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Stability of Chiral Domains Produced by Adsorption of Tartaric Acid Isomers on the Cu(110) Surface: A Periodic Density Functional Theory Study

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Abstract: In the present work the interaction of different bitartrate isomers on the Cu(110) surface has been investigated systematically by using the Vienna Ab-initio Simulation Package (VASP), which performs periodical density functional theory (DFT) calculations. Among all bitartrate isomers the *R*,*R*-configuration is the most stable under the (3 1, 1 2) domain on the Cu surface. Its optical isomer, the *S*,*S*-bitartrate, is 10 kJ mol^{-1} less stable in the same domain. This energy difference is sufficient to produce the distinct chiral assemblies observed after the adsorption of each optical isomer on the Cu surface. The calculations also showed that these domains are not formed due to intermolecular H-bonds, in contrast with the previous proposal by Raval et al.(*Nature* **2000**, *23*, 376). In fact, there is a formation of optimal intramolecular H-bonds in the chemisorption structures. A favorable packing orientation is also needed for the respective chiral domains. For instance, the *S*,*S*-configuration suffers from a destabilizing packing energy of 21 kJ mol^{-1} under the same domain, due to a short contact between the H atoms of the hydroxy groups. These intramolecular H-bonds cause also some distortions on the bitartrate molecule, which appear to be dependent on the relative position of the α-hydroxy groups. The stability of the extended asymmetric domains, when the surface is modified by a chiral additive, might have important consequences for understanding and optimizing the properties of enantioselective heterogeneous catalysts.

1. Introduction

Since 1960 much information has been collected on the enantioselective hydrogenation of *β*-ketoesters over modified Ni catalysts.[2−6] The development of such a heterogeneous catalyst, which is able to synthesize an optical isomer with an enantiomeric excess from a prochiral reagent, would have extreme importance for pharmaceutical and chemical industries. The benefits would not be only due to the production of the chiral molecule itself (in high selectivity) but also due to the catalyst, which is cheaper and easier to handle and to separate than the most common ones that are currently used.

These Ni catalysts are modified by adsorption of an optically active material: α-aminocarboxilic and α-hydroxycarboxilic acids. Data obtained by using infrared experiments[2,7] indicated that the modifier might be adsorbed on the metallic surface as chelate and carboxylate, in case of α-aminocarboxilic and α-hydroxycarboxilic acids, respectively.

Another possibility of forming chiral metal surfaces is to use specific kinked sites of single crystals. An example of such a kinked chiral substrate is the 643 surface of a fcc crystal. Two different studies have followed such procedure; the decomposition of *R*- and *S*-2-butanol on Ag(643)[8] and the electro-oxidation of D- and L-glucose on Pt(643).[9]

Recently, scanning tunneling microscopy (STM) images of the molecular assembly, obtained by adsorption of chiral modifiers on different surfaces, such as Cu(110)[1] and graphite,[10,11] have revealed that each isomer forms different chemisorption domains, which are mirror images on the surface.

In the case of Cu(110), the modifiers were the *R*,*R*-tartaric acid and its mirror image the *S*,*S*-isomer. Their self-assemblies were attributed to the close proximity of the α-hydroxy groups on the neighboring bitartrate, leading to intermolecular hydrogen-bonding interactions. These mirror surfaces are, thus, chiral metal surfaces and may play a central role in rising the enantioselectivity in the hydrogenation reaction. This enantioselectivity is currently known to be strongly dependent on the catalyst preparation and the nature of the modification employed.[6] Despite these important experimental implications, the chemisorption of chiral molecules on a surface has not been previously studied, to our knowledge, from the first principles calculations.

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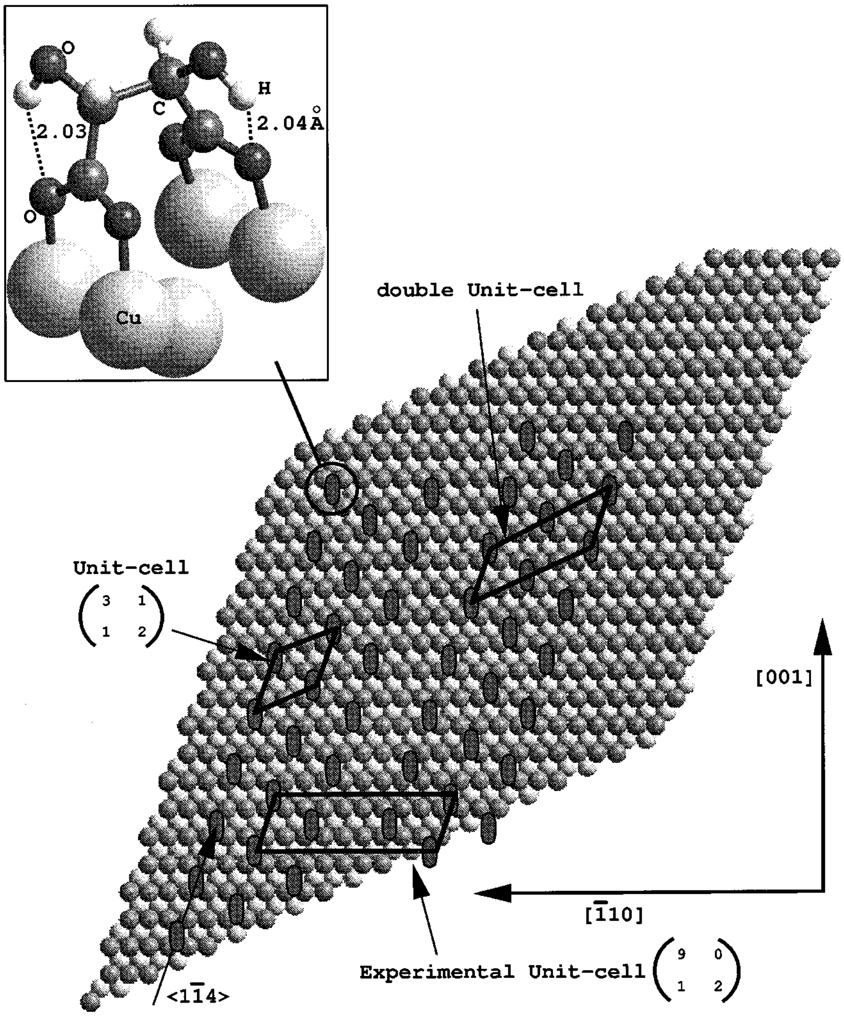

Figure 1. *R*,*R*-bitartrate unit-cells and the optimal structure for the *R*,*R*-bitartrate in the (3 1,1 2) unit cell.

The present work investigates the interaction of the different bitartrate isomers on the Cu(110) surface. Applying ab initio periodic density functional theory (DFT) studies at a molecular level, more insights about the formation and stability of these different domains (*R*,*R*- and *S*,*S*-) have been revealed.

2. Methods and Model Systems

In the work reported here all calculations were performed using the Vienna Ab-initio Simulation Package (VASP).[12,13] This code carries out periodic density functional calculations (DFT) using pseudopotentials and a plane wave basis set. The DFT was parametrized in the local-density approximation (LDA), with the exchange-correlation functional proposed by Perdew and Zunger[14] and corrected for nonlocality in the generalized gradient approximations (GGA) using the Perdew−Wang 91 functional.[15]

The interaction between the core and electrons is described using the ultrasoft pseudopotentials introduced by Vanderbilt[16] and provided by Kresse and Hafner.[17] These pseudopotentials allow a drastic reduction of the necessary number of plane waves per atom, especially for the first row transition metal elements.

In the calculations performed here the Cu(110) surface is modeled by a periodic five layer-slab with a bitartrate adlayer adsorbed on one side of the slab. One slab is separated from its periodic image in the *z* direction by a vacuum space, which is equivalent to eight metallic layers. Only the two bottom layers have been maintained frozen in all optimizations.

To minimize the effect of the stress that occurs due to the constraints in the slab model, the optimal bulk Cu−Cu distance was calculated. The calculated bulk nearest Cu−Cu distance is 2.58 Å, which is in good agreement with the experimental value: 2.56 Å.[18]

The determination of the surface lattice for an adsorbate is a very complicated task. This situation is hence simplified by the fact that the unit cell is known experimentally, and the calculations have been limited to model this unit cell.

Experimentally, the tartaric acid is found to be adsorbed on Cu-(110) as bitartrate, following a 2-dimensionally ordered structure. Each isomer (*R*,*R*- or *S*,*S*-) appears in one of is these “chiral” domains, where the molecules form extended parallel rows along the <1$\bar{1}$4> direction. These rows are assembled in-groups of three, separated by an empty space (channel), see Figure 1. This supramolecular assembly is described for the *R*,*R* and *S*,*S*-isomer by the following matrix notation: [1,7]

$$M_{R,R} = \begin{pmatrix} 9 & 0 \\ 1 & 2 \end{pmatrix} \qquad \text{and} \qquad M_{S,S} = \begin{pmatrix} 9 & 0 \\ -1 & 2 \end{pmatrix}$$

These matrices define the unit cells unambiguously, indicating the new unit-cell vectors.[19]

These unit-cells, however, have 18 metallic atoms per metal layer and three bitartrate molecules. In consequence, the corresponding

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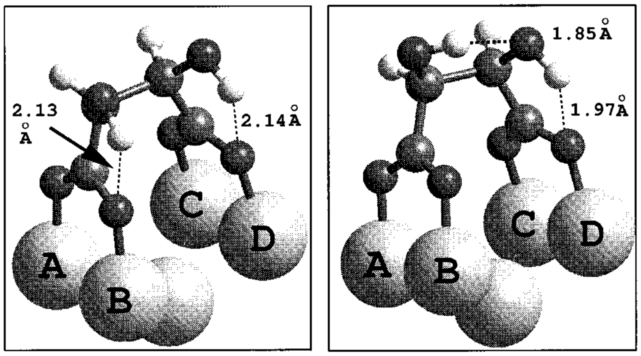
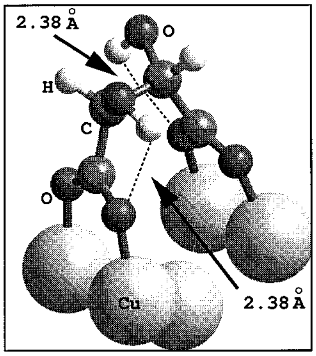


R,S-bitartrate (down) R,S-bitartrate (side)



S,S-bitartrate

Figure 2. Other bitartrate isomers on the Cu(110) surface as optimized with the (3 1,1 2) unit cell.

calculations demand a great computational effort. To minimize this effort, the unit cell was simplified by a periodical repetition of the extended row, instead of groups of three separated by a space, hence modeling the dense part of the adlayer. This means that for the domain of the *R*,*R*-isomer the new matrix notation for the unit-cell vectors will be:

$$M' = \begin{pmatrix} 3 & 1 \\ 1 & 2 \end{pmatrix}$$

The unit-cell is reduced to five metallic atoms per metal layer and one bitartrate molecule, see Figure 1. This matrix representation is referred in the text as (3 1, 1 2) or just *R*,*R*-domain, depending on the case. Although this new bitartrate assembly does not show the empty channel between the three parallel molecular rows found in the original system, it gives the same arrangement between the neighbor molecules in and between adjacent rows. Furthermore, the two chiral domains are still present with this simplified unit cell. The Brillouin-zone integrations have been performed on 2 × 3 × 1 Monkhorst-Pack grid of K-points for all structures, which allows to reach convergence for the calculated energy.

In an additional study, the lateral interaction between the bitartrate molecules and its effects in the molecular assembly were verified. The unit-cell was doubled in order to have in it two molecules from different chains side-by-side, see Figure 1.

All three bitartaric acid isomers have been studied in the present work (the *R*,*R*-, *S*,*S*-, and *R*,*S*-), although the *R*,*S*-isomer was not addressed in the experimental works.

In the case of the *R*,*S*-isomer, two distinct stable configurations adsorbed on Cu(110) surface have been calculated under the (3 1,1 2) domain, so-called "down" and "side".

These denominations correspond to the relative position of the α-hydroxy groups. The position "down" represents the configuration in which both hydroxy groups are interacting with the carboxy oxygen atoms, whereas in the "side" denomination one hydroxy group interacts with the other one, see Figure 2.

The hydrogen atoms, which were released during the formation of the bitartrate phase, were considered to have fast diffusion, to combine themselves and to desorb as molecular hydrogen, which is well-known experimentally at room temperature for Cu-surfaces.[20−22]

3. Results and Discussion

3.1. Different Domains for Different Isomers. From the two adsorption patterns (3 1,1 2) and (−3 1,−1 2) and the *R*,*R*- and *S*,*S*-optical isomers for bitartrate, four distinct theoretical possibilities for the adsorption occur, although only two are observed experimentally.[1] These four possibilities can be sorted in enantiomeric pairs. Thus, only two configurations are needed to be examined, and they are chosen to be the chemisorption of the *R*,*R*- and *S*,*S*-bitartrate under the (3 1,1 2) or *R*,*R*-domain in the present study.

Calculations indicated that the *R*,*R*-bitartrate is the most stable configuration under the (3 1,1 2) domain, which is in agreement with experimental results. The *R*,*R*-isomer is about 10 kJ mol^{-1} more stable than its optical isomer (*S*,*S*-) under the same domain, see Figure 3.

On the basis of the fact that the stability energy of *R*,*R*-isomer under (−3 1,−1 2) or *S*,*S*-domain will be exactly the same as the *S*,*S*-isomer under the *R*,*R*-domain, it is possible to derive the coverage ratio between both the *R*,*R*- and *S*,*S*-domains for the *R*,*R*-optical isomer.

If one assumes an equilibrium among all bitartrate molecules on the surface in most circumstances, the residence time of this molecule on the adsorption site can be estimated by:[19]

$$\tau = \tau_0 \exp\left(\frac{\Delta H_{\mathrm{abs}}}{RT}\right) \tag{1}$$

Moreover, the surface concentration or surface coverage σ will depend on this residence time τ and on the flux of molecules F striking the surface:

$$\sigma = \tau F \tag{2}$$

Combining 1 and 2, one can obtain the coverage as a function of the adsorption energy. Thus, the coverage ratio between the two domains occupied by one optical isomer will be, as the flux F is the same in both cases, equal to:

$$\frac{\sigma_{R,R}}{\sigma_{S,S}} = \exp\left(\frac{\Delta H_{R,R} - \Delta H_{S,S}}{RT}\right) \tag{3}$$

where:

- $\sigma_{R,R}$ is the *R*,*R*-isomer coverage under its own domain.
- $\sigma_{S,S}$ is the *R*,*R*-isomer under the *S*,*S*-domain.

Adding the values of 10 kJ mol^{-1} for the adsorption energy difference and the experimental temperature of bitartrate coverage (405 K),[7] one obtain that the $\sigma_{R,R}$ is 20 times higher than $\sigma_{S,S}$, which means that 95% of the surface is covered by the (3 1,1 2) domain in case of *R*,*R*-bitartrate adsorption. This result is in agreement with the STM images observed by Raval et al.[1]

3.2. The Molecular Assembly and the Hydrogen Bonds. 3.2.1. The Structure of Chemisorption. Raval et al.[1] suggested that a cooperative behavior of the adsorbed bitartrate molecules plays a major role in forming the chiral pattern on the surface. To restrict the supramolecular growth along one particular direction, the locations of the hydroxy groups need to be constrained in space. In this case, it was possible due to the adsorption configuration of the bitartrate: via its carboxy groups.

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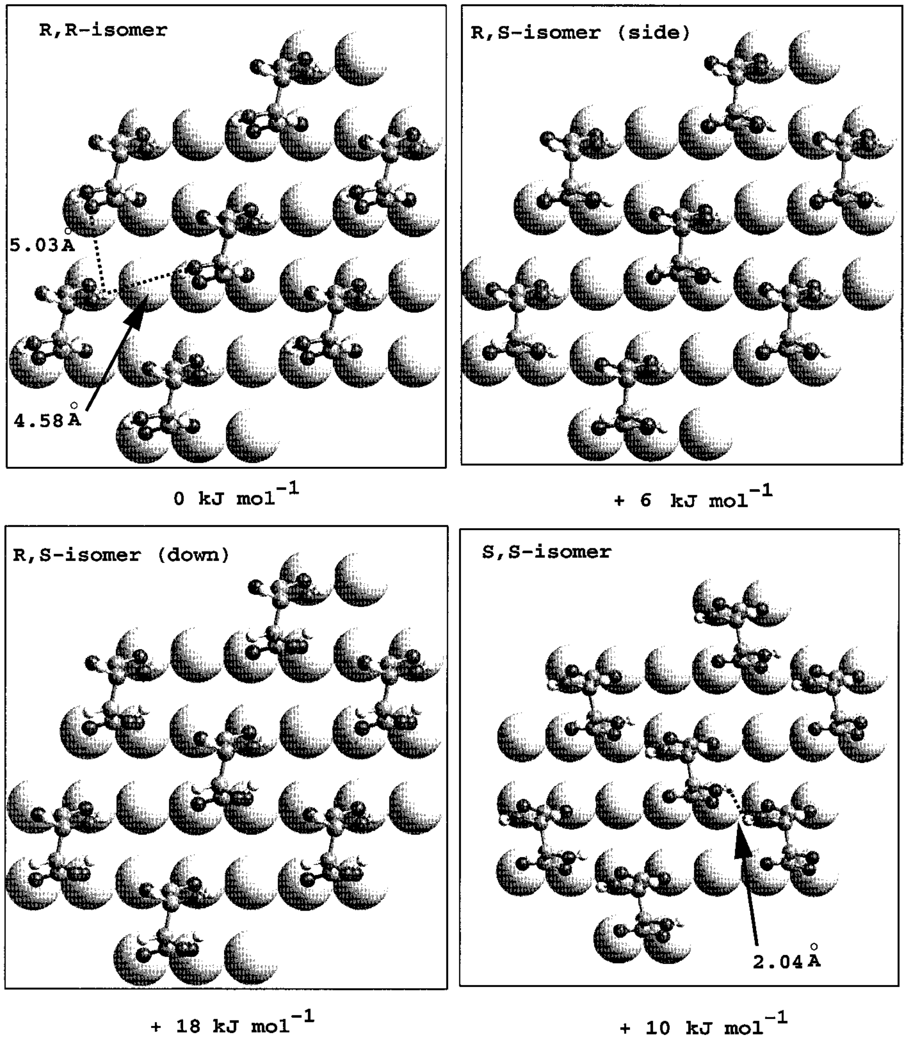

Figure 3. Stability energy of the bitartrate isomers under the (3 1, 1 2) array.

Indeed, similarly to formate[23-25] and acetate,[26] bitartrate adsorbed on Cu(110) with the oxygen atoms of the carboxy groups atop of the neighboring Cu atoms in a short bridge, see Figures 2 and 3.

Four positions a, b, c, and d, which are associated with the nearest Cu atoms bonded to the bitartrate molecule, are defined on the Cu(110) surface, see Figure 2. For all of these positions and all studied molecules, the Cu−O, Cu−Cu (nearest), and Cu−Cu (between the two top layers: interlayer) distances are calculated, see Table 1.

The first point is that the average value for these distances are almost identical for all bitartrate isomers with only small local changes. The average value for the nearest Cu−O distance is equal to 1.97 Å (Table 1), which is in good agreement with the experimental results obtained by surface extended X-ray absorption fine structure (SEXAFS)[27] and photoelectron diffraction (PhD)[23] of the formate on Cu(110) surface: 1.94 ± 0.10 Å and 1.98 ± 0.04 Å, respectively.

For all molecules the Cu−Cu (interlayer) distance has a small expansion from the clean surface value; the maximum value found for the top layer displacement is equal to 0.04 Å, see Table 1. This indicates that these carboxylate molecules do not have a corrosive chemisorption on the Cu surface as found experimentally for the Ni surfaces.[3]

Another interesting fact is that all molecules distribute their Cu−O distances in order to maintain their bond order. Thus, this behavior reminds us of the Bond Order Conservation principle.[28,29] This principle states that each atom has a constant valence to be distributed over its bonds. As a consequence, when one of the bond strength decreases, the others increase, which is noticed by the shortening or lengthening of the atomic bonds.

Although the calculations do not incorporate explicitly the empty channel that appears in the larger (9 0, 1 2) unit cell. They can give a possible explanation for its formation. Upon adsorption, there is an expansion of the Cu−Cu (the nearest distance) spacing in the $\langle\bar{1}10\rangle$ direction (see Table 1); thus, the surface Cu atoms are submitted to a compressive stress. The formation of the empty channel allows a relaxation and release of this stress. Such a mechanism has been observed in the formation of nanostructures at Cu surfaces.[30,31]

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Table 1. Geometric Values for All Species Adsorbed on Cu(110) Surface

molecules	Cu−O (Å)	Cu−Cu (Å) (nearest distance)	Cu−Cu (Å) (interlayer distance)
R,*R*-	1.97^{a} 1.97^{b} 1.96^{c} 1.98^{d} **average value = 1.97**	2.62^{a},^{b} 2.63^{c,d} **average value = 2.63**	1.24^{a} 1.29^{b} 1.27^{c} 1.27^{d} **average value = 1.27**
R,*R*-(double)	1.98^{a} 1.97^{b} 1.96^{c} 1.98^{d} **average value = 1.97**		
R,*R*-(close)	2.02^{a} 1.95^{b} 1.91^{c} 2.07^{d} **average value = 1.99**		
R,*S*-(down)	1.97^{a} 1.95^{b} 1.96^{c} 1.97^{d} **average value = 1.97**	2.63^{a},^{b} 2.62^{c,d} **average value = 2.63**	1.25^{a} 1.23^{b} 1.27^{c} 1.25^{d} **average value = 1.25**
R,*S*-(side)	1.95^{a} 1.97^{b} 1.96^{c} 1.99^{d} **average value = 1.97**	2.62^{a},^{b} 2.62^{c,d} **average value = 2.62**	1.23^{a} 1.28^{b} 1.25^{c} 1.26^{d} **average value = 1.26**
S,*S*-	1.98^{a} 1.96^{b} 1.95^{c} 1.99^{d} **average value = 1.97**	2.62^{a,b} 2.63^{c,d} **average value = 2.63**	1.26^{a} 1.26^{b} 1.20^{c} 1.31^{d} **average value = 1.25**
R,*R*-mirror (*S*,*S*-isomer)	1.97^{a} 1.97^{b} 1.98^{c} 1.96^{d} **average value = 1.98**	2.62^{a,b} 2.63^{c,d} **average value = 2.63**	1.29^{a} 1.24^{b} 1.27^{c} 1.27^{d} **average value = 1.27**
succinic acid (*R*,*R*− domain)	1.95^{a} 1.95^{b} 1.94^{c} 1.97^{d} **average value = 1.97**	2.62^{a,b} 2.63^{c,d} **average value = 2.63**	1.23^{a} 1.26^{b} 1.24^{c} 1.28^{d} **average value = 1.25**
formate values	1.94−2.00^{e} [27] proposed value = 1.98	-	-
Cu (110) clean surface	-	2.58	1.27

[a] The letters *a*, *b*, *c*, and *d* refer to the positions described in Figure 2. [e] Experimental Value.

Table 2. Geometric Values for All Species Adsorbed on Cu(110) Surface

molecules	OH ⋯ O (Å) (intramolecular)	OH ⋯ O (Å) (intermolecular)	C−O (Å) (average value)	O−C−O angle(o) (average value)
R,*R*-(adsorbed)	2.04 2.03	5.03 4.58	1.28	125.8
R,*R*-(double)	2.04 2.03	5.00 4.57	1.28	125.8
R,*R*-(close)	2.05 2.07	4.61 3.65	1.28	125.7
	2.02 2.11		1.28	125.7
R,*S*-(down)	2.13 2.14		1.28	126.1
R,*S*-(side)	1.85 1.97		1.28	125.9
S,*S*-	2.30 2.30	2.50 2.42	1.28	126.2
succinic acid (*R*,*R*-domain)			1.28	125.4
formate values			1.266^{a} [25]	128.7^{a} [25]

[a] Calculated value.

The average values of the C−O distance and of the O−C−O angle are also in good agreement with previous calculated values for formate species on the same Cu surface.[25] Moreover, these values are found very similar for all bitartrate isomers, within a small dispersion, see Table 2.

3.2.2. The Hydrogen Bonds. One may notice that the *R*,*S*-isomers do not have any possibility to interact with their neighbors by intermolecular H-bond, when they are adsorbed under *R*,*R*-domain (or *S*,*S*-domain), see Figure 3. Nevertheless, the *R*,*S*-isomer(“side”) stability is comparable to the *R*,*R*-isomer under the same domain.

Similarly, the distance between the *R*,*R*-isomer molecules are also large to prevent any interaction among the neighbor molecules. In this case, the distance between the hydrogen and oxygen atoms from the α-hydroxy groups of two neighbors is 4.58 and 5.03 Å, respectively, see Figure 3 and Table 2.

In both cases, there are strong intramolecular H-bonds between the α-hydroxy and carboxy groups, viz. the *R*,*R*-isomer or between α-hydroxy groups, viz. the *R*,*S*-isomer(side). An interesting point is that these internal H-bonds are similar to the ones, which occur in the gas-phase configurations of these isomers.

To confirm this preference for intramolecular H-bond, calculations with double unit-cells were done for the *R*,*R*-isomer. Two different systems were tested, see Figure 4. The first system was the *R*,*R*-isomer in a double cell periodicity. This cell was constructed by repeating the molecule in the (3, 1) direction, thus enabling the modification of the interaction of the neighboring molecules. This configuration is so-called *R*,*R*-isomer double.

A different orientation of the OH groups for the two molecules in the unit cell was selected as a starting point. The optimized geometry of the system, however, converged again to a structure with equivalent molecules and identical to the one optimized with the previous small unit cell, see Figure 3. As consequence, there is again no intermolecular H-bond between the neighbor molecules, see Table 2.

By forcing these two neighbor molecules to interact, a second configuration was generated, see Figure 4. This new configuration is so-called *R*,*R*-isomer close. The molecule in the second row was completely distorted for this purpose.

Although the intermolecular H-bonds are shorter than in the previous double cell result, 4.61 and 3.65 Å, the intramolecular H-bonds are still dominating. The distances between the hydrogen and the oxygen atoms from the α-hydroxy and carboxy groups are: 2.05, 2.07, 2.02 and 2.11 Å, see Figure 4. This configuration is around 16 kJ mol^{-1} less stable than the *R*,*R*-isomer double configuration. Thus, one can conclude that the formation of the (3 1,1 2) domain for the *R*,*R*-isomer is not due to intermolecular H-bond as previously suggested by Raval et al.[1]

3.2.3. The Molecular Distortions. Although the C(2)−C(3) bond of the bitartrate molecule retained parallel to the surface, calculations also show that this molecule suffers some structural distortions.

There are two different angular deformations; the first (α) appears in the C(2)−C(3) bond of the backbone structure, whereas the second (β) modifies the O−C−O plane direction from the $<\bar{1}10>$ direction of the surface.

Both distortions are also present in the succinate molecule under the (3 1,1 2) domain but with a much smaller magnitude, see Figure 5. The main difference between the tartaric and

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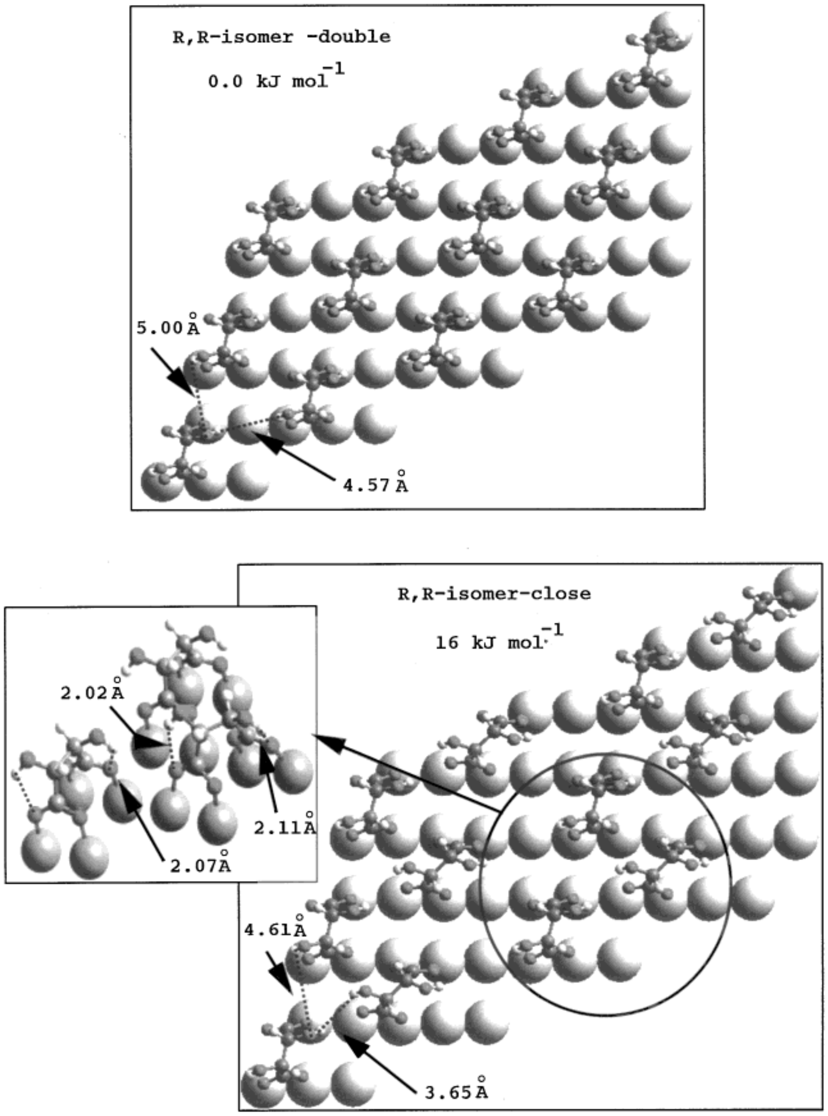


Figure 4. The stability energy of the *R*,*R*-bitartrate isomer: double-cells study.

succinic acids is the absence of the α-hydroxyl groups in the latter molecule, which means that in the succinic acid neither inter- nor intramolecular H-bonds will occur, see Figure 6. Therefore, one can consider that the deviation suffered by the bitartrate isomers, different from the distortion of the succinate, is due to the presence of the α-hydroxy groups.

In the case of *R*,*R*-isomer, the α-hydroxy groups are in different side of the C(2)−C(3) bond. Each of them interacts with one carboxy group producing the backbone distortion ($\Delta\alpha$) equals to +6.2° clockwise.

These internal H-bonds also modify the angle β for both carboxy groups. The final value is −9.1 and −9.3° (anticlockwise), see Table 3 and also Figures 5. In this case, there is an additive effect of these α-hydroxy groups to generate these distortions.

The *R*,*S*-isomer adsorption study also provides more insights about this interesting point. This isomer has both α-hydroxy groups in the same side of the molecule, thus one can expect that each of the α-hydroxy groups will have opposite effect in the molecular distortion. This can be seen in the configuration "down", which has almost no angular distortions $\alpha = 1.8°$ and has opposite deviation $\Delta\alpha = -3.5°$ (anticlockwise) compared to the succinate. The same trend is not observed for the change of the carboxy group plane direction, which the values slightly change, see Table 3.

The other *R*,*S*-configuration ("side"), however, has large angular distortions (α and β), see Table 3. In this case, there is a strong H-bond between both α-hydroxy groups, which twists clockwise the C(2)−C(3) backbone of the *R*,*S*-isomer, and also between the α-hydroxy and carboxy groups, which modifies anticlockwise the carboxy group plane direction. One may note that these results are similar to the ones for the *R*,*R*-isomer.

These angular deformations (α and β) seemed to be achieved in order to provide the best interaction between the α-hydroxy groups, viz. the *R*,*S*-isomer and also between the α-hydroxy and carboxy-surface groups, viz. the *R*,*R*- and *R*,*S*-isomer. Moreover, they are connected to the stability of the molecule on the Cu(110) surface. Both molecular distortion and stability results of the bitartrate isomer under the *R*,*R*-domain follow the same trend:

$$R,R\text{-} > R,S\text{-(side)} > S,S\text{-} > R,S\text{-isomer(down)} \qquad (4)$$

3.2.4. The Intermolecular Interactions. The low stability of the *S*,*S*-isomer in comparison to the *R*,*R*- seems to be due to the unfavorable interaction between the α-hydroxy groups (see Scheme 1), which can be verified by the following steps.

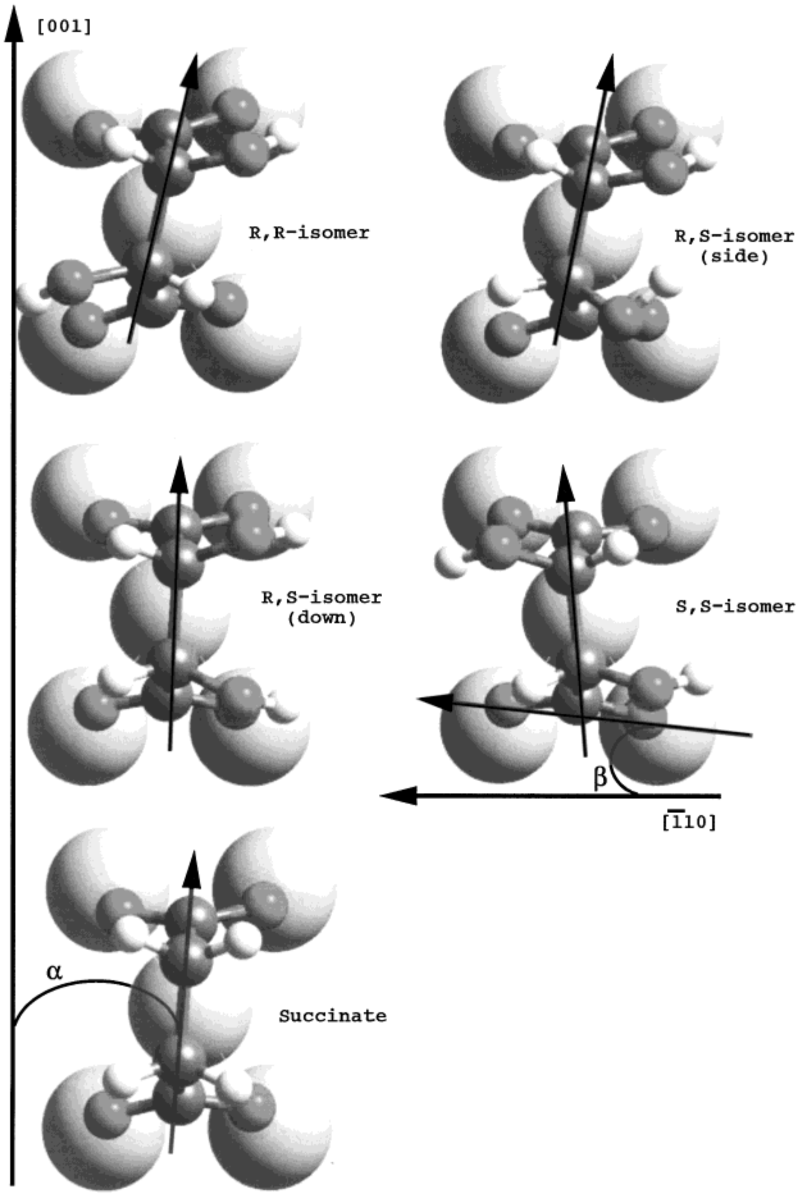


Figure 5. Angular distortions (α) and (*β*) of the molecules on Cu(110) surface for the (3 1,1 2) array.

The first one is to apply a mirror plane transformation to the optimized *R*,*R*-isomer molecule and the Cu atoms of the surface under the *R*,*R*-domain. The mirror plane is chosen to be perpendicular to the <$\bar{1}$10> direction and cross the Cu atom below the molecule. A structure, called *R*,*R*-mirror, is hence obtained for the *S*,*S*-isomer on the *R*,*R*-domain, with the local chemisorption structure identical to the *R*,*R*-molecule, see Scheme 1.

Indeed the *S*,*S*-isomer is less stable by is 35 kJ mol^{-1} in this configuration. This result already indicates that there is a strong repulsive interaction between the hydroxy groups of the *S*,*S*-isomer molecule adsorbed under the *R*,*R*-domain (OH−HO distance: 1.51 Å).

If one optimizes this system, the result is the "optimal" *S*,*S*-configuration under the *R*,*R*-domain, so-called "*S*,*S*-optimized". The angular distortion α is altered from −11.5 (the *R*,*R*-mirror geometry) to −6.1° (the *S*,*S*-optimized), as a consequence the distance of the two H atoms from the adjacent α-hydroxy groups increases to 2.04 Å and there is an energetic gain of 25 kJ mol^{-1} (relaxation energy), see Table 3 and Scheme 1, respectively. This relaxation decreases the lateral repulsion, without being able to completely cancel it.

3.3. The Reason of the Stability of the Molecular Assembly. To understand in more details the stability of the bitartrate molecular assembly on Cu(110), a comparison between the adsorption energy of the bitartrate and the succinic acid under the *R*,*R*-domain was performed.

The adsorption energy was calculated as the difference between the initial system (the gas-phase molecules and the clean surface) and the adsorbed bitartrate or succinate configuration with H_2 in the gas-phase. The value found for the succinate is 72 kJ mol^{-1}, whereas it is 113 kJ mol^{-1} for the *R*,*R*-bitartrate, see Scheme 2.

To understand the adsorption phenomena, this process was decomposed into three distinct elementary steps:

(a) The molecular deformation, which corresponds to the modification of the molecular structure in the gas-phase of the initial configuration to the one found on the surface under the (3 1,1 2) domain.

(b) The molecular packing, which is the arrangement of the already deformed molecules under the (3 1,1 2) assembly in the gas-phase.

(c) The interaction with the surface, which is the adsorption of the deformed and packed molecular assembly onto the

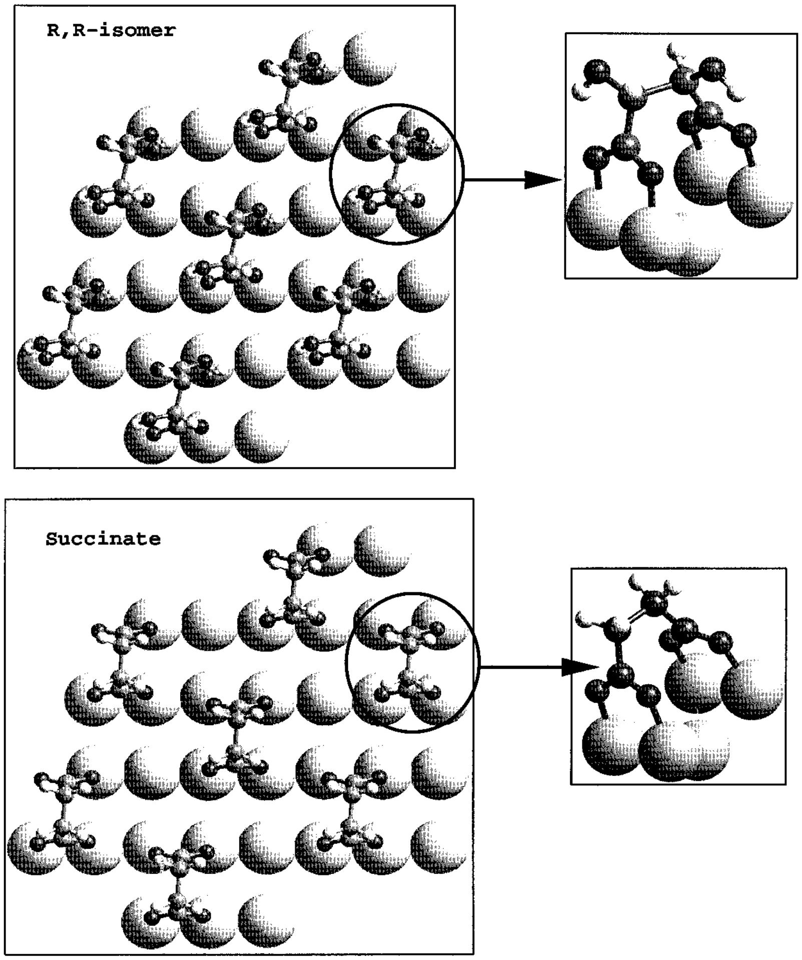


Figure 6. The structure of the bitartrate and succinate molecules on Cu(110) under the (3 1, 1 2) domain.

Table 3. Distortion of the Molecule Adsorbed on Cu(110) Surface[a]

molecules	angular distortion (α) between C−C plane and [001] directions (deg)	$\Delta\alpha$ (deg)	angular distortion (β) between $(\mathrm{O{-}\underline{C}{-}O})$ plane and $[\bar{1}10]$ directions (deg)
R,*R*-	+11.5	+6.2	$-9.1^{a,b}$ $-9.1^{c,d}$
R,*S*-(down)	+1.83	−3.5	$-1.3^{a,b}$ $-3.5^{c,d}$
R,*S*-(side)	+10.4	5.1	$-6.9^{a,b}$ $-7.7^{c,d}$
S,*S*-	−6.1	–	$+7.5^{a,b}$ $+7.8^{c,d}$
R,*R*-(mirror)	−11.5	–	–
succinic acid (*R*,*R*-domain)	+5.3	0.0	$-2.9^{a,b}$ $-3.2^{c,d}$

[a] The letters *a*, *b*, *c* and *d* refer to the positions described in Figure 2.

surface. The surface is allowed to relax during the process and the H_2 is released to the gas-phase.

To estimate the energy balance between these steps, the following procedure was used. All molecules were extracted from the surface, two hydrogen atoms were added to the respective carboxy groups, and a single-point energy was calculated. For the step a, the distance between the periodical images was increased to 10 Å (10 × 10 × 10 Å), whereas in the other two steps the molecules were considered under the (3 1,1 2) array structure, see Scheme 2.

The interaction energies found for the succinate and *R*,*R*-bitartrate isomer is 166 and 164 kJ mol^{-1}, respectively. Both molecules interact with the surface in very similar way, which can also be verified by the average values of the Cu−O distance of both molecules, see Table 1. Therefore, the difference found for the adsorption energies is a consequence of the packing and deformation of the molecule, see Scheme 2.

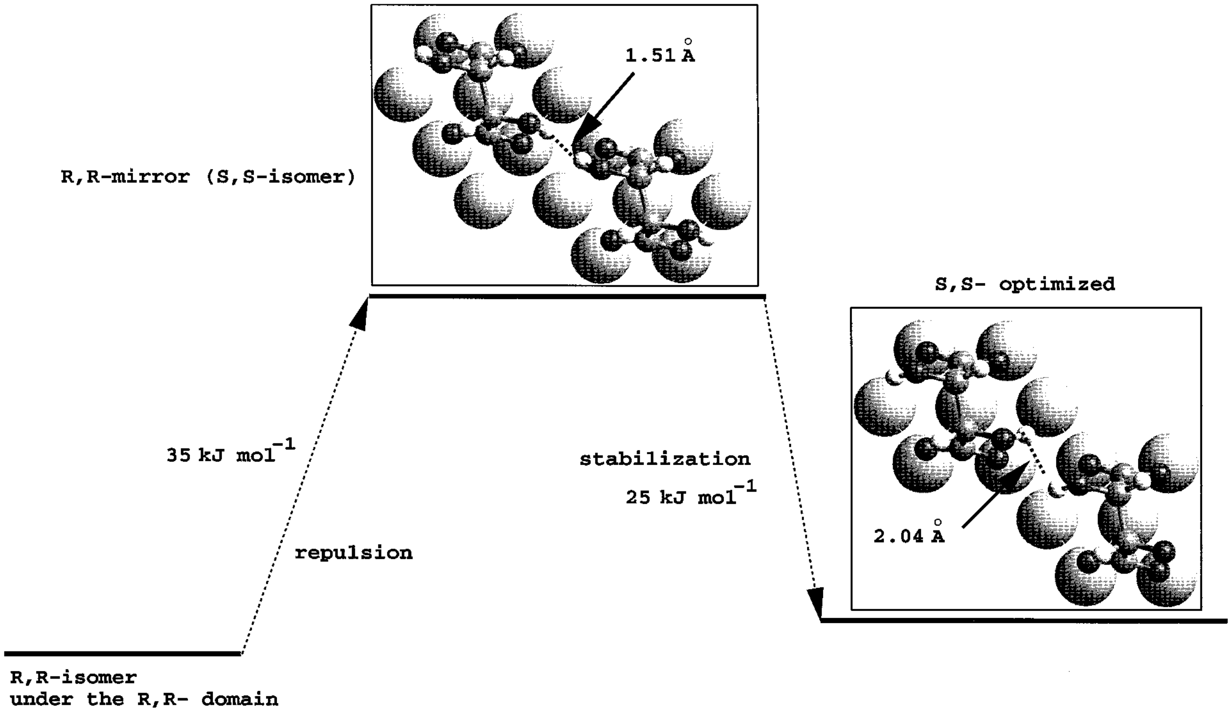
The succinic acid does not have α-hydroxy groups; thus, this molecule is only able to generate H-bonds between the two carboxy groups by distorting its backbone in gas phase. This condition is unattainable on the surface due to the rigid conformation on the surface (see Figure 6); therefore, this molecule suffers a large deformation penalty in order to modify its molecular structure: 94 kJ mol^{-1}.

Although the *R*,*R*-bitartrate molecule loses also energy in order to attain the rigid configuration on the surface, this deformation penalty is the lowest calculated, see Scheme 2. In contrast with succinate, this molecule is still able to align the hydroxy and carboxy groups in order to obtain a stable conformation for the H-bonds, and hence compensate for the loss of these bonds as found in the gas-phase configuration, as seen in the previous section.

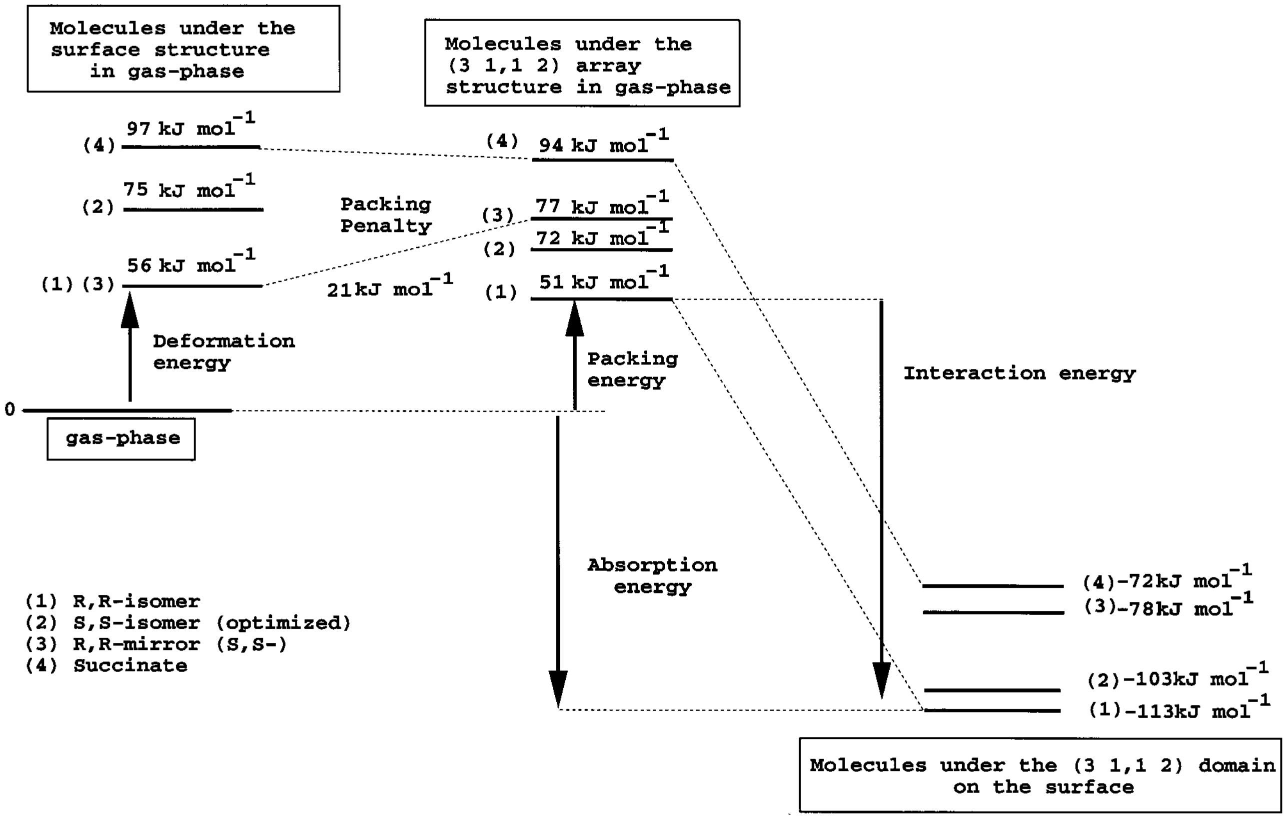
Extending such analysis to the cases of the *S*,*S*-isomer (optimized geometry) and the *R*,*R*-mirror configuration, the lateral interaction problem, which has been already shown, can be clearly identified.

The deformation energy found for the *R*,*R*-mirror is the same as for the *R*,*R*-isomer, since they are mirror images from each other. Once the *R*,*R*-mirror is arranged under the (3 1,1 2) domain, there is a packing cost, which is the difference between the energies of the distorted and packed molecule (about 21 kJ mol^{-1}), see Scheme 2. It is interesting to note that neither the *R*,*R*-isomer, the succinate nor the *S*,*S*-optimized configurations have this packing penalty, thus a negligible influence of the

Scheme 1. Relaxation Energy of the *S,S*-Isomer under the (3 1,1 2) Array



Scheme 2. Energy Diagram of the Bitartrate Optical Isomers and Succinate Molecule Adsorption on Cu(110)



packing. Furthermore, this value is in good agreement with the relaxation energy found in the section 3.2.

Even though the *S,S*-isomer is able to attain a relaxed conformation under the (3 1,1 2) domain, the molecule does not reach its best configuration, which can be verified by the difference between the deformation energies of the *S,S*- and *R,R*-isomer (19 kJ mol^{-1}), see Scheme 2. One may notice that this value is also in agreement with the adsorption energy different between the two optical isomers.

4. Conclusions

In the present work the interaction of different bitartrate isomers on the Cu(110) surface has been investigated systematically. Applying ab initio periodic density functional theory

(DFT), some insights about the formation and stability of these different domains for the *R*,*R*- and *S*,*S*-isomers have been revealed.

Among all bitartrate isomers the *R*,*R*-configuration is the most stable under the (3 1, 1 2) domain on the Cu surface. Its optical isomer, the *S*,*S*-bitartrate, is 10 kJ mol^{-1} less stable in the same domain. This energy difference is sufficient to produce the distinct chiral assemblies observed after the adsorption of each optical isomer on the Cu surface.

The calculations showed that it is unlike that these domains are created due to intermolecular H-bonds, which was suggested previously. In fact, there is a formation of strong intramolecular H-bonds between the carboxy and hydroxy groups. These intramolecular H-bonds cause also some distortions on the molecule, which depends on the relative position of the α-hydroxy groups, encountered in the different bitartrate isomers.

The attractive interaction, which exists between these molecules, as evidenced by the formation of islands at low coverage, is hence not related to H-bonds. It could be, however, assigned to a more general interaction between the adsorbates (through the surface).

There are two factors that promote the molecular stability. The first one is the capability of the molecule to reorganize its internal H-bonds, and hence to reach the chemisorption structure with moderate cost in deformation energy. This explains the larger adsorption energy of the bitartaric acid compared to succinic acid. The second reason is the packing energy cost for the molecules under the (3 1,1 2) domain. This energy only appears for the *S*,*S*-molecule and originates from a short H−H contact. The reduced stability of the *S*,*S*-isomer under the periodic pattern adopted by the *R*,*R*-isomer stems from this repulsive interaction. Therefore these two factors control the formation of different chiral domains for distinct bitartaric isomers.

Although the molecular interactions that have been described here should also appear in the larger experimental unit cell, the magnitude of these interactions should be smaller due to the reduced number of neighbors at the edge of the triple row, where the empty space starts. The expansion of the Cu−Cu spacing in the $<\bar{1}10>$ direction found after the bitartrate adsorption, and the associate surface stress may be a potential explanation for the formation of the empty channel in the experimental (9 0, 1 2) unit cell.

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