Doctoral Thesis

Fundamental aspects of chirally modified metal surface

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Fundamental Aspects of Chirally Modified Metal Surfaces

A dissertation submitted to the Swiss Federal Institute of Technology (ETH) Zurich for the degree of Doctor of Sciences

presented by

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2006
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Summary

Adsorption of a *chiral modifier* on a reactive metal surface is one of the most promising ways of inducing enantioselectivity in a heterogeneous catalytic system. However, little is known about the nature of the active sites present on the modified metal surface and how the modifier imparts chirality to the achiral metal. In addition, it is well-known that modifier concentration, temperature, and catalyst particle size can strongly affect the reaction process.

In this thesis the chirality induced by adsorption of molecules on a metal surface and the role of the metal ensemble size on adsorption geometry and binding strength of the modifier to the metal surfaces are investigated. The methods utilized here are X-ray photoelectron spectroscopy (XPS), temperature programmed desorption (TPD), and low energy electron diffraction (LEED) for investigating the model catalyst (chapters 3, 4 and 7), and attenuated total reflection infrared spectroscopy (ATR-IR) for the study of the catalyst under near reaction conditions (chapters 5 and 6). Basically two types of modifiers are used for enantioselective heterogeneous hydrogenations of β- and α-ketoesters: tartaric acid and cinchonidine-modified metal surfaces, and both have been studied here.

In the first part of the thesis the system racemic-tartaric acid on Cu(110) (chapter 3) and the thermal stability of the modifier on the surface (chapter 4) are addressed. At low coverage after adsorption at 405 K, only locally a chiral surface is created. Two-dimensional conglomerates, showing opposite enantiomorphism, are formed. At higher coverage, a chiral transition from the lateral separated enantiomers into a heterochiral racemic crystal lattice is observed. This transition is directly connected to a change in molecular
adsorbate geometry from a bitartrate complex to monoterartrate species. While the racemic bitartrate undergoes decomposition at the same temperature as the enantiopure system ($T_{\text{dec}} = 447$ K), the racemic heterochiral lattice shows a lower thermal stability ($T_{\text{dec}} = 509$ K) than the enantiopure lattice ($T_{\text{dec}} = 517$ K) of identical periodicity and surface density.

In the second part of the thesis, the influence of the metal ensemble size and morphology on the adsorption behavior of cinchonidine is presented. Metal and bimetallic model thin films with different thickness have been characterized (chapter 5). Monometallic Pt, Pd and Au and bimetallic Pt-Au as well as Pd-Au films with different thicknesses from 0.2 to 2 nm were investigated by AFM and CO adsorption from CH$_2$Cl$_2$ solution using ATR-IR spectroscopy. CO adsorption does not occur on Au. This fact allowed us to study the effect of dilution on the adsorption properties of the surfaces of Pt and Pd on Au. Most prominent changes related to CO adsorption were observed in the case of Pd-Au. The average grain size on Pd-Au surfaces was smaller compared to the monometallic Pd surfaces and at equivalent Pd film thickness, evaporation of Au reduced the amount of adsorbed CO on Pd-Au surfaces. These changes occurred as a consequence of diffusion of Pd into Au, which affects the Pd ensemble size even more significantly than the simple decrease of Pd film thickness in monometallic surfaces. Pt-Au surfaces showed less prominent changes concerning CO adsorption than Pd-Au surfaces.

On the basis of the morphological information, as presented in chapter 5, it was possible to study the adsorption conformation of cinchonidine (CD) on the same bimetallic surfaces (chapter 6). Cinchonidine adsorbs on Au via the lone pair of the quinoline-N, exclusively forming a $\sigma$-bonded (tilted) species on the surface. This species could also be observed on monometallic Pt and Pd films with adsorption strength decreasing in the order Pd > Au $\gg$ Pt. On bimetallic Pt–Au thin model films the population of $\pi$-bonded (flat) species decreased with decreasing Pt film thickness. The $\sigma$-bonding prevailed at very low Pt content.
On bimetallic Pd-Au thin model films cinchonidine σ-bonded to Pd diminishes with Pd content. The reason for these differences are explained such that the π-bonded species requires more surface space than the σ-bonded species and is therefore more sensitive to the size of the metal ensembles. It seems that the platinum group metal ensemble size alters the way the chiral modifier coordinates to the surface and, as a consequence, could affect the enantioselectivity.

Cinchonidine does not form long range ordered structures on Au(111) in ultra-high vacuum (chapter 7). Molecular desorption is observed for multilayers only. It undergoes decomposition upon heating in the first monolayer, as observed by hydrogen desorption above 500 K. This behavior indicates a surprisingly strong interaction of CD with Au. XPS strongly supports this assumption: a strong shift in the N 1s signal to higher binding energies for one of the two N-atoms in the molecules of the first monolayer is observed. Adsorption of the quinoline, the aromatic part of CD, shows similar results in XPS, indicating that the strong shift is due to a strong interaction of the quinoline N with Au.
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Der erste Teil dieser Dissertation behandelt die von razemischer Weinsäure auf Cu(110) (Kapitel 3) herbeigeführte Chiralität und die Stabilität dieses Modifikators auf der Oberfläche (Kapitel 4). Bei niedriger Bedeckung entsteht nur lokal eine chirale Oberfläche, welche aus zweidimensionalen Konglomeraten spiegelbildlicher Enantiomere besteht. Bei höherer Bedeckung entsteht ein heterochirales Razemat –Kristallgitter verbunden mit einem
Übergang von einem Bitartrat-Komplex zu einer Monotartrat-Verbindung. Das lokale chirale System zeigt die gleiche Desorptionstemperatur wie das enantiomer-reine System ($T_{des} = 447$ K). Im Gegensatz dazu zeigt das heterochirale System ($T_{des} = 509$ K) eine geringere Stabilität als das enantiomer-reine System ($T_{des} = 517$ K).


Basierend auf der in Kapitel 5 ermittelten Morphologie, war es möglich, die Konformation von Cinchonidin an gleichen bimetallischen Oberflächen zu untersuchen (Kapitel 6). Cinchonidin adsorbierte über das freie Elektronenpaar des Quinolin-N an Au, was ausschliesslich zu einer geneigten σ-gebundenen Spezies führt. Diese Spezies konnte auch an den Oberflächen dünner monometallischer Pt- und Pd-Schichten beobachtet werden. Die Stärke dieser Bindung sinkt in der Reihenfolge Pd > Au >> Pt. An dünnen bimetallischen Pt-Au Schichten nimmt der Anteil π-gebundener (flach adsorbierten) Spezies mit der Pt-Schichtdicke ab. Die σ-Spezies ist überwiegend bei Pt mit geringer

Im UHV bildet Cinchonidin keine geordnete Phase auf Au(111) (Kapitel 7). Molekulare Desorption wird nur bei Multilagen beobachtet. Über 500 K zersetzt sich die erste Monolage, was durch die Wasserstoff-Desorption festgestellt wurde. Dieses Verhalten weist auf eine starke Wechselwirkung von CD mit Au durch das Quinoline N-Atom hin. XPS unterstützt diese Annahme: Für CD und Quinoline wurde für das N(1s)-Signal die gleiche Verschiebung zu höheren Bindungsenergien beobachtet.
1.1 Chirality

Although chemists have been familiar with the concept of chirality for hundred years, this term has only been used in chemistry since 1870. Chirality means handedness, that is the existence of left/right opposition. For example right hand and left hand are chiral, in other word they are mirror images of each other. The origin of the word chiral is from the Greek word *cheir* which means hand. This word was introduced by Lord Kelvin in 1884. In his lectures in Baltimore on Molecular Dynamics and the wave theory of Light he stated ..."I call any geometrical figure, or group of points, chiral, and say it has chirality, if its image in a plane mirror, ideally realized, can not be brought to coincide with itself. "[1]

The investigation of chiral molecules is an important part of stereochemistry, involving the study of the relative spatial arrangement of atoms within molecules.

L. Pasteur observed in 1849 that salts of tartaric acid collected from wine production vessels could rotate plane polarized light, but salts from other sources did not. This property, the only physical property in which the two types of tartrate salts differed, is due to optical isomerism. In 1874, J.H. van ‘t Hoff [2] and J.A. Le Bel [3] explained optical activity in terms of the tetrahedral arrangement of the atoms bound to carbon. They recognized that when four different groups are attached to a carbon atom, arrayed at the corners of a tetrahedron, there are two possible different arrangements that give two different
molecules called enantiomers. The absolute configuration of chiral centers can be labeled R (for rectus) or S (for sinister) as defined by the Cahn-Ingold-Prelog rules [4, 5] (presented in figure 1.1 for (R) and (S)-alanine). Enantiomers have identical physical properties (boiling point, densities). The only difference is the direction of rotation of plane polarized light. Enantiomers can exhibit distinct chemical behavior and they present different aroma and flavor and more importantly, they have differences in toxicity and biological activity.

![Figure 1.1: The two enantiomeric structures of alanine.](image)

One of the best known demonstrations of the significance of stereochemistry in the pharmaceutical industry is the thalidomide disaster [6]. Thalidomide was a drug prescribed for treating morning sickness of pregnant women. The drug however was later discovered to cause deformation in embryos. The disaster helped to introduce strict drug testing and it was discovered later that one optical isomer of the drug was safe while the other had teratogenic effects, causing serious genetic damage to early embryonic growth and development. In the human body, thalidomide undergoes racemization: even if only one of the two stereoisomers is ingested, the other one is produced [6].
1.2 Asymmetric catalysis

Asymmetric catalysis uses chiral catalysts for the production of single enantiomer compounds for pharmaceutical use and other applications. Because of its importance in 2001 the Nobel prize for chemistry was given to W.S. Knowles and R. Noyori for their work on "chirally catalysed hydrogenation reactions" and to K.B. Sharpless for his work on "chirally catalysed oxidation reactions" [7].

The method used for producing enantiopure products for the pharmaceutical industry is based mainly on homogeneous catalysis. Despite its technical advantages such as higher stability and easier catalyst separation, the use of enantioselective heterogeneous catalysis in pharamaceutical industry is restricted to only few applications. However, experiments performed in the last decades delivered excellent results and show that this method is a promising alternative to homogeneous chiral catalysis [8, 9].

In enantioselective heterogeneous catalysis, metal surfaces that are usually achiral can be endowed with handedness by modification with chiral molecules. The surface-bound molecules (adsorbates) may react enantiospecifically with one another or they may mediate stereoselective reactions. In other cases, atoms in a metal surface assemble in particular patterns, sometimes in response to the presence of adsorbed molecules, thereby leading to the loss of mirror symmetry of the surface.

The two most successful examples of enantioselective heterogeneous catalytic reactions are the hydrogenations of β-ketoesters and β-diketones over tartaric acid modified Ni catalysts [8, 10, 11] and of α-ketoesters and some activated alkenes over cinchona modified Pt and Pd catalysts [9, 12, 13] as presented in figure 1.2.
Modifiers:

<table>
<thead>
<tr>
<th>COOH</th>
<th>COOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>HO</td>
<td>HO</td>
</tr>
<tr>
<td>OH</td>
<td>OH</td>
</tr>
</tbody>
</table>

(R,R)-Tartaric acid

Cinchonidine

Reactants:

<table>
<thead>
<tr>
<th>R-Ketoester</th>
<th>α-Ketoester</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>R</td>
</tr>
<tr>
<td>OR</td>
<td>OR</td>
</tr>
</tbody>
</table>

Figure 1.2: Chiral modifiers cinchonidine and (R,R)-tartaric acid used for enantioselective heterogeneous hydrogenations of α-ketoester and β-ketoesters, respectively.

For example, modifying alumina-supported platinum with cinchonidine, a chiral alkaloid, produces a catalyst that can hydrogenate ethyl pyruvate to (R)-ethyl lactate with an enantiomeric excess as high as 95% [14]. The reaction is shown in figure 1.3 (right).

Figure 1.3: Enantioselective heterogeneous hydrogenation of ethyl pyruvate to (R) ethyl lactate (right) and (S)-ethyl lactate (left).

In addition to α-ketoesters, other reactants used for Pt catalysts include ketopantolactone [15, 16], α-ketoacids [17], α-ketoamides [18] and diketones [19]. Chirally modified Pd is employed in the enantioselective hydrogenation of C=C double bonds for example in α,β-unsaturated carboxylic acid [13, 20-22] and pyrones [23].
Furthermore by changing the absolute configuration of the modifier, for example from cinchonidine to cinchonine (figure 1.4), the chirality of the product is inverted as shown in figure 1.3 (left).

**Figure 1.4:** Chiral modifier cinchonine.

The use of O-Phenylcinchonidine (PhOCD) is also known to efficiently induce inversion of enantioselectivity with respect to cinchonidine (CD) in the enantioselective hydrogenations of various activated ketones on Pt/Al₂O₃ [24] despite the identical absolute configuration of the two modifiers. In addition the influence of solvent was probed in asymmetric heterogeneous reactions [25]. For example it was observed that in the enantioselective hydrogenations of ethyl pyruvate over β-isocinchonine (β-ICN) modified Pt–alumina catalysts, the major enantiomer was (R)-ethyl lactate in toluene, while in acetic acid, (S)-ethyl lactate was formed as shown in figure 1.5. The (R) configuration is opposite to what is expected from the absolute configuration of the cinchonine backbone.
Figure 1.5: Change of the sense of enantioselectivity in the enantioselective hydrogenation of ethyl pyruvate in different solvents.

Besides improving the cinchona platinum catalyst system, extensive efforts have been made in developing a reliable mechanistic interpretation. The most important parameters for the efficiency of the Pt–cinchona system are: i) the structure and concentration of the modifier, ii) the platinum particle size, morphology and support, and iii) the solvent. According to systematic studies three structural elements are crucial for the functioning of the cinchona alkaloids as chiral modifiers: (i) an anchoring part, represented by the flat extended aromatic ring system, (ii) the absolute configuration at C(8) which controls the sense of chirality, (iii) a nitrogen which is able to interact with the reactant through a 1:1 interaction.

With the Raney-nickel system the highest ees have been obtained in hydrogenation of β-functionalized ketones as well as 2- and 3-alkanones in presence of NaBr. Ionic Na might influence the structure of the adsorbed tartrate, while bromide ions are proposed to block racemic sites [26, 27]. Figure 1.6 presents the hydrogenation of methyl acetoacetate to methyl (R)-3-hydroxybutyrate [8] by tartaric acid modified Raney nickel catalysts.
In all examples it was found that reaction parameters like the catalyst morphology, modifier concentration, reaction conditions and solvent are crucial for achieving good results. So there is a demand to understand the origin of the stereospecificity of the reactions and to elucidate their mechanisms. Experimental and computational methods are used to study bonding geometries, molecular conformations and interactions between reactants, surfaces and chiral modifiers. By branching out to model systems, other metals, and a range of experimental procedures, it is possible to collect additional information about the interaction of the chiral modifier with metal surfaces. Although some of these model systems are far from the real catalyst conditions, these studies are useful to get a better understanding of the system.

1.3 Origin of chiral molecules Tartaric Acid and Cinchonidine

TARTARIC ACID (figure 1.7), also dihydroxy-succinic acid, is found in many plants and was known to the Greeks and Romans as tartar. The acid potassium salt derived as a deposit from fermented grape juice. The acid was first isolated in 1768 by C. W. Scheele, who boiled tartar with chalk and decomposed the product with sulphuric acid. Fermentation of the juices of grapes, tamarinds, pineapples and mulberries produces a white crust of potassium acid tartrate known as argol, or lees on the inner surface of the container. Argol, boiled with dilute hydrochloric acid, precipitates as calcium tartrate when calcium hydroxide
is added. Upon addition of dilute sulphuric acid, D-tartaric acid is liberated, which rotates the plane of polarized light to the right.

Another variety, called L-tartaric acid, is identical to D-tartaric acid except that it rotates the plane of polarized light to the left. This acid was first prepared from its sodium ammonium salt by L. Pasteur. Tartaric acid synthesized in the laboratory is a mixture of equal amounts of the D and L acids.

Tartaric acid is used as flavour in foods and beverages. It is used also in photography, in tanning. Potassium hydrogen tartrate, also called cream of tartar, is used in baking powders and in various treatments of metals.

\[
\begin{align*}
\text{HOOC} & \quad \text{COOH} \\
\text{HO} & \quad \text{OH} \\
\text{R} & \quad \text{R} \\
\text{(+)-L-Tartaric Acid} & \quad \text{(-)-D-Tartaric Acid}
\end{align*}
\]

**Figure 1.7:** The two enantiomeric structures of tartaric acid: L-tartaric acid (left) and D-tartaric acid (right).
CINCHONIDINE is an alkaloid isolated from the bark of Cinchona trees (Peruvian Bark) and is most cultivated in India. These evergreen trees grow in the hottest part of the world and constitute the twenty-ninth part of the whole flowering plants of the tropics. Peruvian bark was introduced in Europe in 1640, but the plant producing it was not known to botanists till 1737. Legends say it was named Cinchona after the Countess of Cinchon, who first made the bark known in Europe for its medicinal qualities. It was known and used by the Jesuits very early in its history, but was made official in the London Pharmacopoeia of 1677. The bark is spongy, very slight odour, taste astringent and strongly bitter. Different cinchona alkaloids are shown in figure 1.8. Figure 1.9 illustrates flower and leaves of cinchona.

![Cinchona alkaloids](image)

**Figure 1.8:** Cinchona alkaloids.
1.4 Chirality at the organic/inorganic interface and chiral metal surfaces

As already mentioned, chiral surfaces are of great interest in the field of heterogeneous asymmetric catalysis. Beside the separation of chiral compounds other applications of these surfaces are for example to be found in the development of chemical sensors and nonlinear optical materials. At present, a number of routes are known to produce chiral catalytic surfaces. The principle possibilities for inducing chirality to a metal surface are:

1) generating high index chiral metal surfaces [28, 29]
2) selective poisoning of chiral surface sites of specific handedness [30]
3) chirality induced by chiral support [31-33]
4) surface reconstruction induced by adsorbed chiral molecules [34]
5) supramolecular chirality and chirality induced by adsorbed chiral organic molecule (modifier) [35, 36].

One of the interesting issues for the organic/inorganic interface is how the adsorption of organic molecules bestows chirality to a non-chiral surface. Surface chirality can be identified in a number of ways. It could create local chiral motifs by single adsorption event or create chiral domains arising from the
chiral arrangement of the individual motifs. Also it is important to distinguish between local and global chirality. In local chirality, local chiral adsorption motifs organise into a 2D arrangement but the system as a whole is not chiral. At global level, in contrast, only one of the two possible mirror arrangements is present. The number of allowed space groups rapidly decreases when going from three-dimensional (3D) space (230 space groups) to 2D chiral space group. Each of the space groups can yield two mirror motifs at the surface. A surface with global organisational chirality possesses only of one of two possible mirror motifs as illustrated in figure 1.10.

Figure 1.10: Global chirality on the surface.

Although extensive studies have been carried out in the last two decades, there is still a significant need of information on the crucial surface species. It is a strong hope to utilize surface science methods to gain more details in catalytic systems although it has been difficult to investigate these systems in terms of surface science. The main reason for this difficulty is the existence of the pressure gap. Surface science techniques limit experiments to ultra high vacuum (UHV) environment, since electrons are used to probe the properties of surfaces. One way enabling to bridge the pressure gap between surface science
and catalysis is to apply optical methods which utilize photons to investigate the properties of the surface under more realistic conditions.

We expect through these two approaches (experiments performed in UHV and by spectroscopic methods which can be utilized in UHV and in air) to obtain a complete picture of the adsorbed molecules, binding of molecules and their behavior on the surface and in addition to understand the processes occurring under technologically relevant conditions.

Local structural details such as the chemical nature of the adsorbed species, its bonding and orientation are best obtained by the techniques of reflection absorption infrared spectroscopy (RAIRS), electron energy loss spectroscopy (EELS), X-ray photoelectron spectroscopy (XPS), photoelectron diffraction (PhD), Raman spectroscopy, sum-frequency generation (SFG) and near-edge extended absorption fine structure spectroscopy (NEXAFS). In addition, low energy electron diffraction (LEED) and scanning tunneling microscopy (STM), allow capturing the details of 2D assemblies. Also computational methods assist to propose a possible scenario for enantiodifference.

As mentioned before, adsorption of a chiral molecule on a metal is a fascinating method to fabricate chiral surfaces. Adsorption of cinchona alkaloid on Pt and tartaric acid on Ni and Cu are the most studied systems of this kind. Adsorption of quinoline and 10,11-dihydrocinchonidine (DHC) have been investigated by XPS [37, 38], LEED [38] and NEXAFS [39, 40] under UHV conditions on Pt. Quinoline and 10,11-dihydrocinchonidine were found to adsorb preferentially flat through the π-aromatic system at room temperature, whereas at 323 K on average the quinoline ring was considerably tilted with respect to the surface [39]. Adsorption of the chiral molecule cinchonidine on Pt [41-45] is coverage dependent (figure 1.11). At low coverage, cinchonidine adsorbs on the Pt surface predominantly via the π-system in flat orientation. As the space available on the surface decreases, additional cinchonidine adsorbs in a tilted orientation by formation of α-quinolyl species and N lone pair bonded species [44].
According to ATR-IR studies flat and α-quinolyl species are more strongly bonded than N lone pair species. These adsorption geometries are also confirmed by computational methods [46, 47]. Surface enhanced Raman spectroscopy has been utilized to probe the adsorption of the chiral modifier cinchonidine on polycrystalline platinum. The vibrational properties of adsorbed cinchonidine on platinum in ethanol solutions at 25°C have been probed in situ. It has been observed that the cinchonidine modifier is strongly and irreversibly adsorbed through the quinoline portion by π-bonding with the Pt surface [48]. In addition STM studies indicate that adsorption of cinchonidine occurs without formation of molecular arrays on Pt [45, 49]. LEED studies of DHC also shows no ordered phase on Pt(111) crystal [50]. It has been proposed that the π-bonded species of cinchonidine is involved in enantiodifferentation [51].

Figure 1.11: Suggested adsorption mechanism of cinchonidine on Pt/Al₂O₃ based on ATR-IR experiments. Species 1: π-bonded, 2: α-H abstracted and 3: N lone pair bonded [44].
Adsorption of (R,R)-tartaric acid on Cu(110) has been studied by LEED, STM and FT-RAIRS [52, 53]. Interaction of (R,R)-tartaric acid with Cu(110) produces a complex adsorption phase diagram in which the chemical identity and 2-dimensional order of the adsorbed species vary significantly as a function of coverage and temperature. Different ordered overlayer structures were observed, in which preferred molecular forms, bonding and orientations of the chiral molecules are adopted, depending on coverage, temperature and time. It was proposed that these different adlayers will clearly play a different role in the enantioselective reaction [54]. The STM images reveal that the bitartrate phase is self-assembled in rows of three, each row stacking in parallel with others to form long chains. These long chains do not coincide with any of the symmetry directions present on the Cu(110) surface.

As a result, this molecular growth direction has the effect of destroying all the symmetry elements of the underlying metal, leading directly to the creation of a chiral surface that is non-superimposable to its mirror image.

A detailed study of the adsorption of (R,R)-tartaric acid on the Ni(110) surface was carried out as a function of temperature and coverage and shows that the local nature of the chiral adsorbate changes dynamically as conditions change [55]. STM data of the bitartrate species on Ni(110) do not show any long-range ordered structure of the type observed for Cu(110), instead, random occupation of the surface sites is observed, with a preferential growth of 1-D molecular chains directed along the main <1–10> crystallographic axis.

In addition, DFT calculations show that the bitartrate adsorbate induces a chiral relaxation of atoms at the Ni(110) surface, in order to accommodate a large bitartrate–nickel chiral footprint, thus causing a chirality transfer from the molecule into the metal. Adsorption of (R,R)-tartaric acid on Ni(111) produces two distinct ordered adlayer structures in mono and bitartrate form which are stabilized by intermolecular H-bonding interactions. The former leads to pseudo 1D growth, the latter to ordered 2D adlayers.
Adsorption of succinic acid on Cu(110) is a nice example of generation of local chirality. Succinic acid is a very similar molecule to tartaric acid, the only difference being that the two hydroxyl groups of tartaric acid are replaced by hydrogen atoms leading to a loss of both chiral centres [56]. In contrast to the bitartrate on Cu(110) that possesses global chirality, bisuccinate is locally chiral but globally achiral.

In addition to classical tartaric acid and cinchona systems, there are a lot of systems which have been investigated by the surface science multi-technique approach to study different organic molecules on metal surfaces. It seems that the application of rigorous surface science tools to study organic molecules at surfaces is rapidly increasing.

For example, adsorption of L-cysteine on Au(111) studied by STM shows that the dimers of the molecule appear as paired spots which are aligned with a 20° clockwise rotation relative to certain lattice features. D-cysteine molecules act just like their L counterparts, except that the rotation is counterclockwise, leading to the mirror image [57].

Also it was found that deposition of chiral decacyclene molecules on a copper crystal and moving them with a STM tip, create chiral holes [58]. Adsorption of non-chiral glycine on Cu(110) and Cu(100) [59-61] and on Pt(111) [62, 63] leads to observation of an ordered phase and adsorption of alanine on Cu(110) [64] can create a surface with global point and organisational chirality. Adsorption of S-proline on Cu(110) [65] was studied by RAIRS, LEED, TPD and it has been observed that the S-proline ring tilted with a small angle with respect to the surface plane.

Adsorption of M-[7]- and P-[7]-helicene on Cu(111) [66] has been investigated by LEED. Intact molecules spiral away from surface and form close-packed ordered multilayers.
These and many other examples illustrate how this rapidly expanding research area can assist to understand the possible mechanisms of enantioselective heterogeneous catalysis.
1.5 Aim of the Thesis

Study of the fundamental aspects of chirally modified metal surfaces is the main aim of this work. Modification of metal catalysts by adsorbed chiral auxiliaries is one of the most promising strategies for chiral heterogeneous catalysis. It is still important to increase the knowledge how enantioselective catalysis works on a metal surface modified by adsorbed chiral molecules (modifier). The two systems in focus are tartaric acid modified and cinchona-modified metal surfaces. Different surface sensitive techniques like X-ray photoelectron spectroscopy (XPS), low energy electron diffraction (LEED), temperature programmed desorption (TPD) and attenuated total reflection infra-red spectroscopy (ATR-IR) have been used to study different adsorbates and metals surfaces in UHV and in the presence of a liquid phase. This work tries to answer the open questions such as how do the organic molecule bond to the metal surface, what is the molecular orientation at the surface, is there self-organization at the surface to form ordered structures and how do all the above adsorption characteristics vary with coverage and ensemble size of platinum group metal catalysts?

The thesis consists of two main parts, the first part investigates the behavior of racemic tartaric acid on Cu(110) in UHV and the second part investigates the role of platinum group metal ensemble size (Pt and Pd) on the adsorption mode of the modifier cinchonidine in the presence of a solvent. Comparison of studies performed under realistic conditions with those performed on well-defined model systems should enable to gain new insights into the mechanisms of enantioselective heterogeneous catalysis. In addition to study the adsorption behavior of organic molecules, characterization of the model catalysts by CO adsorption is a significant part of this work.
1.6 References

Introduction

Chapter 2

Experimental Methods

2.1 X-ray Photo Electron Spectroscopy (XPS)

2.1.1 Introduction

X-ray photoelectron spectroscopy (XPS) is one of the widely used surface analysis methods. With this method it is possible to gain information about the elementary composition of surfaces and chemical binding between the elements. The observed depth with this method is about 3 nm.

2.1.2 Principle of the measurement

XPS is based on the photoelectron effect [1-5]. By exciting the atoms, molecules or solids with photons, electrons are emitted and the kinetic energy of emitted electrons is determined. The photoelectrons carry an energy >100 eV so it is possible to study the core electrons and to carry out chemical analysis and consequently this method is called also ESCA (Electron Spectroscopy for Chemical Analysis).

2.1.3 Theory

In XPS a photon is absorbed by an atom in a molecule or solid, leading to ionization and emission of a core electron as shown in figure 2.1. The kinetic energy of emitted electrons can be measured and derived from:

\[ E_{\text{kin}} = h\nu - E_{\text{bin}} - \varphi \, , \]
Here $E_{\text{bin}}$ is the binding energy of the electron referred to Fermi level. In the case of atoms and molecules usually the binding energy of electrons is considered to $E_{\text{vac}}$. The energy of a photon is given by the Einstein equation $E = h\nu$.

![Diagram of XPS process](image)

**Figure 2.1:** In XPS, surfaces are irradiated with X-rays and the energy of the emitted photoelectron is analyzed. The difference between the X-ray energy and the photoelectron energies gives the binding energies (BEs) of the core level electrons which is an atomic characteristic.

For each element, there will be a characteristic binding energy which is associated with each core atomic orbital, i.e. each element will give rise to a characteristic set of peaks in the photoelectron spectrum at kinetic energies determined by the photon energy and respective binding energies. The presence of peaks at particular energies indicates the presence of specific element in the sample under study. In addition the intensity of the peaks is related to the concentration of the element within the sampled region. The most commonly used x-ray sources are those giving rise to:

- Mg K$_\alpha$ radiation: $h\nu = 1253.6$ eV
- Al K$_\alpha$ radiation: $h\nu = 1486.6$ eV.
Since emitted electrons have very short IMFPs (average distance between inelastic collisions (Å)) in solids, this technique is surface sensitive. It is possible to excite more than one electron which leads to shake up and shake off satellite lines. In this process the emitted electron gives some of its energy to another electron. This electron now is able to fill one of the empty binding states (shake up) or empty unbinding states (shake off). In the Auger process, an electron is ejected from a core-level either by a photon (as in conventional photoemission) or by an incident high energy electron. The core-hole is filled by an electron from a higher energy level. The energy lost by that electron may be given up in the form of an X-ray photon or the quantum of energy is transferred (non-radiatively) to another electron in the atom. That electron (the Auger electron) is thus released from the atom. The kinetic energy of the Auger electron, unlike that of a photoelectron, is not dependent on the energy of the incident radiation (or electron) that produced the initial core hole. Thus, Auger electrons have energies that are characteristic of the atom from which they arose and may be used for elemental identification.

2.1.4 Experimental set-up
A XPS spectrometer has 3 main parts: 1) X-ray source, 2) Concentric hemispherical analyzer, 3) Electron detector as shown in figure 2.2. X-ray source is a cathode (filament) and emits electron by heating it to 2-3 A current. The electrons pass through an electric field (10-15 KV) and are accelerated to a metal anode, for example Mg or Al. Emitted electrons hit the anode and emit the electrons from anode thus producing X-ray. After the electrons leave the sample they can be selected with an analyzer according to their kinetic energy and detected with a detector.
Figure 2.2: Experimental set-up of XPS: X-ray source, concentric hemispherical analyzer and electron detector.
2.2 Low Energy Electron Diffraction (LEED)

2.2.1 Introduction

LEED involves the use of an electron gun to bombard a sample with a beam of electrons, the energy of which can be controlled. Diffracted electrons travel away from the sample and pass through a set of retarding grids, which serves to select elastically scattered electrons, and after being accelerated by a high potential they impinge on a phosphor screen. This causes the screen to glow with intensity at each point on the screen proportional to the incident electron flux. LEED can give information quantitatively and qualitatively. In the first use, the intensities of the various diffracted beams are recorded as a function of the incident electron beam energy to generate so-called I-V curves which, by comparison with theoretical curves, may provide accurate information on atomic positions. In the second use, the diffraction pattern is recorded and analysis of the spot positions yields information on the size, symmetry and rotational alignment of the adsorbate unit cell with respect to the substrate unit cell.

2.2.2 Principle of the measurement

In LEED measurements a beam of electrons with a low energy (20-200 eV) incident normally to a sample which is single crystal and well ordered. So a back-scattered electron diffraction pattern can be generated as shown in figure 2.3. Only the elastically-scattered electrons contribute to the diffraction patterns; the lower energy (secondary) electrons are removed by energy-filtering grids placed in front of the fluorescent screen that is employed to display the pattern. Figure 2.4 presents a commercial LEED optics assembly.
Figure 2.3: A typical LEED experimental set-up.

Figure 2.4: LEED optics assembly produced by Omicron (one of the major commercial suppliers of surface science equipment).

2.2.3 Theory

Due to quantum mechanics, a beam of electrons can be regarded as a wave as it incidents normally on a sample and may be scattered by the surface atoms. The wavelength of electrons is given by the de Broglie relation:

$$\lambda = \frac{h}{p},$$
where $h$ is Planck constant ($6.62 \times 10^{-34}$ Js) and $p$ is the electron momentum which is given by:

$$p = mv = (2mE_k)^{1/2} = (2meV)^{1/2},$$

where $m$ is the mass of the electron [kg], $v$ the velocity [ms$^{-1}$], $E_k$ the kinetic energy and $V$ is the acceleration voltage [eV].

In order to detect the atomic spacing it is needed that the range of wavelengths of electrons employed in LEED experiments is comparable with the atomic structure. Consider, first, a one dimensional (1-D) chain of atoms (with atomic separation $a$) with the electron beam incident at right angles to the chain as shown in figure 2.5.

![Figure 2.5: Backscattering of a wavefront from one dimensional (1-D) chain of atoms.](image)

It is clear from the figure that there is a path difference in the distance the radiations from the scattering centers to a detector. In order that a constructive interference occurs when the scattered beams meet and interfere at the detector the following equation has to be satisfied:

$$d = a \sin \theta = n \lambda \quad (n \text{ is an integer}),$$

which is the Bragg condition. The observed LEED pattern is a scaled representation of the reciprocal net of the pseudo-2D surface structure which is defined by reciprocal vectors:

$$a_1^* \ & a_2^* \ (\text{for the substrate}) \ & b_1^* \ & b_2^* \ (\text{for the adsorbate})$$
The reciprocal vectors are related to the real space unit cell vectors by the scalar product: $a_1 \cdot a_2^* = a_1^* \cdot a_2 = 0$ and $a_1 \cdot a_1^* = a_2^* \cdot a_2 = 1$. Similar relations are hold for adsorbate overlayer structure. So the LEED pattern for a given surface can be obtained by superimposing the reciprocal net of the adsorbate overlayer (generated from $b_1^*$ and $b_2^*$) on the reciprocal net of the substrate (generated from $a_1^*$ and $a_2^*$). A simple example is the fcc(110) crystal and its reciprocal net as illustrated in figure 2.6.

Figure 2.6: fcc(110) crystal a), its reciprocal lattice b) and obtained LEED pattern c).
2.2.4 Overlayer structure

Adsorbed species on single crystal surfaces are able to form well-defined overlayer structures. There are two methods for specifying the overlayer structure of an adsorbate in relation to the underlying structure of the substrate. These methods are Wood's notation and the matrix notation. Wood's notation can be used when the two unit cells are of the same symmetry (the angle between \( b_1 \) & \( b_2 \) must be the same as between \( a_1 \) & \( a_2 \)). In this notation the lengths of the two overlayer vectors, \( b_1 \) & \( b_2 \) are specified in terms of \( a_1 \) & \( a_2 \) which is \(|b_1|/|a_1| \times |b_2|/|a_2|\). In matrix notation the vectors \( b_1 \) and \( b_2 \) of the adsorbate are related to the vectors \( a_1 \) and \( a_2 \) of the substrate using \((b_1 \ b_2) = (\ast\ast\ast\ast) (a_1 \ a_2)\) matrix format.

2.3 Temperature-Programmed Desorption

2.3.1 Theory and experimental set-up

Temperature programmed desorption is a technique used for studying surface reactions and molecular adsorption on surfaces which utilize temperature-programming to discriminate between processes with different activation parameters. In this method one or more molecular species adsorbed on the sample surface and while heating the sample in a controlled fashion (a linear ramp) the evolution of species from the surface back into the gas phase is monitored. In this method usually a quadrupole mass spectrometer (QMS) as shown in figure 2.7 is used and the whole process is carried out under computer control in order to monitoring the product. So it is possible to detect different desorbed molecules concerning their mass/charge (m/z) ratio as a function of the desorption temperature and intensity. The area under a peak is proportional to the desorbed particles and the position of the peak (peak temperature) is related to the enthalpy of adsorption, i.e. to the strength of binding to the surface.
Figure 2.7: A quadrupole mass spectrometer.
2.4 Attenuated Total Reflection Infrared Spectroscopy (ATR-IR)

2.4.1 Theory

Attenuated total reflection infrared spectroscopy was invented by Harrick [6] and Fahrenfort [7] in the 1960’s. The method is suitable for adsorption studies and is one of the techniques for characterization of catalysts.

In this method the infrared radiation is passed through an internal reflection element (IRE) which is an infrared transparent crystal of high refractive index (n_{IRE}) and is in contact with the sample. The principle of the method is illustrated in figure 2.8. The infrared radiation propagates through the IRE element which has a higher refractive index (n_{IRE}) at an angle of incidence (\theta) which is larger than the critical angle (\theta_c) and a total reflection occurs at the interface, where an evanescence standing wave is formed that penetrates into the optically thinner medium. If this medium is infrared absorbing, the standing wave is attenuated.

\[ d_p = \frac{\lambda}{2\pi(n_2^2 - n_{IRE}^2)^{1/2}} \]

Figure 2.8: A typical coordinates system in an ATR-IR set-up. A trapezoidal internal reflection element with 5 reflections and an angle of incident of \(-45^\circ\) is shown. The parallel and perpendicular components of the electric field \(E_0\) of the incident radiation are also illustrated.

The penetration depth (\(d_p\)) as shown in figure 2.9, is the distance where the amplitude of the electric field of the standing wave decays to 1/e of its value at the interface according to:

\[ d_p = \frac{\lambda_{IR}}{2\pi(n_2^2 - n_{IRE}^2)^{1/2}} \]
where $\lambda_1 = \lambda / n_{\text{IRE}}$ is the wavelength in the denser medium and $n_{21} = n_2 / n_{\text{IRE}}$. Typically, $d_p$ is in the order of 1/10 of the incident wavelength so that a thin layer of less than 1 $\mu$m is sampled at the interface.

![Diagram](image)

**Figure 2.9:** Penetration depth ($d_p$) is the distance where the amplitude of the electric field of the standing wave decays to 1/e of its value at the interface.

For bulk materials the degree of coupling between the evanescent wave and the absorbing medium is given by the effective thickness ($d_e$), which is a function of the magnitude of the electric field $E_0$, the refractive indices and the angle of incidence: $d_e = n_{21} E_0 d_p / 2 \cos \theta$.

The effective thickness expresses the equivalent path length in hypothetical transmission measurements, which yields the same absorption obtained in an ATR-IR experiment. The very short path length used in ATR-IR spectroscopy, implicit in $d_e$, makes this technique surface sensitive and hence suitable for characterization of heterogeneous catalysts.

### 2.4.2 Experimental set-up

All *in situ* ATR-IR measurements were carried out using the home-built flow-through stainless steel cell shown in figure 2.10. For the ATR-IR experiments commercial trapezoidal Ge internal reflection elements have been used. The transparent window for germanium extends between 5500 and 600 cm$^{-1}$ in the infrared region. The relatively high value of refractive index ($n=4.1$) makes Ge a very good material for studying processes occurring at surfaces.
The spectrometer is equipped with a liquid nitrogen cooled medium band MCT (HgCdTe) photodetector. Using unpolarised light, the spectra are presented in absorbance unit as $A = -\log(I/I_0)$, where $I$ and $I_0$ are the reflected intensity of the sample and reference, respectively. A Thermostat is used to cool or heat the cell. Two water-cooled jackets have been fixed on the two sides of the ATR-IR cell and the temperature was measured with a thermocouple positioned on the bottom part of the cell.

Gases and solutions were passed through the cell according to the scheme of the apparatus shown in figure 2.11. Solvent and solutions were stored in separate reservoirs equipped with glass frits where they could be saturated with a range of gases. A microdosing pump allowed pumping the saturated solutions through the cell.
2.5 Preparation of thin films

Preparation of thin films for ATR-IR experiments was performed in a Balzers BAE-370 vacuum coating system. The Ge crystal has been coated at room temperature with aluminum oxide and metal (Pt, Pd and Au) thin films by electron beam physical vapor deposition (EB-PVD). Raw materials in form of wires (Pt, Pd and Au) and tablets (Al₂O₃) have been used as target. The coating material was heated in a graphite crucible by means of an electron beam generated with an incandescent filament in vacuum of about 1.5x10⁻⁵ to 10⁻⁶ mbar for a metal and a metal oxide. The film thickness was measured with a quartz crystal sensor (microbalance). The distance between the evaporation source and the substrate was about 33 cm resulting in even films over the entire Ge crystal. Figure 2.12 shows a EB-PVD equipment.
Figure 2.12: Scheme of the EB-PVD equipment.

At first the substrate was masked with a shutter until the desired evaporation rate was achieved. In order to have a constant deposition rate, 2 to 10 nm were deposited with the closed shutter for the metal and metal oxide. Then the shutter was opened allowing deposition of the thin film on the substrate. Once the desired thickness had been reached as determined with the microbalance, the shutter was closed, the electron gun switched off and the system was allowed to cool to room temperature before opening to the atmosphere or starting with the deposition of the next material. The crucibles were placed in the rotating four-packet unit of the electron gun thus allowing deposition of several metal oxide and metal films without exposition to atmosphere. The deposition rate for the metals and metal oxides was set to 0.1 to 1.0 Å/s depending on thickness of metal film.
2.6 References:


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Chapter 3

Homochiral conglomerates and Racemic crystals in two dimension: Tartaric Acid on Cu(110)

3.1 Introduction

Chiral molecules crystallize from racemic solution either into homochiral conglomerates or into racemic crystals containing equal number of left- and right- handed molecules [1, 2]. However, the mechanism of the transfer of chirality from single molecules to the resulting enantiomorphous crystals is poorly understood [3]. This is actually part of the general problem that macroscopic crystal shapes are still not predictable from the molecular structure [4]. In particular the solvent or impurities influence the shape of a macroscopic crystal to a large extent. Studying well-defined 2-D chiral model systems on surfaces without such influences, therefore, can help to get more insight into the transfer of chirality from single molecules into larger ensembles [5]. Although the vast majority of chiral molecules crystallize as non-separated racemates, it has been predicated that two-dimensional enantioseparation on a surface should occur more easily than in three-dimensional crystals [6]. Due to confinement in the plane certain symmetry elements, e.g., center of inversion or the glide plane parallel to the surface, are precluded and enhanced chiral interactions are expected [7]. Indeed, only few examples for racemic 2-D crystals are known [8] and most experimental studies confirmed the scenario of spontaneous lateral resolution of chiral molecules into homochiral 2-D crystallites, observed as two-
dimensional enantiomorphism [9]. It is noteworthy here that, due to symmetry breaking upon adsorption, achiral molecules can also form 2-D chiral motifs on the surface [10].

The adsorption of enantiopure (2R,3R)-TA on Cu(110) has been studied in great detail previously [11]. Those studies showed that at room temperature TA is adsorbed as monotartrate with only one carboxylate group interacting with the surface (figure 3.1a). After thermal activation, however, the second carboxylate group also interacts with the substrate, i.e., annealing to 405 K leads to formation of bitartrate species (figure 3.1b). In its sawbuck-like adsorbate geometry, the bitartrate molecule is distorted into a zigzag conformation, as predicted in theoretical studies [12] and experimentally [13]. With increasing coverage, a rearrangement into monotartrate occurs, since this allows a higher adsorbate density [14]. In both species, each carboxylate directly interacts with two copper atoms of the close-packed row along the [1-10] direction. At these temperatures, the dissociated carboxyl hydrogen atoms are not stable on the surface and desorbs as molecular hydrogen. Several ordered surface phases have been observed for the (2R,3R)-enantiomer at 405 K: a (9 0, 1 2) bitartrate phase, a (4 0, 2 1) phase, and a (4 1, 2 5) phase at saturation [11].

The (9 0, 1 2)- and the (4 1, 2 5)-lattices are 2-D-enantiomorphous, i.e., they lack mirror symmetry. The (2S,3S)-enantiomer forms the respective mirror lattices, i.e., (9 0, -1 2) and (-4 1,-2 5), if reflection with respect to the [001] substrate direction is considered. The (4 0, 2 1) lattices of the two enantiomers, however, are undistinguishable, since this lattice expresses no enantiomorphism. In this chapter the ordered adsorbate lattices formed by racemic TA on Cu(110) at 405 K is described and we discuss the results with respect to the findings for the enantiopure TA system.
3.2 Experimental

The experiments have been carried out in a stainless steel ultra-high vacuum (UHV) chamber \((p = 5 \cdot 10^{-10}\text{ mbar})\) equipped with facilities for temperature programmed desorption (TPD) using a quadrupole mass spectrometer, low energy electron diffraction (LEED), and X-ray photoelectron spectroscopy (XPS). The polished copper(110) single crystal (Matek, Jülich) could be resistively heated to 1000 K and liquid-nitrogen cooled to about 85 K. Cleaning of the Cu surface was achieved by prolonged argon ion bombardment in vacuum \((E = 600\text{ eV}, \ p_{\text{Ar}} = 2 \cdot 10^{-5}\text{ mbar}, \ I = 4 \mu\text{A/cm}^2)\). The sputter-damaged surface was annealed at 1100 K for one minute. After several cycles of this treatment, the surface did not show any impurities in XPS and the LEED pattern consisted of a sharp and bright \((1\times1)\) structure with low background intensity. This cleaning procedure was also applied after every TPD experiment (chapters 4 and 7).

Tartaric acid (Aldrich 99.95%) deposition was performed with a homemade Knudsen cell. The Cu-crystal was exposed to the collimated molecular beam effusing from the Knudsen cell which was held at 120°C during sublimation. For the preparation of bitartrate and the \((4\ 0, \ 2\ 1)\)- and \((4\ 1, \ 2\ 5)\)-monotartrate lattices, the Cu sample was held, if not mentioned otherwise, at 405 K during deposition. Relative coverages have been monitored via XPS by measuring the C 1s signal plus normalization to the Cu 3s substrate peak. For the absolute coverage calibration, XPS spectra were taken for the LEED structures which have been previously characterized by Ortega Lorenzo et al. using STM, LEED and FTIR [11]. The sample temperature was measured by a chromel-alumel thermocouple and controlled by a special regulator and ramp generator. The TPD spectra were acquired with a linear heating rate of 4.1 K/s with the surface normal in line of sight of the mass spectrometer. The heating rate variation experiments, from which activation barriers were determined, have been performed with heating rates from 0.8 K/s to 8.5 K/s. Angle resolved TPD
experiments showed no differences in the intensity distribution of different decomposition products. The heats of sublimation for racemate and the pure (S,S)-enantiomer were calculated via the Clausius-Clapeyron equation. The sublimation rates with varying temperatures of both substances were determined with a mass spectrometer mounted in line of sight of the Knudsen cell.

3.3 Results

3.3.1 Tartaric Acid

Tartaric acid exists in three different forms: the natural bi-acid form \((\text{C}_4\text{H}_6\text{O}_6)\), the mon.tartrate form when one of the carboxylic acid groups has deprotonated to give a carboxylate moiety and the bitartrate form in which both acid groups have deprotonated. Figure 3.1 shows the molecular species formed by adsorption of tartaric acid on Cu (110) at 405 K. At low coverage b) we obtain a doubly deprotonated bitartrate and with increasing coverage a) a singly deprotonated mon.tartrate at saturation coverage is created [11].
Figure 3.1: Molecular species formed by adsorption of tartaric acid on Cu (110) at 405 K: a singly deprotonated monocartrate at saturation coverage (a), and a doubly deprotonated bitartrate at low coverage (b).

3.3.2 Adsorption at 405 K: appearance of (9 0, ±1 2) superposition

Figure 3.2 presents the two LEED patterns observed after exposure of the Cu(110) surface, held at 405 K, to racemic Tartaric Acid. A (9 0, ±1 2) lattice forms at lower coverage (figure 3.2 left), while at saturation coverage a (4 0, 2 1) lattice is observed. These sharp superstructure diffraction spots are captured at an electron energy of 20 respectively 38 eV. Both lattices possess the $C_{2v}$ mirror symmetry of the substrate.
3.3.3 Comparison of the coverage for pure and racemic tartaric acid

In order to evaluate the difference in saturation coverage, we compared the signal intensities of the C 1s XPS peaks and of the TPD curves for racemat and the pure enantiomers. Figure 3.3 shows the respective exposure – coverage $\theta$ functions. Indicated dashed lines are the theoretical coverages of the three lattice structures. For the $(9,0,\pm1,2)$ and $(4,0,2,1)$ lattices $1/6$ and $1/4$ molecules per Cu-surface atom have been proposed, respectively [10]. Normalization between both experimental methods has been performed for the values at saturation. For the absolute coverage calibration, the XPS signal area obtained for the racemic $(4,0,2,1)$ lattice has been assigned to a value of $\theta = 0.25$. Because racemic Tartaric acid has a higher heat of sublimation (table 3.1), and all compounds were sublimated at the same temperature, the racemic TA-flux per time was lower, which explain the smaller coverage increase for the racemat as shown in figure 3.3.
Figure 3.3: Comparison of the coverage – exposure relation for pure (2R,3R)-TA (squares) and racemic TA (circles). The data points represent the signal areas obtained from TPD (CO₂ evolution, closed symbols) and XPS (C 1s, open symbols) experiments. The data from both methods were normalized to each other on the average of the values at saturation. Coverage calibration was done by assigning the normalized C 1s XPS intensity from the (4 0, 2 1)-racemic lattice at saturation to a coverage of 0.25. The theoretical coverages for the lattice structures (dashed lines) and the coverage regimes for which these are observable in LEED (arrows) are indicated.
Table 3.1: Comparison of molecular density and thermodynamic stability of TA racemate and enantiomers for the crystalline bulk and the monolayer lattices: The 3-D values for the melting points (m.p.) and the molecular volumes (V-mol) were taken from the literature (references indicated), while the values for the 3-D sublimation enthalpy (ΔH_{sub}), the activation energy for decomposition (ΔE_{dec}), the pre-exponential factor (k) and the saturation coverage (θ_{max}) are from this work.

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<td>129 [17, 18]</td>
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<td>V-mol [Å³]</td>
<td>k [s⁻¹]</td>
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3.4 Discussion

The observed (9 0, ±1 2) LEED patterns must be explained as a superposition of the two enantiomorphous bitartrate lattices of the enantiomers [19]. Therefore, we conclude that this LEED patterns reflects a lattice structure in which the enantiomers are laterally separated into homochiral (9 0, 1 2)-(R, R)-TA and (9 0, -1 2)-(S, S)-TA domains on the surface. The primary electron beam probes an area that contains both enantiomorphous homochiral lattices. The size of homochiral domains can roughly be estimated from the LEED pattern by taking the instrumental resolution, the so-called transfer width, into account. The fact that for an electron energy of 20 eV sharp superstructure diffraction spots are observed, indicates that the domains must have a diameter of more than 20 nm on average [20]. In principle, this LEED pattern might be also explained by the formation of diasteriomeric pairs, which form the two mirror domain by chance. Due to an oblige angle of the adsorbate mesh with respect to the substrate lattice, two equal alignments are possible which can be interconverted only by the mirror operation. However, this scenario was found to be very unlikely in theoretical studies performed on this system. Adsorption of the (S, S)-
enantiomer into the (R, R)-(9 0, 1 2) adsorbate grid is 10 KJ/mol higher in energy than the homochiral arrangement [12]. As already mentioned, the none-nantiomorphous (4 0, 2 1) lattice has been observed for the pure enantiomers as well [11]. This is particularly noteworthy since in three dimensions no case is known so far in which a chiral molecule crystallize in an achiral crystal lattice.

In this 2-D monobartrate lattice the lateral interactions must be substantially lower than for the bitartrate, and the outcome of the long-range structure is governed by the substrate geometry rather than the molecular configuration. The identical (4 0, 2 1) lattices for racemate and pure enantiomers do not allow a conclusion on lateral separation in the racemic monolayer. However, the fact that for racemic TA the (4 0, 2 1) mesh is the monolayer saturation coverage, while for the pure enantiomers a further structure is established at higher coverage, is a strong indication for a racemic (4 0, 2 1) lattice. For homochiral monobartrate crystallites, we could expect, in analogy to bitartrate, the observation of a conglomerate (±4 1, ±2 5) lattice upon further adsorption.

From XPS calibration curve we observed that the saturation coverage for the (R,R)-enantiomer lies slightly above the saturation coverage for the racemate, just outside the estimated error margin of the XPS method (±5%). In order to understand why a higher coverage is achieved for the pure enantiomers, we briefly discuss lattice structures for the enantiopure monobartrate. Figure 3.4 presents tentative structure models for the (4 0, 2 1) and the (4 1, 2 5)-lattice, respectively. The unit cells are indicated. For the (4 0, 2 1) grid one molecule per unit cell, i.e., one molecule per four Cu surface atoms (θ=0.25), is the only reasonable coverage value for a monobartrate species bound to two copper atoms. For the enantiomorphous (4 1, 2 5) lattice, on the other hand, either five or six atoms per unit cell are possible, with coverage of 0.278 (θ=5/18) and 0.33 (θ=6/18), respectively. Our XPS and TPD results show saturation below 0.3 and thus clearly favor a lattice with 5 molecules per unit cell. The (4 1, 2 5) structure model shown in figure 3.4 takes the formation of monobartrate dimmers into
account, as observed via infrared spectroscopy [11]. The alternation of monotartrate dimers and monomers along the $b_1$ adsorbate lattice direction is a chiral motif and has previously been suggested for this lattice as well as for an enantiomorphous $(40, 23)$ monotartrate lattice generated at room temperature [11].

![Figure 3.4: Tentative structure models for the $(40, 21)$ lattice (left) and the $(R,R)-(41, 25)$ lattice (right). The absolute coverages are 5 molecules per 20 substrate atoms and per 18 substrate atoms, respectively. For the $(41, 25)$ lattice, the formation of monotartrate dimers, alternating monotartrate monomers along the $[221]$ direction, is proposed.]

The arrangement of the monomers between the monomer-dimer chains shown in figure 3.4 is one of few reasonable choices. This lattice model rationalized why coverages higher than $\theta=0.25$ are achieved for the enatiopure layer, but not observed for the racemic mixture. An additional TA molecule can only be adsorbed on the site between four monotartrate molecules in the $(40, 21)$ lattice layer if it has the same handedness. This shows that the racemic $(40, 21)$ lattice layer is not separated into homochiral domains, because no further molecule can be added. Therefore, the formation of the enantiopure $(41, 25)$ lattice can be considered as a process in which chiral recognition takes place. Since formation of homochiral dimers was only found for coverages above $\theta=0.25$ in the above-mentioned infrared studies, and for the racemate no lattice structure with $\theta>0.25$
is observed here, we conclude that the chiral recognition is based on the impossibility of heterochiral dimer formation close to monolayer saturation.

3.5 Conclusion
Depending on the coverage, tartaric acid can either become laterally enantioseparated or form a racemic lattice as shown in figure 3.5. In its bitartrate form at lower coverages homochiral enantiomorphous lattice structures are generated, while the monotortrate species present at higher coverage crystallizes into a racemic lattice. Furthermore, a higher lattice density is achieved for the pure enantiomers at saturation coverage. This observation is in contrast to the three-dimensional bulk of crystalline tartaric acid, where the racemic lattice is denser.
Figure 3.5: Local molecular adsorbate geometry determines chiral intermolecular interactions on surfaces. Racemic tartaric acid undergoes lateral enantioselective self-separation into homochiral domains on a Cu(110) surface if adsorbed as doubly deprotonated bitartrate. The singly deprotonated monotertrate species at higher coverages forms a heterochiral lattice.
3.6 References

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Temperature Programmed Desorption of Tartaric Acid on Cu (110)

4.1 Introduction

Molecular recognition of chiral molecules on the surfaces plays an important role in processes like enantiometric separation of chiral compounds [1], crystal growth [2, 3], enantiospecific sensors [4], and heterogeneous asymmetric catalysis [5]. Despite this importance, the mechanism of chiral recognition in these surface processes is poorly understood [6]. Stereospecific interactions with chiral kink sites on surfaces have been also observed for the oxidation of glucose on Pt(643) and for the thermally induced desorption of methyl cyclohexanone on Cu(643) [7]. Here, we report the observation that the handedness of adjacent molecules influences the thermal stability of monotartrate species on the Cu(110) surface. By means of temperature-programmed desorption (TPD) the rapid decomposition, so-called "surface explosion", of monotartrate has been investigated for racemic tartaric acid and the pure enantiomers. The expression "surface explosion" was coined for an autocatalytic increase in reaction rate in thermally induced surface reactions occurring in a very narrow temperature range [8]. This phenomenon has been observed in thermal desorption spectra of decomposition products of formate and acetate species on single-crystal surfaces [9-11] and supported metal catalysts.
Using molecules with mixed or pure chirality, we demonstrate in this chapter that within the close-packed lattice structure the stability of a molecule is influenced by the structure of adjacent molecules, which adds a steric component to the activation barrier.

4.2 Experimental

Experimental methods used in this chapter were the same as presented in chapter 3.

4.3 Results

4.3.1 Temperature programmed desorption of (R,R)-Tartaric acid

Figure 4.1 shows the TPD mass spectra for carbon dioxide (44 amu) formed by after desorption of (R,R)- and racemic TA at 405 K. As molecular species desorbing from the surface, in addition to carbon dioxide, water, and hydrogen have been also identified, all evolving at the same temperature¹. In addition, X-ray photoelectron spectroscopy (XPS) revealed a build-up of carbon on the surface. With increasing coverage, a strong peak shift to higher temperatures is observed. In the case of (R,R)-TA, the three lowest-coverage peaks at about 450 K represent the decomposition of the bitartarate species. The transition to the monotartrate layer is accompanied with a strong increase in desorption temperature as presented by five desorption curves with peak temperatures ranging from 460 to 510 K. Once the (4 0,2 1) structure is completed, a peak with an unprecedented small full width at half-maximum (FWHM) of only 1.6 K is observed (see insert). For the transition from (4 0,2 1) to (4 1,2 5) the peak temperature rises by 3 K, and the FWHM is increased to 2.2 K.

¹ We also observed CO at 28 amu. However, this peak is assigned as fragment of carbon dioxide generated in the mass spectrometer.
Figure 4.1: Reaction induced carbon dioxide desorption spectra for racemic TA (top) and (2R,3R) TA (bottom) with increasing coverage. The peaks for which LEED patterns of best quality have been observed are indicated. The inset illustrates the change in peak shape during the conversion from the (4 0,2 1) lattice to the (4 1,2 5) lattice for the pure enantiomers. The desorption peaks at high coverages are very narrow, indicating an autocatalytic decomposition reaction.

4.3.2 Temperature programmed desorption of Racemic-Tartaric acid

After exposure of the sample to racemic TA at 405 K, a superposition of the two enantiomorphous (R,R)-TA-(9 0,+1 2) and (S,S)-TA-(9 0,-1 2) diffraction patterns was observed via low-energy electron diffraction (chapter 3). Neglecting domain boundary effects, we therefore do not expect to find differences in the decomposition kinetics between racemic mixture and enantiopure structures. Comparing the respective TPD signals confirms this conclusion (figure 4.1 and figure 4.2a). For the low coverage bitartrate lattices, however, no differences between racemat and pure enantiomers are observed. Close to saturation, the desorption peaks become extremely narrow. In contrast to the pure enantiomers, further exposure to racemic TA leads only to the formation of a (4 0,2 1) LEED pattern.
Figure 4.2: (a) Mass 44-TPD signals representing the decomposition of (R,R)- and racemic bitartrate in the (9 0,1 2) structure. No differences in desorption peak temperature are observed. (b) CO$_2$-TPD spectra for the high coverage monotartrate structures prepared at 405 K. The higher decomposition temperatures are found for the pure enantiomers. A ‘racemic’ (4 0,2 1) structure prepared after consecutive dosing of the pure enantiomers shows no substantial differences to the (4 0,2 1) structure prepared via direct exposure to the racemate. The highest stability is observed for the (4 1,5 2) structure. The enantiopure (4 0,1 2) structure exhibits an 8 K higher decomposition peak temperature than the racemic (4 0,2 1) structure.

The surface coverage for the enantiopure (4 1,2 5) structure, as determined via XPS and TPD, was found to be about 10% higher than the racemic and enantiopure (4 0,2 1) structures (chapter 3). With lateral enantioseparation involved, however, the formation of the two enantiomorphous (±4 1,±2 5) structures must be expected for the racemate, leading to a higher coverage than θ = 0.25. Desorption peaks from (4 0,2 1)-monotartrate structures are shown in figure 4.2b. Clearly, the pure enantiomer shows a higher decomposition temperature than the racemate. The activation energies for the reactions, as determined by systematic heating rate variation [12], are 142 ± 3 and 162 ± 3 kJ/mol for racemate and (R,R)-TA, respectively. The comparison of the equal-coverage (4 0,2 1) structures shows an 8 K higher decomposition temperature for monotartrate in the pure enantiomer lattice. Exposure of (R,R)-bitartrate (9 0,1 2) lattice at the coverage of θ = 1/8 to pure (S,S)-TA also shows no

\[^2\] Pre-exponential factors were 10$^{15}$ and 10$^{14}$ sec$^{-1}$ for (R,R) and racemic TA.
difference to racemic TA. In addition it did not lead to other lattice structures nor to higher coverages.

### 4.4 Discussion

On Cu(110), TA undergoes decomposition into gasphase-stable products like CO$_2$, H$_2$O and H$_2$ after the thermal decomposition reaction. We also observed residual carbon on the surface via XPS. With the exception of carbon monoxide, which we assign as fragment of CO$_2$ generated in the mass spectrometer, no other products have been detected. Consequently, the following surface decomposition reaction for mono-and bitartrate is proposed:

\[
\text{HOOC-} \xrightarrow{\text{OH}} \text{C} \xrightarrow{\text{H}} \text{C} \xrightarrow{\text{C}} \text{C} \xrightarrow{\text{O}} \xrightarrow{\text{O}} 2\text{CO}_2 + 2\text{H}_2\text{O} + 2\text{C} + 1/2\text{H}_2
\]

We observed a narrow peak close to saturation. This phenomenon is known for certain decomposition reactions of carboxylic acid on metallic surfaces. In order to see this behavior, the molecular species must be stabilized above the thermal stability of the single molecule on the surface. Therefore, this effect is observed for close-packed adsorbate systems, not allowing upper parts of the molecule to further interact easily with the substrate. The decomposition follows autocatalytic kinetics, because free surface sites serving as catalyst for the reaction are, in turn, generated upon decomposition. Hence, the reaction rate depends on the coverage ($\theta$) and on the number of free surface sites $1-\theta$.

\[
d\theta/dt = A \cdot \theta \cdot (1-\theta) \cdot e^{-k/RT},
\]
Once the decomposition reaction in the close-packed lattice starts, the newly created free surface sites cause an exponential increase in turnover rate. Because the TA decomposition temperature is higher than the desorption temperature of the gasphase-stable reaction products, these desorb instantaneously and cause a relatively large pressure rise above the surface in a small temperature interval. This led to the expression "surface explosion" for this type of surface reaction. The difference between the decomposition temperatures of the racemic (4 0,2 1) and enantiopure (4 0,2 1) can be explained by a chiral ensemble effect. The reaction rate depends not exclusively on the number of molecules and on the number of free surface sites, but is also influenced by the molecular structure of adjacent molecules. Because coverage and periodicity are identical in both (4 0,2 1) lattices, the difference in thermal stability between pure enantiomers and racemat must be due to homochiral lattice in the racemic layer. The observation of a narrower "surface explosion" peak for pure enantiomer compare to racemic is an indication for higher heterogeneity in this transition regime. We recall that the conversion to monotartrate is induced when additional TA is adsorbed onto the homochiral bitartrate domain. The bitartrae species become hydrogenated by "incoming" tartaric acid molecules. The then released substrate binding site becomes occupied by the TA molecules which served as hydrogen donor and actually induced the conversion reaction. This process is independent of the handness of the newly adsorbing TA molecule and consequently leads to a racemic lattice upon exposure to the racemic mixture. In order to test this local racemic mixing model, we exposed a (R,R)-bitartrate (9 0,1 2) lattice at a coverage of \( \theta = 1/8 \) to pure (S,S)-TA as shown in figure 4.2b. This experiment led to a (4 0,2 1) lattice with a saturation coverage of \( \theta = 1/4 \), as determined via XPS. Exposure to more (S,S)- or (R,R)-TA did not lead to other lattice structures nor to higher coverages. In addition the TPD decomposition temperature of this layer was almost identical to the one of the racemic layer. This shows that, no matter if homochiral domains of opposite chirality or a complete bitartrate layer
are present at the beginning, the outcome for a racemic monotaartrate system is the same: a heterochiral (4 0,2 1) saturation lattice. For the monotaartrate lattices generated at room temperature we observed a similar situation: while for (R,R)-TA an enantiomorphous (4 0,2 3) lattices follows a (4 0,2 1) with increasing coverage, the saturation lattice for the racemic is only (4 0,2 1).

The difference of 3 k between the (4 0,2 1) to the (4 1,2 5) can be explained by the higher activation barrier for an interaction with the surface at higher surface density.

To start the decomposition reaction, either an OH- or the COOH-group must be brought into contact with the surface. Besides the availability of reactive surface sites, the local rearrangement or the unhinging of a single monotaartrate from the lattice comes into play. The higher activation barrier for breaking down the close-packed structure, therefore, stems from lateral interactions between the molecules. It has been pointed out recently that the formation of 2-D enantiomorphous bitartrate structures is mediated by substrate rather than governed by intermolecular hydrogen bonds [13, 14]. Although racemate and pure enantiomer form the same monotaartrate lattice structure, i.e., the substrate geometry governs the self-assembly, the formation of intermolecular hydrogen bonds, however, is influenced by the handedness of the molecules and can still have an influence on the lattice stability. In particular, long-range hydrogen-bonded chain structures cannot be established within the (4 0,2 1) heterochiral structure as easily as in the respective homochiral arrangement. The observed higher stability for the enantiopure lattice is in contrast to that of 3D tartaric acid crystals and to most of the other chiral 3D crystals. However, it agrees with the fact that at lower dimensionality homochirality is favored, as observed for the self-assembly of biomolecules via hydrogen bonds.

Interestingly, the system of achiral succinic acid (HOOC-CH₂-CH₂-COOH) on Cu(110) is very similar to racemic TA here. For the bisuccinate, a (9 0,±1 1) lattice has been observed. Due to symmetry breaking interaction with the surface,
this molecule becomes chiral upon adsorption and forms enantiomorphous domains. Because no chiral preference is given, the global outcome is achiral, i.e., both enantiomorphous lattices coexist on the surface and appear as superposition in LEED, just like racemic TA in its bitartrate form. Also identical to the racemic monotartarte here is the (4 0,2 1) or c(4x2) lattice that is formed by the monosuccinate.

Finally we discuss different thermodynamical and structural properties of the racemat and pure enantiomers and compare these for the TA bulk and the 2D crystal on Cu(110) (chapter 3, table 3.1). Stability and density of the enantiopure lattices, with respect to the racemic systems, are higher for the 2D crystal, but lower in the 3D bulk. The pre-exponential factor and the activation energy of the TA decomposition reaction were determined via systematic heating rate variation. Both, the pre-exponential factor and the activation energy are higher for the pure enantiomer lattice. The homochiral lattice is stabilized by an extra 20 kJ/mol with respect to the racemic lattice. The stiffer lattice due stronger lateral binding is also reflected in ten times higher frequency factor. In order to react with the catalytically active substrate sites, an upper part of the molecule must be unhinged from the molecular lattice, and obviously this initial step is influenced by the chirality of the adjacent molecules. Since succinic acid is thermally much more stable than tartaric acid on Cu(110), we further conclude that in initial step of the thermally induced decomposition the OH groups on the TA molecule is involved.
4.5 Conclusion

Compared to the pure enantiomers, the bitartrate lattice are identical in stability, while the racemic monotaartrate lattice has lower stability. The reason for this difference is the fact that within the heterochiral structure, hydrogen-bonded chains cannot be established as easily as in the homochiral arrangement. This observation is in contrast to the three-dimensional bulk of crystalline tartaric acid, where the racemic lattice has a higher thermal stability than the one of the pure enantiomers.
4.6 References

Temperature programmed desorption of tartaric acid on Cu(110)
Chapter 5

CO Adsorption from Liquid Phase on Bimetallic Pt–Au and Pd–Au Surfaces

5.1 Introduction

The major significance of the use of bimetallic surfaces for heterogeneous catalysis is that binary systems often exhibit deviations in terms of catalytic activity and selectivity compared to the individual components [1]. The catalytic properties of noble metals used for hydrogenation reactions have been often tuned upon promotion or formation of bimetallic particles and excellent results have been demonstrated for chemoselective hydrogenation reactions [2, 3]. Although the use of gold for hydrogenation reactions is limited [4] owing to the very high energy barrier against hydrogen dissociation [5], Au has been reported in combination with Pd and Pt for hydrogenation reactions [6-9]. In general, bimetallic catalysts have not yet received much attention in the even more demanding liquid-phase enantioselective hydrogenations of C=O and C=C bonds [10]. This class of reactions requires the surface modification by adsorption of a chiral organic molecule which plays the role of the docking site for the prochiral carbonyl or alkene reactant. Pd-Pt catalysts [11] have been tested for the enantioselective hydrogenation of $\alpha$-ketoesters over Pt/Al$_2$O$_3$ modified by cinchona alkaloids [12, 13]. Based on catalytic data it was proposed that formation of a bimetallic surface greatly reduced the fraction of species of chiral modifier responsible to impart enantioselectivity. Recently, promotion of Pt by Bi and S has been reported to modify undesired reaction pathways and to preferentially direct adsorption of the chiral modifier towards specific sites [14].
On the other hand, adsorption of methylacetoacetate (MAA) [15] and tartaric acid [16] on Ni-Au bimetallic surfaces used for the enantioselective hydrogenation of β-ketoesters on tartaric acid modified Ni [17] has been spectroscopically investigated. Alloy formation has been shown to greatly affect the adsorption behaviour of the chiral modifier and of MAA compared to the unmodified Ni(111) surface. There is no doubt that the use of bimetallic surfaces is of interest to discover new catalytic systems based on the chiral modification of a metal surface, as it has been in the past for chemoselective hydrogenations. Characterization of bimetallic surfaces using traditional methods is complicated by the nature of the metal-metal interaction and because of the microscopic range of this interaction. Among the numerous methods available for the characterization of bimetallic surfaces, adsorption of carbon monoxide represents an efficient tool in order to gain information about the surface structure including both morphological and electronic aspects [18]. CO shows a characteristic dependence of adsorption mode upon coordination, which markedly changes upon variations in the environment of the metallic atoms, i.e. upon change from metal to metal and from metal surface to composite metal surface.

Owing to the improved sensitivity with respect to HREELS, RAIRS has been the preferred tool for investigating CO adsorption on planar single metal surfaces under UHV conditions. On the other hand, the investigation of metal surfaces in contact with a solution requires the use of spectroscopic techniques enabling the efficient subtraction of the large signals of the bulk solvent from the weak features originating from species populating the surface. Sum frequency generation (SFG) [19] and attenuated total reflection infrared (ATR-IR) spectroscopy are two such techniques.

The aim of this chapter is to elucidate the surface properties of bimetallic films prepared using electron beam vapour deposition of Au, Pt and Pd. Surface composition and morphology have been investigated by X-ray photoelectron
spectroscopy (XPS) and atomic force microscopy (AFM), respectively. The adsorption properties of the surfaces are probed by ATR-IR spectroscopy using CO as the adsorbate in the presence of CH$_2$Cl$_2$ solvent.

5.2 Experimental

5.2.1 Materials

Dichloromethane solvent (Baker) was stored over 5A molecular sieves. N$_2$ (99.995 vol%) and H$_2$ (99.999 vol%) gases were purchased from PANGAS, and CO (0.5 vol% in argon) from Sauerstoffwerk Lenzburg. Pt (99.99%), Pd (99.959%) and Au (99.99%) wires and Al$_2$O$_3$ (99.3%) tablets used as a target for electron beam vapor deposition (EB-VD) were supplied by Umicore.

5.2.2 Thin film preparation and characterization

Thin model films were prepared by EB-VD onto the trapezoidal Ge internal reflection element (IRE, 52 × 20 × 2 mm, 45° angle of incidence, Komlas) used for ATR-IR spectroscopy in a Balzers BAE-370 vacuum system equipped with a turret allowing the sequential deposition of four different materials without breaking the vacuum. The methodology has been described in detail elsewhere [20]. Briefly, the materials were evaporated from a graphite crucible using an electron beam (8 kV, to 0.15 mA) at a base pressure of about 1.0 × 10$^{-5}$ mbar and at evaporation rates of 0.5 and 1.0 Å/s for the metals and for Al$_2$O$_3$, respectively. The IRE was polished with 0.25 μm diamond paste after use and thoroughly cleaned with ethanol. Typically, 100 nm Al$_2$O$_3$ was deposited on Ge followed by the metal(s). The mass thickness of each film was measured with a sputtering quartz crystal sensor. Two series of samples were prepared for both Pt and Pd in which the metal thickness was 0.2, 0.5, 1.0 and 2.0 nm. The first series is represented by the monometallic samples, named as M02, M05, M10 and M20, where M is the metal symbol (Pt or Pd). In the second series Pt or Pd was
CO adsorption from liquid phase on bimetallic Pt–Au and Pd–Au surfaces

deposited on 1 nm Au in addition to Al₂O₃ (MAu02, MAu05, MAu10 and MAu20).

The dependence of the composition of the thin films from the metal thickness was investigated using XPS. Photoelectron spectra were acquired on a Physical Electronics (PHI) Quantum 2000 photoelectron spectrometer. The samples were exposed to a monochromatized X-ray (Al Kα = 1486.6 eV) beam with a diameter of 100 μm. Low-energy electrons and argon ions were used simultaneously to partially compensate electrical charging of insulating surface areas during analysis. The spectrometer energy scale was calibrated using the Au 4f₇/₂ line at 84.0 eV. The residual vacuum pressure was typically 3x10⁻⁹ mbar during analysis. Emitted photoelectrons were analyzed with a hemispherical electron energy analyzer equipped with a channel plate and a position sensitive detector. Survey spectra were obtained over a binding energy scale of 0–1100 eV using an analyzer pass energy of 117.4 eV giving a total spectrometer energy resolution of 1.62 eV. High-resolution detail spectra were obtained at a analyzer pass energy of 58.7 eV giving a total energy resolution of 1.05 eV. To compare spectra from different samples, the binding energies of the photoelectron peaks were referenced to the C 1s line at 284.6 eV. Elemental concentrations are given in atomic percent (normalized to a total of 100 atomic percent) using the photoelectron peak areas after Shirley background subtraction (Multi-Pack, Version 6.1, Physical Electronics Inc) and the built-in sensitivity factors.

The grain size distribution of metallic grains and the roughness of mono- and bimetallic films were investigated by atomic force microscopy (AFM). The measurements were performed at room temperature with a Dimension 3100 from Digital Instruments using the tapping operation mode. A standard cantilever with a resonance frequency of about 284 kHz and a stiffness of 42 N/m was employed for all measurements.
5.2.3 Thin ATR-IR spectroscopy

In situ ATR-IR spectra of the solid-liquid interface were recorded on an EQUINOX 55 spectrometer (Bruker Optics) equipped with a liquid nitrogen-cooled MCT detector by co-adding 200 scans at 4 cm⁻¹ resolution. After mounting the coated IRE, the homemade stainless steel flow-through cell was placed on a dedicated ATR accessory (Optispec) and the sample compartment was closed to allow removal of water vapour and CO₂ by dry air overnight. The temperature was maintained at 10° C throughout the experiments.

Measurements were carried out as follows. First, N₂-saturated CH₂Cl₂ provided from a gas bubble tank was contacted at 1 ml/min flow rate with the coated IRE to reach steady state conditions (2 h). Then the gas was changed from N₂ to H₂ in the same glass bubble tank without interrupting the liquid flow and H₂-saturated CH₂Cl₂ was allowed to flow through the cell for 10 min to clean the surface. The last spectrum during cleaning served as the reference spectrum for CO adsorption (ca. 60 min) from CO-saturated CH₂Cl₂ provided from a second glass bubble tank. Finally, H₂-saturated CH₂Cl₂ was again flown through the cell to follow desorption. All spectra are presented in absorbance units and were corrected for the contribution of water vapour where required. The relative CO surface coverage was determined against the intensity of the linear and bridge CO signals of the Pt10 and Pd20 samples, respectively, taken after 60 min on stream.
5.3 Results

5.3.1 Physical characterization of films

X-ray photoelectron spectra of the mono- and bimetallic samples indicated that all metals were in the reduced state. The signals of the Au 4f core level (87 and 83.3 eV) are shown in figure 5.1 and are identified as those corresponding to metallic gold [21]. Broader high binding energy shoulders suggested that a fraction of the Pt-group metals was in the oxidized state [20, 22]. The slower attenuation of the concentration of O compared to that of Al and the increasing concentration of C at increasing Pt film thickness may account for the presence of adventitious carbon contamination and the formation of a thin oxide film. The XPS spectra of the bimetallic PtAu and PdAu surfaces did not exhibit any significant shift in the core level binding energies, which would have indicated electronic modification of either the Au or the Pt-group element [23]. Importantly, the thickness of the metal films evaporated on Au/Al2O3 could be estimated according to ref. [24]. The Au 4d5/2, Pt 4f5/2 and Pd 3d core level lines were used for the estimation. In the case of PtAu surfaces, the Pt film thickness was underestimated in most of the cases, in the worst case by 16% (PtAu20). The excellent values obtained especially for the thinnest samples and the linear correlation (R= 0.99844) between the expected (nominal) and the estimated film thickness using XPS confirmed the reliability of the physical vapour deposition technique. On the contrary, the thickness of Pd in PdAu surfaces was always overestimated by values larger by 50% and more, which is likely due to the overlap between the Au 4d and the Pd 3d signals at all Pd contents.

Figure 5.1 shows the atomic force microscopy images (500×500 nm) of selected monometallic and bimetallic thin films. The images refer to as deposited samples. The Au film is composed of a densely packed layer of agglomerates exhibiting a variable width between about 9 and 30 nm. Comparison with the morphology of the Al2O3 film [20] allows the assignment of these entities to Au particles. Larger agglomerates (up to 65 nm) are also
observed, which might arise from impurities after exposure to air. Similarly to other thin metal films (Cu [25], Pt [20, 26], Pd [22]), the AFM images show the island character of the electron beam deposited films. The average grain size increased when Pt or Pd was evaporated on the Au film, whereas the shape of the grains remained unaffected. For the PtAu05 sample the smallest particles had an approximate diameter of 10–19 nm. The size of the individual particles increased to about 30 nm in the PtAu10 sample. However, the presence of Au did not substantially change the grain size of the Pt-bimetallic films compared to the monometallic film as demonstrated for the Pt05 and PtAu05 samples. On the other hand, a dramatic difference is observed in the morphology of the Pd-containing samples. The smallest particles in PdAu10 are about 15–20 nm large, whereas their size is approximately doubled in the absence of Au (figure 5.1).
Figure 5.1: AFM images (500 × 500 nm) of selected as deposited Pd, PdAu, Pt and PtAu samples together with the Au sample. The inset depicts the Au 4f core level signals of the Au10 sample.
5.3.2 Adsorption of CO from solution

H₂-cleaning of the metal surface is required to follow adsorption of large organic adsorbates and is recommended in the case of CO adsorption where it causes signal enhancement [20]. Briefly, hydrogen-induced removal of CO (Pt, 2033 cm⁻¹; Pd, 1860 cm⁻¹) and carbonates (1540 cm⁻¹), and formation of hydrocarbon fragments (CHₓ species, ca. 1400 cm⁻¹) and ethylidyne species (Pt, 1338 cm⁻¹; Pd, 1325 cm⁻¹) can be followed in the ATR-IR spectra and indicate strong interaction of hydrogen for the Pt and Pd metal surfaces [20, 22]. The changes were negligible for the Au film. The decrease of the film thickness resulted in progressively less pronounced changes, but without any evident difference between mono- and bimetallic surfaces. Obviously, the extent of surface exposed to the contact with hydrogen decreased with metal content.

Adsorption of CO on mono- and bimetallic films is demonstrated in figure 5.2 (Au and Pd) and figure 5.3 (Pt) for experiments carried out under identical conditions and spectra acquired after 60 min of contact with CO-saturated solvent. The insets of figures 5.2 and 5.3 depict the behaviour of the relative CO coverage after 60 min on stream as a function of film thickness. CO adsorbed on Pd20 and Pt10 exhibits two pairs of signals, one above 2000 cm⁻¹ (CO_L; Pt: 2047 cm⁻¹; Pd: 2040 cm⁻¹) assigned to on-top species, and the second below 2000 cm⁻¹ (CO_B; Pt: 1817 cm⁻¹; Pd: 1905 cm⁻¹) indicating population of multi-coordinated species [27]. The CO_B species on the Pd film exhibit a rather broad signal with at least 2–3 components indicating high surface heterogeneity and different adsorption sites. CO frequency above and below 1900 cm⁻¹ can be assigned to CO adsorbed predominantly on bridge (2-fold coordination) and hollow sites (3-fold), respectively. High intensity for the signal corresponding to 3-fold bonded species warrants relatively large domains of reduced metal since the species occupies more space than 2-fold coordinated species. The assignment agrees with the relatively large size of the Pd particles determined by STM [22] and AFM (figure 5.1) and with the low intensity of the signal of on-
top species. The grain size deduced from AFM also suggests that both Pd and Pt particles are mainly composed of (111) facets, the most abundant crystallographic face [28, 29].

Figure 5.2(a) reveals that no CO adsorption occurred on Au. The reason for the lack of CO features can be attributed to either a particle size or a temperature effect. UHV studies indicate that the CO adsorbate layer is completely desorbed at the temperature at which the present ATR-IR experiments have been performed [30], although a signal at 2109 cm\(^{-1}\) (CO\(_L\)) was observed for a 20 nm-thick polycrystalline Au film at ambient temperature under spectroelectrochemical conditions [31]. Moreover, the Au particles could be mainly flat patches exposing (111) facets, in agreement with their relatively large size (figure 5.1). The particles size is a crucial factor for CO adsorption on Au [32]. CO adsorbs preferentially on low-coordinated Au atoms [33], hence on small clusters rather than on extended surfaces, a property which makes Au nanoparticles excellent catalytic materials for CO oxidation compared to bulk Au [34]. It is therefore clear that the polycrystalline Au film shown in figure 5.1 does not expose defects and is not enough corrugated to allow CO adsorption. However, the absence of CO adsorption on the present Au film has the benefit that it allows the investigation of the effect of dilution of Pt and Pd metals in bimetallic surfaces using infrared spectroscopy in comparison to monometallic surfaces without the interference of adsorbed CO on Au.

In the Pt and Pd monometallic samples, the decrease of film thickness from 2 to 0.2 nm was accompanied by a decreased CO adsorption. The frequency of the CO signals in the Pd films was perturbed by the decrease of the film thickness. Pd10 and Pd05 show signals at 2040 and 1870 cm\(^{-1}\). A shoulder at ca. 1800 cm\(^{-1}\) is evident in Pd10. A considerable blue-shift is observed in correspondence of Pd02, exhibiting signals at 2068 and 1887 cm\(^{-1}\) for CO\(_L\) and CO\(_B\), respectively. Similarly, a shift of 35 cm\(^{-1}\) is observed in the CO\(_B\) signal when changing from Pd10 to Pd20 (1905 cm\(^{-1}\)). Very weak signals were observed for Pd05 and Pd02,
less than 5% relative coverage being obtained on Pd02. The decrease of the film thickness more likely modifies the distribution of sites available for adsorption of CO\textsubscript{B} species and the Pd ensemble size [35]. This is best shown in figure 5.2(c-d), where the component at ca. 1800 cm\textsuperscript{-1} completely disappears from Pd10 to Pd05.

A slight blue shift ($\Delta v = 5$ cm\textsuperscript{-1}) accompanied by attenuation of the intensity was observed for the CO\textsubscript{L} signal when the Pt film thickness was decreased from 2 (Pt20, 2045 cm\textsuperscript{-1}) to 1 nm (Pt10, 2049 cm\textsuperscript{-1}) (figure 5.3). The relative coverage of CO decreased to about 40 and 20% on the Pt05 and Pt02 samples, respectively (inset). Similarly to Pd, the Pt02 sample exhibits signals of CO\textsubscript{L} and CO\textsubscript{B} at higher frequency than the other Pt-containing surfaces, i.e. at 2057 and 1827 cm\textsuperscript{-1}, respectively. The inset of figure 5.3 does not depict the relative CO coverage for Pt20 since the second derivative-like shape cuts the CO\textsubscript{L} band conferring a bipolar appearance to the envelope, which reduces the overall intensity. As a result the maximum of the signal also shifts towards lower frequency thus explaining the $\Delta v$. The typical second derivative-like shape associated with the strongest signals of CO on both Pt and Pd can be attributed to the perturbation of the optical properties of the film probed by the IR radiation propagating through the IRE upon adsorption of a strong absorber [25, 36]. The perturbation affects more the appearance of the spectra associated with thicker films. Moreover, the background absorption increased on contact with CO on all surfaces indicating that the optical properties of the metal film also changed owing to the formation of a strong CO adsorbate layer.

Evaporation of 1 nm Au on the Al\textsubscript{2}O\textsubscript{3} film previous to Pd induces important changes in the intensity of the CO signals and hence in the adsorption properties of Pd compared to monometallic surfaces (figures 5.2 and 5.4). CO adsorption occurs at large extent only for PdAu20 and PdAu10, whereas for films thinner than 1 nm extremely weak signals were obtained. The difference with the corresponding monometallic films is obvious. The adsorption sites available for
CO adsorption from liquid phase on bimetallic Pt–Au and Pd–Au surfaces

CO appeared also modified by the addition of Au. Comparison between Pd10 and PdAu10 reveals that the component of the CO\textsubscript{B} envelope located at ca. 1800 cm\textsuperscript{-1} is strongly attenuated or disappeared in the bimetallic surface. Moreover, the maxima of both CO\textsubscript{L} and CO\textsubscript{B} signals are considerably blue shifted to 2059 (\(\Delta\nu = 19\) cm\textsuperscript{-1}) and 1908 (38) cm\textsuperscript{-1}, respectively. The shift could result smaller due to the second derivative shape of the signals in Pd10 but the \(\Delta\nu\) value is so large at least for the CO\textsubscript{B} signals that the contribution of this optical effect can be neglected. To support this argument, it should be noted that the CO\textsubscript{B} signal is found at the same position in Pd10 and Pd05 despite the band shape observed in Pd10. Figure 5.2 also clearly demonstrates that signals due to adsorbed CO are extremely weak in the PdAu05 and PdAu02 samples. On the other hand, CO is clearly visible in the corresponding monometallic surfaces. The effect of changing the distribution of adsorption sites for the CO\textsubscript{B} species with metal thickness might contribute to the exponential behaviour of the relative CO coverage as function of film thickness (inset of figure 5.2). Finally, figure 5.4 shows that CO saturation is achieved at shorter time on stream on bimetallic samples than on monometallic samples, which should hint at morphological changes in the Pd particles.

Changes appear only minor in PtAu surfaces (figure 5.3). Generally, the frequency of the CO\textsubscript{L} signal remains unchanged with decreasing Pt thickness. On the other hand, a blue shift of ca. 13 cm\textsuperscript{-1} is observed for the CO\textsubscript{B} signal which changes from 1812 to about 1825 cm\textsuperscript{-1}. Additionally, the adsorption ability of the bimetallic Pt samples is comparable to that of the monometallic samples in contrast to Pd-containing films. The inset of figure 5.3 shows that the relative surface coverage increased almost linearly with the Pt film thickness.

We note that there are two important differences observed for PdAu and PtAu. In contrast to Pd-containing surfaces, CO adsorption occurs noticeably on all PtAu samples and still about 20% CO coverage was observed on PtAu02. Moreover, the time at which the saturation coverage is achieved is identical
between Pt mono- and bimetallic surfaces (not shown). These observations clearly indicate that the extent of interaction between Au and the two Pt-group metals, as probed by CO adsorption is substantially different.
Figure 5.2: ATR-IR spectra of CO adsorption from CH₂Cl₂ solvent at 10°C on Pd (bold) and PdAu surfaces. Pd film thickness: (b) 0.2 nm, (c) 0.5 nm, (d) 1 nm, and (e) 2 nm. Spectra (a) have been collected for CO adsorption on the monometallic Au surface (1 nm) under equivalent conditions. Spectra (b) and (c) have been magnified 3 and 4 times, respectively for the ease of comparison. The insets show the relative CO coverage as a function of Pd film thickness for (●) mono- and (○) bimetallic Pd-containing surfaces and a further magnification of spectra (b) and (c).
Figure 5.3: ATR–IR spectra of CO adsorption from CH₂Cl₂ solvent at 10°C on Pt (bold) and PtAu surfaces. Pt film thickness: (b) 0.2 nm, (c) 0.5 nm, (d) 1 nm, and (e) 2 nm. The inset shows the relative CO coverage as a function of Pt film thickness for (●) mono- and (○) bimetallic Pt-containing surfaces. Spectra (a) and (b) have been magnified 5 and 3 times, respectively for the ease of comparison.
5.4 Discussion

5.4.1 Model for the bimetallic films

The combination of XPS, AFM and ATR-IR spectroscopy gives valuable information to develop models for the structure of the bimetallic PdAu and PtAu surfaces.

Although surface composition in Pd and Pt increases quite regularly with the amount of deposited metal, it is rather difficult to ascertain whether intermetallic materials are formed. XPS has been used previously to study alloy formation in the Pd–Au binary system but with samples annealed at high temperature [23]. AFM images of ‘as-deposited’ films revealed that Au strongly influences the
morphology of Pd-containing films compared to the monometallic surfaces, whereas much less perturbation was observed in the case of Pt. Obviously, the local surface composition, i.e. formation of intimate Au–metal bonds, cannot be determined using AFM. However, since the ATR-IR spectra exhibit more peculiar features for the Pd-Au bimetallic samples, it appears meaningful to describe primarily the effect of Au on the Pd-containing samples. AFM images indicated that when Pd is deposited on the Au film the average size of the resulting grains was lower compared to Pd films deposited on Al₂O₃ at identical nominal thickness. Together with the ATR-IR spectra obtained during CO adsorption, this fact indicates that the Pd-Au bimetallic surface is not simply composed of two independent Pd and Au films. The decrease of the intensity of the CO signals and the disappearance of some signals with decreasing Pd film thickness on the monometallic surfaces can be related to a particles size effect, which, in turn, decreases the amount of available metal for adsorption, modifies the size of the particles, and affects the sites to which CO can adsorb. Figure 5.2 shows that the decrease in the intensity of the CO signals is much more significant for the bimetallic surfaces at equivalent Pd film thickness. The phenomenon can be associated with a particle size effect as well. However, such effect could arise from the generation of a diffuse Pd/Au interface. Pd and Au form bimetallic surfaces already at ambient temperature due to their good miscibility in solid solutions [23, 37-39]. Alloys have been claimed to form under similar preparation conditions to those used for these ATR-IR measurements and even without any pre-annealing [40]. We propose that the interdiffusion of Pd into Au, i.e. the enrichment of Au at the metal surface exposed to the solution, generates smaller Pd ensembles than on the monometallic Pd films.
The ATR-IR spectra indicate that the morphology of these ensembles is different from the monometallic Pd ensembles. That is, the formation of a diffuse interface produces a geometric effect which influences the adsorption properties of the ensembles showing only Pd character. This is best seen in the formation of prevalently 2-fold adsorbed CO and in the faster decrease of the signal of CO$_B$ compared to CO$_L$. The reduced size of the Pd ensembles is reflected in the reduced interaction with hydrogen and the time at which maximum coverage is reached in bimetallic surfaces. The latter is shorter than for monometallic surfaces. Formation of the diffuse interface has more serious effects at low Pd film thickness (0.2 and 0.5 nm), which possibly best warrants the enrichment of the surface with Au.

Besides geometric (morphological) effects, formation of true bimetallic interfaces is often accompanied by electronic effects [41]. As a result, the adsorption properties of the surfaces are strongly altered and the characteristic absorption features of an adsorbate can experience important shifts. Although rather significant, the blue-shifts observed in the frequency of the CO signals on both the PdAu and the PtAu surfaces (figures 5.2 and 5.3) cannot be attributed to electronic effects since similar shifts have been also found for the monometallic surfaces. Moreover, red-shifts should be expected if truly intermetallic particles are formed due to the charge transfer from one metal into the other one resulting in enhanced back donation into the $2\pi^*$ antibonding orbitals of adsorbed CO.

Small well-defined supported Pd particles typically expose (111) and (100) facets [42, 43], resulting in absorption signals at higher energy than those observed in the present mono- and bimetallic Pd-containing surfaces. Frequencies below 1900 cm$^{-1}$ can be assigned to CO adsorbed predominantly on 3-fold hollow sites.

The increase in frequency of CO$_B$ observed for the bimetallic surfaces indicates a change in the structure of the Pd ensembles induced by the presence of Au,
most probably accompanied by adsorption on 2-fold bridge sites. At very low Pd content (PdAu02) CO adsorption is inhibited to a larger extent and the ratio between on-top and bridge species is close to unity, supporting the diluting effect of Au and the depletion of Pd-like ensembles.

Figure 5.5 depicts a cartoon of the mono- and bimetallic surfaces and of the diffuse interface. At equivalent nominal Pd thickness, the Pd-like ensembles in the PdAu samples are smaller than those that would be obtained if no 'diffusion' of Pd into Au had occurred and those obtained for the monometallic samples. The overall effect can be summarized as an enhanced reduction of the particle size induced by Au, which cannot be obtained by simply decreasing the amount of evaporated Pd. Consequently, the formation of diffused Pd/Au surfaces offers the opportunity to investigate adsorption processes at the solid-liquid interface at a different level than with monometallic surfaces.

Moreover, CO adsorption provides an excellent probe for investigating the structure of the PdAu bimetallic surfaces. However, the interpretation of the PtAu samples seems less straightforward on the base of CO adsorption only. AFM and ATR-IR spectroscopy both indicate that the diffusion of Pt into Au is less probable than in the case of Pd. The only effect observed on Pt and PtAu surfaces is that the decrease of the Pt film thickness results in smaller amounts of adsorbed CO. With the exception of the PtAu10 sample, monometallic and bimetallic surfaces exhibit approximately the same distribution of sites for CO adsorption. PtAu02 and Pt02 samples are significant examples. It can be concluded that evaporation of Pt on Au generates two nearly independent metallic films. It will be shown in the chapter 6 that a chiral adsorbate can be used in place of CO to effectively probe structural changes induced by the presence of Au in these Pt-Au bimetallic surfaces.

In principle, the differences observed for Pd and Pt in the ease of formation of the diffuse interface can be associated with two aspects. At first, the present surfaces have been characterized as prepared, i.e. without thermal treatment,
thus limiting interdiffusion. Secondly, the different electronic structure of Pd and Pt, which is reflected by the observed different catalytic properties of the two metals for identical reactions, does certainly play a role. Pd and Au are well miscible, whereas in the case of Pt and Au a large miscibility gap is observed in the solid solution [44, 45].

The effect of diffusion of Pd into Au observed using CO adsorption can in principle be complicated by surface enhancement (SEIRA) effects, which are due to the interaction between a molecule in proximity of or at metal surface showing island structure and the electromagnetic field present at the metal surface. Au is an excellent substrate for surface-induced enhancement, which is also known but at a lesser extent for the Pt-groups metals [46].
Figure 5.5: Model for the electron beam vapour deposited Pd-Au and Pt-Au surfaces at equivalent metal film thickness. The model represents the observed structural changes when Pd or Pt is deposited on Au or Al$_2$O$_3$. The darkened part of the particles on the right hand side exaggerates the approximate size of the ‘diffuse interface’.

5.5 Conclusion

Pd-Au and Pt-Au bimetallic surfaces have been prepared by electron beam deposition and their structure has been characterized using XPS, AFM and ATR-IR spectroscopy. The changes observed in the infrared frequency and in the shape of the CO signals upon adsorption from the liquid phase indicated that morphological changes occur in the Pd films when decreasing the film thickness from 2 to 0.2 nm and when introducing a 1 nm Au film. In comparison, the Pt-Au surface was less sensitive towards CO adsorption which can be attributed to the large difference in miscibility between Pd, Pt and Au. A diffuse Pd/Au interface is likely formed when Pd is deposited on Au, which results in the interdiffusion of Pd into Au and the enrichment of the surface with Au for very
thin Pd films. This diffuse interface generates smaller Pd ensembles than those obtained by depositing an equivalent Pd film in the absence of Au. This effect could be exploited to investigate the effect of particles size on the adsorption behaviour of larger organic molecules, as will be shown in chapter 6.
5.6 References


CO adsorption from liquid phase on bimetallic Pt–Au and Pd–Au surfaces
Chapter 6

The Influence of Au on the Adsorption Mode of Cinchonidine in Au-containing Bimetallic Surfaces

6.1 Introduction

One of the methods to modulate the adsorption behaviour of the chiral modifier is the changing of the surface composition of a bimetallic catalysts. Although Pt-Pd catalysts have been tested in the enantioselective hydrogenation of ethyl pyruvate and ketopantolactone [1], to date the adsorption of cinchona alkaloids has not been studied on bimetallic surfaces. The main reason for the lower activity and selectivity of Pt-Pd catalysts compared to Pt was traced to the ensemble effect induced by deposition of Pd on Pt, which changes the optimal adsorption geometry of the modifier.

Despite the fact that gold shows poor hydrogenation activity [2, 3], it appears an interesting metal to be combined with Pt and Pd. The main reason for using Au to probe the effect of bimetallic surfaces on cinchonidine adsorption is its suitability to change the ‘ensemble size’ of the platinum group metal [4, 5] and thereby activity and selectivity of hydrogenation catalysts. Both alloying as well as simple ‘blocking’ of active surface metal atoms influence (reduce) the size of the ensembles of the platinum group metal. Hence, binary Pt-Au and Pd-Au films represent interesting model surfaces for investigating the structure sensitivity of cinchonidine adsorption on platinum group metals. A similar
approach has been applied to Ni–Au alloys to investigate the adsorption of methylacetoacetate [6] and tartaric acid [7] used in the enantioselective hydrogenation over Ni catalysts as substrate and chiral modifier, respectively [8]. In this chapter the adsorption of cinchonidine on Pt–Au and Pd–Au thin model films has been studied using attenuated total reflection infrared (ATR–IR) spectroscopy. These films revealed interesting surface properties since evaporation of Au generates a diffuse interface, which reduces the effective size of Pd and Pt domains (ensembles, see figure 5.5). The adsorption was followed in the presence of CH2Cl2 solvent and dissolved hydrogen. Density functional theory calculations of the adsorption of quinoline on platinum and gold clusters are also reported as models for the adsorption of cinchonidine, as a complement to the experimental information on the relative adsorption strength.

6.2 Experimental

6.2.1 Materials

Materials used in this chapter were the same as presented in chapter 5. Cinchonidine (98%) was purchased from Fluka.

6.2.2 Thin film preparation

Thin film preparations in this chapter were the same as presented in chapter 5.

6.2.3 ATR-IR spectroscopy

ATR-IR spectroscopy parameter in this chapter was the same as presented in chapter 5. Cinchonidine (0.1 mM) was used and where needed, water vapour was subtracted from the spectra. Peak integration was performed using the OPUS 5.0 software package.
6.2.4 Theoretical calculations

Adsorption studies have been performed using the Amsterdam Density Functional (ADF) program package [9]. The surface was simulated using rigid Pt 31 and Au 31 clusters. The following level of theory was used. The orbitals up to 1s were kept frozen for the second row elements, while orbitals up to 4f were kept frozen for Pt and Au; the double-\(\zeta\) (DZ) basis functions were used for platinum and gold, while for second row elements and hydrogen double-\(\zeta\) plus polarization (DZP) basis functions were used; Zero Order Regular Approximation for the relativistic Hamiltonian [10-14], and Dirac core potentials for all atoms; Becke-Perdew density functional [15, 16]. A more detailed description of the computational methods used can be found elsewhere [17]. All calculations were run unrestricted. Adsorption energies (\(E_{\text{ads}}\)) were calculated as follows:

\[
\Delta E_{\text{ads}} = E_{\text{cluster+adsorbate}} - E_{\text{cluster}} - E_{\text{free molecule}},
\]

where \(E_{\text{cluster+adsorbate}}\), \(E_{\text{cluster}}\) and \(E_{\text{free molecule}}\) are the energies of the cluster with the molecule adsorbed, of the isolated cluster and of the free molecule, respectively.

For benzene on platinum it was shown that the addition of the BSSE correction and of partial relaxation of the metal cluster lead to contributions of opposite sign which tend to compensate, and that the simple formula used leads to values for the adsorption strength close to the experimental value for both bridge and hollow sites [18].

The bond distances for Pt and for Au were fixed to the experimental value of 2.775 and 2.870 Å for bulk metal [19] Molden [20] was used as graphical interface.
6.3 Results

Previous studies on the adsorption of cinchonidine on platinum [21-23] and palladium [24] have revealed several features that are important for interpreting the ATR-IR spectra measured on Au, PtAu and PdAu surfaces. The characteristic signals of the species typically observed using ATR-IR spectroscopy on platinum metal surfaces are reviewed in table 6.1 for the spectral region of interest. The main difference between flat and tilted species in terms of infrared signals is the resemblance of the spectrum associated to the latter species with the spectrum of cinchonidine in solution. This observation indicates that tilted adsorption does not substantially perturb the molecular structure of the alkaloid. On the other hand, the change of relative intensity of the signal at 1569 cm\(^{-1}\) with respect to that for example at 1509 cm\(^{-1}\) indicates that cinchonidine adapts the molecular structure to the surface, as demonstrated by theoretical calculations [17].
Table 6.1: Assignment of the principal vibrational modes of cinchonidine on Pt, Pd and Au surfaces according to previous ATR-IR studies and the present work. The values for free cinchonidine are also given for comparison.

6.3.1 Adsorption of cinchonidine on Au

The spectrum of cinchonidine on Au10 (figure 6.1(a)) exhibits signals at 1590, 1508, 1452, 1420 and 1376 cm\(^{-1}\). Two signals (not shown) at 2919 and 2854 cm\(^{-1}\) which appear better resolved than on Pt are characteristic of C–H stretch modes of the quinuclidine moiety. Only a very weak signal is observed at ca. 1570 cm\(^{-1}\), otherwise the spectrum indicates that cinchonidine adsorbs on gold predominantly in a tilted mode. Although the position of the signals attributed to the tilted mode on the different metals do not substantially differ (table 6.1), on
The adsorption mode of cinchonidine on Au cannot be properly named 'tilted' as it is on Pt and Pd, as it will become clear in the following.

The absence of the negative signal at 1400 cm\(^{-1}\) enables the observation of modes at 1420 and 1375 cm\(^{-1}\), corresponding to ring deformation and stretch modes, respectively, with a strong contribution from in-plane C–H deformation [21, 25]. These modes have a component normal to the metal surface and hence are infrared active only when the quinoline ring points away from Au. The observation of these modes and the absence of a clear signal at ca. 1570 cm\(^{-1}\) substantiate the dominance of species in which the quinoline ring is strongly tilted with respect to the Au surface. These spectroscopic features should be characteristic of weak adsorption of cinchonidine. On the contrary, the cinchonidine adsorbate shows higher stability against desorption compared to Pt. The origin of this behavior was studied by separately investigating the adsorption of quinoline, the anchoring group on platinum metals. Figure 6.1(c-d) shows that quinoline desorbs from Au as a result of the solvent flow and is easily replaced by cinchonidine. The features appearing during cinchonidine adsorption are more complex and exhibit higher intensity than those of quinoline thus accounting for a relatively denser adsorbate layer. Similarly, the intensity of the signals of cinchonidine on Au is by a factor 3 lower than on Pt (see below).

The absence of the signal at ca. 1590 cm\(^{-1}\) in the case of quinoline strongly suggests a possible different interaction of the aromatic ring of the two molecules with Au, which contrasts with the similarity of the adsorption behavior of these molecules on Pt and Pd [21, 24].
In order to gain further insight, the adsorption of quinoline on Au(111) was simulated using relativistically corrected Density Functional Theory (DFT) and the results are shown in figure 6.2. The adsorption energies calculated for flat-
The influence of Au on the adsorption mode of cinchonidine

like species were found to be 40.4 and 6.9 kcal/mol on Pt and Au, respectively. It is obvious from these values that quinoline is essentially physisorbed on Au, whereas it is chemisorbed on Pt. Furthermore, the adsorption site is shifted from a bridge site on Pt to a site showing a non-specific interaction to Au atoms.

Table 6.2 gives the values of bond lengths for quinoline in vacuum and adsorbed with the aromatic ring approximately parallel to Pt and Au, whereas table 6.3 lists the values of the angles between the hydrogen atoms and the aromatic skeleton. Deviation from the structure in vacuum indicates strong interaction with the metal. Au(111) leaves the structure of quinoline practically unaltered, therefore binding quinoline only weakly, whereas Pt(111) strongly interacts with the heterocyclic ring system. Re-hybridization of the aromatic carbon atoms does not take place on Au (table 3), the distance to the metal increases by more than 1 Å with respect to adsorption on Pt (table 6.2). The bond distances in the carbon skeleton remain practically unchanged on Au compared to the compound in vacuum. Interestingly, adsorption of quinoline with the aromatic ring nearly perpendicular to the Au(111) surface, as shown in figure 6.2, is characterized by an adsorption energy of 9.1 kcal/mol, which is only little higher than that of the flat-like species. This is an important observation because other factors such as the intermolecular forces can enter into play and bias the adsorption state of cinchonidine on Au.
Figure 6.2: Calculated structures for quinoline adsorbed with the aromatic ring on Pt (a, b) and Au (c, d) clusters, and with the N lone pair on the Au (e, f) cluster. Adsorption energies are 40.4, 6.9 and 9.1 kcal/mol, respectively.
Table 6.2: Values of bond distances calculated for free quinoline and for the adsorption of quinoline on Pt and Au on a double bridge site. The atom numbering is given in the top panel. All values are in Å.
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Table 6.3: Values of dihedral angles between hydrogen atoms and quinoline ring skeleton calculated for the adsorption of quinoline on Pt and Au. Atom numbering reference is on table 2. All values are in degrees.

6.3.2 Adsorption of cinchonidine on PtAu and PdAu surfaces

The ATR-IR spectra recorded after contact of the surface with a solution of cinchonidine for 60 min on bimetallic PtAu films are presented in figure 6.3 for increasing Pt film thickness. This time is sufficient to observe all adsorbed species and equilibration between species [21]. The signals at 1612, 1590, 1569, 1530, and 1509 cm⁻¹ are attenuated upon decrease of the Pt content. The signal at ca. 1455 cm⁻¹ is observed with all samples, which might indicate that the quinuclidine moiety also contributes to the adsorption process. Note that experiments with cinchonidine adsorbed on monometallic Pt (and also Pd) with metal film thickness below 1 nm showed only very weak features of the alkaloid compared to Pt10 and to the corresponding bimetallic PtAu samples. As a consequence, the spectra of Pt02 and Pt05 are not shown here. A closer look at the spectra in figure 6.3 reveals that the way the aforementioned signals decrease on PtAu is not identical for all species.
Figure 6.3: ATR-IR spectra of cinchonidine on monometallic Au and Pt (bold), and on bimetallic PtAu. Conditions: $t = 60$ min, CCC= 0.1 mM, $10^\circ$C, $\text{H}_2$-saturated $\text{CH}_2\text{Cl}_2$.

Figure 6.4(A) displays the integrated area of the signals associated with the flat ($1569$ cm$^{-1}$) and tilted ($1509$ cm$^{-1}$) species as a function of Pt thickness. The ratio
of the areas of the two signals (hereafter $A_{1569}/A_{1509}$) is also given assuming that the area is proportional to the relative population of the species. At this point two considerations are needed concerning the band integration: a) although the envelope which these signals belong to is complex, the trends shown in figure 6.4(A) demonstrate that the integration is correct in first approximation; and b) cinchonidine adsorbs also on Au, introducing a source of error. Since PtAu surfaces probably expose also portions of Au at low Pt content, the contribution of the adsorption of cinchonidine on Au should be accounted for when integrating the signal at 1509 cm$^{-1}$. However, it is assumed here that the free portion of Au capable of adsorbing cinchonidine is far smaller than that in the Au10 sample so that the signals observed on PtAu02 can be attributed predominantly to cinchonidine adsorbed on Pt. This assumption is corroborated by the observation on the same PtAu02 sample of $\alpha$-quinolyl species (1530 cm$^{-1}$), which adsorbs only on Pt. It is further demonstrated in figure 6.4(A), where the amount of tilted species on PtAu02 is higher than on Au10.

With these considerations in mind, figure 6.4(A) shows that both flat and tilted species increase with Pt content. However, the simultaneous increase of the $A_{1569}/A_{1509}$ ratio reveals that the flat species is favored at high Pt content, whereas the tilted species dominates at low Pt content and on Au. Equivalent information is obtained when the signals associated with the two species on PtAu samples were also integrated after flowing H$_2$-saturated solvent for 30 min (figure 6.4(B)). The fraction of flat species increases with Pt thickness as clearly shown by the $A_{1569}/A_{1509}$ ratio. The opposite behavior of the two species shown in figure 6.4(B) clearly indicates that the flat species is more strongly adsorbed than the tilted species, similarly to the monometallic Pt surface. However, the adsorption equilibrium is shifted towards the tilted species at low Pt content.
Figure 6.4: (A) Integrated area of the signals associated with the tilted (1509 cm\(^{-1}\), \(\circ\)) and the flat (1569 cm\(^{-1}\), \(\bullet\)) species and of the \(A_{1569}/A_{1509}\) ratio (\(\times\)) as a function of Pt film thickness (A) during adsorption and (B) after flowing H\(_2\)-saturated solvent for 30 min. Lines are drawn to guide the eye.

Beside the difference in adsorption strength between species on the same metal, the adsorbed layer on Au, which is composed of tilted-like species, appears more strongly bound than the tilted species on Pt. This observation is confirmed by the stability of the signal at 1509 cm\(^{-1}\) on Au towards flowing solvent (figures 6.1(b) and 6.4(B)) which contrasts with the removal of the majority of the tilted species from monometallic Pt, PtAu10 and PtAu20 samples.

The typical features of adsorbed cinchonidine on Pt are also found on Pd except for the relative ratio of the signals at 1570 and 1508 cm\(^{-1}\), which is very similar to that observed for cinchonidine in solution (figure 6.5 and table 6.1). This is the major difference between adsorption on the two platinum metals and was attributed to the fact that the tilted species of the alkaloid dominates on Pd [24].

It is obvious from figure 6.5 that the intensity of all signals decreases with Pd film thickness in bimetallic PdAu samples, indicating that the fraction of cinchonidine adsorbed tilted on Pd diminishes with decreasing Pd content.
Figure 6.5: ATR-IR spectra of cinchonidine on monometallic Au and Pd (bold), and on bimetallic PdAu. Conditions: $t = 60 \text{ min}$, $\text{CCD}= 0.1 \text{ mM}$, $10^\circ\text{C}$, $\text{H}_2$-saturated $\text{CH}_2\text{Cl}_2$.

It is worthwhile mentioning here that the difference in the intensity of all signals on Pd20 compared to the PdAu20 samples is likely due to the partial dilution of Pd in the Au film as shown in figure 5.5. This effect produces Pd ensembles, which are smaller than those obtained in the corresponding monometallic films.
Figure 6.6 illustrates the effect of changing Pd film thickness on the integrated areas of the signal at 1508 cm\(^{-1}\) which is representative of the majority of the species present on Pd. During adsorption and when flowing H\(_2\)-saturated solvent for 30 min, the fraction of adsorbed cinchonidine increases with Pd film thickness. It is also found that the adsorbed layer of cinchonidine remaining on the Pd-containing surfaces after solvent flow has a comparable stability to that remaining on Au. However, the origin of this stability is different on the two metals.

\[\text{Figure 6.6: Integrated area of the signal associated with tilted species during cinchonidine adsorption (●) and after flowing H}_2\text{-saturated solvent for 30 min (○) as a function of Pd film thickness in bimetallic PdAu. Lines are drawn to guide the eye.}\]
6.4 Discussion

The behaviour of the quinoline ring of cinchonidine on Au is in agreement with the vertical and/or tilted adsorption mode of N-heteroaromatic molecules on this metal. Isoquinoline [26], 8-hydroxyquinoline [27] and pyridine [28-31] exhibit such adsorption mode on single crystal surfaces with tilting angles of up to 70°. Interestingly, polycrystalline surfaces also allow for parallel geometries [32], a behaviour attributed to the presence of defects. The present DFT calculations provide an explanation for this adsorption geometry based on the very weak bonding of quinoline on Au. This behaviour is attributed to two joint factors, the degrees of overlap of the orbitals of the adsorbate with the d orbitals of Au and the degree of filling of the antibonding states [33].

The ATR-IR spectra demonstrate that cinchonidine readily adsorbs on gold surfaces and forms a fairly stable adsorbed layer. The information contained in the spectra is very similar to that observed on Pd at least with respect to the quinoline ring, which is not oriented parallel to the surface. The spectrum in figure 6.1(c) does not indicate formation of species with the aromatic ring parallel to the Au surface, though their presence might also depend on solute concentration and hence on surface coverage. The theoretical calculations give comparable adsorption energies for local geometries with the quinoline ring adsorbed flat and tilted with respect to the metal.

The stability of the adsorbed layer formed by cinchonidine on the polycrystalline Au surface somehow stands in contrast to the weak adsorption of quinoline. This behaviour is traced to the molecular structure of the alkaloid that has a propensity to form intermolecular interactions both in the liquid [34] and in the solid state [35]. Intramolecular OH–N(quinuclidine) hydrogen bonds are responsible for the formation of ‘chains of [cinchonidine] molecules along alternate screw axes in the solid state’ [35]. These lateral interactions seem to dominate over the weak interaction between Au and the quinoline ring thus generating a stable adsorbed layer, whose overall adsorption energy is increased.
The influence of Au on the adsorption mode of cinchonidine compared to that of the single molecule. Whether ordered structures are formed cannot be concluded from our ATR-IR study and should be addressed using other techniques such as STM or LEED. This possibility cannot be excluded a priori since pyridine is capable of assembling long range ordered structures on Au(111) surfaces [28]. This does not hold true for quinoline and the formation of ordered structures of cinchonidine on Cu(111) is still debated [36, 37]. The much lower intensity of the signals of cinchonidine on Au compared to adsorption on Pt (and Pd) indicates not only that the bonding of cinchonidine is weaker than on the catalytically relevant metals but also that the amount of adsorbed alkaloid is lower on Au. This observation would rather suggest that on Au cinchonidine forms molecular aggregates of variable size organized in the form of islands. Within these islands, the single molecules are statistically oriented with the quinoline ring non-parallel to the surface and with the quinuclidine moiety involved in hydrogen bonds with adjacent molecules. Since the nature of the bonding of the single molecule within the island is significantly different from the bonding of cinchonidine with Pt and Pd, the single species forming the island cannot be properly named ‘tilted’ as it is the case on the enantioselective hydrogenation metals.

This work indicates that a phase transition between single molecule chiral sites and ‘condensation’ of aggregates on the surface can be expected when passing from Pt or Pd to Au.

On the catalytically relevant metals, the transition from a local adsorption geometry in which the quinoline ring is predominantly adsorbed flat to one in which it is tilted away from the metal surface depends on the degree of interaction of the aromatic ring with the metal surface. This interaction can be affected by the size of the metal domains on which adsorption occurs. In the present study the size of platinum group metal domains has been changed by the use of Au-containing Pt and Pd films. We could show that this size alters the way the chiral modifier coordinates to the surface. This property is probably
crucial for understanding the structure sensitivity of supported metals used in enantioselective hydrogenations [38].

Adsorption of cinchonidine on bimetallic PtAu and PdAu surfaces strongly depends on the metal film thickness and on the composition of the surface. On the monometallic Pt and Pd films adsorption of cinchonidine is very dissimilar from that shown in figures 6.3 and 6.5, in the sense that the ATR-IR spectra for Pt films below 1 nm do not provide any information on adsorbates compared to the bimetallic films. The likely reason for this phenomenon is the enhancement effect offered by the combination of the two metal films. Beside Pt giving moderate enhancement [39-41], Au is an excellent substrate for surface-enhanced infrared absorption (SEIRA) spectroscopy [42].

CO adsorption on the bimetallic PdAu thin model films used for cinchonidine adsorption strongly indicated that the size of the Pd ensembles which are able to adsorb the probe molecule are smaller compared to those present in the monometallic Pd surfaces. This has been explained in terms of formation of a diffuse Pd/Au interface, which makes the active Pd particles smaller. This dilution effect is in agreement with the tendency of Pd-Au bimetallic surfaces to form alloys even at ambient temperature [43, 44]. On the other hand, formation of Pt-Au ensembles in PtAu thin model films is more difficult [45] and segregation of the two metals is favored to some extent. This results in comparable CO spectra in mono- and bimetallic samples. The diffuse interface is likely reflected in the adsorption of cinchonidine. Figure 6.3 reveals that there is not much difference in intensity between the spectrum of cinchonidine on Pt10 and on PtAu10. On the contrary, figure 6.6 shows that the spectrum of the alkaloid on PdAu20 is attenuated by about 30% with respect to that of the Pd20 sample, indicating that a smaller fraction of cinchonidine is adsorbed on the PdAu20 sample owing to the reduced size of the free Pd ensembles. Hence, the use of Au reveals to better simulate a particle size effect than simply reducing the film thickness of the noble metal.
It is important to emphasize that the changes in the distribution of the species of cinchonidine on PtAu are much more significant than the changes observed in CO adsorption on the same surfaces (chapter 5). The fraction of flat species is larger at high Pt content, whereas the fraction of tilted species increases with decreasing Pt content. It is obvious that flat species require more Pt atoms to adsorb, since they exhibit a larger cross section than tilted species due to the extended aromatic ring. Hence, cinchonidine appears a better probe to characterize the PtAu bimetallic surfaces because it is more sensitive to the size of the Pt ensembles than CO, which adsorbs mainly on-top on Pt [40]. CO is a good candidate for the PdAu samples because it forms multibonded species on Pd. On the other hand, only tilted species can be observed in the case of adsorption of cinchonidine, which are less sensitive to the size of the metal ensembles.

6.5 Conclusion

The adsorption of the chiral modifier cinchonidine from CH$_2$Cl$_2$ solvent has been investigated using ATR-IR spectroscopy on monometallic Au and on bimetallic Pt–Au and Pd–Au thin model films. The spectroscopic data indicate that on Au cinchonidine adsorbs with the quinoline ring oriented non-parallel to the surface and that the alkaloid adsorbs more strongly than quinoline. DFT calculations indicate that the quinoline ring, the anchoring group of cinchonidine, does not form π-bonds with Au in contrast to Pt. The difference in adsorption strength observed with respect to quinoline and the comparable adsorption energy calculated for flat and tilted quinoline on Au suggest that hydrogen bond-type interactions stabilize the adsorbed cinchonidine layer. These intermolecular interactions likely favor the formation of cinchonidine islands on Au in which the single molecule chirality likely responsible for the enantioselective properties of cinchona modified platinum metals is broken.
On bimetallic Pt–Au thin model films the population of flat species (irreversibly adsorbed) decreases with decreasing Pt film thickness and quinoline ring tilting prevails at very low Pt content. Evaporation of Au before Pt and Pd generates bimetallic surfaces where the role of Au is to modify the effective ensemble size of the noble metal. This modification allows the enhancement of the information that can be gained by simply changing Pt (and Pd) thickness in the absence of Au. In this respect, due to its relatively large molecular size cinchonidine appears a better candidate than CO to probe the ensemble size of Pt–Au films. Cinchonidine seems to prefer a tilted local geometry on very small Pt ensembles. The results obtained on the Pt-Au bimetallic surfaces provide evidence for the sensitivity of the adsorption geometry of the chiral modifier on the size of metal ensembles. This property likely plays an important role in the heterogeneous enantioselective hydrogenation over chirally modified platinum group metals.
6.6 References

The influence of Au on the adsorption mode of cinchonidine
Chapter 7

Adsorption Mode of the Chiral Modifier

Cinchonidine on Au(111)

7.1 Introduction

In chapter 5 bimetallic platinum group metal surfaces containing Au were characterized by CO adsorption from solution by means of ATR-IR spectroscopy and in chapter 6 the adsorption behavior of cinchonidine on the bimetallic surfaces was studied. In order to gather more information on the behavior of cinchonidine adsorption on Au, in this chapter we studied the monolayer structure of cinchonidine and quinoline on Au(111) by means of in vacuo experimental techniques like low energy electron diffraction (LEED), X-ray photoelectron spectroscopy (XPS) and temperature programmed desorption (TPD). Most important objectives of this study were long-range order, chemical structure and local geometric structure of cinchonidine on Au. Adsorption of quinoline is investigated as a reference system in order to identify which nitrogen atom of cinchonidine interacts with the surface. The structure of quinoline is shown in figure 7.1.

![Structural formula of quinoline](image)

Figure 7.1: Structural formula of quinoline.
7.2 Experimental

Experimental set-up in this chapter is the same as in chapter 3. (R8,S9)-cinchonidine (Fluka 98.95%) deposition was performed with a homemade Knudsen cell held at 120°C during sublimation. The relative coverage has been controlled via XPS by normalization of the C 1s peak to the Au 4d substrate signal. Quinoline (Aldrich ≥ 99%) has been further purified by freeze-pump-thaw cycles prior to the adsorption experiments. Exposure of the Au crystal held at 80 K to quinoline has been performed by back-filling the chamber with quinoline partial pressures between $1 \cdot 10^{-8}$ and $1 \cdot 10^{-7}$ mbar. XPS-energy calibration, usually achieved by assigning the Au 4f$_{7/2}$ peak to 84 eV, has been done here by setting the highest intensity C 1s component (obtained via peak fitting) to 285 eV. This procedure has been chosen in order to account for local electrostatic charging effect due to three-dimensional island growth.

7.3 Results and discussion

Prior to evaluation of local bonding geometry and lateral long-range order, we calibrated the amount necessary to form a complete CD monolayer via TPD. The most important results are presented in figures 7.2 and 7.3. Figure 7.2 shows peaks that are indicative for molecular desorption. The most intensive fragment in the mass spectrometer at m/z=136 represents the aliphatic quinuclidine fragment of CD. With the sample held at room temperature (RT), already after 30 sec exposure a peak at 340 K became detectable. However its intensity did not further increase substantially, even at 50 times higher doses. Figure 7.2 further shows the effect on molecular desorption by increasing the exposure from 20 to 27 minutes. Cooling the substrate, on the other hand, increased the intensity of molecular desorption dramatically, even at much smaller doses. This observation must be explained by a relatively high desorption rate from the second layer at RT, i.e., a low sticking probability for
CD on CD. Hence the molecule-substrate interaction is much stronger than the molecule-molecule interaction. However, multilayer growth at RT is observed after very large doses. Apparently, second layer nucleation and growth has to overcome a critical size of nuclei (Ostwald ripening).

![Graph](image)

**Figure 7.2:** Molecular desorption measured via the fragment mass 136 (quinuclidine part of CD) from multilayered films. The strong dependence on substrate temperature indicates a high desorption rate at RT.

Hydrogen desorption signals after exposures of 30 seconds and 30 minutes are shown in figure 7.3. The hydrogen evolves from the thermally induced decomposition of CD on the gold surface. Despite the large difference in exposure, no substantial changes in signal area are observed. It is important to mention that intact CD in the first monolayer at RT on Pt(111) has been observed via ToF-SIMS. Hence, one can safely assume that CD is intact at RT on gold as well.

Taking the first appearance of molecular desorption after 30 sec. into account, we conclude that i) after 30 sec. the monolayer is saturated, ii) no molecular desorption takes place from the first monolayer, and iii) the molecule undergoes thermally induced decomposition at relatively high temperatures on the gold surface. However, going from short to long time exposure, a decomposition
peak observed at 410 K almost disappears and a peak at 505 K shifts by 10 K to higher temperature, while the decomposition steps at 545 K and 610 K do not change with exposure. We assign this observation to a rearrangement of the monolayer due to prolonged CD exposure. Under steady second layer adsorption-desorption conditions, the first layer is still allowed to slowly rearrange towards higher stability, and two of the decomposition reactions become higher activated due to this rearrangement. Since the Au surface is believed to play an active role in all decomposition steps, we conclude that this rearrangement increases the stability by enhanced supra- or supermolecular interactions in the molecular layer, more suppressing the interaction of reactive molecular groups with the substrate. However, we were not able to find any superstructure in LEED for different coverages and temperatures. The thermal stability effect must be therefore assigned to a local rearrangement, either in the single adsorbate complex or between adjacent molecules, but not within a long-range lattice structure.
In contrast to CD, no decomposition of quinoline has been observed here via TPD, i.e., mass 2 and mass 129 peaks appear at the same temperature. From the smallest doses on, molecular desorption has been observed at 161 K from the gold surface. With increasing exposure this peak shifts to higher temperatures (max. 170 K) and a second desorption peak evolves at 180 K, with the peak maximum then shifting to above 200 K. The peak shape of this second peak is typical for zero order desorption kinetics indicating desorption from the multilayer. The low desorption temperature here stands clearly for physisorption. A rough estimate, based on first order desorption kinetics after the Readhead formula [1], delivers a value of 9.6 kcal/mol, in excellent agreement with the 9.1 kcal/mol resulting from DFT calculations for tilted or perpendicular adsorption geometry.

Information on chemical states in the monolayer has been obtained via XPS. The most important feature is presented in figure 7.4, showing the N 1s signals after different doses of CD and quinoline. Basically two peaks are observed for
all species and all coverages. Fitting gaussian peaks under a spectrum acquired with higher resolution for CD gives N 1s binding energies of 399.2 eV and 401.8 eV. The values for quinoline are similar. Both peaks appear at low coverage simultaneously. The high energy peak gets saturated quickly while for multilayer conditions only the low energy peak is increased in intensity.

For undistorted aromatic sp²- or aliphatic sp³-hybridized nitrogen, peaks at 399.0 to 399.8 eV are characteristic [2]. N 1s signals at around 402 eV, however, are an indication for positively charged nitrogen. With the aromatic ring system bound via the π-electron system in a parallel geometry to the surface, we would not expect such strong shift in N 1s binding energy, since the interaction would be spread over the ten atoms of the aromatic system (nine carbon and one nitrogen). For quinoline on Pt(111) this has been confirmed previously [3]. A charge transfer from the quinoline nitrogen to the gold substrate explains the higher N 1s binding energy. For N-containing aromatic molecules, a tilted or perpendicular geometry is quite common, e.g. biquinoline and 8-hydroxyquinoline on silver and gold nanoparticles were found to interact via the N-electron lone pair to the substrate [4]. For pyridine on various Ni, Cu, Ag, Au, Pt and Ru surfaces, this geometry has been found as well [5, 6]. In analogy to the high coverage situation on Pd and Pt, CD is therefore expected to bind to Au via the quinoline nitrogen lone-pair orbital, leading to the tilted adsorbate geometry. The fact that we see a similar chemical shift for quinoline supports this conclusion. Since ATR-IR measurements of CD on Au in CH₂Cl₂ show a tilted quinoline group (chapter 6), it is reasonable to assume that in UHV a similar bonding configuration is present. In contrast to Pt and Pd, the bonding to Au via the aromatic ring is too weak to force the molecule into a parallel adsorption mode, and the bulky aliphatic group at the aromatic ring systems puts a steric constrain to the parallel orientation. This scenario is further supported by DFT calculation of quinoline on Au(111) destabilizing the parallel configuration by 3 kcal/mol (chapter 6). However, adsorbate complexes of pyridine, lepidine
or dihydro-CD on Pt(111) [3, 7], for example, do not show such a strong chemical shift, even when the interaction to the substrate via the N electron lone pair occurs. The same observation has been made for the amino group of naphtylethylamine directly interacting with the Pt surface [8]. On the other hand it has been shown for pyrazine (C₄H₄N₂), that the N 1s binding energy on Au(111) is larger than on Ag(111) [9]. When pyrazine changes its alignment from parallel to perpendicular to the Au(111) surface, an additional peak shift from 399.4 eV to 400.2 eV has been reported [9]. However, the two different nitrogen atoms in the perpendicular configuration were not resolved so that only an average value was determined. In addition the chemical shift for the N bound to the surface is expected to be substantially lower than for quinoline due to an electronic mesomeric effect induced by the second N atom in para position. Without the second nitrogen in the aromatic ring, the positive charge on the nitrogen bound to the substrate must be higher and a larger chemical shift, as observed here, is expected.
After the 30 min CD exposure at RT (figure 7.4d, e), the coverage is just slightly above one monolayer and only the low-energy N 1s peak grows further in intensity with increasing coverage. Therefore, both nitrogen atoms, i.e., in the quinoline and the quinuclidine group in the multilayer show a signal at around
399 eV. For quinoline, the 399.3 eV peak intensity increases for doses above 0.6 L (figure 7.4b), but the 401.8 eV peak is saturated. Again, the low energy peak can be assigned either to the multilayer quinoline not in contact with the gold surface or to a parallel adsorbed molecule. Taking into account, that quinoline is stronger bound via the N-lone pair electrons even at small coverage, and that the low energy peak is substantially increased in the multilayer regime, we assign the low energy peak to quinoline which is not in direct contact with the gold surface. Because it is also observed at initial adsorption, we further conclude that quinoline clusters into 3D islands on gold even at smallest coverage. Up to a dose of 0.6 L the clusters grow in two- and three dimension, and both N 1s peaks are increased simultaneously, until above 0.6 L only the "3D peak" keeps growing. This means that the intermolecular interaction prevail over molecule substrate interaction and is also confirmed here by the shift of the TPD signal to higher temperature with increasing coverage.

Finally, we briefly discuss the fact that quinoline is only physisorbed, while CD undergoes decomposition. A stronger adsorption for CD than for quinoline on gold has been observed by ATR-IR experiments in CH₂Cl₂ (chapter 6). Apparently further interaction, either with the surface or between the CD molecules stabilizes CD substantially. However, the XPS analysis delivers similar electronic bonding conditions for CD and quinoline. But it does not necessarily reflect the situation close to decomposition. The molecule may transfer to a different geometry, and a rearrangement in the monolayer has indeed been observed via the change of the hydrogen desorption signal. Note that due to its rotational flexibility CD can form an intramolecular hydrogen bond between the hydroxyl group and the quinuclidine nitrogen lone pair orbital. For steric reasons, a second N-Au bond of the quinuclidine N is not possible. The tilted or perpendicular oriented aromatic system allows two strong intermolecular hydrogen bonds between OH and N and a π-π interaction between the aromatic moieties. However, we would expect a long-range ordered
structure for such arrangement. On the other hand, the rather weak bond to the surface and stronger intermolecular acting forces will lead to 3D clustering from the beginning on, not allowing long range order.

7.4 Conclusions
Cinchonidine interacts with Au(111) via the nitrogen of the quinoline group and has therefore an adsorption geometry in which the aromatic part is tilted or perpendicular with respect to the surface plane. Although weakly bound, the charge transfer from the nitrogen to the gold is pronounced. In this configuration, quinoline is physisorbed and desorbs intactly upon heating. CD, however, undergoes decomposition in the monolayer, most probably due to strong lateral intermolecular interaction, stabilizing the monolayer.
7.5 References


Adsorption mode of the chiral modifier cinchonidine on Au(111)
Outlook

In this thesis some fundamental aspects of chirally modified metal surfaces have been studied. These investigations were triggered by the increasing importance of asymmetric catalysis on chirally modified metals. We investigated the chirality bestowed by adsorption of chiral molecules on the active metal surface. In addition we studied the influence of changing the ensemble size on platinum group metal surfaces using Au as a blocking component and demonstrated how the ensemble size can affect the adsorption conformation of the modifier on the surface. Additionally we demonstrated how the combination of *in-situ* ATR-IR spectroscopy with surface sensitive methods performed in UHV can help to get new information about the metal/modifier interface.

Nevertheless there are still a lot of open questions in this field which require further investigations. *In-situ* ATR-IR spectroscopy experiments can be extended to investigate complex systems in the presence of modifier and reactant using bimetallic catalyst. It remains to be shown how gold promotion affects the enantiodifferentation in the hydrogenation process. ATR-IR allows to follow the conformational changes induced by modulating the metal ensemble size. In addition UHV investigations could be extended to Pt, Pd and also bimetallic films. Other cinchona alkaloids and derivatives thereof as well as molecules like quinoline, quinuclidine and pyridine could be used as adsorbates. Also the influence of temperature and the use of different gases in ATR-IR experiments could provide information on how these parameters can affect the conformation of the modifier on the surface.

In addition to experimental methods mentioned here, theoretical calculations are another tool to support the experimental results. The combination of surface
science techniques, spectroscopic methods and quantum mechanical calculations is a promising strategy for investigating key aspects of asymmetric catalysis in the future.
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List of Publications

The following publications are based on the present doctoral dissertation. The corresponding chapters are indicated in bracket.

- Homochiral conglomerates and racemic crystals in two dimensions: Tartaric acid on Cu(110).
  S. Romer, B. Behzadi, R. Fasel, K.-H. Ernst
  (Chapter 3)

- Chiral Recognition in Surface Explosion.
  Bahar Behzadi, Sara Romer, Roman Fasel, Karl-Heinz Ernst,
  (Chapter 4)

- CO adsorption from liquid phase on bimetallic Pt–Au and Pd–Au surfaces studied by ATR-IR spectroscopy.
  Bahar Behzadi, Peter Kappenberger, Roland Hauert, Davide Ferri, Karl-Heinz Ernst and Alfons Baiker. (In preparation)
  (Chapter 5)

- The influence of Au on the adsorption mode of cinchonidine in Au-containing bimetallic surfaces.
  Bahar Behzadi, Angelo Vargas, Davide Ferri, Karl-Heinz Ernst and Alfons Baiker. (Submitted, *JPC-B*)
  (Chapter 6)

- Intermolecular interactions of the chiral modifier cinchonidine on Au(111) studied by XPS and TPD.
Other publications and conference contributions:


• Chiral effects in thermally induced chemistry of tartaric acid on Cu(110). B. Behzadi, S. Romer, R. Fasel, K.-H. Ernst *SAOG, Fribourg, Switzerland, Jan 2004. (Poster)*

• Tartaric acid on Cu(110). B. Behzadi, S. Romer, R. Fasel, K.-H. Ernst *Research Market Place, EMPA, Dübendorf, Switzerland, March 2004. (Poster)*


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