

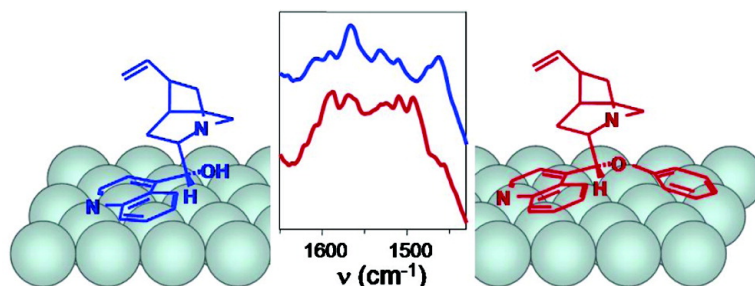
Article

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Competition at Chiral Metal Surfaces: Fundamental Aspects of the Inversion of Enantioselectivity in Hydrogenations on Platinum

Norberto Bonalumi, Angelo Vargas, Davide Ferri, Thomas Bürgi,[†]
Tamas Mallat, and Alfons Baiker*

Contribution from the Department of Chemistry and Applied Biosciences, Swiss Federal Institute of Technology, ETH Hönggerberg HCI, CH-8093 Zurich, Switzerland

Received January 21, 2005; E-mail: baiker@chem.ethz.ch

Abstract: *O*-Phenylcinchonidine (PhOCD) is known to efficiently induce inversion of enantioselectivity with respect to cinchonidine (CD) in the enantioselective hydrogenation of various activated ketones on Pt/Al₂O₃. To understand the origin of the switch of enantioselective properties of the catalyst, the adsorption of PhOCD has been studied by in situ ATR-IR spectroscopy, in the presence of organic solvent and dissolved hydrogen, i.e., under conditions used for catalytic hydrogenation. The adsorption structures and energies of the anchoring group of CD and PhOCD were calculated on a Pt 38 cluster, using relativistically corrected density functional theory (DFT). Both approaches indicate that both modifiers are adsorbed via the quinoline ring and that the spatial arrangement of the quinuclidine skeleton is critical for the chiral recognition. New molecular level information on the conformation of CD relative to PhOCD adsorbed on a surface is extracted from the ATR spectra and supported by DFT calculations. The result is a clearer picture of the role played by the phenyl group in defining the chiral space created by the modifiers on Pt. Moreover, when CD was added to a pre-equilibrated adsorbed layer of PhOCD, a chiral adsorbed layer was formed with CD as the dominant modifier, indicating that CD adsorbs more strongly than PhOCD. Conversely, when PhOCD was added to preadsorbed CD, no significant substitution occurred. The process leading to nonlinear effects in heterogeneous asymmetric catalysis has been characterized by in situ spectroscopy, and new insight into a heterogeneous catalytic *R*–*S* switch system is provided.

Introduction

Chiral recognition on metal surfaces is gaining growing attention and has stimulated various fundamental and applied research,^{1–4} given the potential technological relevance of devices that enable stereochemical control.

Adsorption of a chiral organic compound from solution onto a metal surface is a simple and efficient approach to create a chiral surface.⁵ This strategy has been widely used in (supported) metal-catalyzed heterogeneous enantioselective hydrogenation reactions.^{6–12} Chirally modified metals are synthetically useful solid catalysts that offer over 90% ee in some reactions including the hydrogenation of α - and β -functionalized ketones^{13–16} and 2-pyrones.¹⁷

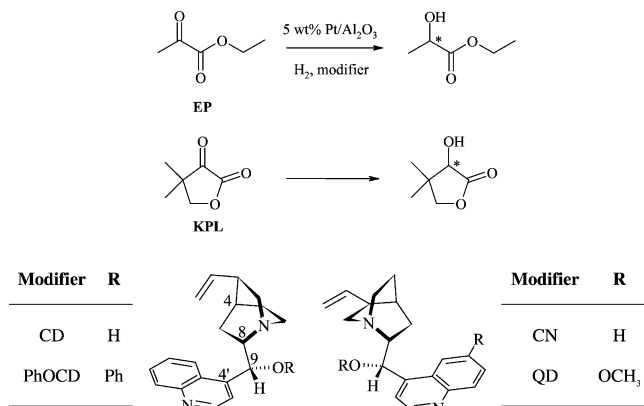
An attractive feature of these catalysts is that the major enantiomer can be switched (i) by changing the reaction conditions or the metal catalyst and (ii) by changing the chiral modifier. Examples for the first category include the inversion of enantioselectivity in the asymmetric hydrogenation of activated ketones by changing the solvent composition, including water and strong acid additives.^{18–23} In the hydrogenation of methyl pyruvate in the presence of cinchonidine (CD, Scheme 1) as chiral modifier, (*R*)-lactate was obtained on Pt/SiO₂, whereas the *S*-enantiomer was produced on iron oxide-supported Pd.¹⁸ Inversion of enantioselectivity by structural variation of the modifier was first reported by Orito,²⁴ who produced the opposite enantiomer in the Pt-catalyzed hydrogenation of α -ketoesters by substitution of CD to its pseudo-enantiomer

[†] Université de Neuchâtel, Institut de Chimie, Av. de Bellevaux 51, CH-Neuchâtel, Switzerland.

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Scheme 1. Enantioselective Hydrogenation of Ethyl Pyruvate (EP) and Ketopantolactone (KPL) on Pt/Al₂O₃ Modified by Cinchona Alkaloids Cinchonidine (CD), Cinchonine (CN), and Quinidine (QD), and by *O*-Phenylcinchonidine (PhOCD)



cinchonine (CN, Scheme 1). The subsequent extensive research by many groups revealed that this type of inversion of enantioselectivity is a general feature of chirally modified Pt and Pd, owing to the change of the absolute configuration of the chiral modifier.⁸

In the hydrogenation of ethyl pyruvate²⁵ and 4-methoxy-6-methyl-2-pyrone²⁶ over Pt/Al₂O₃ and Pd/TiO₂, respectively, an equimolar mixture of two cinchona alkaloids CD and quinidine (QD, Scheme 1) afforded ee's very similar to those obtained with CD alone, although QD alone gave high ee to the opposite enantiomers, and also the reaction rates were similar when the two alkaloids were applied alone. This unexpected behavior was interpreted in terms of different adsorption strengths and adsorption modes of the modifiers, reflecting the different abilities of the alkaloids to modify the metal. This example shows that the enantioselective properties of a chirally modified metal surface can be switched, in principle during a continuous process, simply by addition to the reaction mixture of another, competing chiral modifier.

There are further examples of the nonlinear behavior of modifier mixtures in heterogeneous catalysis although the nonlinearity is not always so striking.^{25,27–31} The phenomenon is closely related to the nonlinear effect (NLE) thoroughly investigated in homogeneous enantioselective catalysis.^{32–34} The asymmetric amplification or depletion in homogeneous catalysis is attributed to molecular interactions between two enantiomers of the auxiliary or ligand. The study of nonlinear effect was later extended to mixtures of two diastereomers and even to two chemically different ligands.^{33,35,36}

An intriguing case of nonlinear behavior of modifier mixtures in heterogeneous asymmetric catalysis is the application of two

modifiers that possess the same absolute configuration but afford the opposite enantiomers in excess due to structural variations. We have found very recently in the Pt-catalyzed enantioselective hydrogenation of some activated ketones that replacing CD with its bulky ether derivatives resulted in the inversion of ee.^{30,31} For example, in the hydrogenation of ketopantolactone CD afforded 79% ee to (*R*)-pantolactone, whereas *O*-phenylcinchonidine (PhOCD, Scheme 1) gave 52% ee to the *S*-enantiomer under otherwise identical conditions. A striking nonlinear behavior was observed when applying a mixture of these two modifiers: less than 0.7% CD in a CD/PhOCD mixture was sufficient to afford the *R*-enantiomer in excess. An important point is that—according to several mechanistic models^{8,37–40}—the OH group of CD is not involved in the reactant–modifier interaction and thus inversion of enantioselectivity by applying ether derivatives of CD was not expected. The feasibility of these mechanisms is confirmed by the observation that CD and its small ether derivatives *O*-methyl-CD and *O*-ethyl-CD afforded the same enantiomer in excess.^{30,31} The explanation for the inversion of enantioselectivity is not yet clear at the molecular level. We propose that the switch depends on the change of the *chiral pocket* experienced by the incoming reactant and the change is connected to the conformational behavior of the adsorbed alkaloid and the bulkiness of the ether group.³⁰

The present study aims at gaining insight in these aspects at the molecular level by combining attenuated total reflection infrared spectroscopy (ATR-IRS)⁴¹ and density functional theory (DFT) calculations. ATR-IRS gives fundamental information on the adsorption behavior of even complex molecules at the metal–liquid interface under conditions close to those relevant in catalysis, i.e., in the presence of the solvent and hydrogen. DFT calculations were performed to gain insight into the molecular phenomena involved in the adsorption process. We will present the experimental evidence for the competitive adsorption of chiral modifiers on Pt and for the change in the shape of the chiral space within which a reactant could be accommodated. The adsorption strength and the variation of the chiral pocket trigger the inversion of the enantioselective properties of the cinchona-Pt system.

Experimental Section

Materials. Cinchonidine (CD, Fluka, 98%) and methoxybenzene (anisole, Fluka, 99%) were used as received. The synthesis of *O*-phenylcinchonidine (PhOCD) has been described elsewhere.³⁰ Dichloromethane solvent (Baker, technical grade) was stored over 5 Å molecular sieves. N₂ (99.995 vol %) and H₂ (99.999 vol %) gases were supplied by PANGAS.

ATR-IR Spectroscopy. The Pt/Al₂O₃ thin film used for ATR-IR spectroscopy was prepared on a 1 mm thick trapezoidal Ge internal reflection element (IRE, 50 × 20 × 1 mm³) by electron beam physical vapor deposition as described in detail elsewhere.⁴² First, 50 nm Al₂O₃ was deposited followed by 1 nm Pt.

In situ ATR-IR spectra were recorded on a Bruker IFS-66/S spectrometer equipped with a commercial ATR accessory (Optispec, Neerach—Switzerland) and a liquid nitrogen-cooled MCT detector.

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Spectra were collected by co-adding 200 scans at 4 cm^{-1} resolution. After cell mounting and optics alignment the probe chamber was purged overnight. The homemade stainless steel flow-through cell was maintained at 293 K throughout the experiments by a thermostat. N_2 -saturated dichloromethane was circulated over the thin film at ca. 1.0 mL/min by a peristaltic pump for about 30 min to reach steady state conditions, under which the infrared spectra did not change significantly. Before adsorption, the Pt film was contacted with H_2 -saturated solvent for about 10 min. This procedure cleans the surface, affording large domains of reduced Pt.⁴² For adsorption studies, an H_2 -saturated solution of the molecule under investigation at the desired concentration was pumped through the cell for about 60 min followed by rinsing with H_2 -saturated solvent in order to remove weakly adsorbed and dissolved species.

The competitive adsorption of the cinchona modifiers was investigated by admitting the PhOCD (or CD) solution to the ATR cell for about 60 min, followed by the CD (or PhOCD) solution under conditions identical to those described above.

ATR spectra are presented in absorbance units, and, where needed, signals from the gas-phase spectrum of water in the $1700\text{--}1400\text{ cm}^{-1}$ range were subtracted. Infrared transmission spectra of CH_2Cl_2 solutions and neat liquids were obtained by co-adding 200 scans at 4 cm^{-1} resolution.

Theoretical Calculations. The vibrational spectrum of anisole was calculated with the GAUSSIAN98⁴³ set of programs using the density functional B3LYP Hamiltonian and the 6-31G** basis set.

DFT calculations of the adsorption geometries and energies were performed using the Amsterdam density functional code.⁴⁴ Two metal clusters were used to simulate the platinum surface: a Pt 31 and a Pt 38 cluster. The smaller was used to study the adsorption of anisole, while the second to study the adsorption of the anchoring group of CD and PhOCD. A frozen core approximation was used for the inner core of all atoms; in particular the 1s frozen core was used for carbon, nitrogen, and oxygen, while the 4f frozen core was used for platinum. The core was modeled using a relativistically corrected core potential created with the DIRAC utility of the ADF program. The core potentials were calculated using the simple X-alpha approximation without gradient corrections, but the fully relativistic Hamiltonian was used, including spin-orbit coupling. The wave function was calculated using a zero-order regular approximation (ZORA) Hamiltonian, where spin-orbit coupling is included already in zero order. ZORA formalism requires a special basis set, including much steeper core-like functions that are implemented in the code. Within this basis set double- ζ (DZ) basis functions were always used for platinum. For second-row elements a DZ basis set was used for the study of anisole and a DZP for the study of the anchoring groups of the alkaloids. The local part of the exchange and correlation functional was modeled using a Vosko et al.⁴⁵ parametrization of the electron gas. The nonlocal part of the functional was modeled using the Becke correction⁴⁶ for the exchange and the Perdew correction⁴⁷ for the correlation. Adsorption energies were calculated as follows:

$$E_{\text{ads}} = E_{\text{cluster+adsorbate}} - E_{\text{cluster}} - E_{\text{free molecule}}$$

where $E_{\text{cluster+adsorbate}}$ is the energy of the cluster with the adsorbed molecule, E_{cluster} is the energy of the isolated cluster, and $E_{\text{free molecule}}$ is the energy of the free molecule. Both Pt 31 and Pt 38 clusters were spin-optimized in order to find the spin state with lowest energy, which was then used for the adsorption studies with the optimized spin. All calculations were run unrestricted. The bond distance for platinum was

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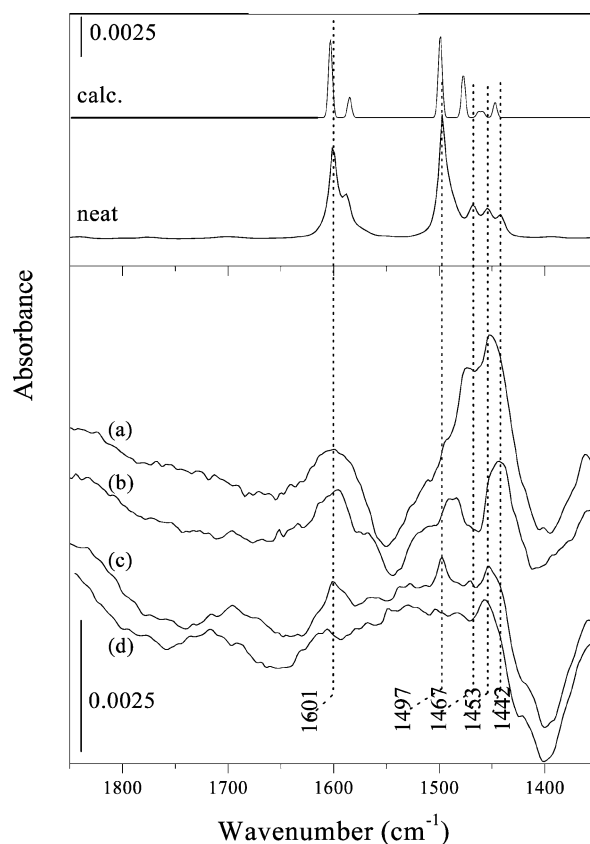


Figure 1. In situ ATR spectra of anisole on $\text{Pt}/\text{Al}_2\text{O}_3$ thin film at 293 K in H_2 -saturated CH_2Cl_2 . The solution concentration is (a) 0.05 mM, (b) 0.25 mM, and (c) 5 mM. Each spectrum refers to an overall adsorption time of 60 min. Spectrum (d) has been collected after admitting H_2 -saturated CH_2Cl_2 for 30 min after acquisition of spectrum (c). The calculated vibrational spectrum and neat anisole are also shown.

fixed during the optimizations to the experimental value of 2.775 \AA for bulk Pt metal,⁴⁸ but the nine central atoms of the Pt 38 cluster were set free to optimize in order to partially reproduce surface reconstruction. All degrees of freedom of the anchoring group were set free to optimize. Molden was used as the graphical interface.⁴⁹

Results

Adsorption of Anisole. The study of the adsorption of anisole was carried out as a model for the surface behavior of the phenyl ring of *O*-phenylcinchonidine (PhOCD). The use of probe molecules simplifies the assignment of IR signals of adsorbed chiral modifiers, as we have already shown for cinchonidine (CD).⁵⁰

Figure 1 displays representative in situ ATR spectra of anisole on $\text{Pt}/\text{Al}_2\text{O}_3$ in CH_2Cl_2 in the $1850\text{--}1350\text{ cm}^{-1}$ spectral range. The intensity of the observed IR signals quickly reached a constant value within a few minutes and thereafter appeared independent from adsorption time at all solution concentrations applied. The ATR spectra exhibit three major positive signals at 1601, 1497, and 1453 cm^{-1} . Depending on the starting concentration, the surface spectrum of anisole differs significantly from the spectrum of neat anisole (Figure 1). The signals at 1601 and 1497 appear weaker and broader in the ATR spectrum at low concentration than in neat anisole, their

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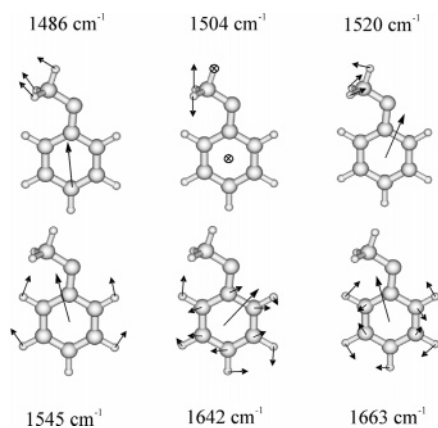


Figure 2. Representative vibrational modes of anisole with the x - y plane coinciding with the plane of the aromatic ring. Arrows indicate atom displacement vectors and the direction of dynamic dipole moments. The calculated harmonic frequencies are also given.

sharpness increasing with solution concentration. Theoretical calculations of the vibrational spectrum of anisole in a vacuum indicate that the two signals belong to modes involving C–C stretching and in-plane C–H deformation of the aromatic skeleton. The calculated vibrational spectrum shown in Figure 1 exhibits modes at 1663, 1642, and 1545 cm^{-1} associated with the ring vibrations, which well match the values measured for neat anisole when scaled by 0.961.⁵¹ Figure 2 depicts the calculated vibrational modes with the corresponding atom displacement vectors. The direction of the dynamic dipole moment is very similar for the two vibrational modes at 1545 (observed 1497) and 1663 (1601) cm^{-1} and is clearly almost parallel to the Ph–O bond. Moreover, the mode centered at 1545 cm^{-1} has a neat strong contribution of the in-plane C–H deformation, whereas the C–C stretching mode also contributes to the vibration at 1663 cm^{-1} .

The relatively broad and intense signal with maxima at 1478 and 1453 cm^{-1} (Figure 1a) is the most prominent band found at low solution concentration in the ATR spectra, whereas at higher concentration the intensity of the signal is remarkably attenuated (Figure 1c). The position of this envelope matches the set of signals observed for neat anisole at 1467, 1454, and 1442 cm^{-1} , corresponding to the asymmetric and symmetric deformation modes of the methyl group (Table 1).

Figure 1d also shows that the signals at 1600 and 1497 cm^{-1} were attenuated upon rinsing with H_2 -saturated solvent after anisole adsorption, whereas the signal at ca. 1453 cm^{-1} remained. A broad feature can still be detected at around 1600 cm^{-1} , but the difference with Figure 1c is obvious.

The evolution of the ATR signals of anisole on Pt suggests the coexistence of at least two adsorption modes. The spectra obtained at low concentration (0.05 mM) are dominated by the vibrational modes of a species adsorbed via the aromatic ring lying parallel to the surface. The relatively broad band at 1453 cm^{-1} represents the deformation modes of the methyl group of this species. According to the surface selection rule,⁵² no strong signal of the aromatic ring should be observed in this configuration. Indeed, only very weak and broad signals of the mixed C–C stretching and C–H in-plane deformation of the aromatic ring can be detected. At higher solution concentration the spectra

exhibit well-defined bands at 1601 and 1497 cm^{-1} that we assign to the appearance of a second species. In the case of a nonparallel adsorption mode of anisole these two modes display a component of the dipole moment perpendicular to the metal surface and become IR active. Since signals due to these vibrations appear at 0.25 mM concentration and are stronger at higher solution concentration, they can be assigned to a species adopting a strongly tilted position with respect to the Pt surface. The resemblance of spectrum (c) in Figure 1 to that of neat anisole supports this assignment and agrees well with the fact that this species is easily removed upon rinsing with H_2 -saturated solvent; that is, it is weakly adsorbed on Pt.

The adsorption of anisole on a Pt 31 cluster was also calculated by DFT, and the results are shown in Figure 3. This adsorption mode corresponds to the bridge adsorption mode of benzene.^{53,54} The structure displayed an adsorption energy of 26.2 kcal/mol, versus 27.8 kcal/mol calculated for benzene at the same adsorption site and at the same level of theory.⁵⁴

As reported for benzene^{53,54} and acetophenone,⁵⁴ this adsorption geometry parallel to the surface involves rehybridization of the aromatic carbons to sp^3 with the consequent loss of coplanarity between the oxygen atom and the ring skeleton. Hence, the O–CH₃ group is forced away from the metal by repulsive interactions and does not contribute to the adsorption process. In this geometry the O–CH₃ group can exhibit a vibrational pattern equivalent to that of neat anisole, whereas the carbon skeleton should show weak or nonexistent IR absorption due to the surface selection rule. This is in fact consistent with the presence of the signal at 1453 cm^{-1} observed at low concentration in the ATR spectra.

The tilting of anisole at high concentration as indicated by the ATR spectra is likely due to surface crowding, which leads to the formation of species only partially interacting with the metal and partially interacting with other adsorbed molecules. Such tilted species were shown to be feasible in the case of benzene on Pt(111) in a previous computational study.⁵³

Note on the Nomenclature of Adsorption Modes for Cinchonidine. Before describing the combined ATR-IR and DFT study of the adsorption of PhOCD, the nomenclature used for identifying adsorbed structures in the existing literature should be briefly discussed.

The literature dealing with the IR and Raman adsorption studies of CD distinguishes between so-called tilted and flat species.^{50,55,56} Tilted species include α -quinolyl and weakly bound N-lone pair bonded species, which are presumably irrelevant in the enantiodifferentiation process.⁵⁰ On the contrary, the flat species, which are assumed to be π -bonded to the metal, are strongly adsorbed parallel to the surface via the quinoline ring of the alkaloid. A computational study of the adsorption of CD on platinum revealed that adsorption modes of CD could be more or less flat on the surface.⁵⁷ Adsorption modes were termed as tilted also when they were neither α -quinolyl or N-lone pair bonded. It has been shown that what was previously named “flat” in the spectroscopic studies could show some degree of tilting. It was also demonstrated that all the strongly

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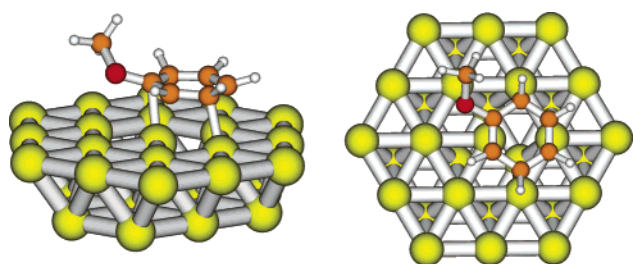
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Table 1. Assignment of the Vibrational Modes of CD, PhOCD, and Anisole in Solution (or neat) and on Pt/Al₂O₃, at 293 K (calculated frequencies are also given for anisole)

CD [§]		anisole					PhOCD ^a				assignment
sol ^b	Pt ^c	neat ^f	Pt ^e	Pt ^d	Pt ^c	calc ^g	sol ^b	Pt ^e	Pt ^d	Pt ^c	
1454	1458 ^{1,2,3}	1442	1449	1443		1504	1458				$\delta_S(\text{CH}_3)$
1463	1458 ^{1,2,3}						1466				$\delta(\text{C-H})$, quinuclidine
		1454	1468		1453	1520					$\delta(\text{C-H})$, quinuclidine
		1467	1478	1468	1470						$\delta_{AS}(\text{CH}_3)$
		1496		1484	1497	1545	1495	1495	1495	1495	$\delta_{AS}(\text{CH}_3)$
1509	1510 ³						1510	1510 ³	1510 ³	1509 ³	$\nu(\text{CC}) + \delta(\text{C-H})$
1570	1530 ²						1571	1530 ²	1530 ²		ring stretching, quinoline
1570	$\sim 1570^{1,2,3}$						1571	1569 ^{1,2,3}		1570 ^{1,2,3}	ring stretching, quinoline
		1588				1663					$\nu(\text{CC})$
1593	1590 ³						~ 1589	1590 ³	1588 ³	1588 ³	ring stretching, quinoline
		1601	1601	1596	1601		1599	1598	1600	1598	$\nu(\text{CC}) + \delta(\text{C-H})$
1635	n.o.						1638	n.o.	n.o.	n.o.	$\nu(\text{C=C})$

^a For adsorbed CD and PhOCD different species are observed. 1 = flat adsorbed, 2 = α -quinolyl, and 3 = N-lone pair bonded species. See text for details. ^b IR spectrum of a 0.01 M solution in CH₂Cl₂. ^c 5 mM solution in CH₂Cl₂. ^d 0.5 mM solution in CH₂Cl₂. ^e 0.05 mM solution in CH₂Cl₂. ^f IR spectrum of neat liquid. ^g A correction factor of 0.961 must be taken into account. n.o. = not observed; δ_S = symmetric bending, δ_{AS} = asymmetric bending.

**Figure 3.** Calculated adsorption mode of anisole. The aromatic ring is adsorbed on a bridge site, and the O-CH₃ group is not chemisorbed to the platinum.

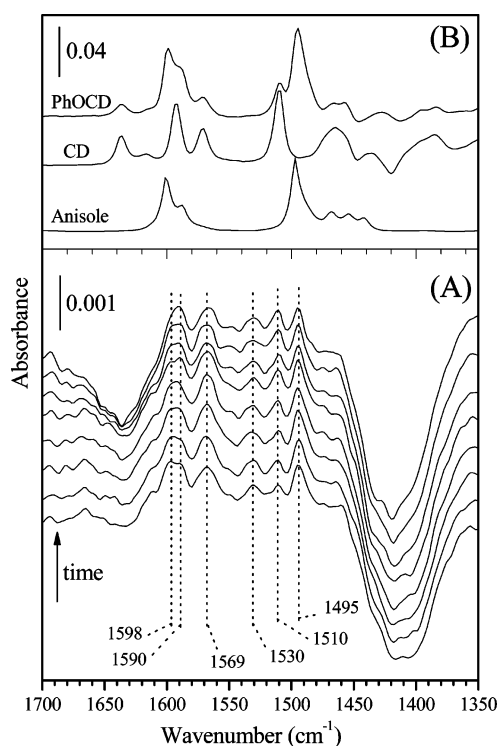
adsorbed species are in fact σ -bonded to the surface and originate from strong directional bonds with the d orbitals of the surface atoms following extensive rehybridization.

In the present investigation, we will explicitly refer to the α -quinolyl or N-lone pair bonded adsorption modes with their names and use the term “tilted” for those species that are strongly adsorbed but deviate from the parallel orientation of the quinoline ring relative to the metal surface.

Adsorption of O-Phenylcinchonidine. Figure 4 reveals that the spectrum of PhOCD dissolved in CH₂Cl₂ is a combination of the vibrational modes of the parent chiral modifier CD and those of the aromatic skeleton of anisole. The 1600–1500 cm⁻¹ region is diagnostic for the vibrational modes of the quinoline group.

The most prominent modes of the ring skeleton of anisole at 1601, 1588, and 1496 cm⁻¹ fall in the same region and dominate over those of quinoline. The quinuclidine skeleton is represented by weak modes located between 1500 and 1400 cm⁻¹,^{50,58} as reported in Table 1. The signal at 1638 (1635) cm⁻¹ observed for PhOCD (CD) in solution belongs to the vinyl group,⁵⁹ which is typically hydrogenated on Pt under the present experimental conditions.^{50,60}

The in situ ATR spectra shown in Figure 4 refer to the adsorption of PhOCD on a Pt/Al₂O₃ film at 293 K from a 0.05 mM solution in H₂-saturated CH₂Cl₂. The relatively lower signal-to-noise ratio and the absorption of the alumina support render the detection of signals below 1200 cm⁻¹ difficult. Upon adsorption of PhOCD, signals appear at ca. 1600, 1569, 1530, 1510, and 1495 cm⁻¹ accompanied by a weaker feature at ca. 1460 cm⁻¹.

**Figure 4.** (A) In situ ATR spectra of PhOCD on Pt/Al₂O₃ at 293 K in H₂-saturated CH₂Cl₂. Solution concentration: 0.05 mM. Spectra have been collected after 0, 2.5, 4, 8, 10, 20, 30, and 60 min on stream (from bottom to top). (B) Transmission spectra of neat anisole (1:25) and solutions of CD and PhOCD (10 mM in CH₂Cl₂).

The band at ca. 1600 cm⁻¹ is clearly given by two overlapping signals whose maxima can be identified at 1598 and 1590 cm⁻¹. The quinuclidine moiety appears only as a very weak band at about 1460 cm⁻¹. Features at 2070 and 1960 cm⁻¹ (not shown)⁶¹ and the negative signals at 1630 and 1400 cm⁻¹ are attributed to the displacement of species already available on the surface (H₂O, CO₃²⁻, C_xH_y, and CO) or formed continuously for example from solvent decomposition.⁵⁰

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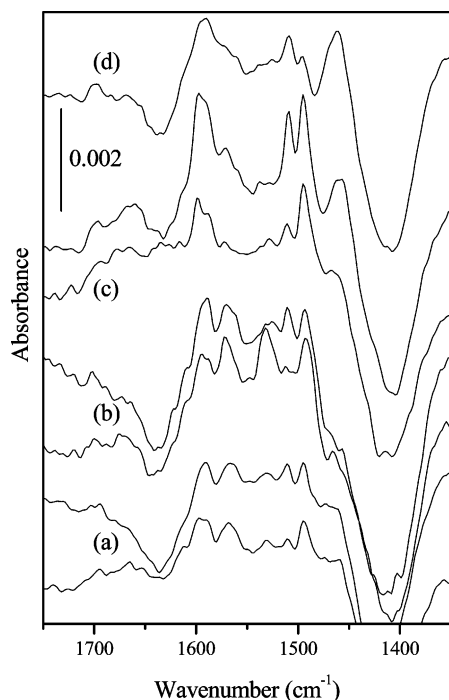


Figure 5. In situ ATR spectra of PhOCD on Pt/Al₂O₃ at 293 K in H₂-saturated CH₂Cl₂ at different solution concentrations. Spectra have been collected at 2.5 (bottom) and 60 min (top) on stream for the (a) 0.05 mM, (b) 0.5 mM, and (c) 5 mM solution concentrations. For the 5 mM concentration spectrum (d), collected when rinsing with H₂-saturated CH₂Cl₂ for 30 min, is also shown.

Although the intensity of the signals in Figure 4A shows only minor changes with time, a careful inspection of the spectra suggests that the signals evolve with different kinetics. In particular, the pair of signals at 1590 and 1510 cm⁻¹ due to quinoline grows in, whereas the signals at 1598 and 1495 cm⁻¹ associated with the phenyl ring are slightly attenuated. The likely explanation is the presence of more than one species.

More information about the adsorption of PhOCD can be gathered by changing the concentration of the chiral modifier in solution and consequently the surface crowding. Figure 5 shows the spectra qualitatively corresponding to low and high coverage recorded at different solution concentrations. Moreover, spectrum (d) depicts the signals observed when admitting H₂-saturated solvent to the cell after adsorption from the most concentrated solution (5 mM, Figure 5c). For lower modifier concentrations only minor attenuation of the bands could be observed between adsorption and desorption, indicating that all features belong to surface species. The spectra clearly show that the amplitude of the signals changes differently with time, in particular for concentrations higher than 0.05 mM, supporting the observation that more than one species evolves on the metal surface depending on time and surface crowding. At all solution concentrations a similar set of signals can be observed between 1600 and 1450 cm⁻¹, whereas Figure 5d shows that both sets of signals at 1590 and 1510 cm⁻¹ and at 1598 and 1495 cm⁻¹ are dramatically attenuated by rinsing with the solvent, suggesting that they must be related to weakly adsorbed species. However, signals that can be associated with more strongly adsorbed species are also detected. Figures 4 and 5 indicate that the signals at 1570 and 1530 cm⁻¹ are rather independent from each other and from the pairs of signals at 1598–1495 cm⁻¹ and 1590–1510 cm⁻¹. The time-dependent behavior of

Table 2. Calculated Adsorption Energies (kcal/mol) of the Anchoring Groups of CD and PhOCD at the Edge of Pt 38 Clusters as Shown in Figure 6

structure	energy
6(a)	68.0
6(b)	65.2
6(c)	80.2
6(d)	61.5

the signals in the 1650–1450 cm⁻¹ spectral region suggests that different species contribute to the spectrum of PhOCD on the Pt surface. The ATR spectra of Figure 4A very much resemble those of CD on Pt/Al₂O₃ model films at 283 K except for the pair of signals due to the phenyl ring.⁵⁰ This resemblance suggests that PhOCD displays similar surface species. Hence, we assign the bands at 1510 and 1590 cm⁻¹ to a species where the interaction with Pt is mainly via the lone pair of the quinoline-N. The band at 1569 cm⁻¹ can be associated with a nearly flat adsorbed species, where the dominant interaction with Pt occurs through the chemisorption of the quinoline moiety. Finally, the feature at 1530 cm⁻¹ is assigned to α -quinolyl-like species, which is also tilted away from the metal and has the quinoline ring adsorbed via both the nitrogen atom and the neighboring α -carbon.

To obtain a clearer picture of the adsorption behavior of PhOCD, DFT calculations have been performed to study the adsorption energies and geometries that may be relevant in this process. The adsorption of PhOCD was calculated by considering the quinoline ring of the alkaloid as responsible for its interaction with the metal. The validity of this assumption is discussed elsewhere;^{62,63} here we only mention that both spectroscopic and theoretical data collected in the past few years strongly support the assumption.^{50,57,60} Table 2 shows the calculated adsorption energies associated with the structures in Figure 6, which will be briefly discussed here. Figure 6a shows the anchoring part of CD, 4(*S*)-(1-hydroxyethyl)quinoline (HEQ, Scheme 2) adsorbed parallel to the surface.

Previous studies on the anchoring part of CD on a Pt 31 cluster,⁵⁷ at a similar level of theory, are not directly comparable to the present one, for what concerns the energies of adsorption, due to the following reasons: (i) a Pt 38 cluster has more free surface; (ii) the previously used cluster was rigid in contrast to the present cluster, where the central nine atoms are set free to optimize to partially reproduce surface reconstruction; (iii) whereas in the former calculations the position of quinoline on the cluster was central, in the present work it was set on one side of the cluster, to leave space for calculating also the ether group and its contribution to adsorption; (iv) although the present calculations use the same Hamiltonian and basis set for platinum as the previously published ones, for second-row elements polarization functions were added. The qualitative picture of the adsorption mode of the quinoline moiety does not change, whereas the adsorption energy undergoes the same changes already noted for the variation of the described parameters.⁵⁴ Figure 6b shows the anchoring part of PhOCD, namely, 4(*S*)-(1-phenoxyethyl)quinoline (PEQ, Scheme 2), also adsorbed parallel to the surface and in the same position. In this geometry, the phenyl ring was found to be physisorbed and slightly tilted

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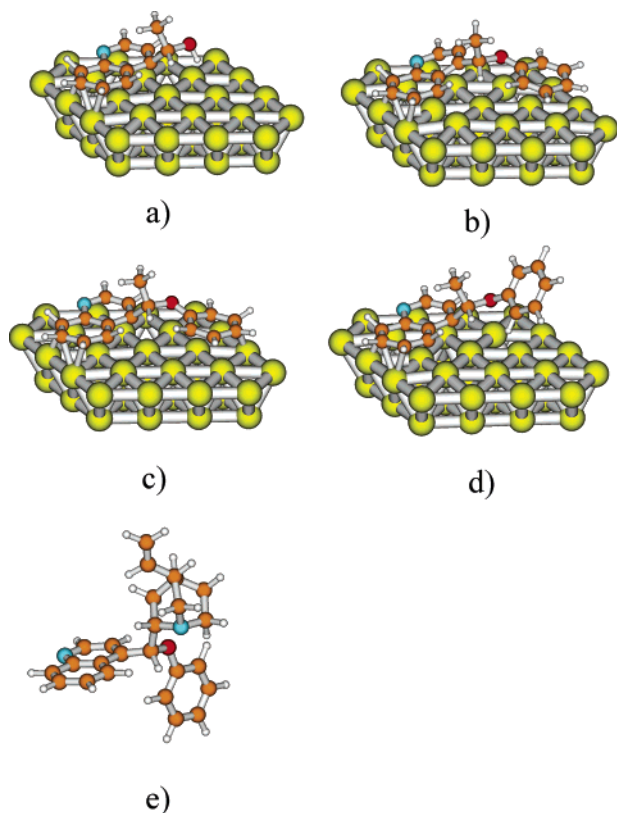
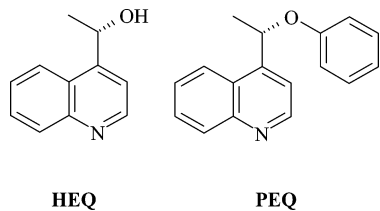


Figure 6. (a) HEQ adsorbed via the quinoline ring lying parallel to the surface, on the edge of the cluster; (b) PEQ adsorbed via the quinoline ring lying parallel to the surface with the physisorbed phenyl ring also adopting a position parallel to the surface; (c) PEQ adsorbed via the quinoline ring lying parallel to the surface with the chemisorbed phenyl ring; (d) PEQ adsorbed via the quinoline ring and with the phenyl ring lying tilted with respect to the metal surface; (e) PhOCD in its minimum energy conformation in a vacuum.

Scheme 2. “Anchoring Moieties” 4(*S*)-(1-Hydroxyethyl)quinoline (HEQ) and 4(*S*)-(1-Phenoxyethyl)quinoline (PEQ) of the Modifiers Used for the DFT Calculations



with respect to the metal surface. Its adsorption energy is smaller by ca. 3.0 kcal/mol than that of HEQ on the same surface site. Figure 6c shows the adsorption of PEQ analogous to that shown in Figure 6b, but with the phenyl ring partially adsorbed on the metal. The formation of chemical bonds to the surface via the phenyl ring results in an adsorption energy over 10 kcal/mol larger than that of HEQ on the same surface site (Table 2). Finally, Figure 6d shows the adsorption of PEQ where the phenyl ring adopts a highly tilted position with respect to the surface. This conformation is the least stable, with an adsorption energy of ca. 61.5 kcal/mol. The DFT calculations confirm the similarity between the adsorption modes of CD and PhOCD and also show that the phenyl ring can occupy the space surrounding the alkaloid with different geometries, increasing or decreasing the total adsorption energy.

Competitive Adsorption. Figure 7 depicts the in situ ATR spectra obtained upon adsorption of PhOCD followed by

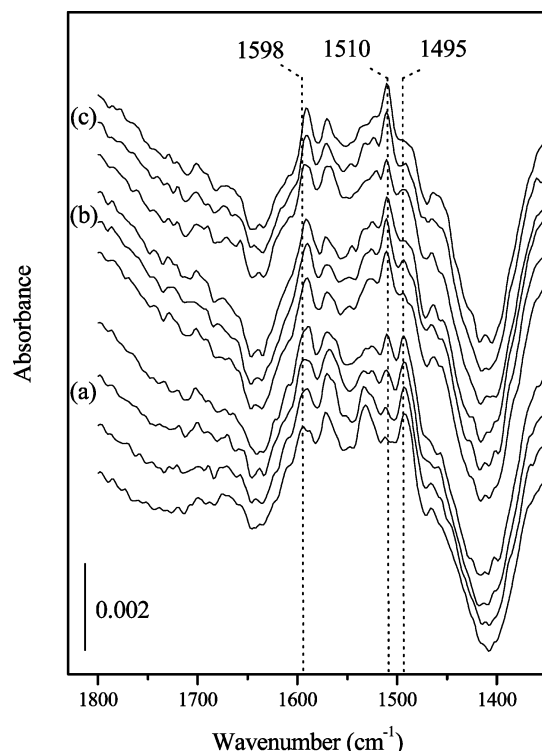


Figure 7. In situ ATR spectra of (a) PhOCD on Pt/Al₂O₃ in H₂-saturated CH₂Cl₂ (spectra taken at 4, 20, 40, and 60 min on stream, from bottom to top) followed by (b) CD in H₂-saturated CH₂Cl₂ (2.5, 20, and 40 min on stream) and (c) the same solution as in (a) (4, 20, and 40 min on stream). The concentration of the chiral modifiers is 0.05 mM.

adsorption of CD. For the two chiral modifiers an identical solution concentration (0.05 mM) was used and their adsorption monitored on a similar time scale.

The signals of PhOCD adsorbed onto Pt have been discussed in the previous section. The evolution of the signals well reproduces the data shown in Figure 4B for the same solution concentration. As expected, the feature assigned to the α -quinolyl species almost completely disappears over 40 min, whereas the signals at 1590 and 1510 cm⁻¹ increase with time, indicating that the surface crowding induces the increase in the population of N-lone pair bonded species. The signal at 1495 cm⁻¹ can be used to qualitatively follow the behavior of PhOCD, when a solution of CD is contacted with the previously PhOCD-modified Pt surface. As previously mentioned, the band is diagnostic for the phenyl ring of PhOCD, as this is the only significant difference in the infrared spectra of the two modifiers in the 1700–1400 cm⁻¹ spectral region. Figure 7b shows that after 40 min under a stream of a CD solution the signal at 1495 cm⁻¹ is completely attenuated, in contrast to the signals at 1510 and 1590 cm⁻¹ which become the most prominent. Simultaneously, the shape of the envelope at around 1590 cm⁻¹ changes due to the disappearance of the high-frequency shoulder (1598 cm⁻¹). We interpret this behavior as the relatively fast displacement of PhOCD from the metal surface by CD. When a solution of PhOCD at the same concentration is again admitted over the modified Pt surface, the signals at 1598 and 1495 cm⁻¹ hardly appear, indicating that the chiral layer formed by CD is more stable than that created by PhOCD and that CD adsorbs more strongly than PhOCD on Pt, under the conditions applied. To further confirm this interpretation, the experiment in the reverse order has also been carried out. At first, CD has been

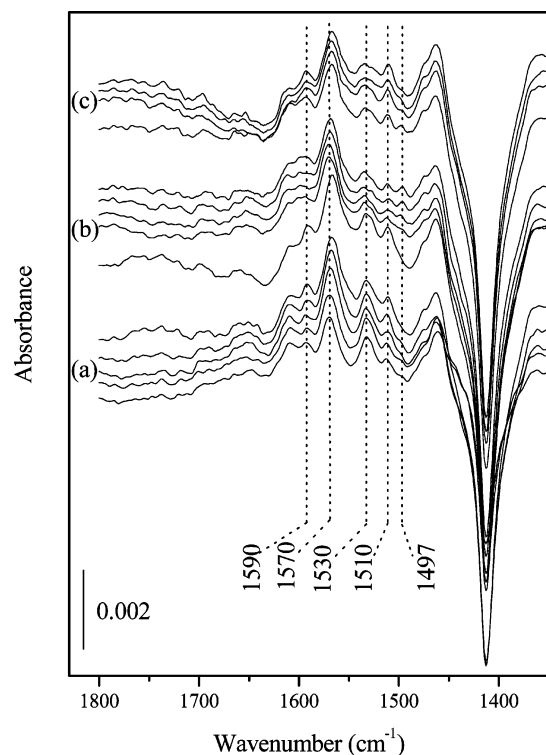


Figure 8. In situ ATR spectra of (a) CD on Pt/Al₂O₃ in H₂-saturated CH₂Cl₂ (spectra taken at 4, 20, 30, 40, and 60 min on stream, from bottom to top) followed by (b) PhOCD in H₂-saturated CH₂Cl₂ (4, 10, 20, 40, and 60 min on stream) and (c) H₂-saturated CH₂Cl₂ (10, 15, 20, and 30 min on stream). The concentration of the chiral modifiers is 0.05 mM.

adsorbed from a 0.05 mM solution in H₂-saturated solvent on a cleaned Pt surface. The spectra in Figure 8a show a significant difference from those depicted in Figure 7b; that is, CD adsorbs preferentially close to parallel to Pt at this concentration on a clean Pt surface. This adsorption mode is indicated by the prominent signal at 1570 cm⁻¹.⁵⁰ Next, changing to a solution of PhOCD (Figure 8b) resulted in the appearance of only a weak signal at 1497 cm⁻¹ and in the attenuation of the signals associated with the N-lone pair bonded species of CD, in agreement with the observation that this species desorbs from Pt when CD is no longer available in solution.⁵⁰ Figure 8c shows that the small amount of adsorbed PhOCD was removed upon rinsing with H₂-saturated solvent, as the signal at 1497 cm⁻¹ disappeared. CD is manifestly still adsorbed, similarly to the situation obtained in Figure 7c, but with the difference that the strongest signals in Figure 7c are associated with the N-lone pair bonded species, whereas the species adsorbed with the anchoring group parallel to the surface largely dominates the spectrum in Figure 8c. Note also the remarkable difference in the intensity displayed by the signal of the quinuclidine moiety, which is pronounced for CD (Figure 8) and practically silent for PhOCD (Figure 7).

Discussion

The study of the adsorption of a cinchona alkaloid onto a metal surface is a major step toward understanding the functioning of the modifier during reaction. The anchoring of the modifier to the metal and the decrease of its degree of freedom to give a defined molecular conformation are key aspects of the overall enantioselective process. The adsorption geometry of the large PhOCD can be better understood by splitting its

molecular structure into subunits and analyzing the adsorption of each single subunit on the metal surface. CD is the major skeleton of PhOCD, and its adsorption from solution has been already reported on Pt and Pd.^{50,55,56,58,60} The additional features of the phenoxy group of PhOCD can be analyzed by using anisole as a model compound. The spectroscopic data suggest that anisole displays at least two species on the metal surface. At low concentration, i.e., at low surface coverage, a species adsorbed via the aromatic ring lying parallel to the surface dominates over a tilted species. DFT calculations clearly show that the energetically favored adsorption mode for anisole on Pt is adsorption via the aromatic ring lying parallel to the surface, and in this position the O-CH₃ group points away from the surface. The ATR spectra match this adsorption mode since the parallel adsorbed surface species is essentially characterized by the deformation modes of the methyl group. Additionally, a second weakly adsorbed species is observed in the ATR spectra at high solution concentration shown in Figure 1, where the phenyl ring of anisole is tilted with respect to Pt.

The presence of anisole adsorbed via the phenyl ring being tilted with respect to Pt is crucial for interpreting the ATR spectra of PhOCD adsorbed on Pt/Al₂O₃ (Figures 4 and 5). Surface species similar to those observed for CD evolve on the metal surface with time, under the same conditions. The observation that the ratio between the signals of the phenyl ring at 1601 and 1497 cm⁻¹ is unaffected by adsorption from solution to the Pt surface, whereas the internal intensity ratio between the signals associated with the quinoline ring significantly changes and corresponds to the typical changes observed for CD adsorption on Pt,⁵⁰ indicates that quinoline is also the main anchoring group of PhOCD.

The evolution of the ATR signals of the quinoline ring of PhOCD suggests that—analogously to the adsorption of CD—three coexisting adsorption modes can be distinguished. These adsorption modes are characterized by (i) the quinoline ring lying nearly parallel to Pt, (ii) the quinoline ring suffering α -H abstraction (α -quinolyl species), and (iii) the quinoline ring being anchored to Pt via the N-lone pair. Different sets of signals belonging to the quinoline ring characterize each single species (Table 1), whereas under the assumption that PhOCD does not adsorb dissociatively on Pt, all detected species bear the vibrational modes belonging to the phenyl ring. This assumption is supported by the resistance against the hydrogenolysis of the ether connectivity of PhOCD under nonacidic conditions.³¹

The three adsorption modes observed for PhOCD show different stability on the metal surface. The α -quinolyl species appears less populated at longer time on stream, probably owing to the rehydrogenation of the α -carbon atom under the continuously reducing conditions and to the increasing surface crowding, favoring the N-lone pair bonded species. This latter species is easily removed from Pt by rinsing with the solvent as indicated by the attenuation of the band at 1510 cm⁻¹ (Figure 5). The species adsorbed via the quinoline ring close to parallel with respect to Pt, characterized by the signal at 1570 cm⁻¹, appears the most stable. The importance of the flat adsorbed species in the catalysis is the major reason for limiting the DFT calculations only to such species, as already demonstrated for CD.⁵⁷

A correct assignment of the observed signals due to the phenyl ring is more demanding. The facts that the ATR spectra exhibit

the bands characteristic of this group at all solution concentrations and the absorbance of these bands (1598 and 1495 cm^{-1}) increases at high concentration (Figures 4 and 5) suggest that the group is tilted with respect to Pt. This conclusion is consistent with the observation that the phenyl ring is not hydrogenated (saturated) on Pt/ Al_2O_3 , in contrast to the reactivity of anisole under identical reaction conditions.³¹ A qualitative distinction between the phenyl group of the flat and N-lone pair bonded species can be done considering that the signal at 1497 cm^{-1} is observed already at low coverage, as clearly shown in the bottom spectra for each concentration in Figure 5. Hence, flat species bear a tilted phenyl ring with respect to the surface. Similarly, after removal of the weakly N-lone pair bonded species by rinsing with H_2 -saturated solvent, strongly bound species display the features of the phenyl ring (Figure 5c,d). However, the signal at 1495 cm^{-1} hardly changes for concentrations below 1 mM , whereas that at 1510 cm^{-1} increases with adsorption time. The net constant intensity of this band is probably due to a combination of two effects. Owing to the strong tilting of the quinoline ring of the N-lone pair species, the phenyl ring is expected to show rotational freedom similar to PhOCD in solution. On the other hand, the increase in surface coverage with time also involves the possible rearrangement of flat adsorbed species into N-lone pair species.⁵⁰ Note that the time-dependent evolution of the three species certainly affects the intensity of these bands due to the possible different orientation of the phenyl ring for each species with respect to Pt.

With HEQ and PEQ being the determining moieties for the adsorption energies of CD and PhOCD, the comparison between the ATR spectra and the computed geometries in Figure 6a–d assists us in assigning the reactive conformations of the adsorbed alkaloids. The DFT calculations identify three possible flat species, having as a corresponding species in the ATR spectra the one characterized mainly by the signal at 1570 cm^{-1} . The computationally most stable conformation is the one shown in Figure 6c, where the phenyl ring contributes to the chemisorption of the alkaloid by forming bonds to the surface. This structure has a predicted adsorption energy of ca. 80 kcal/mol . Catalytic experiments^{30,31} show that following the addition of CD to a platinum catalyst pretreated with PhOCD, an inversion of enantioselectivity occurs; therefore CD must be more strongly adsorbed than the active catalytic PhOCD surface species. This result apparently contradicts the calculations; however, it should be pointed out that PhOCD occupies more surface (larger cross-sectional area), and a critical contribution for its replacement could come from the entropy. This aspect cannot be accounted for in the present calculations, from which only enthalpy differences can be derived. It is therefore not yet clear whether the geometry shown in Figure 6c is responsible for enantio-differentiation. Note that the chemisorption and the flat geometry of the phenyl ring within this species would result in hardly detectable vibrational modes for this group in the considered frequency range. The fact that when rinsing with the solvent the ATR spectra display a signal at 1570 cm^{-1} assigned to species where the quinoline is flat, whereas the signals due to the phenyl group are clearly diminished (Figure 5), suggests the presence of a geometry such as that shown in Figure 6c, consistent with the surface selection rule.

The structure in Figure 6b is less stable than the one in Figure 6a. The physisorption of the phenyl ring does not compensate

for the loss of the hydrogen bond to the surface due to the replacement of the OH group of CD with the phenyl ring, which was estimated to contribute about 5 kcal/mol in a previous study.⁵⁷ Similarly to the former species the phenyl ring would be barely IR active. It is furthermore reasonable to think that the structure in Figure 6b is a precursor to the structure in Figure 6c. Both structures may be destabilized by lateral interactions due to the concomitant presence of more alkaloid molecules on the metal and/or other adsorbates (reactant, solvent). This effect cannot be accounted for quantitatively by the present calculations, but has been reported as a possible cause of destabilization.⁵³

The most stable conformation of PhOCD in a vacuum is shown in Figure 6e. Similarly to all other conformers it displays no coplanarity between the phenyl and the quinoline rings.⁶⁴ Therefore, it seems likely that the adsorption process from solution implies a major rearrangement of the geometry of the alkaloid.

The structure in Figure 6d is consistent with both spectroscopic and catalytic experiments. The difference in adsorption energy from the structure in Figure 6a allows for its substitution by CD in a competition experiment. The position of the phenyl ring with respect to the surface well reflects the retained ratio upon adsorption, indicating little interaction with the metal, and the direction of the local dipole moment associated with the vibrational modes of the ring (Figure 2). It is furthermore important to note that also for anisole the most stable species is chemisorbed, as shown in Figure 3, but tilted species are experimentally observed despite their smaller adsorption strength. This is likely due to surface crowding.

Although the adsorption behavior of CD and PhOCD is similar, some subtle differences with respect to the population of the different species should be considered. For example, a comparison of Figures 4, 5, 7a, and 8a reveals that the ratio between the N-lone pair bonded and tilted adsorbed species can be larger for PhOCD on a clean Pt surface.

A more important difference between the ATR spectra of CD and PhOCD is that on clean Pt the quinuclidine moiety is clearly visible in the case of CD, whereas it is silent in the spectra of PhOCD. This is best shown in Figure 4 for the 0.05 mM concentration. The band at ca. 1460 cm^{-1} is clearly visible only at high solution concentration. This signal results from $\delta(\text{C-H})$ scissor modes inducing a transition dipole moment vector oriented predominantly along the N–C(4) axis (Scheme 1).^{50,58} According to the surface selection rule the observation of a strong band associated with these modes in the spectra of adsorbed CD means that this vector has a strong projection perpendicular to Pt, thus approximately positioning the quinuclidine-N on top of Pt and the N–C(4) axis perpendicular to it. The absence of the band associated with this moiety in PhOCD on Pt strongly suggests that the orientation of quinuclidine with respect to the metal changes. This observation opens the possibility of a deeper insight into the conformation of the different adsorption modes at a molecular level. All recent attempts to monitor CD adsorption on Pt by infrared and Raman spectroscopy^{50,55,56} described in detail the orientation of the quinoline ring but failed to rationalize the position of the quinuclidine moiety with respect to the metal surface. So far,

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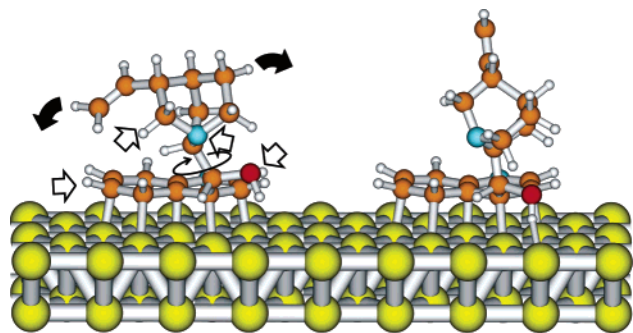


Figure 9. Surface Open(5) (SO5, left) and Surface Open(3) (SO3, right) conformations of cinchonidine on the surface. The circular arrow indicates the rotation of the quinuclidine skeleton around the C(9)–C(8) bond. Black arrows indicate the possible rotation of the quinuclidine skeleton toward and away from the surface around the C(4′)–C(9) bond. Open arrows indicate the elements (quinoline and quinuclidine skeletons, quinuclidine-N, O-connectivity) contributing to attractive and repulsive interactions and forming the chiral pocket on the metal surface.

the Open(3) conformation of CD, which is the most stable in solution, particularly in apolar medium,^{65,66} has been considered to be responsible for enantiodifferentiation, although little or no interaction is possible between the surface and the quinuclidine-N. Clearly, the enantioselection on the Pt surface cannot be understood without clarifying the position of the basic N atom that interacts with the carbonyl group of the reactant.^{8,37–40} More insight can be gathered if the ATR-IR spectrum of CD on a metal surface can be compared to that of one of its derivatives, namely, PhOCD, as made in this work. It should be pointed out that besides the identification of the chiral modifier–reactant interaction,⁶⁷ no spectroscopic investigation is available yet that can describe the configuration adopted by CD on Pt *during* interaction with the reactant. The population and the conformation of the modifier adsorbed on the metal surface in the absence and in the presence of the reactant may be different as a consequence of the easy rotation of the quinuclidine moiety around the C(4′)–C(9) bond. Figure 9 shows two surface conformations of CD corresponding to energy minima obtained by rotation around the C(9)–C(8) and C(4′)–C(9) bonds (Scheme 1).⁵⁷ Following the notation used for the conformations of CD in apolar solvents,⁶⁶ the conformations were called Surface Open(5) (SO5) and Surface Open(3) (SO3). The fact that the quinuclidine moiety appears in the spectra of CD, whereas is absent in those of PhOCD, gives experimental evidence for the flexibility due to this rotational freedom. The position of the quinuclidine-N relative to the metal together with the quinoline ring and the O-connectivity defines the chiral space (*chiral pocket*) as it is depicted in Figure 9.

The most important consequence of the mobility of the quinuclidine skeleton is the change in the conformation of the adsorbed alkaloid resulting in the existence of chiral spaces other than those defined by the SO3 and SO5 generated by rotation around the mentioned bonds.⁵⁷ Recent molecular dynamic calculations confirmed that adsorbed CD could adopt a conformation in which the quinuclidine moiety is close to the metal rather than hanging above the anchoring group as in Open(3).⁶⁸

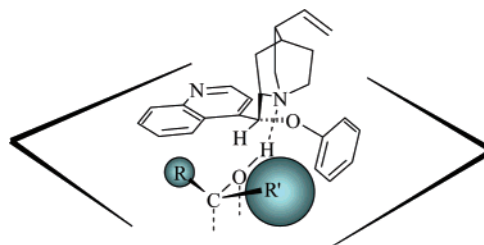


Figure 10. Schematic representation of the attractive and repulsive interactions between the half-hydrogenated state of the activated ketone and the basic quinuclidine-N atom of the chiral modifier and the modifier skeleton, respectively. The size of the spheres is thought to be proportional to the size of the substituents R and R′.

The geometry or shape of the chiral pocket and the adsorption strength of the modifier govern the outcome of the nonlinear behavior of modifier mixtures.

The competitive adsorption of CD and PhOCD on Pt can be followed by the sequence of spectra in Figures 7 and 8, which show that CD is more strongly bound to the metal surface than its *O*-phenyl derivative. The almost complete replacement of PhOCD by CD leads to the formation of a new chiral metal surface, which affords the opposite enantiomer in excess in the hydrogenation of some activated ketones.^{30,31} In heterogeneous enantioselective hydrogenation on Pt-group metal catalysts, the nonlinear behavior originates from the different interaction between adsorbed chiral modifiers and the metal surface. This interaction depends on the chiral space where the reactant is accommodated and interacts with the quinuclidine-N function of the modifier.

Among the proposed mechanistic models for the enantioselective hydrogenation of activated ketones, we favor the model involving an attractive interaction between a half-hydrogenated state of the prochiral ketone and the quinuclidine-N and a repulsive interaction between the skeleton of the modifier and the bulkier side of the ketone,^{40,57} as schematically represented in Figure 10. Since the absolute configuration of CD and PhOCD is identical (Scheme 1), the observed inversion in enantioselectivity^{30,31} is obviously related to the replacement of the OH function of CD by the *O*-phenyl group. The most important consequence of this substitution is that the shape of the chiral space formed by the adsorption of PhOCD onto the metal is modified with respect to that formed by CD.

According to a lock-and-key concept, different chiral spaces can selectively accommodate chiral reactants. In the present case, the surface pro-(*R*)- and pro-(*S*)-EP and KPL experience opposite matching with the chiral spaces generated by CD and PhOCD. On the basis of the present experimental and theoretical data, the most likely roles of the phenyl group in determining the inversion of shape selectivity are (i) restructuring of the chiral pocket formed by adsorption of CD due to the bulkiness of the phenyl ring but preserving the SO3 or SO5 conformations;⁵⁷ and (ii) repositioning of the quinuclidine moiety by rotation around the C(4′)–C(9) bond with respect to the surface, leading to a chiral pocket different from that already described by the SO3 and SO5 conformations.

Both effects may be synergic, since the structure in Figure 6d shows that the phenyl ring is occupying a region in space that was supposed to accommodate the large substituent side of a pro-(*R*) adsorbed ketone,⁵⁷ but can furthermore cause a rearrangement of the quinuclidine moiety, generating a chiral

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space different from SO3 and SO5. A more detailed study of the conformational changes due to the presence of various bulky ether groups is under way in our laboratory, to better characterize the surface binding site experienced by the reactant during the enantioselective hydrogenation.

Conclusions

Chemical devices that can lead to the switch of the enantioselective properties of a heterogeneous catalyst can function according to several principles, one of which is that of the simultaneous tuning of the chemisorption potential of the chiral modifier and fine-tuning of the chiral active space eventually selecting the reactant in a lock-and-key concept. The present investigation was able to witness, through ATR spectroscopy of the two nonlinearly behaving modifiers CD and PhOCD, the process of substitution and remodification of a platinum model catalyst and to observe the changes associated with such modification. High-level electronic structure calculations were also performed as a complement to the spectroscopic data. CD and PhOCD display similar adsorption modes, and in both modifiers the quinoline ring is predominantly piloting the adsorption onto the metal surface. The competition at the surface among the chiral modifiers and the substitution process are governed by the different adsorption strengths of the two chiral modifiers. Replacement of the OH function of CD by a phenoxy group in PhOCD can generate conformations whose adsorption energy is decreased with respect to CD. Another, equally important change is the modification of the chiral pocket obtained upon adsorption of the alkaloid on the metal surface. These changes are sufficient to induce the inversion of enantioselectivity in the hydrogenation of an α -ketoester, an α -ketolactone, α,α,α -trifluoromethyl ketones, and α -hydroxyketones as reported recently.^{30,31,69}

Molecular level information concerning the conformation of the modifiers adsorbed on the metal surface in the presence of hydrogen and an organic solvent could be gathered, in particular concerning the position of the quinuclidine moiety with respect to the metal surface. According to our present understanding of the reaction mechanism, the spatial position of the quinuclidine N atom is critical for description of the reactant–modifier interaction and thus in the whole enantiodifferentiating process.

Several attempts have been made to explain the nonlinear behavior of modifier mixtures in heterogeneous catalysis. The present work represents the first in situ spectroscopic evidence for the competition between chiral modifiers at a metal surface, and the high-level DFT calculations provide the theoretical basis for the striking differences in the adsorption strength and adsorption modes of these modifiers on the Pt surface.

A description of the processes that are believed to be at the base of enantiodifferentiation on chiral metal surfaces has been given. Understanding of the adsorption behavior of modifiers that afford the opposite enantiomers in excess should stimulate the development of *R–S* chemical switches on chiral metal surfaces.

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Supporting Information Available: Complete refs 43 and 44. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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