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Hidden Beneath the Surface: Origin of the Observed Enantioselective Adsorption on PdGa(111)

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Abstract

We unravel the origin of the recently observed striking enantioselectivity of the PdGa(111) surface with respect to the adsorption of a small organic molecule, 9-ethynylphenanthrene, using first-principles calculations. It turns out that the key ingredient to understand the experimental evidence is the appropriate description of van der Waals interactions beyond the widely employed atomic pairwise approximation. A recently developed van der Waals-inclusive density-functional method, which encompasses dielectric screening effects, reveals the origin of the experimentally observed enantioselectivity and provides conclusive evidence of chiral recognition on a bimetallic surface driven by dispersion interactions. The incorporation of dielectric screening

leads to a renormalization of the dispersion interaction range allowing for the appropriate weighting of the molecule-substrate interactions at intermediate distances between 2.5 and 5 Å. Our findings have implications for the structure and stability of complex organic/inorganic systems where dielectric screening effects are expected to be of general importance.

Introduction

PdGa is an intermetallic compound that emerged recently for its catalytic properties in the purification of the feedstock for the polyethylene production.¹⁻⁴ Rameshan et al.⁵ have also shown that PdGa in contact with oxygen or when supported by metal-oxide substrates, can be used as CO₂ selective catalyst in the methanol steam reforming process. Moreover, recently Prinz et al.⁶ demonstrated that PdGa can be potentially used as enantioselective heterogeneous catalyst due to its chiral crystal structure.

The cubic unit cell of PdGa has eight atoms and belongs to the $P2_13$ space group (see Figure-1a, inset). It exhibits two enantiomeric forms, labeled **A** and **B** in the literature.^{7,8} In a recent work⁹ the surface terminations of PdGa(111) and PdGa($\bar{1}\bar{1}\bar{1}$) surfaces obtained by sputter-annealing cycles of a PdGa crystal grown by the Czochralski method¹⁰ were determined. The assignments derived in this work were then confirmed by later experiments and simulations.^{6,11,12} The two surfaces do not present reconstruction, have equal surface symmetry but exhibit different atomic configurations of the Pd atoms. Referring to the **A** form, the most stable ($\bar{1}\bar{1}\bar{1}$) termination (Pd₃ in the literature⁷) is characterized by one Pd trimer per surface unit cell in the outer atomic layer (Figure-1b) while the (111) termination (Pd₁ in the literature⁷) exhibits one isolated Pd site per unit cell (Figure-1c).

Figure 1: Atomistic models of a PdGa:A slab and top views of the Pd₃ and Pd₁ surfaces. Gray (black at the surface) and violet spheres represent Pd and Ga atoms respectively. (a) $[0\bar{1}1]$ view of a PdGa:A slab. The cell, used in our simulations, contains 23 atomic layers terminated by the Pd₁ surface on top and the Pd₃ surface on the bottom. The inset shows the PdGa:A bulk unit cell. (b) Top view of the Pd₃ surface with Pd trimers highlighted in black. (c) Top view of the Pd₁ surface with Pd isolated sites highlighted in black.

For both surfaces the second atomic layer consists of Ga trimers while the third atomic layer is a single Pd atom per unit cell for the Pd₃ surface and a Pd trimer for the Pd₁ surface. Despite the outermost atomic layer of the Pd₁ and Pd₃ surfaces being achiral, the structure of the second and third layer induces a surface chirality (see SI for details).

The difference in adsorption energy of a chiral or prochiral molecule on a chiral substrate is at the origin of chiral molecular selection, a process of crucial relevance in diverse chemical fields ranging from pharmaceuticals to materials science.

We can today optimistically say that the original claim of Jacoby,¹³ on the lacking of exploration of the chiral surface chemistry, was not ignored. Indeed, the theoretical and experimental exploration of chiral inorganic surfaces has been considerably growing in the last decade, particularly with focus on surface steps (see, e.g.,¹⁴). Most studies, however, exploited the concept that enantioselectivity requires the functionalization of the substrate (through steps, adatoms or, in general, nanopatterning) such that three side groups of the adsorbate molecule are confined within a stereoselective environment.^{15–17}

We extend such concepts and note that surface chirality can originate not only from the

functionalization of the surface itself (through steps or defects) but also from the natural termination of bulk chirality, as in the intermetallic compound PdGa which is the focus of this work.

Recently, the possibility to exploit the intrinsic bulk chirality of PdGa has been demonstrated by Prinz and coworkers⁶ for the Pd₁ surface. It was proven that adsorption of the prochiral molecule 9-ethynylphenanthrene (9-EP shown in Figure-2c) on PdGa:A(111)Pd₁ shows enantiomeric excess (defined as $(n_R - n_S)/(n_R + n_S)$ where n_R and n_S are the number of R and S enantiomers, respectively) of more than 0.9 for the R surface enantiomers (and for the S surface enantiomer on the mirror symmetric equivalent surface PdGa:B($\bar{1}\bar{1}\bar{1}$)Pd₁). In their work, Prinz and coworkers study the temperature dependence of the enantioselective process and show that the racemic form obtained after deposition of 9-EP at temperatures below 120 K is transformed to an almost enantiopure ensemble at room temperature. The mechanism responsible for this high enantioselectivity has remained elusive up to now.

Density functional theory^{18,19} (DFT) has been established as a reliable standard for the study of materials properties, however the accurate modeling of adsorption phenomena for organic molecules on metal surfaces on a first-principles level is still challenging, especially due to the large size of atomistic models needed to reliably describe the physics and chemistry of the system under investigation. Moreover, traditional density functional approximations (DFAs) fail to reproduce van der Waals (vdW) interactions that are crucial for the correct estimate of adsorption energies and geometries in adsorbate-substrate systems.^{20,21} In recent years, several vdW-inclusive DFAs have been developed, ranging from pairwise-additive models, over non-local functionals, up to many-body approaches.^{22–28} In particular, it was shown that the inclusion of many-body dielectric screening effects leads to an improved description of geometries and energetics for molecule/surface systems,^{20,21} supermolecular complexes,²⁹ and molecular crystals.^{30–32}

In this work, we unravel the mechanism responsible for the thermally activated enantioselectivity of the Pd₁ surface with respect to adsorption of 9-EP and we demonstrate the

importance of dielectric screening in the description of dispersion interactions in order to understand the surface selectivity. In doing so, we provide the first evidence of chiral recognition on a surface driven by dispersion interactions. Our findings also have implications for complex organic/inorganic systems where dielectric screening effects are expected to be of general relevance.

Results and discussion

To understand the origin of the enantioselective adsorption of 9-EP on the Pd₁ surface we carry out three subsequent analysis steps: i) we show that the assignments made by Prinz and coworkers⁶ on the adsorption geometries of the *R* and *S* form of 9-EP on the Pd₁ surface are correct; ii) we demonstrate how a racemic mixture can be converted in enantiomeric excess; iii) we identify the molecule–substrate interactions responsible for the enantioselectivity assuming that the experimental scanning tunneling microscopy (STM) images were taken at the thermodynamic equilibrium state. Points ii) and iii) required challenging calculations both in terms of computational effort and in terms of accuracy of the underlying methodology.

Adsorption geometry of 9-EP on Pd₁ surface

To demonstrate the *R* and *S* adsorption geometries hypothesized in the experiments, we show in Figure-2 one of the experimental STM images measured by Prinz and coworkers. We focus here on the case of *R* and *S* enantiomers on the defect free surface.

Figure 2: Experimental and theoretical STM images for the adsorption of 9-EP on PdGa:A(111)Pd₁. (a) *R* and *S* adsorbate on the PdGa:A(111)Pd₁ surface. (b) Zoom showing *R* and *S* surface enantiomers. (c) Chemical sketch of the 9-EP molecule laying in the *R* orientation. (d,e) Simulated STM images showing agreement with the experimental data. Experimental images courtesy of Samuel Stolz and Roland Widmer from the nanotech@surface laboratory at Empa.

In the experimental STM images, the 9-EP molecules present an asymmetric three-lobe morphology whose handedness can be inferred from the direction of rotation going from the largest to the smallest lobe (see Figure-2a,b). Prinz and coworkers concluded that the 9-EP molecule is located on top of three isolated Pd atoms belonging to the topmost layer.⁶ A detailed analysis of the STM patterns made evident that two different adsorption sites can be distinguished for both enantiomers: *R* and *R*^{*} as well as *S* and *S*^{*}, where “starred” configurations are located on top of a Ga trimer from the second layer while the “non-starred” configurations are aside of it (Figure-3).

Figure 3: Representation of R and S adsorption geometries of 9-EP on top of the PdGa:A(111)Pd₁ surface. (a) R geometry, located aside of the Ga trimer; (b) R^* geometry, located on top of the Ga trimer; (c) S geometry, located aside of the Ga trimer. (d) S^* geometry, located on top of the Ga trimer. Gray (black at the surface) and violet spheres represent Pd and Ga atoms respectively. Cyan and white spheres represent C and H atoms of the 9-EP molecule, respectively.

We computed the adsorption energies of “starred” and “non-starred” configurations with different functionals and vdW parameterizations (see Table-S1 in SI). All functionals (except BEEF-vdW) predict the R isomer to be the most stable one. However, the energetic ordering of the remaining configurations finds some discrepancies among the different functionals. The assignment of adsorption geometries to respectively R and S or R^* and S^* is better clarified by comparing simulated STM images to experimental ones (See Figure-2d,e; Figure-4). To elucidate the comparison, one should focus on the positions of the dark spots on the surface (whose position is on top of subsurface Pd trimers). For R and S geometries the dark regions are located on the sides of the ethynyl “finger”, while in the R^* and S^* the dark spots are located in front of it (for a comparison to the experimental images of the minority starred configurations we refer the reader to the original work by Prinz et al.⁶). The analysis of the details reveals matching of the geometries proposed in the experiment with the ones considered in the calculations.

Figure 4: Comparison of experimental and simulated STM images of *R* and *S* enantiomers adsorbed on different adsorption sites. (a) Simulated image of *R* configuration. (b) Simulated image of *R*^{*} configuration. (c) Experimental STM image of *R* and *S* configurations. (d) Simulated image of *S* configuration. (e) Simulated image of *S*^{*} configuration. Green circles highlight dark spots on the surface to better recognize the orientation of the ethynyl "finger"

R ↔ S transformation mechanism

The nature of 9-EP/PdGa:A(111)Pd₁ interaction is not purely dispersive, since a contribution from chemical bonding is also evident from a change of the hybridization state of the C-atom connected to H in the ethynyl group of 9-EP (see supporting information). Coexistence of dispersion interactions and chemical bonding results in a high adsorption energy, on the order of -2.5 eV, for the 9-EP molecules. This finding is consistent with the experimental evidence that the molecules do not desorb from the substrate even after annealing cycles up to 670 K (temperature at which dimers are formed on the surface) and rises the question: how is it possible that adsorbed 9-EP molecules switch their chirality from *S* to *R* already at room temperature?

To answer this question we enter the second analysis step with two hypotheses: either the ethynyl group can migrate via a surface mediated reaction from the 9th to the 10th Carbon atom (while Hydrogen does the opposite) or a low energy path exists for the flipping of the molecule at the surface. We discarded our first hypothesis, as discussed in the SI, since at low temperature we could not observe any transition based on this mechanism: the molecule would rather break apart and its constituents chemically adsorb on the surface. On the other hand, flipping of 9-EP molecules requires overcoming a free energy barrier that we estimate in the order of 1.1 eV (at 300 K) thus compatible with the experimental findings at room temperature.

To study the flipping mechanism we used metadynamics³³⁻³⁵ within full DFT simulations. We defined a collective variable (CV) as the angle between the perpendicular to the plane of the 9-EPs central ring and the [111] direction (red arrow and white arrow in Figure-5a).

Figure 5: Flipping of the 9-EP molecule adsorbed on the PdGa:A(111) surface. (a) Description of the collective variable used in the metadynamics simulations to find a possible low energy path for the flipping of 9-EP adsorbed on the Pd₁ surface. (b) Approximate free energy landscape obtained after the first crossing has occurred; the barrier for the flipping is 1.1 eV (at 300 K). The red dashed line is a guide to the eye mimicking the second basin corresponding to the *S* configuration. Superimposed are atomistic sketches of the most relevant configurations for the 9-EP molecule along the flipping path.

Summing up all contributions to the history dependent potential constructed during a converged metadynamics simulation allows to identify the free energy of the system along the set of CVs.³⁴ Our choice for the CV is rather straightforward and could result in an

overestimation of the barrier separating the two free energy basins. Moreover, convergence of the metadynamics simulation is not feasible for such a system at the DFT level of theory. We stop our simulation after the system escapes for the first time the basin corresponding to the initial adsorption geometry (R) and starts filling the basin corresponding to the S adsorption geometry. It is reasonable to consider the depth of the basin obtained immediately after the first crossing as an upper limit for the free energy barrier of the flipping process.³⁶ In our case, for a simulation performed at 300 K, we obtain the mentioned barrier of 1.1 eV.

In addition, we obtain an estimate of the potential-energy barrier for the flipping process (1.6 eV) performing a nudged elastic band (NEB)³⁷ simulation starting from the path identified along the metadynamics trajectory. In this case the barrier obtained corresponds to a zero-temperature scenario and could be related to experimental conditions through the term $\Gamma e^{-\Delta E/k_B T}$ (being ΔE the energy difference between transition state and initial state) in the Arrhenius formula, if the attempt frequency Γ would be known. Direct calculation of Γ would be prohibitive, however assuming a value of 10^{13} , standard for processes at surfaces,³⁸ reveals that at 300 K a flipping event happens on a timescale of seconds. Therefore, the flipping mechanism is compatible with the experimental evidence of a low temperature activation of the transition between the racemic mixture and the R enantiomeric excess.

Origin of the high enantioselectivity

At this stage the third point of our investigation remains to be clarified: what is the origin of the high enantioselectivity experimentally observed? Given the impossibility to investigate properly the role of entropic/kinetic effects in the process, that would require at least properly converged metadynamics simulations, we explore in the following thermodynamic arguments based on the energy difference between R and S adsorption geometries ($E_{RS} = E_R - E_S$, where E_R and E_S are the computed adsorption energies of R and S respectively). In the experiments conducted by Prinz et al.,⁶ due to the high mobility of 9-EP on the Pd₁ surface, there is no direct measurement of R/S enantiomeric excess at a specific temperature. To

obtain a stable STM image the authors had to cool down the system to 5 K and, assuming that the cooling process was fast enough to freeze the equilibrium state obtained after annealing, they could identify the temperature dependence of the observed excess rate.

Under this hypothesis, we can estimate the free energy difference between R and S configurations, $\Delta_r G^0 = -RT \ln([R]/[S])$, referring to the information that at room temperature the enantiomeric excess for PdGa:A is 0.94 ± 0.02 .⁶ Therefore, an energy difference in the order of 80 meV is required to explain the experimental findings in terms of thermodynamic arguments (see SI for the derivation of the energy difference required at thermodynamic equilibrium to justify the enantiomeric excess observed).

The chiral nature of the PdGa bulk can contribute to the 9-EP adsorption energy in two ways: through chemisorption contributions and through dispersion interactions.

We computed E_{RS} employing several vdW-inclusive DFAs. First, we consider those available within the CP2K code distribution: PBE³⁹-D3,²³ revPBE⁴⁰-D3,²³ optB88-vdW,⁴¹ rVV10-vdW,⁴² BEEF-vdW⁴³ as well as the conventional PBE³⁹ functional without vdW correction. In the PBE-D3 and revPBE-D3 calculations the C_9 term, describing three-body dispersion effects, was included and the damping function by Chai and Head-Gordon⁴⁴ was employed.

The values of E_{RS} are illustrated in Figure-6 decomposed into the vdW contribution and the remainder (abbreviated with DFT in the figure). E_{RS} varies considerably for the thus far mentioned methods, ranging from -0.052 eV to +0.013 eV, with BEEF-vdW being the only approach which describes the S configuration as the most stable one. All adsorption energies as well as all corresponding adsorption heights are available in the SI. Figure-6 reveals that rVV10-vdW and BEEF-vdW imply a large vdW contribution to E_{RS} . However, in both cases the remaining DFT part is repulsive enough to reduce E_{RS} to less than 0.020 eV.

For all other DFAs, the DFT contribution amounts always to about -0.04 eV, while the vdW contribution is always smaller than 0.01 eV. Furthermore, the calculated adsorption heights differ up to 0.3 Å between all thus far discussed approaches. In general, the R

enantiomer has a slightly smaller adsorption height than the *S* enantiomer. All calculations were performed with a surface model matching the PdGa lattice constant pertinent to the respective functional (see SI), yielding a spread of about 3 % among all discussed methods. PBE-D3 yields the smallest lattice constant and rVV10-vdW the largest. In order to determine if this lattice constant difference could lead to a qualitative change in the relative adsorption energy or the vdW contribution, we repeated the PBE-D3 calculation with the largest computed lattice constant. This approach is labeled PBE-D3* in Figure-6. In general, increasing the lattice constant leads to decreasing Pauli repulsion. This enables smaller adsorption heights which leads to a larger vdW attraction. Therefore, the absolute values of the adsorption energies increase in magnitude with increasing lattice constant. However, the studied increase of the lattice constant results in an even positive vdW contribution to the adsorption energy difference E_{RS} and it also reduces the *DFT* contribution in magnitude, resulting in a decrease of E_{RS} by 0.02 eV. Increasing the lattice constant yields in this case ≈ 0.05 Å smaller adsorption heights but results in no qualitative changes in the enantioselectivity, i.e. the vdW contribution in the D3 method has only a minor role in the adsorption energy difference. This is in contrast to more accurate vdW methods as we will argue below.

Figure 6: Adsorption energy differences E_{RS} obtained with several vdW-inclusive DFAs (total). The total adsorption energy difference is also decomposed into a dispersion contribution (vdW) and the remaining energy (DFT). The dashed blue line represents the minimal adsorption energy difference necessary to explain the experimentally observed enantiomeric excess. In the PBE-D3* approach the lattice constant used for the generation of the surface was increased from 4.886 to 5.018 Å.

In general, despite the thus far discussed results for E_{RS} correctly indicate the R enantiomer as more stable than the S one, the adsorption energy differences are far too small to explain the experimentally determined enantiomeric excess.

Therefore, we went one step further in the description of dispersive interactions employing the DFT+vdW^{surf} method,⁴⁵ which accounts for the collective response of the underlying substrate by modeling screened vdW interactions based on the Lifshitz–Zaremba–Kohn theory.^{21,46–48} The vdW^{surf} method is based on the pairwise Tkatchenko-Scheffler²⁴ (TS) dispersion model and includes screening effects of the substrate electrons by using renormalized “atom-in-a-solid” vdW parameters. The derivation of the parameters for Pd and Ga atoms within PdGa is available in the SI.

The PBE+vdW^{surf} adsorption energies for both enantiomers were calculated using the full-electron code FHI-aims.^{49–52} In addition, we also computed the adsorption energies with

the many-body dispersion (MBD) method^{27,53} utilizing the renormalized vdW parameters from vdW^{surf} . This approach will be referred to as MBD^{surf} . The resulting adsorption energy differences are shown in Figure-6.

The $\text{PBE}+\text{vdW}^{\text{surf}}$ and $\text{PBE}+\text{MBD}^{\text{surf}}$ approaches provide E_{RS} of -0.077 and -0.070 eV in favor of the R enantiomer, respectively. While the DFT contribution is comparable to other functionals, the magnitude of the vdW contribution is now ≈ 0.04 eV, corresponding in both cases to about 50 % of E_{RS} .

The result from both $\text{PBE}+\text{vdW}^{\text{surf}}$ and $\text{PBE}+\text{MBD}^{\text{surf}}$ is compatible with the experimental findings, confirms the thermodynamic origin of the enantioselectivity and highlights the dominant role of dispersion interactions in the enantioselectivity. We stress that only $\text{PBE}+\text{vdW}^{\text{surf}}$ and $\text{PBE}+\text{MBD}^{\text{surf}}$ methods yield E_{RS} values large enough to correspond to the experimentally observed enantiomeric excess of the R enantiomer.

We now discuss the origin of the observed stabilization of the R enantiomer in the $\text{PBE}+\text{vdW}^{\text{surf}}$ method. Figure-7a,b shows histograms of the absolute value of the vdW interaction between the adsorbed molecule and the surface atoms at a given interatomic distance for both enantiomers (E^{vdW}). The main qualitative difference between the two enantiomers originates from adsorbate-Ga interactions at distances between 2.5 Å and 5 Å. In Figure-7c we show the vdW interaction energy difference between the R and S enantiomers when only contributions between atoms having interatomic distances smaller than a cutoff distance r are included. It can be seen that stabilization of the R enantiomer with respect to the S enantiomer mainly originates from distances smaller than 5 Å (2.5-5.0 Å range). Note that the difference in the interaction energies is not exactly equal to the difference in the adsorption energies, since this analysis does not account for differences originating from within the adsorbate and from within the metal surface.

Figure 7: (a,b,d,e) Histograms of the absolute value of the vdW interaction between the adsorbed molecule and the surface atoms for a given interatomic distance: vdW^{surf} interaction energies for the R (a) and S (b) enantiomer; vdW interaction energies obtained with the traditional Tkatchenko-Scheffler (TS) approach without screened free-atom parameters but calculated with the PBE+ vdW^{surf} geometries for the R (d) and S (e) enantiomer, respectively. The values are decomposed in contributions between adsorbate atoms and Pd and Ga atoms, respectively. (c) E_{RS}^{vdW} — difference in vdW interaction energie between the adsorbate molecule and the surface atoms contributed by interactions between atoms which have an interatomic distance smaller than r . (f) Number of C-Ga pairs for a given atomic distance (aligned to the plot of c).

To better illustrate the geometrical dissimilarity between R and S enantiomers we plotted the number of C-Ga pairs as a function of interatomic distance (Figure-7f). The plot is aligned to the graph of Figure-7c. The subplot in Figure-7f focuses on the region 2.5 - 5.0 Å. The first relevant vdW contribution is coming from the C-Ga pairs whose interatomic distances are smaller than 3 Å. Those interactions favor the R configuration with respect to S , since S does not have any C-Ga contributions at this range (see Figure-7b,f). Then every half of Ångstrom we observe alternating results with respect to R and S stability: 3.0 - 3.5 (R most stable), 3.5 - 4.0 (S), 4.0 - 4.5 (R), 4.5 - 5.0 (S). At distances larger than 5.0 Å E_{RS}^{vdW} essentially becomes a straight line with minor oscillations.

In order to demonstrate the importance of dielectric screening, Figure-7c-d contain the same analysis performed using the PBE+vdW^{surf} structures but evaluating the vdW energies with the traditional Tkatchenko-Scheffler (TS) approach,²⁴ i.e. using free-atom parameters as a starting point. In this case, there is almost no energetic difference between the two enantiomers (as for the case of DFT-D3 results).

Accounting for dielectric screening decreases the magnitude of the adsorption energies and modifies the range of the employed damping function. Here, this leads to an increased stabilization of the *R* enantiomer originating from short-range adsorbate-Ga interactions. Indeed, the most important effective change in the interaction scheme by moving from TS to vdW^{surf} is the rescaling of the vdW radius R_{vdW} of the Ga atom from the TS value of 2.22 Å to 1.30 Å. We note that this change directly originates from the dielectric constant determined from first-principles calculations. This suggests that the screening properties of the substrate material strongly affect the appropriate weighting of the interactions at intermediate distances, which in turn is the factor determining enantioselectivity. Our analysis also demonstrates that the gallium atoms in PdGa are not simply acting as a “spacers”: they actively affect the adsorption energies of carbon-based molecules, as was recently pointed out by Bechthold and coworkers.⁵⁴

Methods

The simulations performed to obtain adsorption geometries and STM images relied on the CP2K code^{55,56} implementing DFT within a mixed Gaussian plane waves approach.⁵⁷ The surface/adsorbate systems were modeled within the repeated slab scheme⁵⁸ i.e. a simulation cell contained 23 atomic layers of PdGa along the [111] direction, the adsorbate and 40 Å of vacuum. As indicated in Figure-6 we used different possible exchange correlation functionals and parameterizations for the van der Waals interactions. For each functional we determined the corresponding bulk lattice parameter of PdGa.

All calculations with the vdW^{surf} , and MBD^{surf} methods were performed within the all-electron code FHI-aims^{49–52} by using the Perdew-Burke-Ernzerhof (PBE) density functional.³⁹ The derivation of the necessary screened free atom parameters is available in the SI. The unit cell of PdGa was optimized with $\text{PBE}+\text{vdW}^{\text{surf}}$ and $\text{PBE}+\text{MBD}^{\text{surf}}$ within FHI-aims using a $12 \times 12 \times 12$ k-grid and tight species default settings. The obtained lattice parameters have been used to create the surface structures for each method. The adsorbate/surface complex was optimized for both enantiomers with both methods within FHI-aims. All calculations were performed with a $2 \times 2 \times 1$ k-grid, tight species default settings for integration grids and basis functions, and the scalar-relativistic ZORA (zero-order regular approximation) approach. Convergence criteria of 10^{-5} eV and 10^{-5} electrons/ $\text{\AA}^3$ were used for the total energy and the charge density, respectively. The structures have been optimized until all atomic force components were smaller than 0.01 eV/ $\text{\AA}$.

Conclusions

In summary, we provided evidence of the van der Waals nature of the enantioselectivity properties of the PdGa:A(111)Pd₁ surface with respect to the adsorption of 9-ethynylphenanthrene. The chirality of the flat surface originates from the chiral nature of the PdGa crystal and expression of enantioselectivity was first reported by Prinz and coworkers but the chemical and physical origin of it was unknown up to now. Our investigation reveals the possibility of a van der Waals driven chiral recognition on a solid chiral surface.

After demonstrating the correctness of the adsorption geometries proposed in the experiments, we proved that flipping of the molecules at the surface is possible at room temperature and is indicated as the mechanism for the transition from a racemic mixture to enantiomeric excess. Finally, we analyzed in details the molecule/substrate interaction and identified the van der Waals contribution from the subsurface Ga atoms as the main factor in the enantioselectivity. Our work, based on recently developed van der Waals-inclusive density-

functional approximations, which include dielectric screening effects, stresses the importance of a proper modeling of dispersion interactions in the description of adsorbate–substrate systems. Indeed, simplified models for the dispersion interactions without account for dielectric screening effects did not allow to explain the enantioselectivity of the PdGa surface. In contrast, a proper description of dielectric screening leads to an appropriate weighting of the vdW interactions at intermediate distances (2.5 - 5 Å) and to an energy landscape in agreement with experiments.

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Supporting Information Available

Description of the surface chirality; description of the charge density difference between adsorbate system, isolated molecule and clean substrate; description of metadynamics simulations; table of adsorption energies for the different adsorption geometries; methods details. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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