Adsorption of Dichlorobenzene on Au and Pt Stepped Surfaces Using van der Waals Density Functional Theory

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ABSTRACT: The adsorption of dichlorobenzene on flat (111) and stepped (332) Au and Pt surfaces was studied using density functional theory with both a conventional generalized gradient approximation (GGA) and a fully nonlocal van der Waals density functional (vdW-DF). The equilibrium geometries and adsorption energies were computed for several different adsorption configurations. The two functionals yielded qualitatively different results, with the GGA functional predicting only weak binding compared to vdW-DF, demonstrating the importance of including nonlocal dispersion. By analyzing the electronic density and projected density of states, it was found that the interaction of dichlorobenzene with the two surfaces caused a charge redistribution, especially for the stepped surfaces. Moreover, adsorption on the step edge on Au(332) was dominated by nonlocal dispersion, whereas adsorption on the Pt(332) step was dominated by chemical bonding.

1. INTRODUCTION

Graphene nanoribbons (GNRs) have a nonzero band gap, and the band structure can be tuned by changing the width and shape of the edges, which makes them very appealing for electronic applications. To tailor defect-free, atomically precise GNRs with desired properties, a well-controlled growth mechanism is required. Among the different synthesis methods recently applied, a bottom-up approach using surface-supported synthesis is a powerful technique because of its ease in controlling the quality of the nanoribbons.1 Surface-supported GNR fabrication converts halogenated aromatic precursor molecules into linear polyphenylenes, which are then transformed into extended fully aromatic structures by cyclodehydrogenation. Many experimental and theoretical studies have focused on understanding the details of these chemical processes. Theoretical studies, in particular, have investigated the cyclodehydrogenation of individual molecules and the self-assembly of molecules on surfaces as well as the effect of the substrate on such processes.2–6 Much less is known about the adsorption, diffusion, and self-assembly of molecular precursors into polymer chains. Improved control of the growth setup and of the final products stems from a fundamental understanding of the initial stages of GNR fabrication and, in particular, on the interaction between molecular precursors and metal surfaces. Corrugated surfaces (such as high-index vicinal surfaces,8–10 or superstructures formed due to lattice mismatch11) have been proposed to be more suitable than flat surfaces for building ordered 2D molecular structures12–15 since, especially at low coverage, step edges are preferential adsorption sites.16–18 Using low-temperature scanning tunneling microscopy (STM), Pascual and co-workers17 found that benzene molecules preferentially adsorb on step edges, while terraces remain free of molecules for low coverage. Increasing the coverage resulted in single rows of molecules adsorbed at the step edges. Very recently, Zhang et al.18 investigated the adsorption properties of iron-phthalocyanine on the $22 \times \sqrt{3}$ reconstructed Au(111) surface with monatomic steps using a combination of low-temperature STM and density functional theory (DFT) calculations, and they also reported adsorption at the step edges. A study by Treier et al.12 of the large organic molecule hexa-peri-hexabenzocoronene on the Au(11 12 12) surface used a combination of STM, synchrotron-based X-ray photoelectron diffraction (XPD), and DFT calculations and found that the stable adsorption structure is tilted and situated on kink sites. Although there are many studies on the adsorption behavior of aromatic molecules, such as benzene, pyridine, pyrazine, thiophene, cyclopentadienyl, and n-butane,19–22 on different metal surfaces, only few are concerned with halogenated molecules. Despite the fact that it is not possible to grow GNRs from dichlorobenzene (DCB), DCB is a simple prototype for larger and more complex GNR precursors. For example, Milosevic et al.23 investigated experimentally the constitutional meta–para isomerization of DCB adsorbed on Ag(111) and Cu(111) surfaces, but gave no details about the adsorption behavior. Fagan and co-workers24,25 explored the interaction of 1,2-DCB with semiconducting and metallic single-walled carbon nanotubes (SWCNTs) based on both DFT calculations and experiments. However, none of these studies revealed any information about the adsorption properties of DCB molecules on metal surfaces.

In this work, we perform first-principles calculations to investigate the role of van der Waals (vdW) interactions on the adsorption of the 1,4-DCB molecule on flat (111) and stepped Au and Pt surfaces. Even though high-index metallic surfaces exhibit complex reconstructions,26 we here consider (332) as-cleaved metal surfaces as model step-terrace systems, with a relatively small size and a well-defined geometry that permits comparisons between different metals at an affordable
computational cost. We employ the vdW density functional (vdW-DF) for general geometries proposed by Dion et al.\textsuperscript{27} using the implementation described by Gulans et al.\textsuperscript{28} Adsorption sites, geometries, energies, and electronic densities are explored using vdW-DF, and the results are compared to those obtained using a conventional GGA functional. Furthermore, the effect of the substrate is also explored by comparing the adsorption properties of DCB on Au and Pt surfaces, which have different electronic structures, that is, fully occupied d band (Au) versus partially occupied d band (Pt).

2. THEORY AND METHODS

All calculations were performed within the framework of DFT as implemented in the VASP 4.6 package.\textsuperscript{29,30} The electronic wave functions were expanded in a plane-wave basis set, and frozen-core all-electron projector augmented wave (PAW)\textsuperscript{31} potentials were used to describe the core electrons. The VASP code was adapted to include vdW interactions via a self-consistent implementation of the vdW-DF functional.\textsuperscript{27,28} Both the PBE version\textsuperscript{32,33} of the generalized gradient approximation (GGA) and the vdW-DF functional\textsuperscript{27,28} with PBE exchange were used. This fully nonlocal vdW functional has been successfully applied to a broad spectrum of systems, including layered structures, such as graphite\textsuperscript{34} and boron nitride,\textsuperscript{35} dimers of atoms and small molecules,\textsuperscript{28} polycyclic aromatic hydrocarbons (PAHs),\textsuperscript{36} silicon\textsuperscript{37,38} and metals,\textsuperscript{21,39} polymers\textsuperscript{40} and carbon nanotubes (CNTs).\textsuperscript{43}

Four different surfaces were used as substrates: the flat Au(111) and Pt(111) surfaces and the stepped Au(332) and Pt(332) surfaces. The Au(Pt) flat surface has a hexagonal unit cell with dimensions $a = 2.95(2.81)$ Å for PBE and $a = 2.99(2.85)$ Å for vdW-DF. Both the flat and the stepped surfaces have four atomic layers with the two bottom layers fixed during the simulations. In the stepped surfaces, the terraces have a (111) orientation and the steps are spaced just over five atomic rows apart. A vacuum region of 30 Å separates adjacent slabs, and the cutoff energy for the plane waves was 400 eV. The Brillouin zone integration was performed using the Monkhorst–Pack scheme with $4 \times 4 \times 1$ and $2 \times 3 \times 1$ mesh for the flat and stepped surfaces, respectively. All structures were optimized with a convergence criterion of 10 meV/Å for the forces and 0.1 meV for the energy. Several test calculations for the convergence of results with the number of fixed bottom layers and vacuum space were also carried out. The binding energy for DCB on Pt decreases by 0.02 eV from fixing the bottom two layers to fixing only the bottom layer. Increasing the vacuum region from 20 to 40 Å increased the binding energy by 0.001 eV. For the adsorption calculations on (111) surfaces, a $4 \times 4$ unit cell was constructed, corresponding to a coverage of 0.0625 monolayers (ML), where one ML is defined here as one molecule adsorbed on one surface unit cell.

The adsorption energy, $E_{\text{ads}}$, at a given vertical distance $z$ of the molecular plane from the surface, is defined by

$$E_{\text{ads}} = E_{\text{molecule}} + E_{\text{surface}} - E_{\text{total}}$$

where $E_{\text{total}}$, $E_{\text{molecule}}$, and $E_{\text{surface}}$ are the total energies of the adsorbed system, the isolated DCB molecule, and the clean metal surface, respectively. A positive value of $E_{\text{ads}}$ means that the adsorbed system is energetically favorable relative to the isolated state. The adsorption energy and distance from the surface at equilibrium is denoted by $E_{\text{ads}}^0$ and $z_{\text{eq}}$, respectively.

3. RESULTS AND DISCUSSION

3.1. Adsorption Structure and Energy. The adsorption of DCB on Au(111) and Pt(111) surfaces is investigated for flat-lying orientations, in which the center of the molecule is positioned on the top (T), bridge (B), or fcc hollow (H) sites. For each site, two orientations are considered, with an angle of $\theta = 0^\circ$ or $30^\circ$ between the Cl–Cl vector and the (100) axis, as shown in Figure 1.
function of the perpendicular distance ($z$) between the metal surface and the center of the molecule. For both Au and Pt, the PBE functional predicts a negligible equilibrium binding energy of about 0.1 eV, whereas vdW-DF yields equilibrium binding energies of 1.0–1.1 eV. This shows that, in both systems, dispersion forces are the dominant interaction, as previously demonstrated for benzene on gold.\textsuperscript{22} Furthermore, inclusion of the vdW interaction brings the molecule closer to the surface and decreases $z_{eq}$ by 0.1–0.2 Å.

The equilibrium distances, $z_{eq}$, and adsorption energies, $E_{ads}^\text{eq}$, of DCB on the high symmetry sites of Au(111) and Pt(111) using vdW-DF are displayed in Table 1. We found that the most favorable adsorption site for Au(111) is H-30 with $E_{ads}^\text{eq} = 1.01$ eV and $z_{eq} = 3.46$ Å. The difference in adsorption energy between this site and the least-favorable one (T-30) is only 0.05 eV. The energy differences between the various configurations of DCB on Au(111) are at the limit of the accuracy of DFT-based approaches, and thus, our calculations cannot be conclusive about the optimal geometry but, instead, indicate that the potential energy surface of DCB on Au(111) displays several nearly equivalent minima. For Pt(111), the energy differences between different adsorption sites are also small ($\sim0.1$ eV), but the adsorption of DCB on Pt(111) is slightly stronger than on Au. The adsorption energy of the optimal configurations (H-30 and B-30) is 1.19 eV, and the equilibrium distance is shorter by 0.2–0.3 Å than on the Au(111) surface. For the B-30 configuration, both Cl atoms lie on low-symmetry surface sites, and the molecule is found to lie flat on both Au and Pt surfaces. In contrast, for the H-30 configuration on Au(Pt), one Cl atom lies on a top site and the other on a hollow hcp site, with a coordination of one and three metal atoms, respectively. This leads to a tilted adsorption structure, where the Cl atom on the top site is closer to the surface by 0.08(0.33) Å than the Cl atom on the hcp site. The corresponding tilt angle of the H-30 configuration on Au and Pt is 1° and 3.5°, respectively. The adsorption differences between Au and Pt stems from the stronger coupling between the p bands of the DCB to the d bands of Pt, as will be discussed in depth in the following sections. While it is expected that DCB interaction with Au is almost exclusively dispersive, it is surprising that the different position and electronic occupation of the d band of Pt, with respect to Au, produces only minor effects in the adsorption of DCB on the (111) surfaces.

Diffusion barriers for the (111) surfaces were calculated using the nudged elastic band (NEB) method\textsuperscript{44,45} implemented in the VASP code. Only configurations with $\theta = 30°$ were considered, and it was found that there are no barriers between the three high symmetry sites (hollow, top, and bridge). Therefore, an upper limit for the diffusion barrier can be estimated as the difference between the adsorption energies of the highest- and lowest-energy configurations, which is $\sim 0.05$ eV for Au and $\sim 0.13$ eV for Pt. This low diffusion barrier is consistent with previous results regarding benzene diffusion on metal surfaces. STM images showed that, even at 4 K with low coverage, benzene molecules were mobile over the Au(111) surfaces with diffusion barriers $\sim 0.15$ eV.\textsuperscript{46} While benzene molecules on Pt(111) were frozen at 4 K, they were able to diffuse at room temperature,\textsuperscript{47} and in the 280–520 K temperature range, the diffusion barrier was measured to be $\sim 0.43$ eV.\textsuperscript{48,49} Recent vdW-DF calculations reported by Berland et al.\textsuperscript{50} slightly underestimated the diffusion barrier for benzene on the Cu(111) surface.

We now consider the adsorption behavior of DCB on the (332) stepped surfaces. The lower symmetry of the (332) surfaces yields several inequivalent adsorption sites along the step edge, several of which are shown in Figure 3. Note that, for

\begin{table}[h]
\caption{Adsorption Sites (See Figure 1), Angles ($\theta$), Energies ($E_{ads}^\text{eq}$), Equilibrium Distances ($z_{eq}$), and Charge Displacement ($\Delta Q$) for Dichlorobenzene on Au(111) and Pt(111) Surfaces from vdW-DF Calculations}
\begin{tabular}{|l|c|c|c|c|c|c|c|}
\hline
 & \multicolumn{2}{|c|}{Au(111)} & \multicolumn{2}{|c|}{Pt(111)} \\
\hline
site & $\theta$ (°) & $E_{ads}^\text{eq}$ [eV] & $z_{eq}$ [Å] & $\Delta Q$ [eV] & $E_{ads}^\text{eq}$ [eV] & $z_{eq}$ [Å] & $\Delta Q$ [eV] \\
\hline
T & 0 & 1.00 & 3.51 & 0.26 & 1.12 & 3.41 & 0.46 \\
T & 30 & 0.97 & 3.51 & 0.22 & 1.06 & 3.48 & 0.30 \\
H & 0 & 1.00 & 3.50 & 0.25 & 1.14 & 3.34 & 0.44 \\
H & 30 & 1.02 & 3.46 & 0.29 & 1.19 & 3.29 & 0.60 \\
B & 0 & 1.01 & 3.49 & 0.25 & 1.17 & 3.31 & 0.54 \\
B & 30 & 1.01 & 3.48 & 0.26 & 1.19 & 3.23 & 0.62 \\
\hline
\end{tabular}
\end{table}

Figure 3. Schematic diagram of the Au(332) surface showing DCB with various initial adsorption configurations. Upper and lower panels show the top and side views, respectively, and the black lines indicate the unit cell of Au(332). The step-edge Au atoms are shown with white spheres. The details of the configurations are given in Table 2. The optimized (c) and (e) configurations have a tilted DCB structure similar to, but less tilted than, configuration (g).
terrace sites (denoted as Tr in Table 2). This is indeed the case for both Au and Pt: $E_{\text{ads}}$ and $z_{\text{eq}}$ are nearly the same on the (111) surface and (332) terrace. On Au(332), only configuration (g), in which DCB lies on the step with the Cl atoms aligned with the step edge, has a larger equilibrium adsorption energy than the terrace sites, with $E_{\text{ads}}^\text{eq} = 1.10 \text{ eV}$. This adsorption energy is only 0.08 eV larger than that on the flat (111) surface, indicating that there is no substantial difference in the chemical interactions between the two situations and that, for both flat and stepped Au surfaces, the nature of the interaction is predominantly dispersive. This interpretation is supported by the calculation of the S-T$_\text{tilt-0}$ configuration at the PBE level, which yields $E_{\text{ads}}^\text{eq} = 1.12 \text{ eV}$, which is only ~0.05 eV larger than that of the configurations on the flat surface. On Pt(332), the chemical behavior is rather different, and the binding energy on the step is much larger. For example, the S-B-0, shown in Figure 3c, has an adsorption energy of $E_{\text{ads}}^\text{eq} = 1.14 \text{ eV}$ compared to 1.19 eV (B-30 site) on the flat surface. Differences between the binding energies on flat surfaces and at the step edge are very large also at the PBE level. The PBE energy of the S-T$_\text{tilt-90}$ configuration is $E_{\text{ads}}^\text{eq} = 1.14 \text{ eV}$, which is ~1 eV more attractive than the configurations on Pt(111).

By comparing vDW-DF versus PBE calculations, flat versus stepped, and Au versus Pt surfaces, it is clear that the electronic properties of the substrate have an important effect on the binding properties; that is, $E_{\text{ads}}^\text{eq}$ of DCB on Au is smaller than that of Pt for both functionals and surface types. The higher adsorption energies of the configurations on the step edges are due to the different atomic environment, such as the coordination of the step atoms, which leads to different electronic properties and a higher reactivity of the stepped surface (Smoluchowski effect). Moreover, for the Au stepped surfaces, the dominant interaction still arises from vDW forces.

Table 2. Adsorption Configurations (See Figure 3), Angles ($\theta$), Energies ($E_{\text{ads}}^\text{eq}$), Equilibrium Distances ($z_{\text{eq}}$), and Charge Displacement ($\Delta Q$) for Dichlorobenzene on Au(332) and Pt(332) Surfaces Using the vDW-DF Functional$^a$

<table>
<thead>
<tr>
<th>configuration</th>
<th>$\theta$ [°]</th>
<th>$E_{\text{ads}}^\text{eq}$ [eV]</th>
<th>$z_{\text{eq}}$ [Å]</th>
<th>$\Delta Q$ [e]</th>
<th>$E_{\text{ads}}^\text{eq}$ [eV]</th>
<th>$z_{\text{eq}}$ [Å]</th>
<th>$\Delta Q$ [e]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) S T$_\text{auto}$</td>
<td>0</td>
<td>0.92</td>
<td>3.24</td>
<td>0.38</td>
<td>1.84</td>
<td>2.27</td>
<td>2.72</td>
</tr>
<tr>
<td>(b) S T</td>
<td>0</td>
<td>0.91</td>
<td>3.54</td>
<td>0.48</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(c) S B</td>
<td>0</td>
<td>0.89</td>
<td>3.25</td>
<td>0.39</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(d) Tr H</td>
<td>0</td>
<td>0.98</td>
<td>3.41</td>
<td>0.34</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(e) S H</td>
<td>0</td>
<td>0.90</td>
<td>3.43</td>
<td>0.33</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(f) S T$_\text{tilt}$</td>
<td>90</td>
<td>0.99</td>
<td>3.42</td>
<td>0.61</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(g) S T$_\text{tilt}$</td>
<td>90</td>
<td>1.10</td>
<td>2.95</td>
<td>0.60</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(h) Tr T</td>
<td>90</td>
<td>0.96</td>
<td>3.40</td>
<td>0.31</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tr T</td>
<td>30</td>
<td>0.96</td>
<td>3.48</td>
<td>0.25</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tr T</td>
<td>60</td>
<td>0.98</td>
<td>3.53</td>
<td>0.30</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tr H</td>
<td>30</td>
<td>0.99</td>
<td>3.40</td>
<td>0.36</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Abbreviations: S, step; Tr, terrace; T, top; B, bridge; H, hollow. $\theta$ is the angle that the Cl−Cl vector makes with the step edge. $z_{\text{eq}}$ is the perpendicular distance between the geometric center of the molecule and the average height of the terrace atoms, except for configuration (g), which is tilted on the step, where it is the perpendicular distance between the plane of the geometric center of dichlorobenzene and the step edge atoms.
whereas in the case of the Pt step, the main contribution to binding energy is due to chemical bonding.

3.2. Electronic Structure. To further interpret the chemistry of the adsorption processes, we analyzed charge density and partial density of states (PDOS). For both Au and Pt, we consider the H-30 structure on the (111) surfaces and configuration (f) on the (332) surfaces. In Figure 4a,c, we show the PDOS for DCB on Au(111) and Au(332), respectively. The top panel in each case shows the Au 5d states, and the bottom panel shows the 2s(3s) and 2p(3p) states of the C(Cl) atoms of DCB. When DCB adsorbs on Au(111) with the H-30 configuration, neither the PDOS of the gold surface nor the molecule changes significantly, except for small differences in the C 2p and Cl 3p valence states just below the Fermi level, as seen in Figure 4a. The adsorption of DCB on Au(332) has a more pronounced effect on the molecular states, which shift and decrease in intensity, indicating a mixing between the electronic states of DCB and the d band of Au, as seen in Figure 4c.

The higher adsorption energies of DCB on Pt surfaces imply that there should be a stronger hybridization between the molecular and the surface states compared to the Au case. The PDOSs of DCB on Pt(111) and Pt(332) are shown in Figure 4b,d, respectively. The change in the molecular PDOS of DCB on Pt is clear even for the (111) surface, where the three highest occupied molecular states and the two lowest unoccupied molecular states are slightly shifted and their intensity is reduced by the interaction with the surface. For DCB on Pt(332), the two highest occupied states and the unoccupied C 2p states are almost bleached, as seen in Figure 4d. Furthermore, while there is no significant effect of DCB adsorption on the d states of the flat surfaces, the d states of both Au(332) and Pt(332) are coupled to the p states of the molecule, leading to a stronger metal/adsorbate interaction. However, the effect on the d band of Au is smaller than that on Pt.

The difference between the adsorption of DCB on flat and stepped surfaces is further analyzed by examining the electronic charge density. The charge density difference or deformation due to the adsorption of the molecule on the surface is calculated as

$$\Delta \rho = \rho_{\text{total}} - \rho_{\text{surface}} - \rho_{\text{molecule}}$$

where $\rho_{\text{total}}$ is the electronic charge density of DCB adsorbed on the surface, $\rho_{\text{surface}}$ is the charge density of the Au or Pt slab in the adsorbed configuration without the presence of DCB, and $\rho_{\text{molecule}}$ is the charge density of the molecule in the adsorbed configuration in vacuum. For a more quantitative analysis, the average charge density difference profile, $\Delta \rho_{av}(z)$, is calculated by averaging over the plane perpendicular to the (111) surface for both the flat and the stepped surfaces

$$\Delta \rho_{av}(z) = \int \Delta \rho \, dx \, dy$$

The total charge densities and electronic density differences of DCB with configuration H-30 (and benzene, which will be discussed below) on Au(111) and Pt(111) are shown in Figure S. When DCB is adsorbed on the Au or Pt surface, it has an overall positive charge and there are regions of electronic density accumulation ($\Delta \rho_{av} > 0$) and depletion ($\Delta \rho_{av} < 0$) in the metal. For DCB on Au(111), the charge accumulation (blue regions in Figure Sb) is localized above the top layer of atoms (Figure Sa,b), whereas for Pt(111), the charge displacement is larger and penetrates into the subsurface layer (Figure Sd,e). In addition to the charge accumulation at the surface, there is also a small area of charge depletion between
the surface and the Cl atom on the top site. As mentioned previously, this Cl atom is closer to the surface by 0.33 Å, which corresponds to the observed tilt of 3.5° between the DCB plane and the Pt surface. This alternating charge density pattern between the surface and the Cl atom induces a dipole. The averaged electronic density difference profile, Δρ_{av}(z), reveals that there is almost no dipole formation for the lower layers of the Au(111) surface, whereas for Pt(111), the charge difference oscillates down to the lowest layers. For the lowest two layers, the oscillation is very small and decreases toward the bottom surface layer, which can also be seen in the 3D electronic density difference (Δρ; see Figure 5b,e).

To elucidate the specific role of the chlorine atoms, we compare the electronic structure of DCB on metal surfaces with benzene on metal surfaces. The latter system has been widely investigated both experimentally and theoretically. Theoretical calculations, which used the same vdW-DF and exchange functionals as the present study, predicted an adsorption energy of ∼0.8 eV for benzene on Au(111), in reasonable agreement with experiment and in good agreement with other calculations. The PBE calculations together with experiments show that benzene is chemisorbed on Pt(111). This is qualitatively different from the case of DCB on Pt(111), which has a PBE adsorption energy of around 0.1 eV, showing that DCB is not chemically bonded to the surface. The different binding properties of benzene and DCB on Pt(111) arise because the large Cl atoms keep the aromatic ring structure farther from the surface, thus preventing chemical bonding. The electronic density differences of benzene on Au(111) and Pt(111) are shown in Figure 5. For both surfaces, the shape of Δρ_{av}(z) for benzene and DCB is very similar, although, for benzene, the amplitude of the charge fluctuations is larger, especially on the Pt surface. This is due to a larger overlap of the electronic states of benzene and the d band of Pt. The 3D electronic density differences, Δρ_{av}, of benzene on Au and Pt, shown in Figure 5c,f, respectively, provide more information about the electronic properties of these structures. For benzene in the H-30 configuration, all the hydrogen atoms are on low-symmetry sites, which preserves the symmetry of the system, resulting in a completely flat molecule lying on the surface with a symmetric charge distribution (see Figure 5c,f), in contrast to the asymmetric and tilted DCB molecule with the same configuration (see Figure 5b,e).

The charge reorganization due to the adsorption of the molecule on the surface can be analyzed quantitatively by integrating the charge density difference profile. Following ref 60, we define the charge displacement as
\[ \Delta Q = \int \left| \Delta \rho(r) \right| \, d^3r \]  

(4)

The values of \( \Delta Q \) are reported in Tables 1 and 2. \( \Delta Q \) correlates well with binding energies and is inversely proportional to adsorption distances. This general trend is not completely fulfilled for the case of dispersive adsorption of DCB on Au; however, adsorption on step sites leads to larger \( \Delta Q \) than on flat surfaces. A stronger relation between binding energy and \( \Delta Q \) is found for DCB on Pt, as different charge displacements reflect different types of bonding, from physisorption to chemisorption. For DCB on Au(111), \( \Delta Q \) is about 0.29 \( e^- \), and for benzene on Au(111), \( \Delta Q = 0.49 \) \( e^- \). On Pt(111), \( \Delta Q \) is 0.62 \( e^- \) for DCB and 1.18 \( e^- \) for benzene. Consistent with the 3D plots, it is clear that benzene has a larger charge displacement on both surfaces than DCB and that the Pt surface has a large charge displacement than Au.

The work function of a surface is defined as \( \Phi_{\text{metal}} = E_{\text{vac}} - E_F \), where \( E_{\text{vac}} \) and \( E_F \) are the electrostatic potential in the center of the vacuum region and Fermi energy of the systems, respectively. The deformation dipole due to the charge rearrangement at the interface mentioned above is thus partly responsible for the decrease of the work function upon adsorption. The calculated \( \Phi_{\text{Au}(111)} \) and \( \Phi_{\text{Pt}(111)} \) are 5.47 and 5.98 \( \text{eV} \), which are in good agreement with the experimental results of 5.31 \( \text{eV} \) and 5.70 \( \text{eV} \) respectively. The adsorption of DCB(benzene) on flat Au and Pt surfaces decreases the work function by 0.15(0.23) and 0.25(0.41) \( \text{eV} \), respectively. This is rather small in the case of DCB and indicates that there are no significant dipoles formed between DCB and the surfaces.

For the stepped surfaces, we explore the electronic density differences taking configuration (f) as an example. The electronic density difference profiles, \( \Delta \rho_{\text{av}}(z) \), are rather different from those of the flat surfaces, as shown in Figure 6. For DCB on Au, the region between the surface and the subsurface layers has a small accumulation of charge (see Figure 6c). For DCB on Pt, the fluctuations are much larger and the region between the surface and the subsurface layers has both accumulation and depletion regions (see Figure 6d). A small charge depletion can be seen in the region between the surface and the lower part of the DCB molecule. Within the range of the DCB molecule, there is a large accumulation layer, followed by a charge depletion region, the magnitude of which is larger than the accumulation part. Furthermore, for the stepped surfaces, there is a weak polarization of the electronic states, which penetrates only into the Au subsurface layer but continues down to the bottom layer for Pt. From the 3D representation of electronic density difference, shown in Figure 6e,f, it is observed that the dipole is formed along the direction perpendicular to the DCB molecule through the step edge. For configuration (f) on Au(332), shown in Figure 6c, the charge displacement is equal to 0.60 \( e^- \). Configuration (f) on Pt(332) has \( \Delta Q = 2.72 \) \( e^- \). This demonstrates the large difference in the type of bonding of DCB to Au and Pt stepped surfaces. The charge rearrangement between the aromatic regions of DCB adsorbed on both Au and Pt steps is more pronounced than on flat surfaces. This is supported by both the 3D electronic density difference plots and the total integrated charge displacement data.

4. CONCLUSIONS

We investigated the adsorption properties of dichlorobenzene on flat (111) and stepped (332) Au and Pt surfaces using DFT calculations with a conventional GGA-PBE and a vdW-DF functional. We found that adsorption on both Au(111) and Pt(111) surfaces is governed by dispersion interactions. The slightly stronger binding energy of DCB on Pt(111) compared to Au(111) stems from the larger interaction between the d orbitals of Pt and the highest occupied molecular orbitals of DCB.

For the stepped surfaces, the step edges were found to be preferential adsorption sites; however, large differences are observed between Pt and Au. DCB on the Au(332) surface binds only slightly more strongly than on the flat surface with a difference in adsorption energy of around 0.1 eV, and the interaction remains mostly dispersive. In contrast, on the Pt(332) surface, DCB is chemisorbed at the edge of the steps with an adsorption energy 0.4—0.6 eV larger than that on the terrace or flat surface.

In view of exploiting stepped metallic surfaces as supports to grow GNR, we can conclude that, for Au, the very small differences in adsorption energies between steps and terraces may be insufficient to induce a significant alignment of graphene precursors along the edge of the steps at room temperature. The diffusion barriers of DCB on (111) surfaces were found to be very low, for both Au and Pt surfaces. Therefore, on the stepped surface, molecules will diffuse freely along the terraces, but in the case of Pt, they would get trapped at step edges. This investigation of adsorption and diffusion of small precursor molecules should provide valuable information to improve the synthesis of GNRs. However, further work is needed to elucidate the kinetics of molecular diffusion on the surfaces on larger scales. Future work will focus on the coupling of precursor molecules and multiscale modeling of the diffusion and dynamics of molecules on gold surfaces.

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**Notes**

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