Potential Energy Landscape of Monolayer-Surface Systems Governed by Repulsive Lateral Interactions: The Case of \((3 \times 3)\)-I-Pt(111)

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Combined density functional theory (DFT) and Monte Carlo (MC) approach is applied to study the potential energy landscape of four iodine atoms adsorbed on the Pt(111) surface in a \((3 \times 3)\) unit cell. Three critical points were identified: \((3 \times 3)\)-sym and \((3 \times 3)\)- asym, corresponding to structures well known from experimental studies, while the third one \((3 \times 3)\)-zigzag is a new structure not reported before. An interaction model fitted to DFT calculations allows us to explain the difference between arrangements of iodine monolayer in vacuum, air, and solution environments as a result of different repulsion regimes.

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Investigation of potential energy landscapes of different systems, such as clusters, biomolecules, and glasses, have attracted much attention over the last years [1]. The availability of high quality interaction potentials makes possible detailed analysis of minima and saddle points in order to gain valuable insight into kinetics and dynamics of these systems. On the other hand, adsorbates on well-ordered surfaces represent a system where interaction potentials are available in very few cases, mainly for rare gases adsorbed on metal surfaces [2]. For many chemisorption systems, not even a phenomenological picture of interactions is available yet. Density functional theory (DFT) calculations allow a detailed description of the potential energy surface (PES) and nowadays are routinely applied for the description of the adsorbate-substrate systems [3,4]. The shortcoming of DFT is the time required to perform the calculations, restricting the sampling of the PES to about \(10^2 - 10^3\) points even for adsorption systems with few atoms. Different methodologies have been proposed for constructing complete analytic PES based on a limited number of DFT energies [5–7], but they are restricted to systems with a small number of dimensions and still require considerable computational effort. On the experimental side, the wealth of data available for the structure of different adsorbate-substrate systems [8] makes the detailed theoretical study of their energy landscapes very interesting. In this Letter, we use combined DFT and Monte Carlo (MC) approach to analyze the PES of four atoms of iodine adsorbed on the Pt(111) surface in a \((3 \times 3)\) unit cell. We identify three extreme points on the PES. Among the three extremes, two of them correspond to experimentally known structures and one is a new non-reported structure for this system. From characterization of the Hessian matrix and MC simulations, one can conclude that the stabilization of different structures can be rationalized by two different repulsion regimes. High-repulsion regime corresponds to experimental results in air and solution environments, while low-repulsion reproduces vacuum results.

The I-Pt(111) system is one of the most well studied in the surface science and electrochemistry community [9–19]. From the experimental point of view, it is easy to prepare and maintain stability in vacuum, air, and solution environments, which was demonstrated in numerous studies so far [19]. I-Pt(111) shows four different commensurate structures: \((\sqrt{3} \times \sqrt{3})R30^\circ\), \((\sqrt{7} \times \sqrt{7})R19.11^\circ\), \((3 \times 3)\)-sym, and \((3 \times 3)\)- asym. The \((3 \times 3)\) unit cell with four atoms is particularly interesting because of coexistence of two structures with different symmetry. Early low energy electron diffraction (LEED) studies of the I-Pt(111) system [9] found indication of the \((3 \times 3)\) structure. The sym and asym symmetries could not be distinguished, because their LEED patterns are essentially the same. Scanning tunneling microscopy (STM) experiments in air by Schardt et al. [10] distinguished between sym and asym structures and showed the topographic differences between the two. Several other STM studies in air and in solution confirmed the coexistence of both structures and found them in approximately the same concentration at the Pt(111) surface [12,14,19]. More recent tensor LEED study in vacuum [16] could only find evidence of the \((3 \times 3)\)-sym structure at coverage \(\theta = 4/9\). The structure with \((3 \times 3)\)- asym symmetry could not be fitted to experimental LEED spectra.

The DFT calculation procedure used in this work is based on a slab model that includes five layers of substrate Pt atoms with iodine atoms (monolayer) adsorbed on both sides of the slab. The electronic structure was calculated within the Kohn-Sham DFT formalism [20] using the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional form [21]. The Kohn-Sham equations were solved using a plane-wave expansion truncated at 40 Ry within the DFT ++ program [22]. The core electrons were not treated explicitly and norm con-
In order to map the stationary points of the \( (3 \times 3) \)-I-Pt(111) system, we performed the relaxation of a systematic and uniform sample of the \( (3 \times 3) \) unit cell within the hexagonal symmetry restriction (the cell parameters were always kept fixed). This set of structures has been recently analyzed in a geometrical study of the \( (3 \times 3) \)-I-Pt(111) system [25]. The choice of starting points with hexagonal symmetry was motivated by experimental results where only hexagonal structures have been found. We identified three different extreme points, shown on Fig. 1, which we will call \((3 \times 3)\)-sym, \((3 \times 3)\)-asym, and \((3 \times 3)\)-zigzag [26]. The first two structures are well known from different experimental studies [10,12,14,16], while the third one has never been observed for I-Pt(111). Note that the \( \text{sym} \) and \( \text{asym} \) structures possess almost perfect hexagonal order inside the \((3 \times 3)\) unit cell, while the iodine atoms positioned close to fcc and hcp sites in the \((3 \times 3)\)-zigzag structure relax around 0.3 Å from the perfect hexagonal arrangement. In order to classify the extreme points, we analyzed the Hessian matrix eigenvalues, formed by numerical second derivative evaluation for the four iodine atoms in the unit cell, which showed that \((3 \times 3)\)-sym and \((3 \times 3)\)-zigzag are minima, while \((3 \times 3)\)-asym is a saddle point. The adsorption energies of these structures and their geometrical parameters, as obtained from GGA calculations, are presented in Table I. The structural parameters show the expected trend [24], namely, that atoms in threefold sites have the lowest equilibrium positions, with bridge and atop following. A simple reaction coordinate can be established between \( \text{sym} \) and \( \text{asym} \) structures. It is formed by collective movement of all four iodine atoms in the unit cell following a linear trajectory on the \( X-Y \) plane with one bridge atom sliding into the closest fcc site. We have calculated the energy of ten different points along that trajectory by fixing the \( X-Y \) position of the adsorbate atoms and allowing the vertical positions to be relaxed. We found that the adsorption energy decreases monotonically, thus confirming the fact that \((3 \times 3)\)-asym is indeed a saddle point. Such simple reaction coordinate cannot be established for transitions between the structures with \( \text{sym} \) or \( \text{asym} \) and \( \text{zigzag} \) symmetry, due to the noticeable atomic relaxation inside the unit cell of the \( \text{zigzag} \) structure.

Considering that \((3 \times 3)\)-sym and \((3 \times 3)\)-asym are the unique structures observed in experiments [10,12,14,16], at first glance it is surprising that \((3 \times 3)\)-asym is a saddle point and \((3 \times 3)\)-zigzag is a local minimum. Experimental studies in solution and air environments have found a mixture of \((3 \times 3)\)-sym and \((3 \times 3)\)-asym at the Pt(111) surface. In contrast, a recent study in vacuum [16] indicated that no evidence for \((3 \times 3)\)-asym structure could be found. Our DFT results are closer to the vacuum experimental situation and this explains why the saddle point, \((3 \times 3)\)-asym, has not been observed. The experimental study in vacuum did not analyze the possibility of formation of the \((3 \times 3)\)-zigzag structure, because it has never been reported before.

In order to determine the reason for the stabilization of the observed structures in air, solution, and vacuum environments, we use a simple energy expression. Following many other adsorption studies [2,4], we separate the I-Pt(111) interaction potential into adsorbate-substrate and adsorbate-adsorbate parts:

\[
E = \sum_{i}^{N} \left[ V(x_i, y_i) + \sum_{j>i}^{N} [A \exp(-B r_{ij})] \right],
\]

where \( r_{ij} \) is the distance between particles \( i \) and \( j \), while \( A \) and \( B \) are parameters. \( N \) is equal to 4 for \((3 \times 3)\) cell with coverage \( \theta = 4/9 \). The second summation is cut after 15 Å. Tests with larger cutoff did not affect our results.

We assume a simple exponential interaction between the iodine atoms in the adsorbed monolayer. Although, clearly a simplification, several experimental studies point out that the interaction between adsorbed iodine atoms is repulsive in a wide range of coverages [18]. Furthermore, the \((3 \times 3)\) cell with coverage \( \theta = 4/9 \) is the most compressed one observed in experiments. In order to set limits on the \( A \) and \( B \) parameters, we performed calculations of iodine adsorbed on the fcc site in \((\sqrt{3} \times \sqrt{3})R30^\circ \) cell with \( \theta = \frac{1}{4} \) and in the \((1 \times 1)\) cell with \( \theta = 1 \). We use the adsorption energy of the \( \sqrt{3} \) structure to fix the \( A \) parameter, while the variation of \( B \) parameter allows us to simulate the effect of repulsion between iodine atoms in the monolayer. The
the unit cell and the MC simulation procedure was as follows: 100 MC runs (without Boltzmann factor) were performed for each value of B in the interval 4.5 ≤ B ≤ 5 with increments of 0.01. We did additional runs around B = 4.74 in order to verify that all three structures do not coexist for any value of B. Each MC run consisted of the following steps: (1) initializing randomly the X-Y positions of all four atoms in the unit cell, (2) randomly moving one of the four atoms within a circle of radius 0.001 reduced unit cell coordinates, (3) the step is accepted if the energy of the adsorption site is lower than the previous one, (4) repeating steps (2)–(3) until reaching convergence. The final configuration was accepted if the energy did not change more than 10⁻⁴ in 5000 MC steps. For B < 4.74, (3 × 3)-sym and (3 × 3)-asy are the only minima, while for B ≥ 4.74, (3 × 3)-sym and (3 × 3)-zigzag were obtained exclusively. We could not find any value of B around 4.74, which showed the existence of the three structures as minima. Therefore, one could conclude that the deformation of the PES around B = 4.74 is abrupt, with asym structure most probably becoming saddle point and zigzag structure most probably becoming saddle point and zigzag.

### Table I. GGA adsorption energies (Ad.) and \( X, Y, Z \) structural parameters of four iodine atoms for the three structures of the (3 × 3)-I-Pt(111) system. The energies are reported in kcal/mol, \( X-Y \) structural parameters in reduced unit cell coordinates, and \( Z \) positions in Å measured relative to the first Pt(111) surface layer.

<table>
<thead>
<tr>
<th></th>
<th>( I_1(X, Y, Z) )</th>
<th>( I_2(X, Y, Z) )</th>
<th>( I_3(X, Y, Z) )</th>
<th>( I_4(X, Y, Z) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(3 × 3)-sym</td>
<td>217.9 (−0.001, −0.001, 2.774)</td>
<td>(0.503, −0.007, 2.255)</td>
<td>(−0.005, 0.503, 2.276)</td>
<td>(0.504, 0.505, 2.248)</td>
</tr>
<tr>
<td>(3 × 3)-asy</td>
<td>210.0 (−0.112, 0.222, 2.091)</td>
<td>(0.389, 0.220, 2.499)</td>
<td>(−0.117, 0.725, 2.483)</td>
<td>(0.391, 0.726, 2.490)</td>
</tr>
<tr>
<td>(3 × 3)-zigzag</td>
<td>212.2 (0.078, 0.002, 2.612)</td>
<td>(0.587, −0.002, 2.612)</td>
<td>(0.909, 0.472, 2.204)</td>
<td>(0.564, 0.534, 2.129)</td>
</tr>
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</table>

The adsorbate-substrate interaction \( V(x, y) \) for the iodine atom with the Pt(111) surface is represented by the unequal-sphere packing (USP) potential, which has been shown to give an astonishing agreement with experimental structures of the I-Pt(111) system [25,27].

\[
V(x, y) = k \left[ \sqrt{(R_1 + R_2)^2 - (x - x_s)^2} - (y - y_s)^2 \right] + b.
\] (2)

The quantity between the parenthesis is the equilibrium \( Z \) distance of an iodine atom measured relative to the first Pt surface layer, \( R_1 \) is the surface atoms metallic radius, \( R_2 \) is the adsorbate radius and \( (x_s, y_s) \) is the closest substrate particle position. \( k \) and \( b \) are the parameters to be fitted to ab initio data. Note that \( R_3 \) is set to represent the equilibrium bond lengths of the adsorbate atoms. The \( b \) parameter is only needed for absolute energy values. Therefore, \( k \) is the only parameter which needs to be fitted for the adsorbate-substrate interaction potential. It is related to the corrugation of the potential. We fit the parameters of USP potential with the adsorption energies and equilibrium \( Z \) positions of fcc and atop sites from our previous DFT study [24]. The values of parameters of the USP model used here are \( R_1 = 1.3875 \) Å, \( R_2 = 1.8122 \) Å, \( k = -22.8140 \) kcal/mol, \( b = 96.9091 \) kcal/mol. In Fig. 2, the excellent performance of the USP potential in comparison to DFT calculations is shown (see Fig. 2 caption for more details). The linear relation between \( E \) and \( Z \) obtained in DFT calculations is striking and it would be interesting to look for such behavior in other adsorbate-substrate systems.

According to Eq. (1), once we define the parameters for \( V(x, y) \) and the constant \( A \), the global interaction is a direct superposition of a single parameter — \( B \), which defines different repulsion regimes and induces deformation of the PES as it will be shown below. We have performed Monte Carlo (MC) simulations with the interaction potential of Eq. (1), exploring the PES of the (3 × 3)-I-Pt(111) system containing four iodine atoms per unit cell. Periodic boundary conditions have been used for the \( X \) and \( Y \) directions of the unit cell and the MC simulation procedure was as follows: 100 MC runs (without Boltzmann factor) were performed for each value of \( B \) in the interval 4.5 ≤ \( B \) ≤ 5 with increments of 0.01. We did additional runs around \( B = 4.74 \) in order to verify that all three structures do not coexist for any value of \( B \). Each MC run consisted of the following steps: (1) initializing randomly the \( X-Y \) positions of all four atoms in the unit cell, (2) randomly moving one of the four atoms within a circle of radius 0.001 reduced unit cell coordinates, (3) the step is accepted if the energy of the adsorption site is lower than the previous one, (4) repeating steps (2)–(3) until reaching convergence. The final configuration was accepted if the energy did not change more than 10⁻⁴ in 5000 MC steps. For \( B < 4.74, (3 \times 3)\)-sym and (3 × 3)-asy are the only minima, while for \( B ≥ 4.74, (3 \times 3)\)-sym and (3 × 3)-zigzag were obtained exclusively. We could not find any value of \( B \) around 4.74, which showed the existence of the three structures as minima. Therefore, one could conclude that the deformation of the PES around \( B = 4.74 \) is abrupt, with asym structure most probably becoming saddle point and zigzag structure most probably becoming saddle point and zigzag.
simulations. Such effect is not present in vacuum been used for an appropriate description in Monte Carlo can be related with a dipolar repulsive interaction and has DFT calculations of an isolated iodine monolayer with body effect that modifies the I–I interaction. In order to test in Fig. 2 of Ref. [19] and the related discussion. This effect halogen-metal adsorption systems, as could be seen, e.g., could indicate smaller effective repulsion between them higher repulsive regime in solution can be traced back to in this work, could explain the vast amount of experimental could indicate smaller effective repulsion between them small van der Waals radius of bromine atoms, which experimental study of Br–Pt(111) system is essentially the important to notice that the (3 × 3)-zigzag symmetry is an intriguing possibility. Along this vein it is important to notice that the (3 × 3/2)-rect structure found by Orts et al. [28] in their experimental study of Br–Pt(111) system is essentially the same as (3 × 3)-zigzag. The fact that zigzag structure has been observed for Br–Pt(111) could be rationalized by the smaller van der Waals radius of bromine atoms, which could indicate smaller effective repulsion between them in the adsorbed monolayer.

It is noticeable that a simple model, as the one proposed in this work, could explain the vast amount of experimental results in (3 × 3)-I–Pt(111) system. The origin of the higher repulsive regime in solution can be traced back to an induced charge transfer as has been observed in other halogen-metal adsorption systems, as could be seen, e.g., in Fig. 2 of Ref. [19] and the related discussion. This effect can be related with a dipolar repulsive interaction and has been used for an appropriate description in Monte Carlo simulations [29]. Such effect is not present in vacuum because the charge transfer is quite small [24]. In the presence of air the repulsion could be related to a three-body effect that modifies the I–I interaction. In order to test possible effect of the air environment, we have performed DFT calculations of an isolated iodine monolayer with N2 molecule on top and on the bridge positions. When the N2 molecule is positioned 2.5–3.5 Å away from the monolayer, visible repulsion effect can be noticed in the monolayer interaction curve, which is increased when the molecule is closer.

In conclusion, we have performed combined DFT and MC study of the potential energy landscape of iodine adsorbed on the Pt(111) surface in (3 × 3) unit cell. Such an approach turned out to be powerful enough to rationalize differences between I–Pt(111) system in solution, air, and vacuum environments. We have found a new structure called (3 × 3)-zigzag and we believe it is worth to pursue additional experimental studies of the I–Pt(111) system to confirm its existence.

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[26] In Fig. 1(c) one can see that if the atoms onfcc and hcp sites are connected, a zigzag pattern emerges. One could also see that zigzag structure is characterized by the largest atomic relaxation inside the unit cell compared to the sym and asym structures.