# Detailed characterization of (3×3) iodine adlayer on Pt(111) by unequal-sphere packing model

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A simple unequal-sphere packing model is applied to study the iodine (3×3) adlayer on the Pt(111) surface. By using a newly introduced parameter, defined as the average adsorbate height, three characteristic adlattices, (3×3)-sym, (3×3)-asym, and (3×3)-lin, have been selected and characterized in great detail, including the exact adatom registry. The (3×3)-sym iodine adlattice, observed in many experimental studies, appears to be, on average, the closest one to the substrate surface. A special contour plot of average adsorbate height vs *X* and *Y* positions of the (3×3) iodine unit cell indicates the existence of two local minima, which are related to preferential formation of (3×3)-sym and (3×3)-asym iodine adlattices. Our model gives good agreement with experimental findings, and explains the mechanism of preferential appearance of (3×3)-sym and (3×3)-asym structures. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1856458]

## I. INTRODUCTION

Detailed atomic level characterization of adsorbate-substrate systems, including identification of the adsorbate registry, is of a great interest for better understanding of adsorption phenomena, interaction between different materials, and properties of modified surfaces. So far, it has been a subject of many theoretical and experimental studies.[1–5] Techniques, such as Low-Energy Electron Diffraction (LEED), Angular Distribution Auger Microscopy (ADAM), Scanning Tunneling Microscopy (STM), and others have been successfully used in such studies, and a great amount of data has been collected for a variety of adsorbate-substrate systems. A frequently investigated and particularly well-known system in surface science and surface electrochemistry is the iodine adlayer on the Pt(111) substrate.

It is known that iodine on Pt(111) forms three distinct lattices: $(\sqrt{3}\times\sqrt{3})R30°$, $(\sqrt{7}\times\sqrt{7})R19.1°$, and (3×3), for which reliable data on surface coverage, adsorbate atomic registry, and interatomic distances already exists. These lattices have been characterized by LEED,[6–12] ADAM,[13] STM,[14–16] and Surface X-ray Scattering (SXS).[17–21] The same type of iodine adlayer on Pt(111) was found for preparations from gas phase[12–14] and from aqueous solution.[6–11,15,16] Experimental data also show that an iodine adlayer with (3×3) unit cell structure can form two distinct lattices,[10,13–16] in which iodine-iodine interatomic distance (4.162 Å) and surface coverage are the same, but iodine adatoms possess different registries. They are known as the (3×3)-sym and (3×3)-asym adlattices. Indeed, (3×3)-sym was called (3×3)-hex in previous literature.[13–16] Interestingly, both were found in approximately equal proportions on the Pt(111) surface.[14–16] Also, to our knowledge, no experimental procedures have been developed to exhibit exclusively one or another type of (3×3) iodine adlayer. Although description and characterization of these two structures have been reported in the literature extensively,[13–15] the issue is still intriguing in respect to the mechanism of (3×3)-sym to (3×3)-asym adlattice transformation, stability, and the structures which the iodine (3×3) adlayer can form at the Pt(111) substrate. In addition, it is interesting to establish the parameters, which influence the appearance of the (3×3)-sym and (3×3)-asym structures.

In view of these questions, the present study focuses on the characterization of the (3×3) iodine adsorbate layer on Pt(111), with primary emphasis on how many different structures (in respect of the atomic registry) iodine adatoms could form on the Pt(111) substrate, identification of parameters which determinate appearance of (3×3)-sym and (3×3)-asym iodine adlayers, and understanding of the transformation mechanism between (3×3)-sym and (3×3)-asym arrangements. For methodology, we use unequal-sphere packing modeling procedure,[22] developed in our laboratory, which could simulate adatom arrangement in a multilayer adsorbate-substrate system. The whole approach is based on simple hard-sphere geometrical modeling, which adequately simulates the (3×3) iodine adlayer at the Pt(111) surface. By this means, different adsorbate adlattices, with distinct atomic registry, were described. For each structure, detailed analysis was carried out in order to determine exact iodine adatom registry and calculate the value of the adsorbate-substrate distance (center to center of the hard balls).

Among numerous iodine adlayer arrangements, formed as result of the adlayer translation over the Pt(111) substrate, the (3×3)-sym and (3×3)-asym arrangements were identified and selected as the most probable. The selection was based on use of a newly introduced parameter defined as the *average adsorbate height*, which measures the adsorbate-substrate distance calculated for each iodine adatom within a single (3×3) unit cell. Using this new parameter, we found that, on average, the iodine adlayer with (3×3)-sym struc-

ture is the closest one to the Pt(111) substrate in our simulation studies. Also, it was found that iodine adlayers with $(3\times3)$-sym, $(3\times3)$-asym, and $(3\times3)$-lin structures possess the minimum number of different atomic registries (two). Other iodine adlattices possess three or even four different adatom registries. With a contour plot, which allows us to trace average height of the iodine $(3\times3)$ adlayer from the Pt(111) substrate as a function of its position at the substrate surface, we are able to demonstrate why iodine adsorbs preferentially in $(3\times3)$-sym and $(3\times3)$-asym arrangements. As our simulations show, this is related to the existence of two well-defined local minima in the contour plot. Furthermore, our findings are in agreement with the experimental observations.

We believe that our findings lead to a new level of understanding of the adsorbate-substrate system and that such simulations could be useful for explanation of other processes involving atomic adlattices.

## II. DESCRIPTION OF THE ALGORITHM

Modeling of different atomic arrangements was based on use of our software, ALSA (atomic level surface assembler). This is a homemade program developed on a Linux platform, based on modeling of the geometrical arrangement of unequal spheres (hard-ball contact model) over the crystalline substrate. In comparison to numerous models developed and used before in the field of surface science,[1,2,23–26] ALSA has certain advantages. ALSA allows simulation of single or multiple adlayers on flat or stepped substrates having different symmetry. Adlayers can be assembled using individual atoms or complete layers, and can be easily translated or rotated in any direction at the substrate surface. The adlayer-substrate system can be presented in different modes such as two-dimensional (2D) transparent hard-ball models or 3D STM like image mode, which simplifies the understanding and qualitative and quantitative interpretation of the experimental data. In our study, ALSA was useful for identification of atomic registry as well as for evaluation of the height variations of the iodine adatoms in the $(3\times3)$ lattice on the Pt(111) surface.

The first step of our simulation involves definition of substrate and adsorbate layers in terms of geometrical models (unequal-sphere concept). The Pt(111) substrate surface is represented by close-packed hexagonally ordered spheres touching each other, with normalized radius $R_{\mathrm{Pt}}=1$. The iodine adlayer consists of hexagonally ordered spheres of larger normalized radius, $R_I=1.5$. These particular radii are chosen so that iodine can be arranged in a $(3\times3)$ unit cell at a surface coverage $\theta=\frac{4}{9}$. In the process of simulation, the iodine adlayer was translated (shifted) over the Pt(111) surface in different directions; however, during this process both substrate and adsorbate maintained their rigid hexagonal order, while adatoms were allowed to change registry on the substrate surface. Figure 1 shows schematically three possible directions of movement, as well as an example of shifting in the $X$ direction by a $\Delta x$ increment to a new position marked $a'$. The shifting of the iodine $(3\times3)$ ordered adlayer over the (111) substrate is a collective movement in which all iodine atoms undergo the same displacement along a particular direction. Our methodology is based on collection and analysis of changes in the adatom registry.

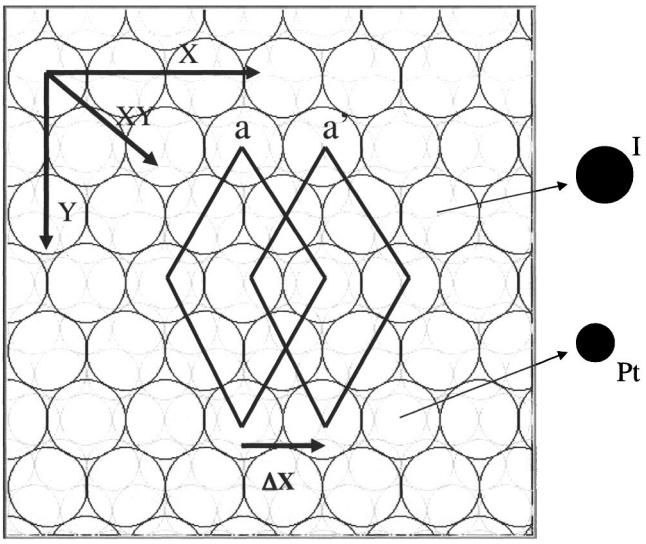


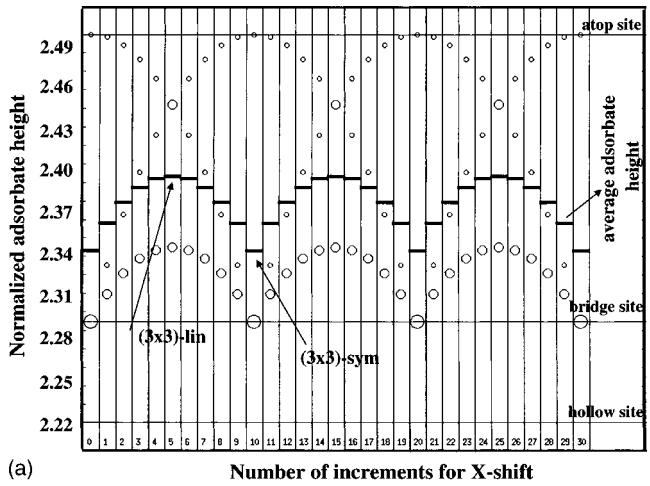

FIG. 1. Illustration of translation of the adsorbate layer with $(3\times3)$ unitcell on the flat Pt (111) substrate.

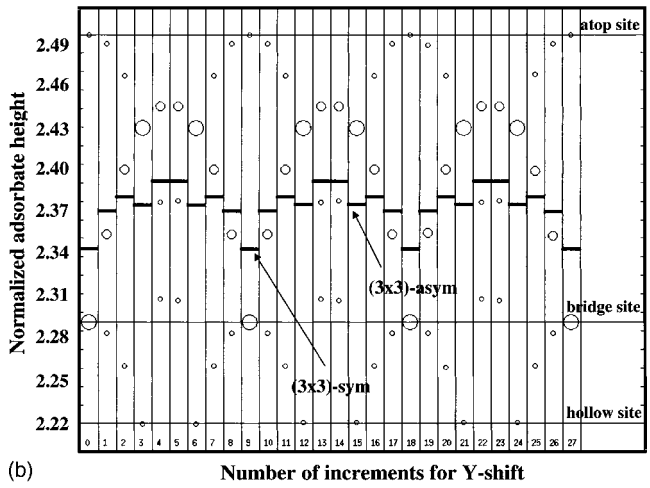
The height of each sphere in the adsorbate layer is determined after the sphere is lowered in the surface-normal direction until it contacts one or more substrate spheres. By definition, contact is made when the distance between the adsorbate and the substrate spheres reaches the sum of their radii, regardless of the contact direction.

In order to systemize large number of data (structures) we introduce a new parameter defined as the average adsorbate height of the iodine adlayer, which is based on a calculation of the vertical position (distance between the adsorbate and substrate layers) for every adatom within the $(3\times3)$ unit cell. Use of this parameter allows us to satisfy most of the aims of our study.

## III. CHARACTERIZATION OF THE (3×3) IODINE ADLAYER DURING SHIFTING OVER THE Pt(111) SURFACE

The $(3\times3)$-sym lattice was used as a starting point prior to imposing any translation movement. This is a well-known structure, in which one of the iodine atoms in the unit cell is placed in an atop site and surrounded by six neighbors, equally positioned on the bridge sites.[13–16] This particular structure was shifted in different directions with small increments. Figure 2(a) shows results obtained by translation of the $(3\times3)$-sym structure along the $X$ direction. The movement was carried out in increments equal to $0.1R_{\mathrm{Pt}}$ which means that after ten increments the iodine adlayer again possesses the full symmetry of the $(3\times3)$-sym lattice. During simulation, each iodine adatom position within the unit cell was monitored. Based on these observations, two parameters have been extracted and plotted vs magnitude of the $\Delta x$ shift. The first parameter is the normalized adsorbate height (NAH) (equal to adsorbate distance from the substrate surface), which is represented in Figs. 2(a)–2(c) by circles of different size, placed at different distances from the sub-



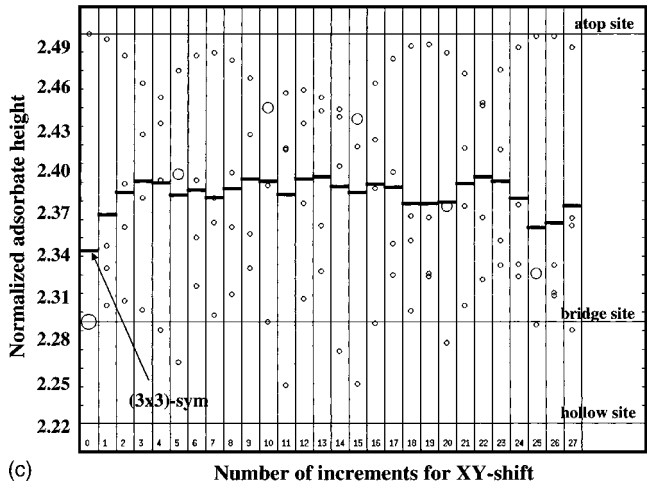




FIG. 2. Distribution of adsorbate atom heights during translation along *X* (a), *Y* (b), and *XY* (c).

strate. Positions of these circles represent the distance of certain adatom populations from the substrate, while the sizes of circles are related to the percentage of atoms at a particular position. The distance between the lowest and the highest positioned circles represents the corrugation or thickness of the iodine adlayer. As a separate parameter Fig. 2(a) shows the average adsorbate height of the iodine adlayer, which is our newly introduced parameter.

To elucidate our results, let us describe the structure at *X* shift equal to 0, which has one of four atoms (25% of the total population) in an atop site (see small circle at vertical distance equal to 2.500 NAH units). Three additional atoms (75%) in the $(3\times3)$-sym unit cell are placed on the bridge sites (note a big circle at the bridge site at 2.291 NAH units). This plot shows two things: first that the majority of atoms are on bridge sites and second that there is a large difference between the highest and the lowest atoms within the unit cell (0.209 NAH units). Thus, the average adsorbate height value of 2.344 NAH units is closer to the lowest positioned atoms at the bridge site. During the first shift, the iodine adlayer shows a tendency to diminish the difference between the lowest and the highest adatoms; the average adsorbate height increases and iodine adatoms within unit cell occupy three different registry positions. All of them, without exception, are between the bridge and atop site, with population density of 25%-25%-50%, respectively, relative to the circle size. This tendency continues, up to the fifth shift, when again, adlayer registry is limited to two specific places, with iodine adatoms placed between atop and the bridge sites. At this point, the average adsorbate height for the iodine adlayer reaches its absolute maximum value (2.397 normalized units). As will be described later, this particular structure will be named $(3\times3)$-lin because of formation of linear iodine rows over the Pt(111) substrate. Another interesting characteristic of the $(3\times3)$-lin structure is a rather small difference between the highest and lowest iodine adatoms in the adlayer $(2.450-2.345=0.105)$. In another words, the iodine adlayer with $(3\times3)$-lin structure is, on average, very far from the platinum substrate, but is the less corrugated. Between fifth and tenth shift, the situation is reversed and the $(3\times3)$-sym arrangement is recovered, with the adlayer again gaining in thickness.

Taking into account the obtained average adsorbate height, adlayer thickness, and number of different registry sites within the $(3\times3)$ unit cell, the $(3\times3)$-sym and $(3\times3)$-lin are identified as the limiting options for the iodine arrangement during the shift along the *X* direction. Interestingly, the process involving rising and falling of the iodine adlayer is continuous with a certain frequency involving complete repetition every ten increments in the *X* direction. After ten regular cycles, the $(3\times3)$-sym will be reestablished. As clearly seen from plot on Fig. 2(a), during the *X* shifting the iodine adlayer will accommodate to the Pt(111) surface by placing itself, on average, closer or farther from the surface but individual adatoms will always be placed only between atop and bridge sites, as limiting options. Respectively, the adlayer thickness will vary between 0.105 and 0.209 NAH units. The average adsorbate height varies in the range of 2.344 for $(3\times3)$-sym up to 2.397 for $(3\times3)$-lin, which makes difference of 0.053 in the NAH units.

Figure 2(b) shows the results of our modeling when the $(3\times3)$ iodine adlayer was shifted over Pt(111) surface in the *Y* direction. During the first two shifts by increments of $0.13R_{\mathrm{Pt}}$, the average adsorbate height increases, but adatoms within the $(3\times3)$ unit cell now occupy one additional (in total three) adsorbate registries. One (25%, small circle) of the four atoms in the unit cell shows a tendency to move closer to the substrate. Indeed, after the third shift, the aver-

age adsorbate height slightly drops, and one of four iodine atoms in the $(3\times3)$ unit cell already occupies a hollow site. Another 75% (three of four) are somewhere between atop and bridge sites. This lattice has been reported and described as $(3\times3)$-asym. In the STM image,[14–16] it is easily recognizable due to a specific image pattern with one atom down (in the hollow site) and its neighbors in so-called "asymmetric" sites,[7] which from our plot are equal to 2.432 NAH units. Corrugation or the adlayer thickness of the iodine $(3\times3)$-asym is 0.215 NAH units, which is 0.006 units bigger than that for $(3\times3)$-sym adlayer. The average adsorbate height for $(3\times3)$-asym is 2.379 normalized units, which is 0.035 units higher than that for $(3\times3)$-sym. Interestingly, during the next two shifts iodine adatoms occupy almost the same registry. Further shifting between the fifth and the ninth, along the *Y* direction, induces rearrangement and mirrors distribution of atomic registry as observed for the first five shifts, but in the reverse order. Essentially, the $(3\times3)$-sym lattice will be formed again after each nine cycles and $(3\times3)$-asym will be repeated after the 3rd, 6th, 12th, 15th, 21st, and so on shifts. Structures found after 4th, 5th, 13th, 14th, 22th, and 23th shifts possess minimum adlayer thickness (0.135 normalized units), which is the most compact adlayer among all found during shifting along the *Y* direction. The rest of the structures, including $(3\times3)$-sym and $(3\times3)$-asym, are thicker, as described before. One could also observe that during the shift in the *Y* direction, iodine adatoms within the $(3\times3)$ unit cell have two or three registries; however, in comparison with shifting in the *X* direction, values of the NAH vary over a larger range, from the atop site to the hollow site (0.283 normalized units). The average adsorbate height varies only between 2.344 and 2.393 normalized units; the total difference over which the adlayer could vary on the Pt(111) surface is 0.049 NAH units, which is smaller than for shifting in the *X* direction.

From the above considerations, the $(3\times3)$-sym and $(3\times3)$-asym have been identified as unique lattices with only two possibilities for the adsorbate registry sites. In addition, $(3\times3)$-sym is the only one to have atom in the atop site, and $(3\times3)$-asym is the only one to have at least one atom in the hollow site. In respect to the normalized average adsorbate height, the iodine adlayer with the $(3\times3)$-sym structure is the closest to the platinum substrate, while $(3\times3)$-asym is farther for 0.035 normalized units. In respect to appearance of $(3\times3)$-sym and $(3\times3)$-asym arrangements during the shifting, it is obvious that they occur with different frequencies and periodicity.

In the case of shifting along the *XY* direction, the periodicity is lost [Fig. 2(c)]. The $(3\times3)$-sym arrangement presented during the zero shift could not be repeated even after 27 and more shifts. Within a single $(3\times3)$ unit cell, the iodine adatoms occupy two [only in the case of $(3\times3)$-sym arrangement], three (seldom, after 5th, 10th, 15th, 20th shift, and so on) or in the most cases, even four different registries. This means that each adatom within the unit cell is occupying different registry. In respect to the normalized adatom-substrate distance (NAH) it is obvious that iodine adatoms could occupy a large span of values. However, no atom was found to reach a hollow or atop site exactly. Thus, the total range for the NAH is slightly shorter than 0.283 normalized units, as seen in shifting along the *Y* direction. Despite determination of exact values for the iodine adlayer thickness, it was difficult to estimate the range and direction of change for average adsorbate height values. In general, we found that during such *XY* shift, iodine adlayers are neither thicker nor thinner than those observed during separated *X* and *Y* translations. The same behavior was observed for variations of the average adsorbate height.

These three examples clearly show that the appearance of one or another type of iodine adatom arrangement, with characteristic adatom registry, depends on the direction of translation over the Pt(111) substrate. However, only a few structures possess specific characteristics, which could be used for selection of the most likely arrangement of adsorbed iodine on Pt(111) with $(3\times3)$ symmetry. In our analysis, the following parameters have been taken into account: the average adsorbate height (the closest adlayer to the substrate surface), minimum number of registry positions, and thickness of the adsorbed iodine layer (minimum vs maximum). For example $(3\times3)$-sym is closer to the substrate surface, while $(3\times3)$-asym is the thickest adlayer and $(3\times3)$-lin is the thinnest adlayer, as we demonstrated and described in the paragraph before.

Finally, as result of such analysis, we selected the following three structures, $(3\times3)$-sym, $(3\times3)$-asym, and $(3\times3)$-lin, for a more detailed characterization.

## IV. DETAILED CHARACTERIZATION OF THE (3×3)-SYM, (3×3)-ASYM AND (3×3)-LIN IODINE ADLAYERS

Figures 3(a)–3(c) show these three structures. They are presented in the 3D STM-like mode (upper part of the image) with bright spheres representing higher iodine adatoms and darker spheres representing lower ones. The lower part of this figure is the same image presented in 2D transparent mode, which shows registry of iodine adatoms (big circles) on the Pt(111) surface (small circles). These two particular modes allow identification of differences among the adatom registry sites in a very practical way. Figures 3(a)–3(c) show $(3\times3)$-sym, $(3\times3)$-asym, and $(3\times3)$-lin structures, respectively.

Figure 4 shows a different kind of presentation: top view cross section with iodine adatoms (big circles) placed on the Pt(111) substrate (small circles), side view cross section, and scaled view cross section, which we use in evaluation of quantitative parameters in our study.

Figure 4(a) shows analysis of the $(3\times3)$-sym structure with iodine adatoms positioned at atop and bridge sites, and a difference of 0.209 normalized height value between these two positions (adlayer corrugation). In order to convert the normalized adsorbate value to real distance one should multiply it by the radius of Pt substrate atoms (1.388 Å). This conversion leads to a value of 0.290 Å which is bigger than recent LEED data (0.100 Å) (Ref. 12) but lower than previously reported from STM studies (0.450 Å) (Ref. 15) and ADAM studies (0.800 Å).[13]

In the case of the $(3\times3)$-asym structure [Fig. 4(b)], the

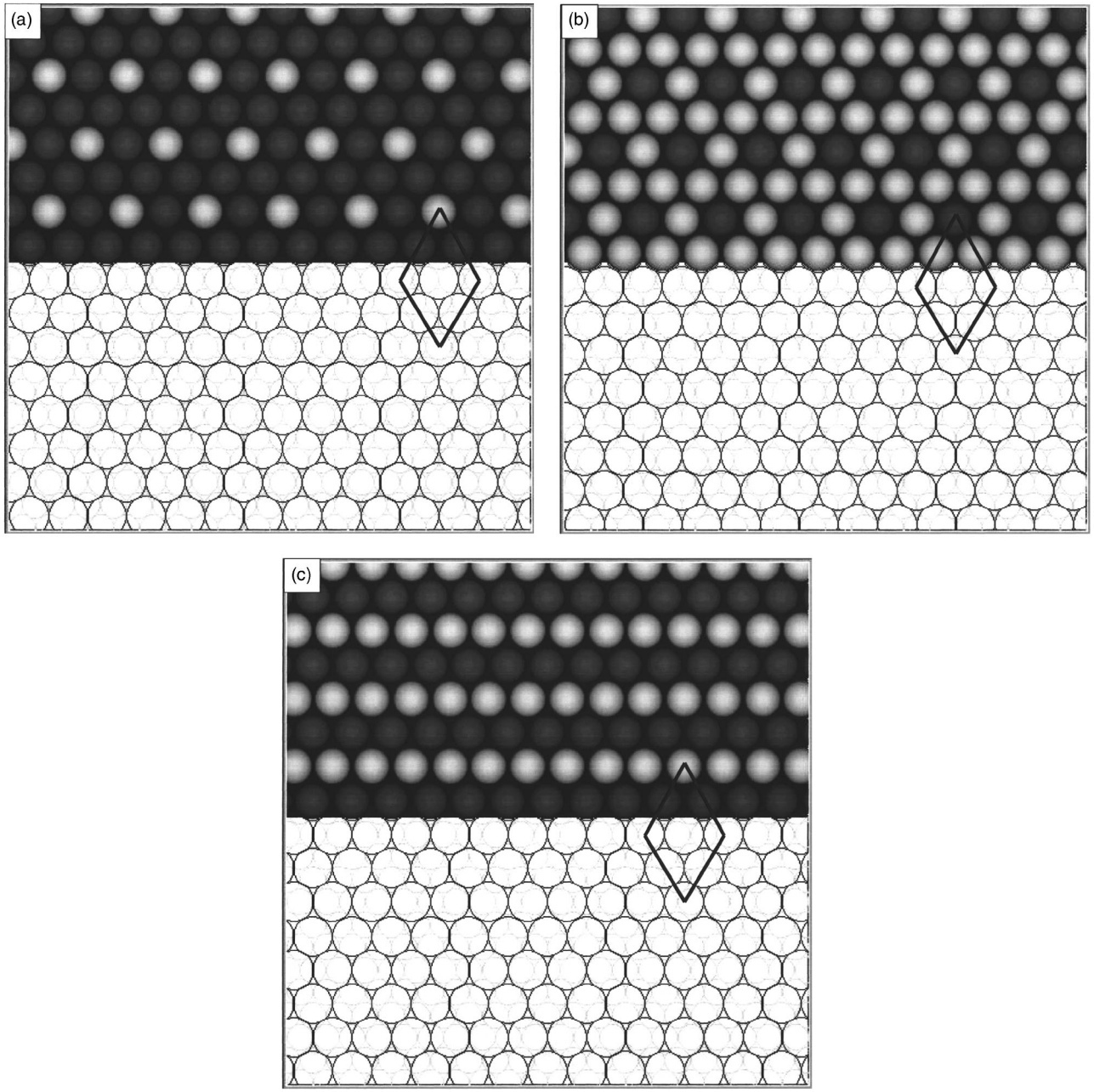



FIG. 3. Combined STM-like and transparent mode illustration of three characteristic $(3\times3)$ structures of the iodine adlayer: $(3\times3)$-sym (a), $(3\times3)$-asym (b), and $(3\times3)$-lin (c).

distance between upper (asymmetric site) and lower (hollow site) adatoms is 0.215 normalized units or 0.298 Å. This value of adlayer corrugation is much smaller than previously published data (1.000 Å).[13,26] In addition, from our data [Fig. 4(b)] we also could see that distance from the Pt(111) substrate for iodine adatoms at asymmetric site is 2.432 normalized units (3.374 Å) and 2.217 normalized units for iodine adatoms in the hollow site (3.076 Å). The iodine-platinum distance for hollow site is higher than reported from Surface Extended X-ray Absorption Fine Structures (SEXAFS) analysis (2.670 Å).[21] However, we found that the distance between iodine adatoms at atop and hollow sites, 0.283 normalized units (0.393 Å) is close to the recent LEED observation (0.500 Å).[12]

One possible reason for such differences could be related to STM evaluation, which is based on determination of the tunneling efficiency, which often is controlled by factors other rather than the true topographic position. In the case of ADAM,[3] also, a true geometrical approach was not used. Position of adatoms in $(3\times3)$-sym and $(3\times3)$-asym structures was estimated according to best theoretical ADAM patterns. Contrary, our data is derived from a purely geometrical model, taking into account only topographic position. However, it is very interesting to compare our findings with LEED, STM, ADAM, and SEXAFS data, in order to understand additional mechanisms, which control the appearance of different adatom patterns. In respect to the SEXAFS analysis one must admit a possibility that in real iodine-

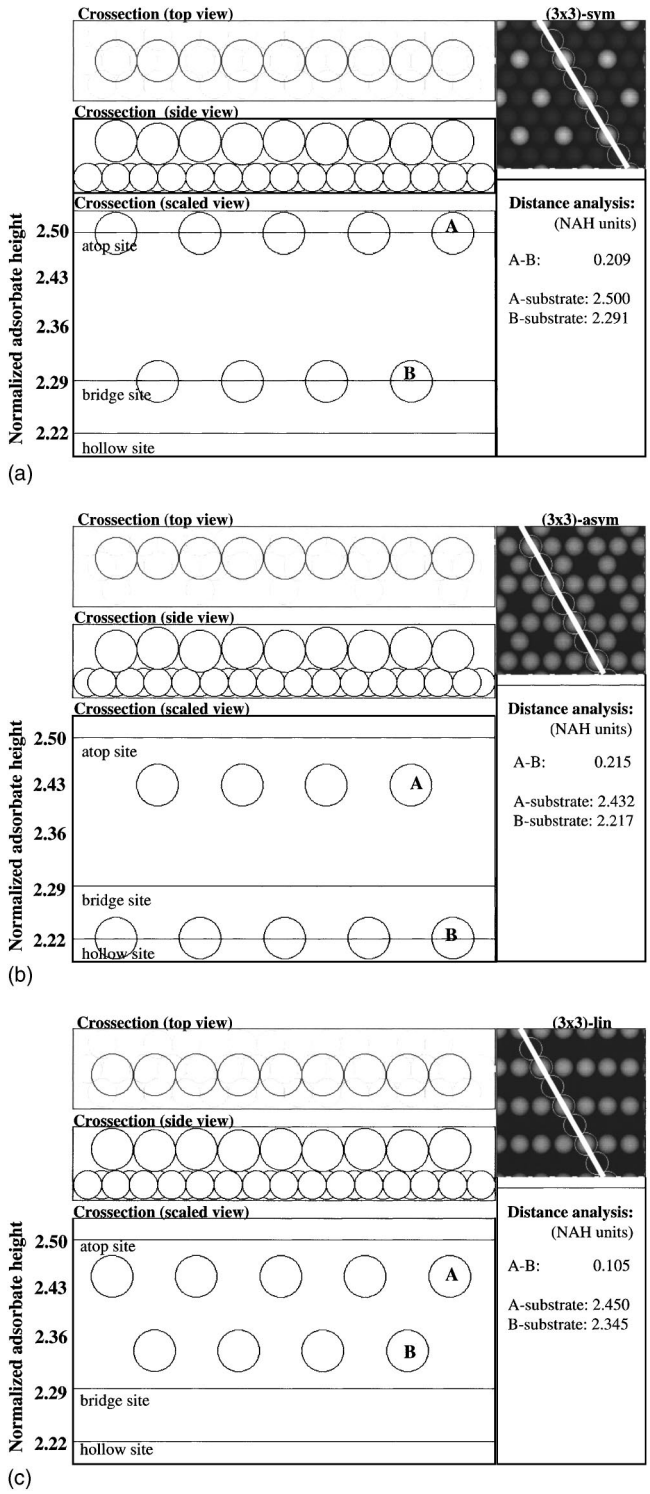



FIG. 4. Cross sectional analysis of characteristic $(3\times3)$ structures showing exact registry and height of the iodine adatoms in $(3\times3)$-sym (a), $(3\times3)$-asym (b), and $(3\times3)$-lin (c) iodine adlattices.

Pt(111) system, due to formation of chemical covalent bonding, iodine adatoms are closer to the substrate than is allowed by a purely geometrical model.

Figure 4(c) is related to the $(3\times3)$-lin structure, and adlayer corrugation is only 0.105 NAH units (0.146 Å). It is important to note that an iodine adlayer having the $(3\times3)$-lin structure has not been observed experimentally as yet. Indeed, the first indication of this type of arrangement comes from work by Yamada,[27] with whom one of the authors collaborated on development of software for interpretation of the STM images based on hard-sphere models.

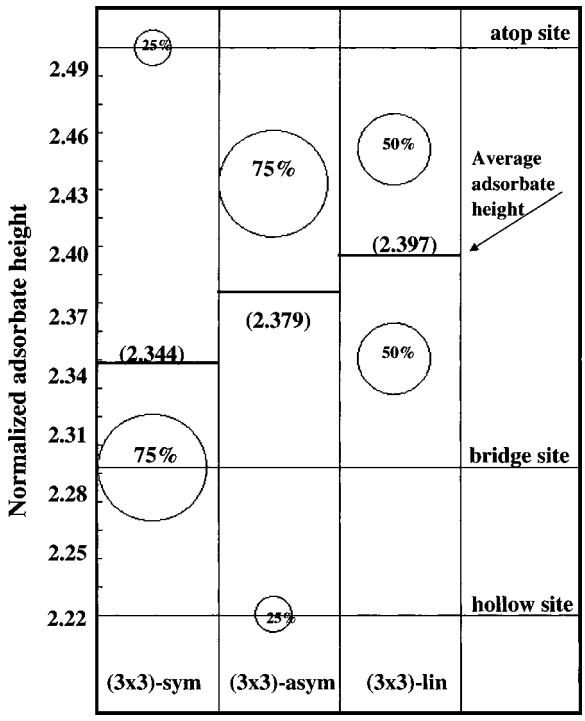



FIG. 5. Quantitative analysis of the normalized adsorbate height parameter for characteristic $(3\times3)$ iodine structures: $(3\times3)$-sym, $(3\times3)$-asym, and $(3\times3)$-lin.

## V. DISCUSSION

Figure 5 summarizes the results of the above-mentioned analysis. One should read this plot in the same way as the data in Fig. 2. The NAH, the average adsorbate height, and registry distribution for $(3\times3)$-sym, $(3\times3)$-asym, and $(3\times3)$-lin iodine adlayers, are presented. For $(3\times3)$-sym we clearly see that one (25%) of four iodine adatoms is in atop site and three (75%) of four are in the bridge site. On average, the whole iodine adlayer is 2.344 NAH units away from the substrate. In the case of $(3\times3)$-asym structure, one (25%) of four atoms is in the hollow site, the closest to the substrate; however, all of its neighbors are high up, close to atop sites, on so-called "asymmetric" sites. Because of this, on average iodine adlayer with this particular arrangement is 2.379 NAH units away from the substrate, farther from the substrate than $(3\times3)$-sym. In the $(3\times3)$-lin adsorbate arrangement, iodine occupies two types of registry, defined in Figs. 3 and 4. Both of these sites are intermediate between atop and bridge. The $(3\times3)$-lin adsorbate layer is very thin, half of the other two arrangements, but at the same time on average is very much farther from the Pt(111) substrate (2.397 normalized units). This graph is very interesting and offers plenty of information about characteristics of the iodine arrangements within $(3\times3)$ unit cell on the Pt(111) surface, which could be related to the experimental findings. First of all, as we mentioned in the Introduction, it is well known that in all experiments only the $(3\times3)$-sym and $(3\times3)$-asym arrangements have been found.[13–16] In respect to

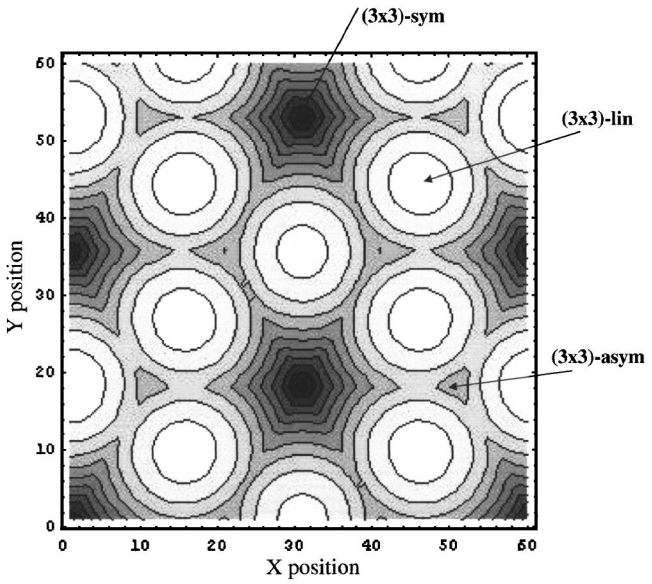



FIG. 6. The contour plot of the average adsorbate height vs adsorbate position ($X$ and $Y$) obtained for $(3\times3)$ iodine adlayer on the Pt(111) substrate.

our data, one could say that those two, which have been found, in average terms are closer to the substrate, than the $(3\times3)$-lin adlayer. Indeed, it should be noted that, on average, $(3\times3)$-sym is situated closest to the Pt(111) surface. This could lead us to the next issue of the stability of different structures. However, we need to know more about relation between average adsorbate height (adsorbate distance from the substrate) and the adsorption energy of iodine on the Pt(111) surface, as well as to estimate how different bonding at fcc and hcp hollow sites could influence the adatom structure.

In continuation, it is also interesting to note that many experiments indicate that the $(3\times3)$-sym and $(3\times3)$-asym structures appear almost simultaneously. Based on our simulation and criteria of the average adsorbate height, the $(3\times3)$-sym structure will be formed preferentially due to closeness to the Pt(111) substrate. Interestingly, in the earlier discussions about ordering of the iodine adlayer on Pt(111), iodine contact with Pt(111) via hollow site was recognized as an important or even crucial reason for preferential bonding. We believe that the crucial parameter is, in fact, the average adsorbate height or the adsorbate (iodine) distance from the substrate surface.

In order to address the final issues related to selective appearance of $(3\times3)$-sym and $(3\times3)$-asym structures, their stability, and the transformation pathway from one to another, we construct the plot of average adsorbate layer height (adsorbate-substrate distance) vs $X$ and $Y$ positions of the iodine adlayer with $(3\times3)$ cell. It is a contour plot in Fig. 6. Note that, in this plot, higher values for average adsorbate height are shaded brighter. When, on average, the adsorbate layer is closer to the substrate, the position is shaded darker. In this particular plot, we can see all simulated positions equivalent to 60 shifts in $X$ and $Y$ directions. Several contour zones of different shading can be seen. The darkest one (contour plot minimum) corresponds to iodine adlayer with $(3\times3)$-sym structure, which is on average the closest one to the Pt(111) substrate. Another local minimum (shaded rather darkly) was found at the position characterized by $(3\times3)$-asym iodine adlayer structure, which we already found that is farther from the platinum substrate. The completely bright zones (circles) correspond to the $(3\times3)$-lin structure, which is far away from the Pt(111) substrate. Indeed, only two local minima have been found for $(3\times3)$-sym and $(3\times3)$-asym structures. This plot indicates that, taking into account the average adsorbate height, only these two positions are preferential. In the remaining cases, iodine adlayer on average is on the walls of the wells, and would gain stability from reaching one of these two minima. This probably could explain why in experiments only these two particular structures have been found. Although the minimum associated with $(3\times3)$-sym structure is deeper, the iodine adlayer once trapped into the $(3\times3)$-asym minimum could not come out easily. This could be the reason why in most experiments both structures have been observed simultaneously. To transform $(3\times3)$-asym to $(3\times3)$-sym it would require considerable additional energy. The opposite would also be difficult.

## VI. CONCLUSION

Using the unequal-sphere packing model, based on geometrical arrangement, the iodine adlayer with $(3\times3)$ unit cell on Pt(111) has been studied, and exact determination of iodine atomic registry has been achieved. This simulation procedure is based on translation of the hexagonally ordered iodine $(3\times3)$ adlayer over the Pt(111) substrate and determination of the NAH (adatom distance from the substrate), adsorbate layer thickness (corrugation), and number of atomic registry per $(3\times3)$ unit cell. In order to select from among many structures having $(3\times3)$ unit cells, we introduce a new parameter defined as the average adsorbate height, which is based on determination of distances between iodine atoms and the substrate for all adatoms in the $(3\times3)$ unit cell. This allows us to select three structures of special interest: $(3\times3)$-sym, $(3\times3)$-asym, and $(3\times3)$-lin, which have been characterized and simulated in great detail, with respect to adatom registry, height, etc. Results obtained by our detailed analysis can be compared to the experimental findings obtained by LEED, STM, ADAM, and SXS. This shows that the average adsorbate height is a useful parameter for selecting among alternative iodine adlayer structures. In addition, results of our simulation show that $(3\times3)$-sym and $(3\times3)$-asym lattices will be favored at the Pt(111) surface. According to our simulation, the formation of $(3\times3)$-sym, which we found to be closer to the substrate, is a favorable process.

Such exhaustive analysis based on the unequal-sphere-packing model reveals many additional details not known before and important for better understanding of the mechanism of formation of $(3\times3)$ iodine structures. Although our modeling is based on a simple, geometrical approach, we have demonstrated its ability to address such complex system as iodine atomic arrangements on the Pt(111) surface. In general, we believe that our approach will be particularly useful for better understanding of the adsorbate-substrate

(modified surfaces) systems, interpretation of experimental STM data and valuable in the future design of the nanodevices at the atomic level.

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