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Molecular dynamics simulations of adsorption and diffusion of Xe on bare and Xe covered Pt(111)

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Abstract

Molecular dynamics simulations are used to calculate adsorption probabilities and diffusion coefficients of Xe on Pt(111) and Xe/Pt(111). Experimental trends are reproduced. The adsorption mechanism is found to be the modified Kisliuk model, with the addition of direct and indirect insertion in the Xe islands. Up to almost saturation coverage, adsorption via migration to island borders is the most important way of adsorbate assisted adsorption. Stimulated desorption is observed at high incidence energies.

1. Introduction

A lot of attention has been paid to the adsorption of Xe on bare Pt(111), both experimentally by means of molecular beam experiments [1-7] and theoretically by means of computer simulations [4,6,7]. However, for adsorption behaviour on Pt(111) surfaces with nonzero Xe coverages, only one experimental study was published thus far [8], and no theoretical study at all. For surface diffusion of Xe on Pt(111), only one experimental study was published until now too [9], and again no theoretical study. In this study we present adsorption data and some diffusion data of Xe on Pt(111) at Xe coverages ($\theta = N_{\text{Xe}}/N_{\text{Pt}}$), varying from zero to 0.33 ($= \theta_c$, commensurate monolayer coverage), obtained by molecular dynamics simulations.

We investigated whether and how stimulated desorption occurred and whether the adsorption mechanism at nonzero coverages according to the modified Kisliuk model proposed by Arumainayagam et al. [8] is valid. This mechanism operates through adsorbate assisted adsorption (see Fig. 1); a Xe atom may adsorb either on bare Pt or on a Xe island. If adsorbed on a Xe island, it may migrate to bare Pt and adsorb there, or it may desorb before the edge of the island is reached. In this model the coverage dependent overall adsorption probability $S(\theta)$ is given by

$$S(\theta) = [1 - (\theta/\theta_s)] S_{\text{Pt}} + (\theta/\theta_s) S_{\text{Xe}}(\theta), \quad (1)$$

with

$$S_{\text{Xe}}(\theta) = S_0 \frac{k_m g(\theta)}{k_d + k_m g(\theta)}. \quad (2)$$

Here is θ_s the saturation coverage (about equal to 0.42 [8]), S_{Pt} the probability of adsorption directly on bare Pt and S_{Xe} is the probability of

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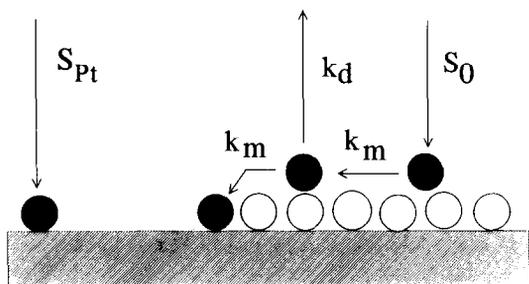


Fig. 1. Schematic view of the modified Kisliuk model. S_{Pt} adsorption probability on bare Pt, S_0 initial trapping probability on Xe island, k_m rate constants for migration, k_d rate constants for desorption.

adsorption on Pt via a Xe island. S_{Xe} depends on the initial adsorption probability on a Xe island (S_0), the rate constants for migration (k_m) and desorption (k_d) and a geometry factor for islands ($g(\theta)$). The geometry factor $g(\theta)$ approaches one for very low coverages or very small islands and zero for very high coverages or very large islands. It appeared that in most cases examined either migration goes much faster than desorption or the islands are small. This implies that $k_m g(\theta) \gg k_d$. Then Eqs. (1) and (2) reduce to

$$S(\theta) = (S_0 - S_{Pt})(\theta/\theta_s) + S_{Pt}. \quad (3)$$

A large number of interatomic potentials for the Xe/Pt(111) system can be found in the literature [4,6,7,10-18]. To our knowledge, none of these was ever tested on the whole range of processes, as different as scattering, desorption, diffusion, island formation and phase transitions. We have decided not to add another potential to the list. We have used a potential that we used before in a study on desorption in the same system [16,17]. Though this potential does not give accurate numerical results for adsorption, we think it is accurate enough, because we have concentrated on trends and on the mechanisms underlying the adsorption and diffusion. These are probably not very sensitive to details of the potential.

2. Computational details

We performed MD simulations in a box with periodic boundary conditions in two dimensions: modelling the Xe-covered Pt(111) surface by two layers with 48 Pt atoms each, and a number of Xe atoms varying from 1 to 16 (commensurate monolayer coverage). We assumed a $\sqrt{3} \times \sqrt{3}R30^\circ$ commensurate structure for monolayer coverage, in which every third threefold face-centered-cubic (fcc) site is occupied, and which has a Xe-Xe nearest neighbour distance of 0.4801 nm. We used the generalised Langevin formalism as developed by Tully to include the effect of the rest of the substrate [19]. The coupling to the ghost particles was calculated by DePristo's method [20]. In order to reduce the length of the simulations only the coupling of each ghost particle with one Pt atom was retained. This coupling was scaled to get approximately the same amplitudes for the vibrations of the Pt atoms as when all coupling terms with the ghost particles would have been included [16,17].

The Pt-Pt interaction is given by the harmonic form

$$\phi_{ij} = \frac{1}{2}\lambda_{ij}[(\mathbf{u}_i - \mathbf{u}_j) \cdot \hat{\mathbf{r}}_{ij}]^2 + \frac{1}{2}\mu_{ij} \left\{ (\mathbf{u}_i - \mathbf{u}_j)^2 - [(\mathbf{u}_i - \mathbf{u}_j) \cdot \hat{\mathbf{r}}_{ij}]^2 \right\}. \quad (4)$$

The \mathbf{u} 's are the displacements from the equilibrium positions, and $\hat{\mathbf{r}}_{ij}$ is a unit vector connecting the equilibrium positions. The Pt atoms were placed at bulk positions with a nearest-neighbour distance of 0.2772 nm. The parameters λ_{ij} and μ_{ij} were determined for nearest and next-nearest neighbours so that they gave the correct elastic constants and bulk specific heat. The Xe-Pt and the Xe-Xe interactions were fitted to TPD spectra [21,22]. Both interactions were represented by the Morse potential

$$\phi(R) = D_e x(x-2), \quad (5)$$

with

$$x = e^{-\alpha(R-R_e)}.$$

The potentials were originally constructed to describe desorption data [17]. We used a cutoff distance $R_c = 0.83$ nm which was dictated by the minimal image convention [23]. The depth of the potential D_e and the parameter α of the Pt-Xe potential were fitted to the adsorption energy and the harmonic vibrational frequency of a Xe atom perpendicular to the surface [17]. The interaction of a Xe atom with the Pt surface was calculated by summing over all Pt atoms within a distance R_c . We also added a contribution of the Pt atoms farther away by integrating over the region of the Pt surface farther than R_c , assuming it to be a continuum [17]. D_e and α of the Xe-Xe Morse potential were fitted to thermal desorption data as follows [17].

A good potential for the direct interaction between Xe atoms is known derived by Barker et al. [24], but this potential gave a desorption peak in the TPD spectra at a temperature which is 20 K too high: the potential is too strong. Work by McLachlan [25] and by Kohn and Lau [26] showed that the dispersion interaction may be reduced by as much as 1/3 by substrate-mediated effects if the substrate is modeled by a continuum. When we took only 2/3 of the dispersion interaction, the desorption peak was lying only 10 K too high. An additional repulsion between the Xe atoms may be present because of charge transfer [27]. This charge was estimated from the change in the work function. Using a change in the work function of 0.6 V at full coverage [28], a dipole moment of 8.7×10^{-31} C m was obtained. The location of the negative charge is unknown. Supposing that it is located in the top Pt layer we found, with the Xe-surface distance of 0.245 nm as the charge separation, $q_{Xe} = +0.022e$.

If the negative charge in the Pt is localised, the electrostatic Xe-Xe interaction should be a dipole-dipole interaction. But if it is delocalised, a Coulomb interaction between the Xe atoms is better. We have used the strongest of the two. At R_c , the Coulomb repulsion is thrice as strong as the dipole-dipole repulsion. This Coulomb interaction was added to the direct Xe-Xe interaction with diminished dispersion interaction. With this potential, a desorption peak was found

Table 1
Parameters of the potentials (nn nearest neighbour, nnn next nearest neighbour)

PtPt	λ_{nn}	36651	$\text{kJ mol}^{-1} \text{nm}^{-2}$
	μ_{nn}	-2007	$\text{kJ mol}^{-1} \text{nm}^{-2}$
	λ_{nnn}	3155	$\text{kJ mol}^{-1} \text{nm}^{-2}$
	μ_{nnn}	-3145	$\text{kJ mol}^{-1} \text{nm}^{-2}$
PtXe	D_e	3.016	kJ mol^{-1}
	R_e	0.32	nm
	α	12.27	nm^{-1}
XeXe	D_e	1.318	kJ mol^{-1}
	R_e	0.4527	nm
	α	15.306	nm^{-1}

which was lying only 3 K too high. Our Morse potential was fitted to this potential. At R_e , it has only 56% of the strength of the direct Xe-Xe potential.

The Xe-Xe interaction was calculated by summing over all the Xe atoms less than R_c apart. All potential parameters are given in Table 1. Even though the physical ground on which the potential is based is suspect, we feel that the magnitude of the interaction between Xe atoms on Pt(111) is reasonably well represented.

All simulations were performed with a time step of 10.0 fs and at a temperature of 95 K, unless otherwise stated. All systems were allowed to relax from their initial equilibrium positions for at least 5 ps.

For the determination of diffusion coefficients we used

$$D = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{d}{dt} \langle [\Delta r(t)]^2 \rangle \quad (6)$$

from Ref. [29]. The linear region of $\langle [\Delta r(t)]^2 \rangle$ started at about 100 ps, and we measured it up to 200 ps.

Adsorption probabilities were determined by counting the number of scattered Xe atoms. Typically, 1000 simulations of 25 ps each were required to obtain data with statistical uncertainties well below the experimental errors. Determining such an adsorption probability took about 4 to 9 cpu h for $\theta = 0$ to θ_c , respectively, on a Silicon Graphics Iris Indigo workstation.

3. Results and discussion

3.1. Diffusion coefficients

At $\theta = 0$ we found a diffusion coefficient of about $9 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ at both 80 and 95 K. Experimentally [9], about $8 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ was found at 80 K. Taking into consideration that the experimental error is about a factor of five, the agreement is reasonable, although the difference might also be caused by a corrugation that is slightly too large in our simulations. As the dependence of the adsorption probability on angle and energy of incidence is correct (see Section 3.2) the latter factor cannot be large. In accordance with the experiment, we find that the diffusion coefficient decreases strongly with increasing coverage, because collisions with Xe islands limit diffusional motion [9]. At $\theta = 0.083$ and 95 K we find $D = 4 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$. At θ_c and 95 K we observed no diffusion at all. The experimental data give $D = 6 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ and $D = 1 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$, respectively (calculated for $T = 95 \text{ K}$ from data in Ref. [9]). Our simulation box is too small to allow for the necessary rearrangements at θ_c that would make diffusion of a Xe atom in the monolayer possible. For the diffusion of a Xe atom over a commensurate Xe layer at θ_c we found $D = 4 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ at 95 K.

3.2. Adsorption on bare Pt(111)

Our adsorption probabilities are about twice as large as the experimental values, as can be seen from Fig. 2. Apparently the Pt-Xe interaction, which was originally fitted to describe desorption data [17], fails to reproduce the adsorption probabilities in a quantitative manner. But the trend is described very well: Our adsorption probabilities are found to scale with $E_i \cos^{1.6}(\theta_i)$ (Fig. 2), in contrast with the experiments of Arumainayagam et al. [4], where scaling with $E_i \cos(\theta_i)$ is reported (E_i is the incidence energy and θ_i is the angle of incidence), but in accordance with the experiments of Rettner et al. [2] who reported scaling with $E_i \cos^{1.6}(\theta_i)$ too. This is in accordance with

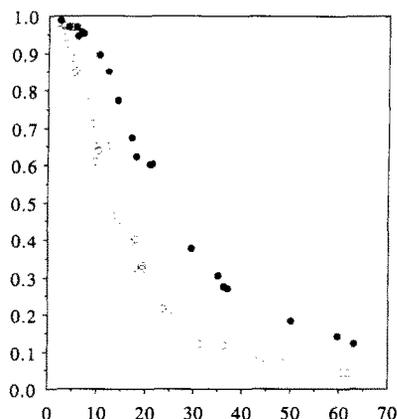


Fig. 2. Adsorption probability on bare Pt as a function of $E_i \cos^{1.6}(\theta_i)$. $E_i = 6-63 \text{ kJ mol}^{-1}$, $\theta_i = 0-60^\circ$. \circ = experimental values [2], \bullet = our simulations.

the defect densities of the surfaces used [6]. Arumainayagam's was 1%, Rettner's was 0.1%, and ours 0.0%. Hence, provided the influence of the defects at 0.1% defect density on the adsorption probabilities is negligible, our potential describes the surface corrugation well.

Desorption after more than one collision with the surface we found to be very rare. In about 20000 simulations we found only 10 desorptions after two collisions, only one after three collisions, and no desorption after four or more collisions at all.

3.3. Adsorption at nonzero Xe coverages

All simulations in this section were carried out at normal incidence. We determined adsorption probabilities at $\theta = 0$ to θ_c , at an incidence energy of 34 kJ mol^{-1} . We were not able to model higher coverages (the real saturation coverage is θ_s) because our simulation cell was not large enough to model the incommensurate phases which occur above θ_c [12,13,18,30,31].

The results are shown in Fig. 3. Again, as in Fig. 2, we see that the adsorption probabilities of the simulations are higher than the experimental ones. However, the experimental [8] trend is clearly reproduced very well by our simulations. The adsorption probability increases with coverage up till close to θ_c (our "saturation cover-

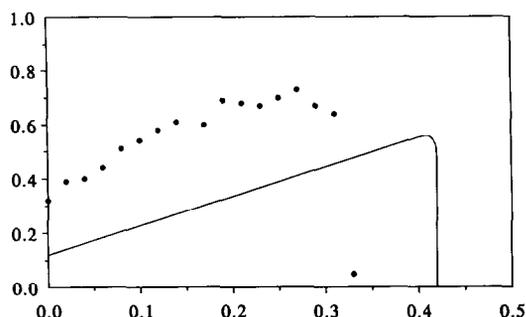


Fig. 3. Adsorption probability as a function of Xe coverage at normal incidence and $E_i = 34 \text{ kJ mol}^{-1}$. — = experimental result [8], • = our simulations.

age”) indicating adsorbate assisted adsorption. Hence, the modified Kisliuk model seems to be correct. However, it was already observed by Arumainayagam et al. [8] that an alternative explanation for the modified Kisliuk model is that incoming atoms are incorporated into the monolayer at or near the impact point by a local relaxation of the adsorbed layer, without migration over large distances. At 34 and 63 kJ mol^{-1} we have found this direct insertion in 4 and 12%, respectively, of the hits on the Xe islands. Hence direct insertion is not the most important adsorption route, but its influence on the overall adsorption probability is not to be neglected. As is to be expected, it occurs more often for higher energies.

Apart from adsorption after migration to the edges of an island and direct insertion into an island we encountered also an in-between mechanism; first adsorption on top of an island, followed by migration over the island and “indirect insertion” into the island before the edge is reached. At θ_c and 34 kJ mol^{-1} we found this in 5% of the hits on top of the adatom layer. This is in accordance with simulations at this coverage in which a Xe atom is placed on top of the adatom layer: 95% desorbs and 5% inserts.

A scheme of the modified Kisliuk model of Arumainayagam et al., extended with both direct and indirect insertion, is shown in Fig. 4. Eq. (2) must be replaced by

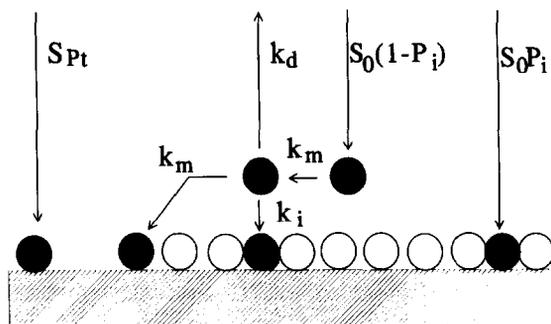


Fig. 4. Schematic view of the extended adsorption model. S_{Pt} adsorption probability on bare Pt, S_0 initial trapping probability on Xe island, k_m , k_d and k_i rate constants for migration, desorption and indirect insertion, respectively, P_i probability that an adsorbed incoming Xe atom inserted.

$$S_{Xe}(\theta) = S_0 \left[\frac{k_i + k_m g(\theta)}{k_d + k_i + k_m g(\theta)} \times (1 - P_i) + P_i \right]. \quad (7)$$

Here P_i is the probability that an adsorbed incoming Xe atom inserts directly and k_i is the rate constant for indirect insertion. If $k_i + k_m g(\theta) \gg k_d$, as is the usual case, Eqs. (1) and (7) still reduce to Eq. (3). Hence, on the basis of the experimental adsorption data, the various mechanisms cannot be distinguished, as was also observed by Arumainayagam et al. But our simulations clearly show the modified Kisliuk model to be operative, with two alternative ways of adsorption besides.

We found $S_0 = 0.85 \pm 0.05$ (exp. 0.63 [8]) and $S_{Pt} = 0.32 \pm 0.02$ (exp. 0.12 [8]), at 34 kJ mol^{-1} and normal incidence. As in the experiment, the initial trapping probability on a Xe island is much higher than on bare Pt. This is due to the matching of masses of the collision partners in case of a collision on an island, which enhances multiple collisions, thereby facilitating energy loss. Pt has a larger mass and the Pt surface is stiffer than the Xe overlayer, which results in fewer collisions with enough energy loss to lead to adsorption [8]. This is in accordance with the fact that desorption after more than one collision with the bare Pt surface is very rare, whereas it happens in the majority of the colli-

sions on a Xe island.

We found $k_d = (2.4 \pm 0.1) \times 10^6 \text{ s}^{-1}$ and $k_i = (1.3 \pm 0.3) \times 10^5 \text{ s}^{-1}$, at θ_c and $T = 95 \text{ K}$. The average residence time of a Xe atom adsorbed on a commensurate monolayer at θ_c we found to be $(4.0 \pm 0.2) \times 10^{-7} \text{ s}$. We think that k_d will be in reality much smaller than in our simulations, because in our simulations the Xe in the second layer is in fact bound too weakly. This can be seen in Fig. 3. Experimentally, the trapping probability increases linearly with coverage up to almost θ_s . In contrast, our data show a deviation from the linear behaviour at coverages somewhat below θ_c , though linear behaviour should have persisted to almost θ_c . Apparently, a lot of Xe atoms desorb from the island before reaching its borders and adsorbing there. Hence desorption goes too fast compared to diffusion over the island. The cause of this is that our Xe-Xe potential does not depend on the distance to the surface. It was fitted in order to describe the Xe-Xe interaction between two Xe atoms on the surface [17], which is weakened to 56% of the strength of the gas phase Xe-Xe potential because of charge transfer [3,32]. Hence, at larger distances to the surface it is too weak compared to the actual Xe-Xe potential which approaches the gas phase Xe-Xe potential with increasing height. Indeed some simulations with a height dependent Xe-Xe potential showed a steady linear dependence of the adsorption probability on coverage up to almost θ_c . It may well be that the interaction between a Xe atom on top of the adlayer and the atoms in the adlayer is well nigh equal to the gas phase Xe-Xe potential. This follows from the consideration that it is experimentally possible to determine the trapping dynamics unto a really saturated monolayer at θ_s , in which insertion of course is impossible. In order for the experiment to be successful, k_d must be many orders of magnitude smaller than we found. This cannot be explained by only taking the 26% larger Xe density in a θ_s compared to a θ_c layer into account.

Will k_i be smaller too? The indirect insertion process consists of hopping of a Xe atom over the Xe adlayer until it can slip into a hole in the adlayer which was there momentarily due to

the thermal motions of the adatoms. This process is mainly governed by entropy effects, and much less so by energy effects. Hence the real k_i will not be very different from our k_i . But since the real k_d is many orders of magnitude smaller, $k_i \gg k_d$. Hence the average residence time in the second layer without adsorption at borders equals $t_r = k_i^{-1} = 7.7 \times 10^{-6} \text{ s}$. In this time, the distance covered through diffusion over an island equals $\sqrt{\langle [r(t)]^2 \rangle} = \sqrt{6Dt_r} = 42 \text{ nm}$. If the dimensions of the island are smaller than about this value, the majority of the Xe atoms moving on top of the island will reach the border of the island and adsorb there. But if islands are larger, or empty sites are rare, close to θ_c , the majority will desorb before reaching the island border. A circular island with radius 42 nm consists of approximately 7000 Xe atoms. Since in reality Xe islands are much smaller [9], indirect insertion will be unimportant compared to migration with subsequent adsorption at the borders, at coverages varying from zero to close to θ_c : $k_m g(\theta) \gg k_i$. The conclusion is that in real systems, at coverages from zero to almost θ_c , $k_m g(\theta) \gg k_i \gg k_d$. Hence, the condition for using Eq. (3), $k_i + k_m g(\theta) \gg k_d$, is met almost invariantly. Only close to or above θ_c , $g(\theta)$ of course will be very small or zero, respectively. In these cases insertion, both direct and indirect, followed by phase transitions to incommensurate phases will be the most important or the only way of adsorption, respectively.

At sufficient high energies of incidence stimulated desorption occurs. At 34 kJ mol^{-1} and θ_c this effect is all but negligible; only 0.5% of the simulations leads to stimulated desorption of one Xe atom, while in all of these cases the incoming atom adsorbs. At 63 kJ mol^{-1} stimulated desorption occurs already in 15% of the cases; 12% consists of adsorption of the incoming atom and desorption of another, and 3% consists of scattering of the incoming atom and desorption of one adatom. Adsorption of the incoming atom and desorption of two others was never observed. The fact that scattering with stimulated desorption has just started at 63 kJ mol^{-1} should be compared with the desorption energy of Xe from a commensurate full Xe layer on Pt(111),

which is $28.1 \pm 0.6 \text{ kJ mol}^{-1}$ [17]. Hence, scattering with stimulated desorption theoretically might start at about 30 kJ mol^{-1} . The fact that it does not, together with the fact that adsorption with stimulated desorption starts only at about 34 kJ mol^{-1} , leads to the conclusion that energy transfer from the incoming atom to the adsorbed Xe atoms is very inefficient. A direct insertion into the monolayer leads to stimulated desorption three times as often as a hit on top of the monolayer. About half of the desorbed adatoms desorbed directly, the other half was kicked to the top of the monolayer and desorbed from there. Since in reality desorption is expected to be much slower, the latter half probably is overestimated in the simulations, because re-insertion will take place much more often in reality.

4. Conclusions

We have shown that molecular dynamics simulations, even with a small simulation box, is very well fit to reproduce the trends in the experimental diffusion and scattering data. The surface corrugation of Pt(111) is described well. Also the decrease of the diffusion coefficient with increasing coverage due to collisions with Xe islands is reproduced. A clear view of the adsorbate assisted adsorption was obtained, consisting of the modified Kisliuk model, with in addition direct and indirect insertion. Initial trapping on Xe islands appeared to be easier than trapping on bare Pt, due to mass matching of the collision partners. Furthermore, we were able to determine that the migration over an Xe island with subsequent adsorption on bare Pt is the most important way of adsorption at higher coverages, up to almost θ_c , where insertion takes over.

However, in order to provide for data which would be even accurate in a quantitative manner, the potentials would have to be modified. A height dependent Xe–Xe potential would be required, especially in order to give a better description of desorption from the second Xe layer. The Pt–Xe potential would need some modification too.

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