A theoretical study of the parameters affecting the kinetics of gas adsorption on solid surfaces

2 **AUTHORS**, INCLUDING:

Francisco Zaera
University of California, Riverside

376 PUBLICATIONS   **12,214** CITATIONS

A theoretical study of the parameters affecting the kinetics of gas adsorption on solid surfaces

T. Nordmeyer and F. Zaera
Department of Chemistry, University of California, Riverside, California 92521

The nondissociative adsorption of gas phase molecules onto a spatially homogeneous square lattice was studied using a Monte Carlo computer simulation method which accounts for the existence of an extrinsic precursor state. The parameters affecting the adsorption kinetics were varied systematically in order to compare our simulations with a model for adsorption originally proposed by Kisliuk [J. Phys. Chem. Solids 3, 95 (1957)]. Our studies indicate that in the presence of precursor mobility, the sticking coefficients obtained from our simulations are consistently lower than those obtained using Kisliuk's equation. Upon further investigation, we found two reasons for this discrepancy, namely, islanding of the adsorbates on the surface, and site revisiting in the precursor state. We found that some degree of islanding within the chemisorption layer occurs as a direct consequence of the nature of the precursor mediated adsorption process and that the extent of this clustering is controlled by the competition between mobility within the physisorbed layer and desorption; when mobility dominates, islanding formation is enhanced. Site revisiting within the precursor state was also found to affect the adsorption kinetics; we were able to derive here an analytical expression for the sticking coefficient that accounts for this factor and that correlates well with results from the corresponding simulation. Finally, we show that sticking coefficients are affected by surface geometry.

I. INTRODUCTION

The kinetics of many nondissociative adsorption processes can be described by a simple model first proposed by Langmuir in which incoming molecules chemisorb on empty surface sites but bounce off occupied sites; in those cases, the value of the sticking coefficient decreases linearly with surface coverage.[1] In some systems, however, the sticking coefficient remains almost constant until coverages near saturation are reached, at which point it drops rapidly to zero.[2,3] In 1957, Kisliuk[4] proposed an explanation for such behavior which considers the formation of mobile physisorbed precursor states similar to those first conceptualized by Taylor and Langmuir.[5] In Kisliuk's model, incoming molecules may physisorb over either empty (intrinsic precursors) or occupied sites (extrinsic precursors), and those physisorbed molecules may then either desorb back into the gas phase or move within the second layer until a site for chemisorption is found. Based on these ideas, he derived an analytical expression for the sticking coefficient s for nondissociative adsorption in terms of the probabilities for chemisorption given by

$$s/s_0 = P_c(1) + P_c(2) + P_c(3) + \cdots, \qquad (1)$$

where s_0 is the initial sticking coefficient and $P_c(n)$ is the probability of chemisorption after visiting n sites—$P_c(1)$ is the probability for chemisorption on the initial site, $P_c(2)$ corresponds to physisorption at an initial site followed by a move and chemisorption at a neighboring site, etc. This expression can be written in the form of a geometric series and expressed in closed form as[4]

$$s/s_0 = \frac{(1-\theta)}{(1-\theta+K\cdot\theta)}, \qquad (2)$$

where θ is the fractional coverage of chemisorbed molecules and K is a parameter that describes the nature of the physisorbed layer, which according to Kisliuk can be expressed in terms of the relative probabilities involved in the adsorption process. For the case where molecules are not allowed to be trapped into an intrinsic precursor state, K is given by

$$K = \frac{k_d}{k_d + k_m} = P_d, \qquad (3)$$

where k_d and k_m are the rate constants for desorption and diffusion from the extrinsic precursor state, respectively, and P_d is the probability for desorption to occur over migration. From this expression, it can be seen that $K = 1.00$ corresponds to a case where the precursor state has no mobility at all and where the adsorption kinetics is described by a Langmuir equation, while low values of K represent cases with high precursor mobility where the sticking coefficient remains at s_0 until near-saturation coverages.

King and co-workers have derived an alternative expression for the kinetics of chemisorption which also includes precursor states,[6] and Monte Carlo simulations of precursor mediated chemisorption have been done as well,[7] but up to now no direct comparisons have been made between the analytical models and the corresponding computer simulations. In this paper, we compare the results obtained from our simulations with those obtained using the model proposed by Kisliuk. We have found that the

values for the sticking coefficient obtained from our simulations are consistently lower than those predicted by the model. We show that this discrepancy is due to two effects which were not included in the derivation of the original equation, namely, the formation of islands within the chemisorbed layer, and the finite chance for an extrinsic precursor to visit a given site more than once during its migration within the physisorbed layer (site revisiting). The magnitude of these effects were assessed—islanding was found to account for about one-third of the discrepancy, while site revisiting was responsible for the rest. We have also derived a new analytical expression for the sticking coefficient that reproduces quite well the results obtained from our simulations.

II. THEORETICAL BACKGROUND

The Monte Carlo simulations described in this paper are based on a stochastic method for adsorption kinetics similar to that used by Gillespie to model reaction kinetics in homogeneous media.[8,9] This stochastic approach, unlike the deterministic analog, is based on a comparison of probabilities for all possible choices of individual events taking place during the overall reaction. Three rate constants are used to describe the behavior of the system—the two mentioned earlier, i.e., k_m and k_d for movement and desorption of molecules within the precursor state, respectively, and a third one, k_i, that provides the frequency of impingement of gas molecules with the target. The reaction rates R_m, R_d, and R_i associated with those three processes are given by

$$R_m = k_m \cdot \theta_p, \tag{4}$$

$$R_d = k_d \cdot \theta_p, \tag{5}$$

$$R_i = k_i, \tag{6}$$

and

$$R_T = R_m + R_d + R_i, \tag{7}$$

where θ_p is the fractional coverage of physisorbed molecules. The time evolution of the system could then be calculated by using these expressions and the so-called master equation,[10] but since solving such an equation analytically can only be done for a few limited systems,[8] we have chosen an alternative approach that uses the reaction probability density (RPD) function instead. This RPD function is ideally suited for numerical simulations of processes that can be described as a sequence of discrete events because it allows for the calculation of both the time elapsed between events and the type of event that takes place next. The time interval between successive events, τ, can be expressed as

$$\tau = \frac{1}{R_T} \ln\left(\frac{1}{x}\right), \tag{8}$$

where x is a random number between 0 and 1, and the type of event chosen to occur next, μ, is determined by the expression

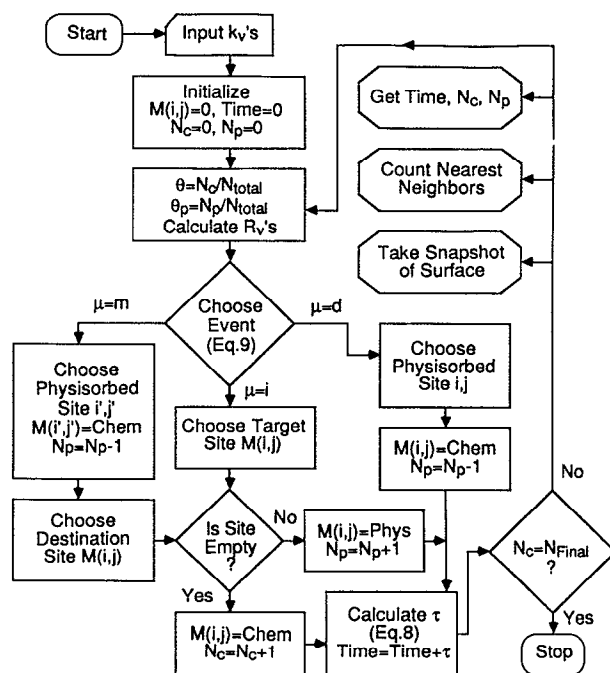$$\sum_{v=i}^{\mu-1} R_v < y \cdot R_T \leqslant \sum_{v=i}^{\mu} R_v, \tag{9}$$

FIG. 1. The flow chart for the main Monte Carlo algorithm used to simulate the adsorption kinetics of gas phase molecules impinging onto a square lattice. (i,j) denotes a position on the square matrix M with a total of N_{total} sites which is used to represent the surface, and N_p and N_c correspond to the number of physisorbed and chemisorbed species on the target, respectively.

where y is a second random number between 0 and 1, and μ stands for i (impingement), m (mobility), or d (desorption).

III. SIMULATION DETAILS

A 10 000 site square target (100×100) was used to represent a section of an ideal surface; larger targets would have required prohibitive amounts of time on the computer used in these simulations (Vax system 8820). Cyclic boundary conditions were added to eliminate edge effects—a molecule moving past an edge reappears on the opposite side of the matrix, making the target in effect infinite in two dimensions. We also guarded against buildup of the physisorbed layer by choosing a rate of impingement such that only a small concentration of precursors existed at any time, thus avoiding complications such as hindered diffusion and collisions of gas phase molecules with the physisorbed layer (later in this paper we will discuss some results obtained by increasing the rate of impingement). A flow chart outlining the algorithm used for our simulation is given in Fig. 1. After initializing the appropriate variables, the rates for the three processes are calculated, the event to take place is selected using Eq. (9), the chemisorbed and physisorbed layers are modified according to the event chosen, and the time interval is calculated using Eq. (8); this process is repeated many times until the desired coverages are obtained. In addition to acquiring kinetic information about the system, we also devised codes for counting nearest-neighbor distributions

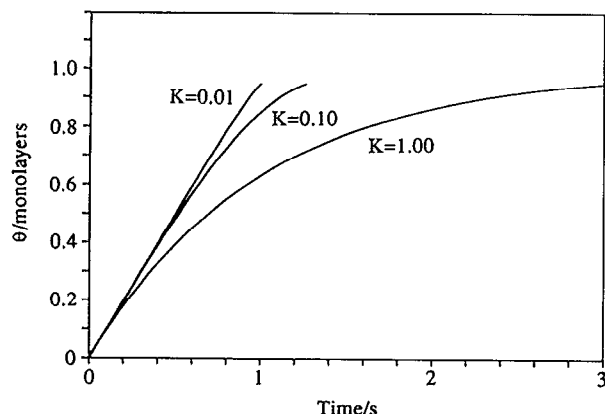## Uptake Curves as a Function of Surface Mobility

FIG. 2. Uptake curves calculated using our simulation program showing the coverage of chemisorbed species θ as a function of time for three different values of K representing various degrees of mobility. The parameters used for these simulations are given in Table I.

and for taking snapshots of the target at periodic intervals. The code for the random number generator used in the program was taken from a recent book on numerical methods.[11]

Figure 2 displays results from typical simulations showing the changes in surface coverage for the chemisorbed species (θ) vs time for three cases—$K=0.01$, $K=0.10$, and $K=1.00$ (Table I). All simulations reported in this paper are the result of averaging 18 runs using different sequences of random numbers [a single simulation for the $K=0.10$ case used about 18 min of central processing unit (CPU) time and required about 45 000 events to reach a final coverage of $\theta=0.95$]. Relative sticking coefficients s/s_0 were calculated as a function of coverage by taking the derivative ($d\theta/dt$) of curves such as those shown in Fig. 2; an example for the $K=0.10$ case is shown in Fig. 3. Given the high level of noise present in the raw data several smoothing techniques were tried, including filtering of the frequency spectra obtained by Fourier transform using various low pass filters, averaging using boxcar and combinatorial windows, and second polynomial least-squares fits; a 31-point moving window second-order polynomial least-squares fit was found to give the best results (Fig. 3). The window size was chosen to be large enough to average out local fluctuations while still retaining the general shape of the curve, and the coefficients in the second-order polynomial were calculated using the Gauss–Seidel method.[12]
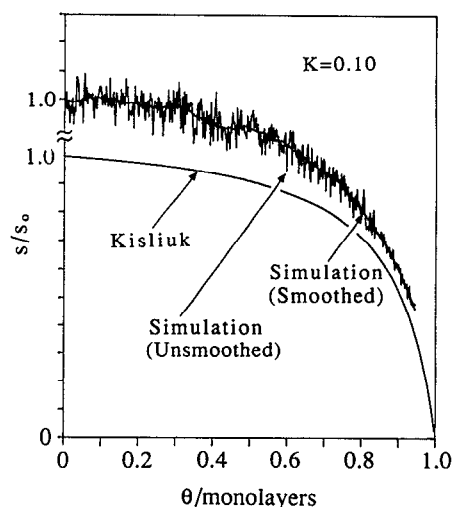
Sticking Coefficient vs. Coverage

FIG. 3. Sticking coefficient vs coverage for $K=0.10$ as obtained from our simulation results before (upper curve, noisy line) and after smoothing (upper curve, smoother line). A curve for the same value of K calculated by using Eq. (2) is also shown for comparison (lower trace).

Several tests were performed to ensure that our stochastic method reproduces accurately the adsorption kinetics. First we made sure that in the absence of precursor mobility ($K=1.00$), simple Langmuir adsorption kinetics was observed: this is not only evident from the results displayed in Figs. 2 and 4 ($K=1.00$), but also from the fact that the chemisorbed species were found to be randomly distributed within the lattice (see below). In addition, we also checked for inconsistencies in the simulations by
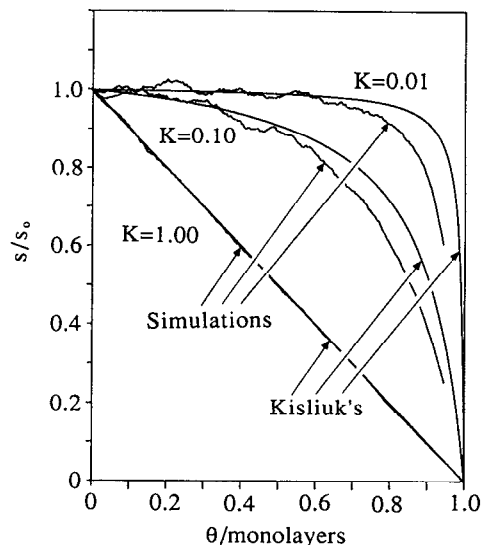
Sticking Coefficient vs. Coverage

FIG. 4. Sticking coefficient vs coverage results obtained from our Monte Carlo simulations (noisy lines) and calculated by using Kisliuk's equation (smooth lines) for three different values of K.

TABLE I. Rate constants and K values used in our simulations.

K	k_d (s^{-1})	k_m (s^{-1})	k_i (molecule site^{-1} s^{-1})
1.00	1.0×10^4	0	1.0
0.10	1.0×10^4	9.0×10^4	1.0
0.01	1.0×10^4	99.0×10^4	1.0

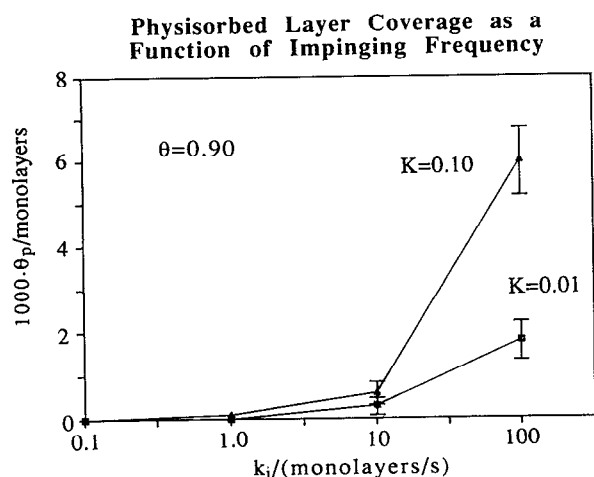## Physisorbed Layer Coverage as a Function of Impinging Frequency

FIG. 5. The population of physisorbed species at a chemisorbed coverage of $\theta=0.90$ as a function of impingement rate for two different values of K.
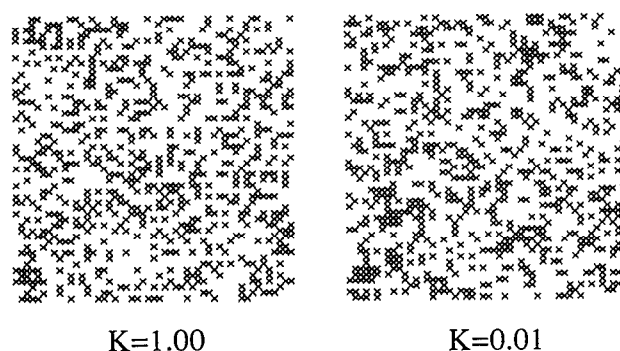
Snapshot of surface for $\theta = 0.3$

FIG. 6. Snapshots of the chemisorbed layers obtained at a coverage of $\theta=0.30$ for $K=1.00$ (left) and $K=0.01$ (right). These pictures have dimensions of 50×50 sites.

changing the program's code in order to simulate the same system via a different logic, and by varying the target size while keeping periodic boundary conditions; in all cases, we found complete consistency between the simulations and the expected results.

IV. RESULTS

A. General

As mentioned above, the changes in the sticking coefficient with surface coverage were calculated for three different values of K corresponding to varying degrees of precursor mobility. The dependence of the surface coverage on time (Fig. 2) follows the general trends expected, i.e., an exponential increase in the absence of precursor mobility and an almost linear relationship for high mobility rates. The corresponding sticking coefficient vs coverage curves are shown in Fig. 4 together with values calculated using Kisliuk's equation. Note that while there is good agreement between our calculations and Kisliuk's prediction for $K=1.00$, a clear discrepancy exists for the other values of K—the sticking coefficients obtained from our simulations at intermediate to high coverages are consistently lower than those predicted by the analytical equation. In the following sections, we will discuss three possible reasons for this discrepancy, namely, a buildup of molecules in the precursor state, islanding in the chemisorbed layer, and site revisiting during migration within the physisorbed layer.

B. The effect of the rate of impingement

The effect of the rate of impingement (changes in gas pressure) on the sticking coefficient was studied first. If the rate of incoming molecules is too high, the population of molecules in the physisorbed layer is expected to build up and some hindrance in diffusion within that layer as well as an increase in collision frequency of the incoming particles with physisorbed species should be observed. Figure 5

shows the final physisorption coverages obtained as a function of the rate of impingement after reaching a coverage of 0.90 in the chemisorbed layer; results are displayed for two different values of K (0.10 and 0.01), where the rates of mobility and desorption were held constant as k_i was varied. It can be seen from this figure that the concentration of molecules in the precursor state becomes significant only after the rate of impingement reaches values above 100 monolayers/s (an equivalent pressure of about 10^{-4} Torr); we chose a value of 1 monolayer/s in our simulations in order to rule out pressure effects as the cause of the differences with Kisliuk's theory.

C. Islanding

A second possible reason for why the results obtained in our simulations differ from those calculated using the theoretical model of Kisliuk relates to the formation of islands of chemisorbed species on the surface. Snapshots of the target were taken at different times during the simulations in order to help visualize the adsorption arrangement on the surface during the chemisorption process. The results of two such snapshots for a 50×50 portion of the target are illustrated in Fig. 6 for two values of K. It can be seen that while Langmuir kinetics ($K=1.00$) seems to yield a randomly distributed pattern, some clustering occurs in the case of high precursor mobility ($K=0.01$).

In order to obtain more quantitative information about the degree of islanding present on the surface, we developed a statistical method for characterizing this surface

TABLE II. Normalized nearest-neighbor matrix for $K=0.01$.

θ	Z_0	Z_1	Z_2	Z_3	Z_4
0.1	1.00	1.16	1.40	2.75	10.0
0.3	1.00	1.16	1.43	1.88	2.76
0.5	1.00	1.13	1.30	1.56	1.94
0.7	1.00	1.06	1.15	1.27	1.43
0.9	1.00	1.02	1.04	1.08	1.12

TABLE III. Statistical islanding factor (SIF) for three values of K.

K	SIF
1.00	1.00
0.10	1.27
0.01	1.36

grouping. For a given value of K, the number of nearest neighbors around each chemisorbed molecule was determined as a function of coverage, and the resulting distributions were normalized by numbers corresponding to a random distribution. The resulting parameters $Z_i(\theta,K)$ are given by the following expressions:

$$Z_0(\theta,K) = (\phi_0 + \phi_1 + \phi_2 + \phi_3 + \phi_4)/\theta,$$

$$Z_1(\theta,K) = (\phi_1 + 2\cdot\phi_2 + 3\cdot\phi_3 + 4\cdot\phi_4)/4\cdot\theta^2,$$

$$Z_2(\theta,K) = (\phi_2 + 3\cdot\phi_3 + 6\cdot\phi_4)/6\cdot\theta^3,$$

$$Z_3(\theta,K) = (\phi_3 + 4\cdot\phi_4)/4\cdot\theta^4,$$

$$Z_4(\theta,K) = (\phi_4)/\theta^5, \qquad (10)$$

where ϕ_i is the fraction of chemisorbed sites with i nearest neighbors obtained from the simulations. These parameters provide a measure of the degree of islanding present on a given surface—values close to 1.00 indicate that the distribution of target species in the simulation is random, while numbers greater than 1.00 correspond to some clustering of surface species. A "normalized nearest-neighbor" matrix was then constructed for each K by calculating the $Z_i(\theta,K)$ values obtained for a series of surface coverages. For the $K=1.00$ case, i.e., a random distribution, all the values in the matrix were found to be unity to within experimental error (about 2%) as expected. The values for $K=0.01$, on the other hand, show that the distribution of molecules within the target is nonrandom, which indicates that some degree of islanding does indeed take place (Table II). For instance, in the example shown in Fig. 6, the total number of paired chemisorbed molecules was estimated to be about 15% larger than that expected for a random distribution, and there were almost three times as many molecules surrounded by four neighboring filled sites as those seen in the Langmuir case.

In order to compare the extent of islanding among different simulations, a more convenient way to represent the matrix described above is needed; we have arbitrarily chosen to average the ratios for $Z_i(\theta=0.5, K)$ and call this the statistical islanding factor (SIF)

$$\text{SIF}(K) = \sum_{i=0}^{4} \frac{Z_i(\theta=0.5, K)}{5}. \qquad (11)$$

Table III shows the SIF values obtained for the three different values of K used here. It is clear from these data that island formation is enhanced as precursor mobility is increased (lower K values). It must be emphasized that the islanding is due exclusively to the nature of the precursor state since no mobility of the chemisorbed molecules is allowed in our simulations. This result is easily understood

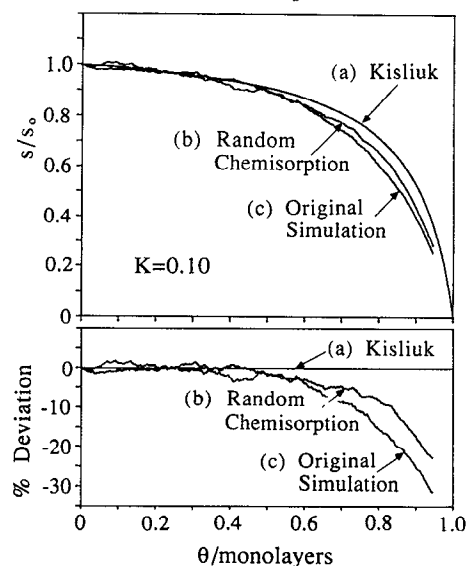## Simulation Results Using the Random Chemisorption Routine

FIG. 7. (Top) Sticking coefficient vs coverage for $K=0.10$ as calculated using (a) Kisliuk's equation, and by employing two different versions of our simulation program, namely, (b) the random chemisorption routine and (c) the original algorithm. (Bottom) Percentage deviations between the results of our simulations and the value obtained from Eq. (2).

when considering that the molecules that chemisorb from a physisorption site do so at the edge of an island, after migrating there through movements on the second layer. This means that the selection of sites for the chemisorption of physisorbed molecules is not an aleatory process as is the direct adsorption from gas phase; the preference for chemisorption next to another chemisorbed molecule introduces the bias towards island growth observed in our simulations.

In order to test the effect that island formation may have on the sticking coefficient, we devised an alternative "random chemisorption" version of our simulation algorithm where the precursor is allowed to move as usual except for when the chosen ending site is vacant, in which case, instead of allowing chemisorption to take place at that site, an alternate site is chosen randomly among all possible sites for chemisorption; this mechanism was introduced in order to eliminate the correlation observed in the original version of the algorithm by which physisorbed molecules always chemisorb at the edge of an island. The result of simulations using this code is a random distribution of surface molecules in all cases, as confirmed by the SIF obtained from these simulations, which for $K=0.10$ was 1.00, as compared to 1.27 for the unaltered simulation. Figure 7(b) shows the sticking coefficient curve obtained for this value of K. We see that roughly one-third of the deviations between the original simulation (7c) and the values obtained using Kisliuk's formula (7a) are accounted for by the elimination of islanding in the chemisorbed layer.

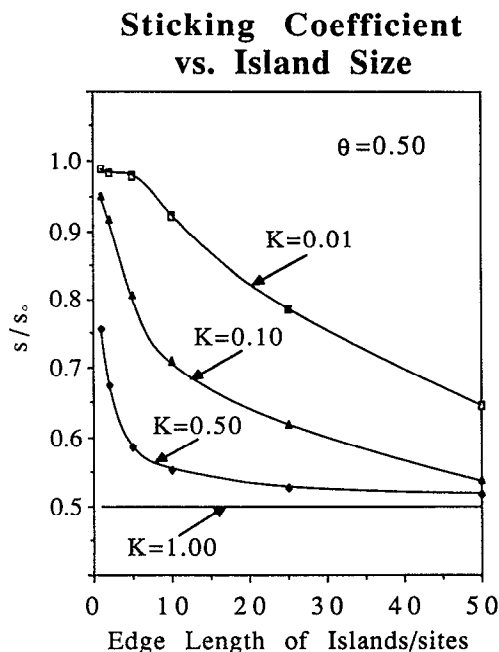## Sticking Coefficient vs. Island Size

FIG. 8. Sticking coefficient vs island size at a surface coverage of 0.50 for three different values of K (the Langmuir value $K=1.00$ is also shown for comparison). These islands were set artificially at the beginning of the simulation and were arranged in a square checkerboard pattern.

Islanding effects are expected to be more pronounced in systems where the chemisorbed layer displays an appreciable diffusion rate and where there are noticeable attractive and/or repulsive interactions within the adsorbed species.[7] To study the effect of islanding on a larger scale, we performed some additional calculations in which islands were created artificially in a checkerboard pattern within the chemisorption layer by alternating between empty squares and chemisorbed squares, thus establishing a surface coverage of 0.50. The number of chemisorbed species in each square was then varied to see how island size affects the sticking coefficients (Fig. 8). There is a direct correlation between the degree of mobility within the physisorbed layer and the size of the islands as to how they affect sticking coefficients—more mobile systems (smaller K) require larger islands to yield the same sticking coefficient values. This is expected since any increase in the sticking coefficient from the Langmuir value of 0.5 is due to the finite probability that physisorbed molecules have to reach an island edge and chemisorb before desorbing; that probability decreases as the islands become larger because more steps are required to reach the edge, but, it increases with decreasing values of K. Also, the sticking coefficient does approach the value of 0.50 as the island size increases, indicating that in such extreme most molecules in the precursor state desorb before reaching an empty site. This limiting value, which, as mentioned above, corresponds to the Langmuir case, can be obtained easily in systems where the precursor states have reasonable mobility if the island size is large enough (e.g., $K=0.50$ and islands about 10 molecules wide), so great caution must be exercised in

assuming Langmuir-like behavior in cases where there is strong evidence for island formation.

D. Site revisiting

Even though islanding does indeed affect sticking coefficients, the routine described above shows that it only accounts for a fraction of the deviations between Kisliuk's model and our simulations. A third potential explanation for the observed differences is based on the fact that the mobility of the precursor state within the second layer is not a Markovian process,[13] i.e., each move that a physisorbed molecule makes within the second layer is not only dependent on the configuration of the immediately preceding state, but also on all the previous steps that it took to get there. Hence, the probability that a precursor will find an empty site for chemisorption is not directly proportional to the fraction of empty sites available as commonly thought because there is a finite probability of returning to a previously visited occupied site during migration in the physisorbed layer; given that the chemisorbed molecules are not allowed to move in our calculations, the probability for chemisorption on such a site is zero. To see this more clearly, let us follow the path of a molecule physisorbed initially on top of a site occupied with another chemisorbed molecule in the first layer: that physisorbed species can either move to a neighboring site or desorb. If it moves to one of the neighboring sites which also has a molecule already chemisorbed on it, the molecule will physisorb there and have a 25% chance (on a square lattice) of returning to the initial site of physisorption on the next move; the probability for chemisorption in that case is zero, not 0.25 as assumed in Kisliuk's derivation. Extending this idea to the whole migration process, one can see that at any time after the first hop there will be a 25% chance of returning to the site from which the molecule just came from the move before, and in fact, any even number of moves can result in the precursor molecule returning to a site that has been visited previously. This site revisiting within the physisorbed layer causes a decrease in the sticking coefficient from what would be expected in a Markovian process and needs to be included in any derivation involving random precursor migration.

To test the effect of site revisiting on the sticking coefficient, we wrote a "random physisorption" version of our program that removes the correlation between successive moves within the diffusion layer. The probability for mobility is calculated as usual, but when the event selected results in movement to another physisorption site, instead of allowing physisorption at that site, an alternate site is chosen randomly among all the possible sites available for physisorption. The net effect of these changes is to remove all site revisiting while retaining most of the islanding effect. The SIF obtained for $K=0.10$ with this algorithm was 1.20, compared to 1.27 for the unaltered version and to 1.00 for a random distribution of chemisorbed species. Figure 9(b) shows the corresponding sticking coefficient curve obtained this way—most of the discrepancy between the

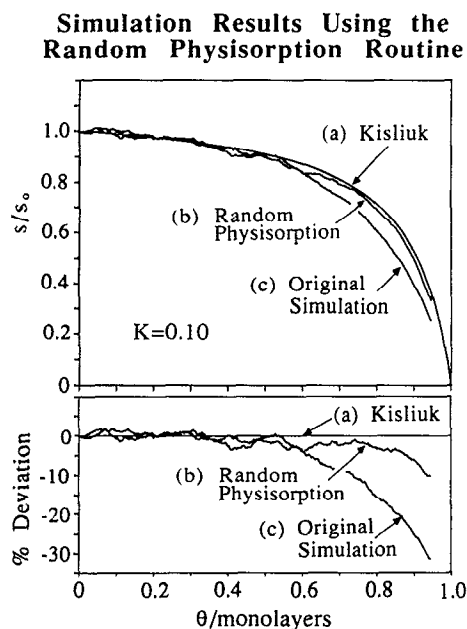## Simulation Results Using the Random Physisorption Routine

FIG. 9. (Top) Sticking coefficient vs coverage for $K=0.10$ as calculated using (a) Kisliuk's equation and by employing two different versions of the simulation program, namely, (b) the random physisorption routine and (c) the original algorithm. (Bottom) Percentage deviations between the results of our simulations and the value obtained from Eq. (2).

original simulation curve (c) and the values obtained using Kisliuk's formula (a) are indeed accounted for by the elimination of site revisiting. Some islanding was unavoidably suppressed in this version of our algorithm as well, but
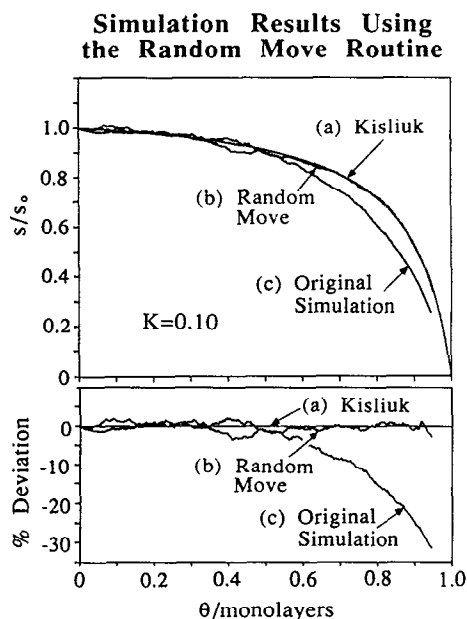
Simulation Results Using the Random Move Routine

FIG. 10. (Top) Sticking coefficient vs coverage for $K=0.10$ as calculated using (a) Kisliuk's equation and by employing two different versions of the simulation program, namely, (b) the random move routine and (c) the original algorithm. (Bottom) Percentage deviations between the results of our simulations and the value obtained from Eq. (2).

Comparison Between Theory and Results Using the Random Chemisorption Algorithm
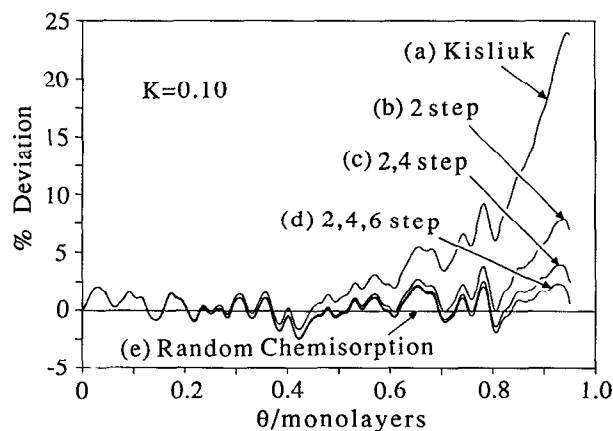

FIG. 11. Percentage deviation in the sticking coefficient between values obtained using the random chemisorption routine and those calculated using the analytical expressions provided in the text. Four theoretical values are shown, three of which include site revisiting probabilities: (a) Kisliuk's prediction; and equations including (b) two; (c) two and four; and (d) two, four, and six step paths.

the changes were not remotely as drastic as to affect the qualitative conclusion given above.

Finally, a "random move" version of our simulation program was developed to remove both islanding and site revisiting effects simultaneously. Normally, a molecule in the precursor state moves to one of the four adjacent positions; however, in this version of the program, every time a migration event is chosen, the molecule is moved to a randomly selected site anywhere on the target. The results from simulations using this program show the combination of the effects seen in the random chemisorption and the random physisorption versions, i.e., both islanding and correlation between successive moves within the physisorbed layer are eliminated; the SIF for $K=0.10$ using this version was found to be 1.01, indicating a random arrangement of the chemisorbed molecules within the first layer. Figure 10(b) shows the results using the random move algorithm along with the results obtained with the initial version of our program (c) and those calculated using Kisliuk's equation (a). It can be seen from these data that by removing all correlation between moves, we were able to duplicate the results obtained using the Kisliuk equation, which shows that the reason for the discrepancies are due to the combination of both site revisiting and islanding.

V. NEW ANALYTICAL EXPRESSION FOR THE STICKING COEFFICIENT

Having identified site revisiting on the physisorbed layer as the main factor responsible for the inaccuracy of Kisliuk's theory, in this section we proceed to develop a more complete analytical equation for the sticking coefficient that includes this effect. We begin by finding expressions for site revisiting probabilities. The probability for a precursor to return to a previous site in a square lattice,

$P_{rs}(n)$, is calculated by counting the number of unique paths for a given number of steps n that would result in a precursor returning to the starting site and dividing this by the total possible paths, i.e., 4^n. For instance, in a two step

path, there are 16 total possible routes, from which four result in a return to the starting site, and so the probability for site revisiting is 4/16 (or one-quarter). Using this method, we arrive at the following expressions:

$$P_{rs}(2)=4/16=0.2500, \quad P_{rs}(4)=20/256=0.0781, \quad P_{rs}(6)=176/4096=0.0430,$$

$$P_{rs}(2,4)=P_{rs}(2)+P_{rs}(4)=0.3281, \quad P_{rs}(2,4,6)=P_{rs}(2)+P_{rs}(4)+P_{rs}(6)=0.3711, \tag{12}$$

$$A=[1-P_{rs}(2)]\cdot\theta+P_{rs}(2), \quad B=[1-P_{rs}(2,4)]\cdot\theta+P_{rs}(2,4), \quad C=[1-P_{rs}(2,4,6)]\cdot\theta+P_{rs}(2,4,6).$$

Next, we need to express the sticking coefficient as the sum of the probabilities for chemisorption on the nth move [Eq. (1)].[4] Let us define $P_p(n)$ and $P_c(n)$ to be the probabilities for physisorption and chemisorption, respectively, after the nth site is visited. Using Eqs. (12), the first few of those probabilities are given by

$$P_c(1)=1-\theta, \quad P_p(1)=\theta,$$

$$P_c(2)=P_p(1)\cdot P_m\cdot(1-\theta)=\theta\cdot P_m\cdot(1-\theta), \quad P_p(2)=P_p(1)\cdot P_m\cdot\theta=\theta^2\cdot P_m,$$

$$P_c(3)=P_p(2)\cdot P_m\cdot(1-\theta)\cdot[1-P_{rs}(2)]=\theta^2\cdot P_m^2\cdot(1-\theta)\cdot[1-P_{rs}(2)], \quad P_p(3)=P_p(2)\cdot P_m\cdot A=\theta^2\cdot P_m^2\cdot A,$$

$$P_c(4)=P_p(3)\cdot P_m\cdot(1-\theta)\cdot[1-P_{rs}(2)]=\theta^2\cdot P_m^3\cdot A\cdot(1-\theta)\cdot[1-P_{rs}(2)], \quad P_p(4)=P_p(3)\cdot P_m\cdot A=\theta^2\cdot P_m^3\cdot A^2, \tag{13}$$

$$P_c(5)=P_p(4)\cdot P_m\cdot(1-\theta)\cdot[1-P_{rs}(2,4)]=\theta^2\cdot P_m^4\cdot A^2\cdot(1-\theta)\cdot[1-P_{rs}(2,4)], \quad P_p(5)=P_p(4)\cdot P_m\cdot B=\theta^2\cdot P_m^4\cdot A^2\cdot B,$$

$$P_c(6)=P_p(5)\cdot P_m\cdot(1-\theta)\cdot[1-P_{rs}(2,4)]=\theta^2\cdot P_m^5\cdot A^2\cdot B\cdot(1-\theta)\cdot[1-P_{rs}(2,4)], \quad P_p(6)=P_p(5)\cdot P_m\cdot B=\theta^2\cdot P_m^5\cdot A^2\cdot B^2,$$

$$P_c(7)=P_p(6)\cdot P_m\cdot(1-\theta)\cdot[1-P_{rs}(2,4,6)]=\theta^2\cdot P_m^6\cdot A^2\cdot B^2\cdot(1-\theta)\cdot[1-P_{rs}(2,4,6)],$$

$$P_p(7)=P_p(6)\cdot P_m\cdot C=\theta^2\cdot P_m^6\cdot A^2\cdot B^2\cdot C,$$

$$P_c(8)=P_p(7)\cdot P_m\cdot(1-\theta)\cdot[1-P_{rs}(2,4,6)]=\theta^2\cdot P_m^7\cdot A^2\cdot B^2\cdot C\cdot(1-\theta)\cdot[1-P_{rs}(2,4,6)].$$

Note that the probability $P_{rs}(n)$ for site revisiting after n moves does not enter into these expressions until after that move has occurred. For example, $P_{rs}(2)$ first appears in $P_c(3)$ because it is only when the molecule visits the third site that a two step path is first possible. Substituting Eqs. (13) into Eq. (1) and reorganizing some terms, we arrive at an expression for the sticking coefficient given by

$$s/s_0=(1-\theta)\cdot(1+\theta\cdot P_m)+\theta^2\cdot P_m^2\cdot(1-\theta)\cdot[1-P_{rs}(2)]$$

$$\cdot(1+P_m\cdot A)+\theta^2\cdot P_m^4\cdot(1-\theta)\cdot A^2\cdot[1-P_{rs}(2,4)]$$

$$\cdot(1+P_m\cdot B)+\theta^2\cdot P_m^6\cdot(1-\theta)\cdot A^2\cdot B^2\cdot[1-P_{rs}(2,4,6)]$$

$$\cdot(1+P_m\cdot C+P_m^2\cdot C^2+\cdots). \tag{14}$$

Finally, we make use of the relation $P_m+P_d=1$, which, together with Eq. (3), says that $P_m=1-K$. Substituting $1-K$ for P_m and writing the geometric series in closed form, we arrive at the final expression

$$s/s_0=(1-\theta)\cdot[1+\theta\cdot(1-K)]+\theta^2\cdot(1-K)^2\cdot(1-\theta)$$

$$\cdot[1-P_{rs}(2)]\cdot[1+(1-K)\cdot A]+\theta^2\cdot(1-K)^4$$

$$\cdot(1-\theta)\cdot A^2\cdot[1-P_{rs}(2,4)]\cdot[1+(1-K)\cdot B]+\theta^2$$

$$\cdot(1-K)^6\cdot(1-\theta)\cdot A^2\cdot B^2\cdot[1-P_{rs}(2,4,6)]/$$

$$[1-(1-K)\cdot C]. \tag{15}$$

This equation, which depends only on two variables (θ and K) accounts for two, four, and six step site revisiting probabilities, and yields results that are within 2% of those expected from the random chemisorption version of the simulation. A simpler expression for the sticking coefficient that includes only two step return paths and accounts for 75% of site revisiting for the $K=0.10$ case was reported previously.[14] Figure 11 displays the differences in sticking coefficients as a function of coverage between simulations using the random chemisorption version of our program and three analytical expressions that included two, two and four, and two, four, and six step paths, respectively. The revisiting probability for paths with eight or more steps are negligible and therefore were not included. Finally, recall that the SIF obtained in the simulations using the random chemisorption algorithm was 1.00, because in this case islanding effects were removed while site revisiting was still retained.

We have also obtained an expression similar to Eq. (15) for the case of a hexagonal lattice. The sticking coefficient is expected to depend on surface geometry because site revisiting probabilities are affected by the lattice geom-

etry. There are two main differences between hexagonal and square lattices, each affecting the sticking coefficient in an opposite way. On the one hand, the return probabilities for a given path are lower in the latter case because of the larger number of possible paths available, but on the other, site revisiting is possible after either odd or even numbers of steps in the hexagonal lattice, whereas only even numbers of steps can result in path crossing on a square sub-

strate. Site revisiting probabilities on an hexagonal lattice P_{rh} were calculated the same way as before by counting return paths and dividing by the total number of possible paths, i.e., 6^m, where m is the number of steps (any positive integer). The derivation is similar to that given for the square lattice, except that odd numbers of steps are also included in the expression. We obtain

$$P_{rh}(2) = 6/36 = 0.1667, \quad P_{rh}(3) = 12/216 = 0.0556, \quad P_{rh}(4) = 54/1296 = 0.0417, \quad P_{rh}(5) = 192/7776 = 0.0247,$$

$$P_{rh}(2,3) = P_{rh}(2) + P_{rh}(3) = 0.2222, \quad P_{rh}(2,3,4) = P_{rh}(2) + P_{rh}(3) + P_{rh}(4) = 0.2639,$$

$$P_{rh}(2,3,4,5) = P_{rh}(2) + P_{rh}(3) + P_{rh}(4) + P_{rh}(5) = 0.2886, \quad D = [1 - P_{rh}(2)] \cdot \theta + P_{rh}(2),$$

$$E = [1 - P_{rh}(2,3)] \cdot \theta + P_{rh}(2,3), \quad F = [1 - P_{rh}(2,3,4)] \cdot \theta + P_{rh}(2,3,4), \quad G = [1 - P_{rh}(2,3,4,5)] \cdot \theta + P_{rh}(2,3,4,5)$$

and

$$s/s_0 = (1-\theta) \cdot [1 + \theta \cdot (1-K)] + \theta^2 \cdot (1-K)^2 \cdot (1-\theta) \cdot [1 - P_{rh}(2)] + \theta^2 \cdot (1-K)^3 \cdot (1-\theta) \cdot [1 - P_{rh}(2,3)] D + \theta^2 \cdot (1$$
$$-K)^4 \cdot (1-\theta) \cdot [1 - P_{rh}(2,3,4)] \cdot D \cdot E + \theta^2 \cdot (1-K)^5 \cdot (1-\theta) \cdot [1 - P_{rh}(2,3,4,5)] D \cdot E \cdot F / [1 - (1-K) \cdot G]. \quad (17)$$

(16)

Figure 12 shows the percent difference in sticking coefficients between hexagonal and square lattices for three values of K as calculated using Eqs. (15) and (17). The sticking coefficient on the hexagonal target was found to be always higher than on the square target because the probabilities for revisiting a site on the hexagonal lattice are smaller. Also, as the mobility in the precursor state initially increases, the differences in sticking coefficients between the two lattices increases, but at higher mobility ($K = 0.01$), the trend is reversed. We believe that this last result is due to the fact that at higher mobilities, the molecule has more than ample number of moves to locate an empty site for chemisorption, so even though a few extra sites are revisited, this does not appreciably decrease the sticking coefficient. All these effects are more pronounced at very high coverages, where sufficiently large islands are formed and therefore high mobility is needed to find the few remaining empty sites. Also note that the behavior discussed in this paragraph is based solely on site revisiting effects; differences in islanding between the square and hexagonal lattices are also expected to affect sticking probabilities, but at this point, we are not able to predict the overall outcome without further simulations.

VI. COMPARISON WITH OTHER CALCULATIONS

In this report, we have focused on a comparison between our simulations and a model proposed by Kisliuk.[4] Even though Kisliuk's derivation was published about 25 years ago, it is still the equation most commonly used today to describe any adsorption kinetic process influenced by the existence of a precursor state.[15–18] There have been, nevertheless, some more detailed theoretical studies published on this type of systems in more recent years. For one, both Schönhammer[19] and King[6,20] have derived alter-

native statistical equations for precursor state affected adsorption which have turned out to be equivalent to those provided by Kisliuk. In fact, those models suffer from the same shortcomings as the original equation. For instance, in King's paper, F'_m, defined as the probability that an extrinsic precursor moves to an empty site, is considered to be proportional to the coverage θ,[6] an assumption that disregards the non-Markovian nature of this process. A chemical reaction kinetic approach has also been used for describing adsorption dynamics[21] and even the effect of lateral interactions have been brought into the picture,[22,23] but none of those derivations have yielded results that cannot be reduced to Kisliuk's expression. No study has to the

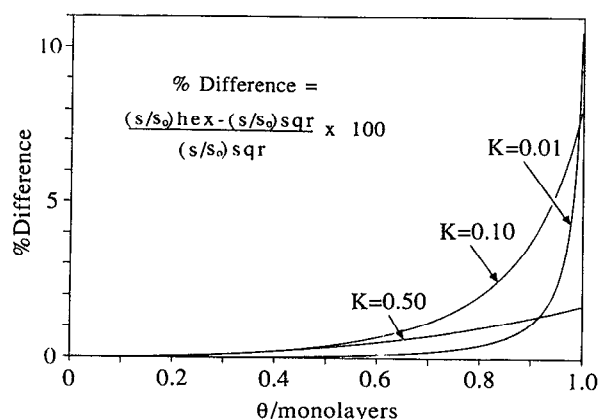### Comparison of the Sticking Coefficient Between Hexagonal and Square Lattices

FIG. 12. Percentage deviation in the sticking coefficient values between hexagonal and square lattices for three values of K.

best of our knowledge, addressed any deviations between the real systems and the models due to either the formation of islands or the non-Markovian nature of the overall process.

We also would like to point out that issues on chemical bonding and potential energy surfaces are not considered explicitly in our simulations; they only enter through the use of phenomenological rate constants. Calculations of sticking coefficients using potential energy surfaces are a matter of extensive work at the present time[24] and are beyond the scope of our simulations.

VII. CONCLUSIONS

We have demonstrated that the Kisliuk model of adsorption does not account for either nonrandom distributions of adsorbed molecules on the surface (islanding) or non-Markovian processes within the precursor state (site revisiting). The deviations between Kisliuk's model and the simulation results are more noticeable in cases of high precursor mobility. For example, when the simulation corresponding to $K=0.01$ is fit to Kisliuk's equation (2), a value of about $K=0.02$ is obtained. In addition, we have shown that systems where adsorbate–adsorbate interactions can induce islanding in the chemisorbed layer will result in even greater deviation from Kisliuk's model. We have derived a new analytical expression for the sticking coefficient which includes non-Markovian effects and accounts for about two-thirds of the discrepancy between the model and our simulations, but in order to correct for the remaining differences, the inclusion of islanding into these equations is needed. A surprising finding from these studies is the dependence of the sticking coefficient on lattice geometry. To our knowledge, this is the first study to show that, everything else being equal, differences in surface geometry can affect the sticking coefficient because of differences in site revisiting probabilities.

[1] I. Langmuir, J. Am. Chem. Soc. **40**, 1361 (1918).
[2] J. A. Becker and C. D. Hartman, J. Phys. Chem. **57**, 157 (1953).
[3] G. Ehrlich, J. Phys. Chem. **60**, 1388 (1956).
[4] P. Kisliuk, J. Phys. Chem. Solids **3**, 95 (1957).
[5] J. B. Taylor and I. Langmuir, Phys. Rev. **44**, 423 (1933).
[6] A. Cassuto and D. A. King, Surf. Sci. **102**, 388 (1981).
[7] E. S. Hood, B. H. Toby, and W. H. Weinberg, Phys. Rev. Lett. **55**, 2437 (1985).
[8] D. T. Gillespie, J. Comp. Phys. **22**, 403 (1976).
[9] D. T. Gillespie, J. Phys. Chem. **81**, 2340 (1977).
[10] J. S. Turner, J. Phys. Chem. **81**, 2379 (1977).
[11] W. H. Press, B. P. Flannery, S. A. Teukolsky, and W. T. Vetterling, *Numerical Recipes in Pascal* (Cambridge University, New York, 1989), p. 220.
[12] H. G. Hecht, *Mathematics in Chemistry: An Introduction to Modern Methods* (Prentice–Hall, Englewood Cliffs, N.J., 1990), p. 171.
[13] D. A. McQuarrie, in *Physical Chemistry* (Academic, New York, 1975), Vol. 11B, p. 643.
[14] T. Nordmeyer and F. Zaera, Chem. Phys. Lett. **183**, 195 (1991).
[15] C. T. Campbell, G. Ertl, and J. Segner, Surf. Sci. **115**, 309 (1982).
[16] K. Christmann, Surf. Sci. Rep. **9**, 1 (1988).
[17] K. D. Rendulic, Surf. Sci. **272**, 34 (1992).
[18] L. Q. Jiang, B. E. Koel, and J. L. Falconer, Surf. Sci. **273**, 273 (1992).
[19] K. Schönhammer, Surf. Sci. **83**, L633 (1979).
[20] D. A. King, Surf. Sci. **64**, 43 (1977).
[21] R. Gorte and L. D. Schmidt, Surf. Sci. **76**, 559 (1978).
[22] D. A. King and M. G. Wells, Proc. R. Soc. London Ser. A **339**, 245 (1974).
[23] M. A. DeAngelis, A. M. Glines, and A. B. Anton, J. Chem. Phys. **96**, 8582 (1992).
[24] D. J. Doren and J. C. Tully, J. Chem. Phys. **94**, 8428 (1991).