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Molecular dynamics of haloalkane corral formation and surface halogenation at Si(111)-7×7

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Long-chain organic molecules, 1-halododecane, RX ($X=\text{Cl}, \text{Br}$), adsorbed on Si(111)-7×7 were shown to form stable dimeric corrals; type I around corner holes and type II around corner adatoms S. Dobrin *et al.* [Surf. Sci. Lett. **600**, L43 (2006)]. Here we examine the molecular dynamics of corral formation, in which mobile physisorbed adsorbates spontaneously convert to immobile. At high coverage the mechanism gives evidence of involving collisions between mobile vertical monomers, giving types I and II immobile horizontal dimers, $v_D + v_D \rightarrow h_2$ (I, II). At low coverage mobile vertical monomers collide with immobile horizontal ones to form largely type-II corrals, $v_D + h \rightarrow h_2$ (II). Thermal reaction of corrals with $X=\text{Br}$ brominates the surface by two distinct molecular pathways, thought to have more general applicability: “daughter-mediated” reaction of vertical v_A with a low activation energy (here $E_a \sim 5 \text{ kcal mol}^{-1}$) and “parent-mediated” reaction of horizontal h or h_2 with high activation energy (here $E_a = 29 \text{ kcal mol}^{-1}$). © 2006 American Institute of Physics. [DOI: 10.1063/1.2352745]

I. INTRODUCTION

In three preceding papers^{1–3} we described studies of circular dimeric corrals of long-chain haloalkanes (1-fluorododecane, 1-chlorododecane, 1-bromododecane, and 1-chlorooctadecane) adsorbed on the Si(111)-7×7 surface. The corrals are stable up to temperatures of over 100 °C. Two main types of corral were described, which we label as type I and type II. Type-I corrals surround a corner hole; these were shown to cause thermally activated switching of the adatom enclosed by the jaws of the corral.³ Type-II corrals center on an adatom whose electronic energy was shown to be shifted by -1 eV ($-23 \text{ kcal mol}^{-1}$).¹

The first paper of the present series reported a preliminary study of the dynamics of formation of the corrals on the Si(111)-7×7 surface, with measurements made at both low temperature and room temperature. The most studied molecules, 1-chlorododecane and 1-bromododecane, were found to behave in a similar fashion to one another. In the present work we present a model of dimer formation that we have found to be general for both these halogenated alkanes, as well as for dihalogenated and nonhalogenated alkanes. The model describes the molecular dynamics of formation of the two main types of corral structure that we have observed, types I and II, by competing molecular pathways.

The relative yield of dimers to monomers was studied as a function of both the silicon surface temperature and the rate of deposition of the two main molecules studied, 1-chlorododecane and 1-bromododecane. Lowering the sur-

face temperature or lowering the rate of deposition suppressed formation of horizontal dimers (i.e., corrals, h_2) and increased the percentage of adsorbed horizontal monomers (h). From the effect of cooling we conclude that corral formation is due to diffusion of the molecules adsorbed in a vertical mobile precursor state (v , to be described below).

At 50 K we directly observed the molecules in their mobile precursor states. Because the adsorption sites were highly localized, we identify these features in our scanning tunneling microscope (STM) images at 50 K as vertical adsorbates v . When v molecules converted to the horizontal state (h if monomer or h_2 if dimer), multiple points of physisorption attachment were evident in the STM topograph, rendering the molecules immobile. The v molecules were observed to be especially mobile when on the dimer rows between the unit cells, where they were seen to collect and diffuse. The dimer rows (joining corner holes) do not contain dangling bonds; this may account for the observed rapid diffusion. [The features of the Si(111)-7×7 reconstruction are well known and were recently reviewed, see, for example, Ref. 4.]

The mechanism of corral formation that we propose can be described briefly as follows.¹ At fast rates of deposition, gas-phase molecules first form mobile vertical precursors (v_A) on top of an adatom; the vertical precursors v_A then diffuse to a silicon-dimer row where they are termed v_D . The dimer rows act as a conduit to transport of v_D across the surface. In the metastable precursor states v_D , the molecules can desorb or lie down to give horizontally adsorbed h molecules, stabilized by physisorption at adjacent silicon adatoms. Although the horizontal molecule has CH_2 groups in register with only three adatom sites (bright in the STM images), all the CH_2 's will experience some degree of phys-

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isorption attachment to the surface beneath. For halogenated and dihalogenated alkanes, one or two of these points of attachment will be affected to some extent by the C–X dipole interaction with silicon, the other(s) being due to the physisorption interaction of nonhalogenated CH₂ groups of the molecule's alkane chain with silicon atoms below.

When a pair of mobile v_D molecules collides, they can stabilize by lying down to form the observed immobile horizontal corral structures ($v_D + v_D \rightarrow h_2$). This process is in competition with both desorption and lying down to form immobile horizontal monomers ($v_D \rightarrow h$). The overall mechanism is noteworthy, since it provides a means both to the mobility necessary for self-assembly (as v_D) as well as to the immobility desirable for permanence (as h). The mobile to immobile transition is due to the conversion of single-point attachment to subsequent multiple attachment. The effect on mobility (as we have pointed out by analogy to vertical and horizontal skiers¹) is marked. For slow deposition rates we find evidence that v molecules exist for long enough prior to encountering a collision partner to convert thermally to monomers h , favoring subsequently a new dynamical pathway for corral formation, $v_D + h \rightarrow h_2$.

The second part of this work examines the reactions of 1-chlorododecane and 1-bromododecane with the silicon surface. In previous work^{5–10} it was shown that reaction of physisorbed halide molecules XR at a silicon surface led to localized atomic reaction (LAR) to form “daughter” atoms X , as X –Si, in the vicinity of the parent molecule. Halogenation of the surface occurred via two molecular pathways: “daughter mediated” and “parent mediated.”^{11–13} The former pathway was associated with events in which X –Si was observed in isolation at the surface (the organic residue R having escaped into the gas), whereas the latter gave adjacent Si– X and organic residue R –Si. In the present work we show for the first time that the activation barrier for the more direct daughter-mediated reaction dynamics is markedly less than for parent-mediated dynamics. This is likely to be due to the daughter-mediated pathway bringing the reactive halogen atom into optimal proximity to the surface. Whereas, in the parent-mediated reaction dynamics the bonds attaching the parent to the surface and those attaching the daughter to the parent together restrict the C–Br–Si alignment and the Br–Si reactive separation, thus providing a barrier to formation of covalently bound Br–Si at the surface.

II. EXPERIMENT

Measurements were made using a room-temperature scanning tunneling microscope (STM) RHK-400 described in a previous paper.^{6,11} Low temperature measurements were made with either an Omicron VT-STM (Ref. 7) or with an RHK-300 described below.

The RHK-300 apparatus was operated from 50 to 400 K. Cooling was by liquid helium. Vibration isolation was achieved by a Stacis 2000 active control system on the floor to decrease low-frequency noise and pneumatic isolation legs (Newport) mounted above to combat high-frequency noise. Pains were taken to ensure rigidity in this two-tier structure.

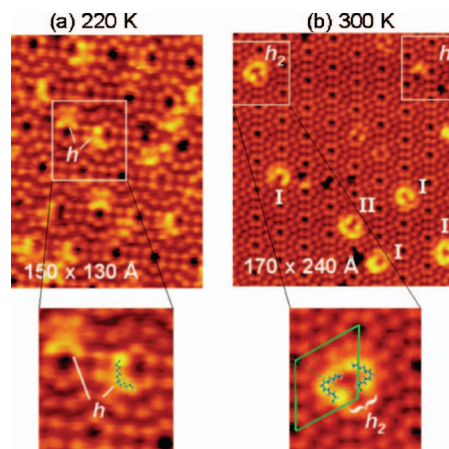


FIG. 1. (Color) STM images ($V_s = 1.5$ V, $I_{\text{tun}} = 200$ pA) of 1-chlorododecane obtained at (a) 220 K and (b) 300 K. Image (a) contains h type monomers, while image (b) contains monomers h and dimers h_2 . The absence of dimers at 220 K is ascribed to the slow diffusion of v_D molecules at this temperature, mitigating against formation of dimers by $v_D + v_D$ or $v_D + h$ in favor of monomers by $v_D \rightarrow h$.

Imaging was by 0.25 mm tungsten STM tips electrochemically etched in a 2.0M NaOH solution. The STM was operated in the constant-current mode at a tunneling current of 0.2 nA.

All reagents were from Aldrich, purified by freeze-pump-thaw cycles using liquid nitrogen, prior to introduction into the UHV chamber through a variable leak valve for background dosing. The composition of the dosant gases was checked using a residual gas analyzer (SRS RGA-200). Exposures are reported in langmuirs ($1 \text{ L} = 1 \times 10^{-6}$ Torr s) with pressure measured at an uncorrected ion gauge (calibrated for N_2). Where stated, to take into account the high sensitivity of the ionization gauge for long-chain alkane molecules,¹⁴ the gauge readings were divided by 10 to yield an approximate “true” pressure for the haloalkane.

The Si(111) samples ($2 \times 9 \text{ mm}^2$) were cut from n -type phosphorus-doped silicon wafers ($250 \pm 25 \mu\text{m}$ in thickness) with a resistivity of 0.02 – $0.05 \Omega \text{ cm}$ (Virginia semiconductor). Samples were cleaned in UHV by several cycles of direct current heating to 1500 K for ~ 1 min. Temperatures were measured with an optical pyrometer (Minolta, $\epsilon = 0.63$) in the applicable temperature range. The STM images of the surface cleaned in this way showed a (7×7) reconstruction and a small number ($< 0.2\%$) of surface defects.

III. RESULTS AND DISCUSSION

A. Adsorption of haloalkanes: 50–300 K

Figure 1(a) shows predominantly horizontal (h) single molecules of chlorododecane and Fig. 1(b) shows predominantly dimers h_2 of types I and II. These images were recorded following deposition at 5×10^{-10} Torr (corrected) for 200 s ($= 0.1 \text{ L}$). This is the “high” rate of deposition, see below. Type-I dimers, as previously reported,^{1,2} are centered on a corner hole and cover a total of five corner adatoms, whereas type-II dimers are centered on a corner adatom and cover six adatoms (two middle and one corner adatoms for each half of the corral). Other types of corrals were occasion-

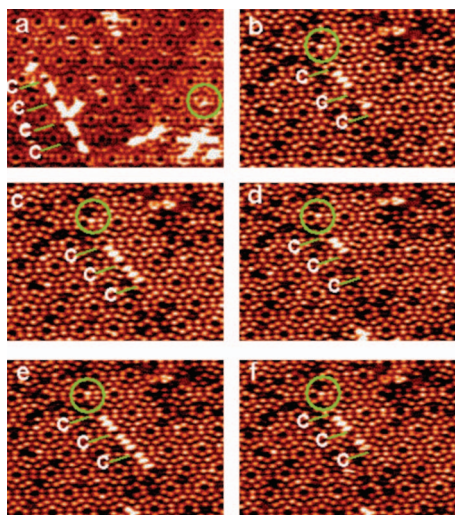


FIG. 2. (Color) STM images of (a) 1-chlorododecane molecules (Ref. 1) ($V_s=1.5$ V, $I_{\text{tun}}=100$ pA), “c” are corner holes, and [(b)–(f)] 1,12-dibromododecane molecules ($V_s=1.5$ V, $I_{\text{tun}}=100$ pA) adsorbed on Si(111)-7×7 at 50 K, in their mobile precursor states v_A and v_D . Two types of adsorption are indicated; v_A molecules on the adatom dangling bond [an example is circled in (a)–(f)] or v_D molecules on the dimer rows [mobile lines of molecules in (a)–(f)]. Panel (a) shows a line of stacked v_D molecules propagating over four intervening corner holes, and panels (b)–(f) show a sequence of images taken at equal intervals of 100 s. The high mobility of molecules adsorbed on the dimer rows is evident as they disperse and reform as lines of varying lengths between the corner holes.

ally observed covering five or six adatom sites. The increased yield of dimeric h_2 relative to monomeric h at the higher temperature will be linked, in what follows, to the increased rate of diffusion of v_D across the surface.

At the lowest achievable surface temperature of 50 K, very different structures were seen, pictured in Fig. 2.

Figure 2 shows STM images of (a) 1-chlorododecane and [(b)–(f)] 1,12-dibromododecane on a surface at 50 K. Both molecules display similar behavior; each forming two slightly different molecular features, both of which are mobile and markedly different from those obtained at higher temperature (cf. Fig. 1). The two features are single circular bright spots on top of adatoms (v_A molecules on single adatoms, circled in Fig. 2), and mobile lines of oval bright spots (v_D molecules, covering a dimer pair) along the Si(111)-7×7 dimer rows that border half-unit cells, joining corner holes. As these features are only observed at low temperature, we identify them as precursor molecules. Since they are localized at single points of attachment, we believe these mobile features to be vertically attached to the surface (as v_A molecules and v_D molecules) in contrast to the horizontal h and h_2 features that exhibit extended topographs consistent with multiple points of attachment.

From consecutive STM images obtained at 50 K [of which one is shown as Fig. 2(a)], it was found that chlorododecane molecules that adsorbed on adatoms (v_A) were less mobile than those on dimer rows (v_D), with an average lifetime of 5 min in the v_A state. Displacement of a vertical molecule adsorbed on an adatom (v_A) is due either to desorption or migration to a dimer row which serves as a conduit for rapid diffusion.¹ Migration from an adatom to an adjacent dimer row requires a jump of only 3.6 Å, since every adatom

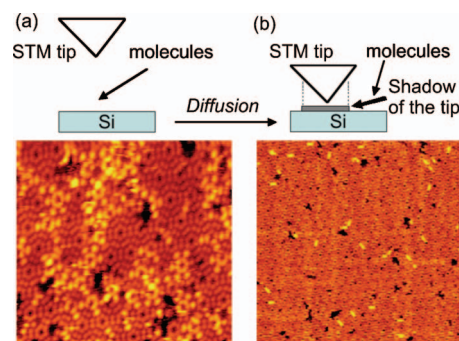


FIG. 3. (Color) STM images of dodecane molecules adsorbed on the Si(111)-7×7 at 160 K ($V_s=+2$ V, $I_{\text{tun}}=200$ pA). Image (a) shows v_D molecules adsorbed on dimer rows and on single adatom dangling bonds circling corner holes (corner adatoms), while image (b) by the diffusive deposition of dodecane under the shadow of the STM tip shows only adsorption on dimer rows (predominantly lines of three molecules). This indicates that diffusion of v_D molecules occurs along dimer rows.

is located adjacent to a dimer row. From the (mean) measured residence time of the v_A molecule on the adatom (5 min), an activation energy of ~ 3.5 kcal mol^{−1} was estimated for removal from the adatom, using a standard Arrhenius equation. At room temperature the corresponding lifetime will be ~ 38 ps. In principle removal can be by desorption ($E_{\text{des}} \sim 12$ kcal mol^{−1} from a dimer row; see Appendix); in fact, we believe that the dominant removal process is diffusion, as discussed below.

In Figs. 2(b)–2(f) we show a sequence of images of 1,12-dibromododecane adsorbed on the Si(111)-7×7 surface at 50 K. As for chlorododecane, oval bright spots attributed to the v_D molecules were observed only below 100 K. Sequential STM images [Figs. 2(b)–2(f)] showed that molecules adsorbed on the dimer rows (v_D) were very mobile. Their lifetime on average was shorter than 100 s (the minimum time interval between sequential STM scans). This gave an upper limit for the energy barrier to diffusion along a dimer row (assuming, as above, a standard preexponential factor of 10^{-13} s), $E_{\text{diff}} < 3.42$ kcal mol^{−1}.

In order to arrive at an estimate of the diffusion length of v_D molecules on the dimer rows, we made an experiment with dodecane at 160 K in which direct deposition to the area being scanned was prevented by the proximity of the STM tip during deposition. The tip was located at a distance of about 100 nm from the surface, for which distance we have found that gas-phase molecules are shadowed by the tip, arriving at the area under the tip predominantly by diffusion. The same tip-shadowing technique has previously been used in the Ho laboratory to study diffusion of O₂ on Pt(111).¹⁵ A STM scan (Fig. 3) of the shadowed area showed only v_D molecules adsorbed on dimer rows, with many instances of three molecules adjacent to one another on these rows. This was evidence that diffusion occurred along the dimer rows. It also showed, additionally, that the characteristic diffusion length at 160 K exceeded several hundreds of nanometers, the approximate radius of the circle shadowed by the tip. It is noteworthy that the sequences of stacked v_D molecules in Fig. 3(b) never exceeds 3. From this we can conclude that the hydrogen bonding between the tails of the

alkane molecules is too weak to cause the sequences to bridge corner holes at 160 K [cf. Figs. 2(a)–2(e) recorded at 50 K].

A STM scan performed at 220 K did not permit observation of 1-chlorododecane molecules in the v_D state due to their short lifetime but yielded information concerning h -type monomers, see Fig. 1(a). At 200 K it was found that monomers were formed almost exclusively, while at room temperature many more dimers than monomers were obtained. This is thought to be because diffusion along dimer rows is sufficiently slow at 220 K to allow time for v_D to convert to h , precluding a $v_D + v_D \rightarrow h_2$ or $v_D + h \rightarrow h_2$ encounter. The h monomers were found to be stable and did not diffuse even at elevated temperatures of $\approx 100^\circ\text{C}$.¹

The shapes and location of monomers formed at 220 K were different from those formed at room temperature. At low temperature the monomers were predominantly formed on corner adatoms adjacent to a corner hole, whereas at room-temperature monomers were typically found to cover one corner adatom and two middle adatoms. In order to form corrals the room-temperature monomer must reorient on the surface during corral formation. The initial attachment as monomer is between three adjacent adatoms within one half-unit cell (one corner and two middle adatoms); by contrast the final attachment as part of a corral covers two adjacent adatoms within one half-unit cell and a third adatom in an adjacent half-unit cell.

B. Kinetics of corral formation

To study the kinetics, the 1-chlorododecane deposition rates at constant coverage were varied and the yields of monomers (h) and dimers (corrals, h_2) were measured. Subsequently the yields of h and h_2 were obtained as a function of coverage for a constant deposition rate. In addition to monomers and dimers, occasional clusters of three or more molecules were observed; these have not been included in the analysis that follows.

In “slow deposition” experiments the chlorododecane was deposited at 10^{-10} Torr (corrected) during 1000 s to obtain 0.1 L. In “fast deposition” experiments the adsorbate was dosed at 10^{-9} Torr (corrected) for 100 s, i.e., at ten times the rate, once more yielding 0.1 L. In both cases the surface was scanned after the deposition and the number of adsorbed monomers h and dimers h_2 were counted. The h/h_2 ratio as a function of deposition rate is shown in Fig. 4. This ratio is high at slow deposition rates (many more h than h_2) and low at high deposition rates.

We interpret this result as follows: at fast rates of deposition, there is a high steady-state coverage of the vertically attached molecules v_D , so that these molecules are likely to collide with each other to form dimers by way of $v_D + v_D \rightarrow h_2$. At slower deposition rates the interval of time between $v_D + v_D$ is sufficiently great for $v_D \rightarrow h$ to intervene, i.e., thermal motion causes vertical molecules to “lie down” to form immobile monomers.

We can make a simple estimate of the lifetime of the v_D molecules at room temperature. From previous experimental and theoretical studies of methyl bromide, we know that the

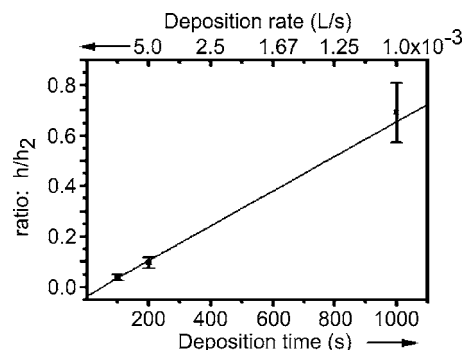


FIG. 4. Ratio of the number of h monomers to h_2 dimers (corrals) per unit cell as a function of deposition rate (top axis) and time (bottom) to achieve a set coverage of chlorododecane, namely, 0.1 L (pressure corrected).

energy of attachment to the Si(111)- 7×7 surface is around 9.2 kcal mol^{-1} (0.4 eV).⁷ Given the larger size of the molecule and the possibility of some additional binding to the surface even in the approximately vertical state, we use a binding energy for vertical (single-point) attachment of 1-bromododecane of $11.5\text{ kcal mol}^{-1}$ (0.5 eV). Inserting this energy into the Arrhenius expression together with the standard preexponential factor of 10^{13} s^{-1} yields a lifetime for the v_D state of around 10^{-4} s (a quantity which will be required in the following section). This 10^{-4} s lifetime is consistent with our measurement of the h/h_2 ratio obtained at various deposition rates, as discussed in the Appendix.

1. Repeated doses at a slow rate of deposition

To further elucidate parameters in our model of the surface reactions, we examined the effect of repeated doses at a slow rate of deposition. This had the advantage that all processes could be considered to be complete before an additional dose took place, simplifying the analysis.

In these experiments we deposited 1-chlorododecane onto the Si(111)- 7×7 surface in small doses at a slow dose rate. Each dose was 10^{-10} Torr (corrected) for 200 s (0.02 L). After each deposition, we examined the surface by STM and counted the number of single molecules and molecular dimers. Provided the rate $k_{v\rightarrow h}$ allowed a steady state of v molecules to be reached on a time scale small compared with the dose-length time, this was equivalent to making measurements of h and h_2 concentrations at intervals of $t = 200\text{ s}$ during continuous dosing. As the lifetime for the v_D state is estimated as 10^{-4} s , this condition is fulfilled.

The results are shown in Fig. 5. The abscissa shows the number of gas-phase molecules impinging per unit cell, governing the coverage at a given surface temperature (1 corresponds to 8.3 molecules of 1-chlorododecane impinging per unit cell, see below). The coverage of single molecules increased during the first several doses and then became stationary. The coverage of dimers monotonically increased, becoming linear after the first several depositions. These trends can be qualitatively described by a simple kinetic model given below.

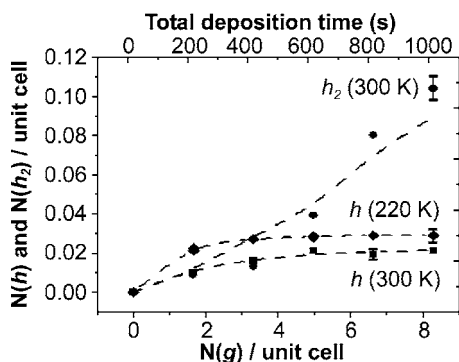


FIG. 5. The number of horizontal dimers (corrals) h_2 (at 300 K) and the number of horizontal monomers h (single molecules) per unit cell (at both 220 and 300 K) are shown as counted after each of five sequential depositions; representative error bars are shown on some points. Each deposition was 0.02 L (after pressure correction). Theoretical fits to the $h(t)$ concentrations at 220 and 300 K, and to the $h_2(t)$ concentration at 300 K are given by dashed lines. Although depositions were made separately, the kinetics are such that this corresponds to five concentration measurements made during a continuous deposition; hence time t is shown as an alternative axis above.

2. Simple kinetic model

The main features of the full kinetic model are described pictorially in Figs. 6(a) and 6(b) below. Firstly we consider the fate of single molecules arriving at the surface [Fig. 6(a)]. Single long-chain haloalkane molecules arrive at the surface and are adsorbed into a precursor state (v_A) atop an adatom. From the atop-adatom position the molecule can transfer to a dimer row, in which state (v_D) it is highly mobile. From the mobile precursor v_D state, molecules can either desorb, react by imprinting a halogen atom X , or lie down to form an immobile h monomer. The immobile h monomer can later react by imprinting an X atom and an organic residue R ; the organic residue is usually found to cover either one or two adatoms.

Secondly we consider the mechanism for formation of molecular dimers (corrals) h_2 on the surface [Fig. 6(b)]. Two reactions can lead to the formation of dimers: $v_D + v_D \rightarrow h_2$ and $v_D + h \rightarrow h_2$. The $v_D + h \rightarrow h_2$ reaction forms two types of corral, type I and type II, both with head-to-head orientation as we observe for high rates of deposition. The $v_D + h \rightarrow h_2$ reaction leads to formation of type-II corrals with both head-to-head and head-to-tail orientations, both of which were observed at slow rates of deposition where corral formation is predominantly by the $v_D + h \rightarrow h_2$ mechanism.

As described above (text and Fig. 2), we have made direct observations of the vertical precursor states, v_A and v_D , at low temperature (50 K) but were not able to image these precursors at higher temperatures. Instead we have investigated and analyzed the concentrations of h and h_2 molecules under differing conditions of temperature, dose rate, and total dose.

We now describe the model for monomer and dimer formation in the limit of zero coverage of monomers (h) and dimers (h_2). In this model we do not consider the chemical reactions of the monomers or dimers with the surface.

As already noted (Fig. 5) we have found it informative to control the deposition rate. The following analysis examines the role of the deposition rate in controlling the ob-

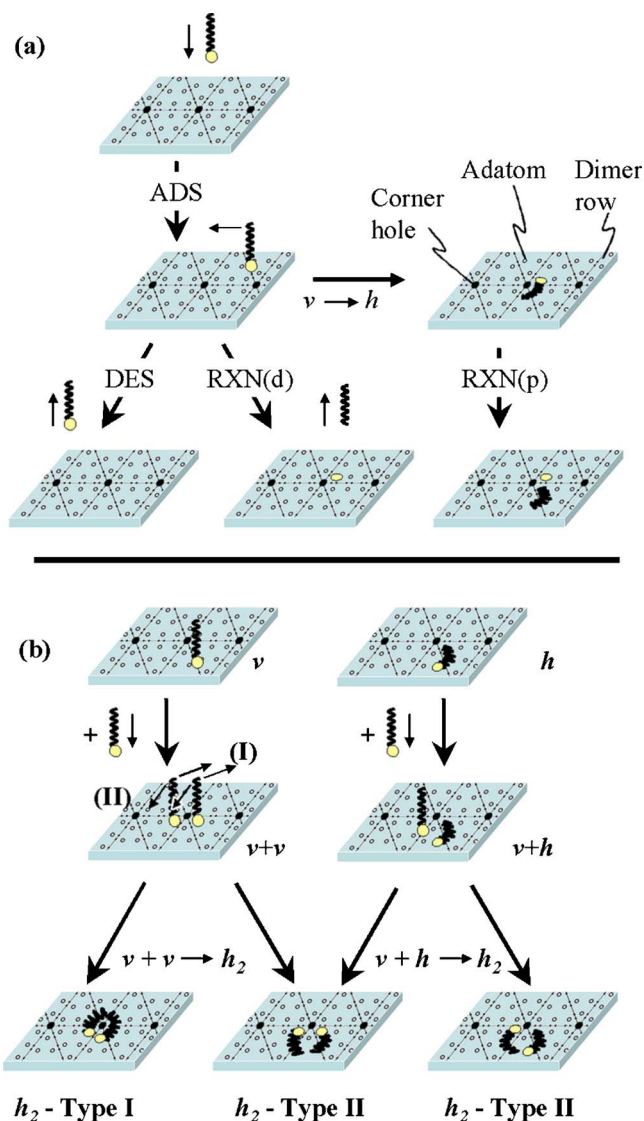
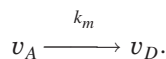


FIG. 6. (Color online) (a) Pictorial representation of adsorption and reaction of single long-chain haloalkane molecules. The wavy lines indicate vertical or horizontal alkane chains on an idealized Si(111)-7×7 surface, the relevant features of which (corner holes, adatoms, and dimer rows) are indicated. “RXN(d)” exemplifies the daughter-mediated dynamics (attachment of the reagent to the surface is by way of the daughter halogen atom, shown as a red dot). “RXN(p)” exemplifies the parent-mediated dynamics (attachment of the reagent to the surface is by physisorption of the parent molecule, lying down on the surface); the resultant radical is shown. (b) Proposed model for corral (dimer) formation of types I and II. Sequential adsorption of a pair of long-chain haloalkane molecules. After adsorption the vertical molecules are trapped in their mobile precursor state (v), from which they can either desorb, react by imprinting a halogen atom X , or lie down individually to form immobile h monomers or together to form h_2 dimers. At left column $v + v \rightarrow h_2$ (corral), whereas at the right $v + h \rightarrow h_2$. The $v + v \rightarrow h_2$ dimerization leads to the formation of type-I and type-II corrals (to form type I the pairs of vertical molecules fall to the right, and to form type II they fall to the left), all with head-to-head orientation (the “head” being the halogen atom, shown as a gray (yellow online) dot). The $v + h \rightarrow h_2$ dimerization leads to formation of type II corrals only, but with both head-to-head and head-to-tail alignment being observed (Ref. 2) (see text for explanation of these outcomes).

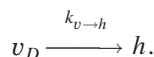
served yields of h and h_2 . Considering the concentration of gas-phase molecules to be g , these impinge on the surface at rate Z with sticking coefficient S to form the precursor state v_A ,



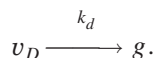
where $gk_{\text{abs}} = ZS$. Precursor molecules atop adatoms v_A can migrate to dimer rows to form highly mobile v molecules designated as v_D ,



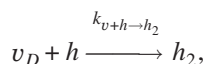
The highly mobile precursors v_D can lie down exoergically to give h but are regarded as unlikely to revert to h ,



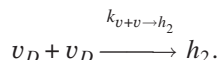
They can also desorb,



Reaction of monomer and precursor to form a dimer is also considered to be irreversible,



as is the reaction of two precursors to form a dimer,



This model gives a set of coupled differential equations that describe the kinetics of corral formation,

$$\frac{dv_A}{dt} = ZS - k_{\text{des}}v_A(t) - k_mv_A(t), \quad (1)$$

$$\begin{aligned} \frac{dv_D}{dt} = & k_mv_A(t) - k_{v \rightarrow h}v_D(t) - k_dv_D(t) - k_{v+v \rightarrow h_2}v_D(t)^2 \\ & - k_{v+h \rightarrow h_2}v_D(t)h(t), \end{aligned} \quad (2)$$

$$\frac{dh}{dt} = k_{v \rightarrow h}v_D(t) - k_{v+h \rightarrow h_2}v_D(t)h(t), \quad (3)$$

$$\frac{dh_2}{dt} = k_{v+v \rightarrow h_2}v_D(t)^2 + k_{v+h \rightarrow h_2}v_D(t)h(t). \quad (4)$$

A full solution of the equations requires numerical integration, but physical insight can be obtained from a simplified model as shown below.

We expect a rapid equilibration of vertical monomers (v_A and v_D) at the surface. The rate of deposition of v_A is given by the impingement rate Z multiplied by a sticking probability S . For a perfect gas, $Z = n\bar{c}/4$,¹⁶ where n is the number density of molecules in the gas phase and \bar{c} is the average molecular speed. Assuming a Boltzmann distribution at temperature T and pressure p for molecules of mass m gives, in Systeme International (SI) units,

$$Z = p/\sqrt{2kT\pi m}.$$

We assume that both $v_A(t)$ and $v_D(t)$ reach their steady-state concentrations, v_A and v_D , rapidly on a time scale determined by the average lifetime of a v_D molecule, that is, $\approx 10^{-4}$ s.

We can then solve Eqs. (3) and (4) with $v_D(t) = v$, analytically, to yield

$$h(t) = \left(\frac{k_{v \rightarrow h}}{k_{v+h \rightarrow h_2}} \right) (1 - e^{-v k_{v+h \rightarrow h_2} t}), \quad (5)$$

$$h_2(t) = (v^2 k_{v+v \rightarrow h_2} + v k_{v \rightarrow h}) t - h(t). \quad (6)$$

For numerical calculations, we use as a unit area of the surface the 7×7 unit cell, which is a $27 \times 27 \text{ \AA}^2$ rhombus with an area of 627 \AA^2 .

3. Fitting experimental $h(t)$ and $h_2(t)$ to the model

The solutions (5) and (6) are shown as a fit of the experimental data in Fig. 5 (we have used the corrected pressure obtained by multiplying the pressure measured at the ion gauge by the factor of 0.1, as described in the Sec. II). For room-temperature measurements the best fit (with UC \equiv unit cell) was found to be $h(t)/\text{UC} = 0.022[1 - \exp(4 \times 10^{-3}t)]$, giving $(k_{v \rightarrow h}/k_{v+h \rightarrow h_2}) = 0.022$ (rate constant for $v_D \rightarrow h$ markedly less than for $v_D + h \rightarrow h_2$). While for the experiment where deposition was made at a reduced surface temperature of 220 K, the best fit was obtained with $h(t)/\text{UC} = 0.029[1 - \exp(7.9 \times 10^{-3}t)]$, giving $(k_{v \rightarrow h}/k_{v+h \rightarrow h_2}) = 0.029$. From the estimate of $v_D = 1.1 \times 10^{-4} \text{ UC}^{-1}$ at fast deposition and room temperature (see Appendix) and the fitted exponent $v k_{v+h \rightarrow h_2} = 4 \times 10^{-3}$, we find $k_{v+h \rightarrow h_2} = 5.96 \times 10^3 \text{ UC s}^{-1}$ and hence [from $(k_{v \rightarrow h}/k_{v+h \rightarrow h_2}) = 0.022$] $k_{v \rightarrow h} = 0.17 \text{ s}^{-1}$.

For the approximately horizontal portion of the graphs, steady state in $h(t)$ has been reached and the rate of deposition of the intermediate h is equal to the rate of removal of the intermediate h by dimerization. At this steady-state stage of the kinetics, the coverage of dimers h_2 increases linearly with time. The best fit to $h_2(t)$ is also shown in the figure. Qualitatively the fit shows the correct characteristics, tending to a linear monotonic increase for long times.

C. Dimers of type I and II: head-to-head and head-to-tail

We compare dimers formed by two different mechanisms: $v_D + v_D \rightarrow h_2$ which predominates at fast deposition and $v_D + h \rightarrow h_2$ at slower deposition rates. Dimers h_2 formed by both these mechanisms are predominantly located close to corner holes. The same is true of monomers h . This can be explained by v_D molecules slowing down near corner holes. For dimers the $v_D + v_D \rightarrow h_2$ mechanism therefore becomes more likely at corner holes. For the second mechanism, $v_D + h \rightarrow h_2$, the preference for formation of dimers near corner holes is likely to be connected with our observation that h monomers form near corner holes, presumably by the lying down of a single slowed v_D molecule: $v_D \rightarrow h$.

The most likely encounter of the first kind, $v_D + v_D \rightarrow h_2$ (I, II), is that two v_D molecules approach the corner hole from opposite directions, moving along dimer rows. When they collide, their hydrocarbon tails make attractive contact (hydrogen bond) across the corner hole. We have evidence of such bridging of the corner holes in the images at 50 K [Fig. 2, especially (a), (c), and (e)] which show a

procession of vertical molecules spanning a succession of the 11.5 Å corner-hole gaps. The horizontal dimer h_2 ultimately formed in this fashion, can be of either type I (around the corner hole) or type II (to one side of the corner hole) depending on the direction in which the v_D molecular pair falls [see arrows in Fig. 6(b)]. Vertical molecules coming along dimer rows from opposite directions provide a likely explanation of the invariable observation (for 1-chloro dodecane and 1-bromododecane dimers) of an 11.5 Å separation between the “heads” of the component monomers.²

For the $v_D + h \rightarrow h_2$ formation dynamics, which dominates at slow deposition rates, one molecule is already immobilized in a horizontal position when another v_D molecule approaches it. The second molecule lies down near the first. In this case the molecules do not engage across a corner hole: consequently molecular dimers of type-II (*adjacent* to a corner hole) are formed rather than of type I (around the corner hole). This sequence of events is pictured at the right in Fig. 6(b).

To obtain more insight into the structures of the dimers, in an extension of the work reported previously,² we have located the position of the halogen atoms within them. The halogen end of each monomer was deduced (see the following section) by observing Cl-atom imprinting on the silicon surface at 70 °C. It was found that the Cl atom reacted with the silicon at the location where the STM image of the intact molecule exhibited heightened brightness. This strongly suggests that the brightest part of the STM image of the intact molecule was due to the halogen atom, as previously postulated.^{1,2}

We have used this observation to classify h_2 dimers of both type I and type II into four subgroups that could, in principle, occur: (i) “head-to-head” dimers, where halogen atoms are adjacent to one another and directed toward the corner hole; (ii) “tail-to-tail,” where the nonhalogenated ends of molecules are adjacent to one another and directed toward the corner-hole; and as the equivalent configuration of (iii) “head-to-tail” or (iv) “tail-to-head.”²

The present experiments show that for type-I dimers (around the corner hole), formed through the $v_D + v_D \rightarrow h_2$ process, exclusively the head-to-head configuration was observed. Conversely for type-II dimers, formed by $v_D + v_D \rightarrow h_2$ or $v_D + h \rightarrow h_2$, we found that dimers were formed in approximately 1:1 ratio as head-to-head or head-to-tail structures. This observation is consistent with the mechanisms discussed above. Tail-to-tail corrals are occasionally observed.² Such corrals must be formed from v -precursor states in which the molecules are attached to the surface by their nonhalogenated ends. We know from our experiments with nonhalogenated dodecanes that this mechanism exists (see Fig. 3). However, the attachment energy for $X-R-Si$ is markedly less than for $X-R-Si$. This accounts for the fact that tail-to-tail corrals were only rarely observed.

For the $v_D + v_D \rightarrow h_2$ mechanism, the v_D molecules with halogen atom (head) down should always approach in the head-to-head configuration found to be formed on the surface. For $v_D + h \rightarrow h_2$, the v_D molecule moving along a dimer

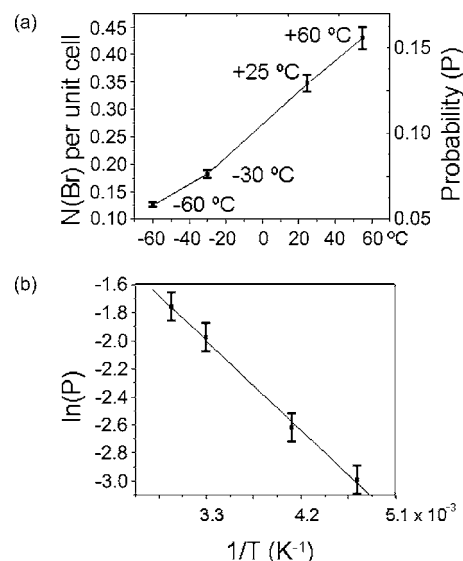


FIG. 7. (a) Coverage of Br atoms imprinted on the surface through the daughter-mediated mechanism as a function of deposition temperature [experimental uncertainties are for $N(\text{Br})$ and are taken as $\sqrt{N(\text{Br})}$]. The left-hand ordinate shows the number of Br atoms per unit cell counted in the experiment, and the right-hand ordinate shows the probability of reaction, P , which was calculated using the true pressure (corrected by a factor of 10). (b) Arrhenius plot: logarithm of reaction probability per incident molecule, $\ln(P)$, as a function of $1/T$, where T stands for the surface temperature during the deposition of 1-bromododecane and the slope of the plot is E/R , where $E = E_r - E_d$ (see text).

row may approach either the head end or the tail end of the immobile h molecule, giving rise to the head-to-head or head-to-tail configuration.

D. Dynamical pathways for surface halogenation

As discussed above, haloalkane molecules can exist on the silicon surface in two principal forms: short-lived vertical states (v_A molecules and v_D molecules) with a lifetime in the range of 10^{-4} s at room temperature (see Appendix) and the long-lived horizontal state (h). Both of these adsorbed states give rise to halogenation of the surface. Reaction from the v_A state is termed daughter mediated and that from the h state parent mediated. This terminology was previously introduced in our studies of halogenation reactions of dibromobenzene at the 7×7 surface.^{4,11} In daughter mediated reaction the molecule is previously attached to the surface through the reactive halogen atom. In parent mediated the parent molecule is attached to the surface by covalent,^{4,11} or, in the present case, noncovalent physisorption bonding prior to reaction.

From our experiments we were able, for the first time, to experimentally determine activation energies for both daughter-mediated and parent-mediated reactions of the reagent molecule.

1. Daughter mediated reaction

The yield of daughter-mediated reaction was measured by observing its products, the incident bromododecane molecules that had been converted to Br, at the earliest feasible observation time. These bright Br-Si features were unaccompanied by dark R-Si, indicative therefore of daughter medi-

ated reaction. The activation energy of the bromination reaction was obtained by measurement at various surface temperatures, from -60 to $+60$ °C. In each experiment we dosed for the same pressure (5×10^{-10} Torr, corrected) and time (500 s) at the desired surface temperature. After deposition we counted the number of imprinted Br-atoms (present as Br-Si) to determine an absolute probability of bromination per incident molecule. The experimental results were analyzed with an Arrhenius plot shown in Fig. 7.

For a reaction probability per adsorbed molecule of less than unity, the lifetime of the molecule in its precursor state must be limited by a competing process. The competing processes in the present case are diffusion to the dimer row and desorption; both are first order processes and so can be considered together, with an effective rate constant and lifetime. Since diffusion from an adatom to a dimer row is fast, this can be expected to dominate (see the previous discussion). In our experiments at 50 K molecules physisorbed on an adatom were observed to leave an adatom site (i.e., diffuse) after a mean time of approximately 5 min (cf. Fig. 2). Since diffusion led to population of dimer rows and since we never saw bromination reaction at dimer rows in the temperature range examined, diffusion can be treated as a means of removal. The case of concurrent reaction and removal is well known in the literature.¹⁷ In the (common) circumstance that the rate constant for reaction is small compared with the competing rate, diffusion in the present instance, the phenomenological activation energy [slope in Fig. 7(b)] gives $E_r - E_d$, where subscript r refers to reaction and d to the removal process diffusion. The intercept of the Arrhenius plot at $1/T=0$ equals the ratio of preexponential factors, A_r/A_d .

The slope of the Arrhenius plot is $1.5 \text{ kcal mol}^{-1}$, and the ratio of A factors $A_r/A_d=1.5$. According to the model, using $E_d=3.45 \text{ kcal mol}^{-1}$ and an assumed normal $A_d=10^{13}$ yields, for the daughter mediated bromination reaction at silicon, $E_r^D=4.94 \text{ kcal mol}^{-1}$.

2. Parent mediated reaction

The rate of the parent mediated reaction was studied by viewing STM images of the same area of the surface dosed with 1-chlorododecane or 1-bromododecane at measured time intervals. For this purpose the surface was heated to 75 °C prior to exposure of 0.1 L of chlorododecane (5×10^{-10} Torr, corrected, for 200 s=0.1 L) or 0.1 L of bromododecane (deposited with the same conditions). Both adsorbates formed dimers at the surface. (Chlorododecane with its strong C-Cl bond, in contrast to bromododecane, did not give daughter-mediated reaction and consequently was not considered in the previous section.) Over a period of up to 2 h, the same group of dimers could be observed to form steadily increasing amounts of atomic halogen at the surface, X-Si, together with dark features, R-Si. The area of surface viewed by repeated scans over this period was $\sim 2.15 \times 10^6 \text{ Å}^2$. In the experiment with chlorododecane, we were able to observe the same area of the silicon surface for 160 min, which was long enough for the halogenation reaction to occur to a detectable extent. In the experiment with

bromododecane, parent-mediated surface reaction was faster and the observation time could be reduced to 30 min.

Two processes were observed at 75 °C: (1) a surface halogenation reaction and (2) desorption of the dimers. No diffusion of the dimers was observable. At the beginning of the experiment, we found that the total amount of adsorbed dimers was for 1-chlorododecane (1-bromododecane) 305 ± 17 (79 ± 9). Parentheses will be used for Br values. (Errors are here calculated as a square root of the total counts; they do not represent uncertainty in the count, but the uncertainty in the result was the same experiment to be repeated and a new count taken.) After 160 min (30 min) of scanning with uneven intervals 180 ± 13 (39 ± 6) dimers were counted for 1-chlorododecane (1-bromododecane). The number of dimers decreased because 51 ± 7 (39 ± 6) dimers reacted, by producing an imprinted Cl atom (Br atom), and 74 ± 9 (1, no uncertainty calculable) desorbed. In the great majority of cases an organic residue (dark spot) was found near the imprinted Cl atom (Br atom) for this slow thermal reaction. Desorbed intact dimers did not leave any residue.

Using these numbers and assuming exponential decay in the number of adsorbed dimers, average lifetimes were calculated for the reaction and desorption processes for 1-chlorododecane (1-bromododecane) as 874 min (43 min) and 576 min (≥ 30 min), respectively. Using an Arrhenius equation with a standard pre-exponential factor of 10^{13} s^{-1} activation energies for the reaction and desorption were calculated as $E_r^P=28.13 \text{ kcal mol}^{-1}$ ($26.05 \text{ kcal mol}^{-1}$) and $E_d=27.84 \text{ kcal mol}^{-1}$ ($\geq 25.8 \text{ kcal mol}^{-1}$) respectively.

The desorption energy of the intact chlorododecane (bromododecane) dimers may be compared with the desorption energy of unsubstituted dodecane dimers. Unsubstituted dodecane dimers were observed to desorb (after adsorption on the surface at 200 K) following flash heating to 425 K for approximately 1 s. Taking the desorption time to be 1 s at 425 K, we obtain an activation energy of desorption of the dodecane as $E_d' \sim 25.2 \text{ kcal mol}^{-1}$. Evidently the physisorption energy of the molecule owes more to the entire hydrocarbon chain than to the single halogen since E_d' for dodecane is less by only a few kcal mol^{-1} than E_d for the halododecanes.

IV. CONCLUSIONS

In this work we have shown that the formation of self-assembled haloalkane corrals (dimers) on Si(111) can be accounted for by two dynamical mechanisms, one in which pairs of mobile vertical molecules encounter one another and dimerize, $v_D + v_D \rightarrow h_2$ (I, II), and one in which a mobile vertical molecule encounters an immobile horizontal one, $v_D + h \rightarrow h_2$ (II). The bracketed numbers in the foregoing refer to the types of corrals h_2 found to be formed by each mechanism: type I centered on a corner hole and type II on an adatom.

We reported studies of the dependence of the relative yields of h_2 as a function of the haloalkane deposition rate. At a greater deposition rate the high concentration of v_D favored dimerization, $v_D + v_D \rightarrow h_2$. At a slower deposition rate the coverage of v_D was less and that of h greater, since

the interval between $v_D + v_D$ collisions was longer. This permitted $v_D \rightarrow h$, so that the dominant pathway for dimerization became $v_D + h \rightarrow h_2$. These changes were analyzed by means of a simple kinetic model.

Dimerization (corral formation) by the first pathway, $v_D + v_D \rightarrow h_2$, could also be suppressed by cooling the surface to 220 K and thereby increasing the time interval between $v_D + v_D$ encounters, once again favoring $v_D \rightarrow h$.

Cooling to 50 K made possible the direct observation of the vertical molecules v_A at isolated adatoms. They were also seen to proceed across the surface as fast-moving self-assembled lines of v_D molecules stacked along dimer rows at 50 K. The alkane tails of these vertical molecules gave evidence of being long enough to guide the self-assembled lines readily across corner holes, since the stacked molecules could be seen to propagate linearly across a succession of such holes.

The halododecanes were found to react with silicon to produce imprinted halogen atoms (X–Si), sometimes accompanied by adsorbed organic residues (R–Si). We investigated two mechanisms for this surface halogenation, daughter mediated (from v_A molecules) and parent mediated (from h molecules), and determined for the first time their activation energies. For daughter mediated reaction, the activation energy for the Br-atom imprinting was approximately 5 kcal mol⁻¹ over the temperature range from -60 to +60 °C, whereas for parent mediated reaction (measured at 75 °C) the activation energy was much greater, approximately 29 kcal mol⁻¹.

This difference can be understood in terms of adsorbate approaching its halogen atom to within optimal bonding distance of a surface dangling bond for daughter-mediated reaction in the vertical state, in contrast to the parent-mediated reaction in the horizontal state in which the prior binding of the long-chain molecule to the surface sets the X–Si separation at a value less favorable for atom transfer. We note the unique utility of STM in uncovering the differing molecular pathways (daughter and parent mediated, here) by which a given reagent can engage in a chemically identical surface reaction.

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APPENDIX: ESTIMATED LIFETIME OF v_D PRECURSOR MOLECULES

We can estimate an average lifetime τ_v of a single v_D molecule using our observation that dimers were rare at the slow deposition rate but dominated at the fast deposition rate. An average lifetime for a single v_D molecule is determined both by the rates of desorption and of the $v_D \rightarrow h$ reaction, which together provide a probability per second $P_1 = 1/\tau_v$ of the elimination of the molecule from the v_D

state. The average lifetime of a v_D molecule in the presence of other v_D molecules is additionally affected by the probability per second P_2 of the $v_D + v_D \rightarrow h_2$ reaction; P_2 increases quadratically with the coverage of v_D -molecules. At high v_D coverages P_2 becomes higher than P_1 and dimers are predominantly formed. At some intermediate coverage $P_2 = P_1$; we equate this approximately with the fast deposition. From this we can estimate the lifetime of the v_D state τ_v , as shown below.

The collision-free diffusion length of a single molecule in the v_D state can be estimated as $l_d = u\tau_v$, where τ_v is the v_D state lifetime and u is the average velocity of the v_D molecule. A mean distance between molecules on the dimer row can be estimated as $l_v = L/v_D = L/(N\tau_v/T)$, where L is the length of the dimer row perimeter per unit cell (97 Å), v_D is the number of v_D molecules simultaneously found on this perimeter, and N stands for the total number of gas-phase molecules deposited in the v_D state during time T . The condition that at fast deposition $P_2 = P_1$ can be written as $l_d = l_v$, but as $u\tau_v = l_d = L/(N\tau_v/T)$ we find $\tau_v = \sqrt{L/(Nu/T)}$.

At the fast deposition, $T = 100$ s and $N = 0.83$ molecules/UC (assuming a unit sticking probability and that all deposited molecules arrive on the dimer row). We also assume that $u = 200$ ms⁻¹ (the equilibrium gas-phase thermal velocity) and thereby obtain $\tau_v \approx 10^{-4}$ s as found in the previous calculation, in the text. Using a standard preexponential factor of 10^{13} s⁻¹ in the Arrhenius expression we calculate an activation energy, which visibly is due to desorption, as $E_{\text{des}} \approx 12$ kcal mol⁻¹. Using this lifetime we can estimate an average coverage of v_D molecules as $v_D = l/l_v$. At slow deposition it gives us 0.23×10^{-6} and 0.46×10^{-6} UC⁻¹ at fast deposition (0.1 L per 100 s). These coverages are approximately four orders of magnitude less than the coverages of h monomers.

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