

STM Study of the Conformation and Reaction of Long-Chain Haloalkanes at Si(111)-7 × 7

Sergey Dobrin, K. Rajamma Harikumar, and John C. Polanyi*

Lash Miller Chemical Laboratories, Department of Chemistry and Institute of Optical Sciences, University of Toronto, 80 St. George Street, Ontario M5S 3H6, Canada

Received: December 15, 2005; In Final Form: February 17, 2006

Scanning tunneling microscopy (STM) has been used to study the adsorption of 1-fluoro-, 1-chloro-, and 1-bromo-substituted C_{12} alkanes at the Si(111)-7 × 7 surface, at temperatures from 300 to 500 K. We report self-assembly of these physisorbed adsorbates, $C_{12}H_{25}X$, to form approximately circular corrals, $(C_{12}H_{25}X)_2$, with charge transfer to a corralled adatom in each case (cf. Dobrin et al. *Surf. Sci.* **2006**, 600, L43). The corrals comprised pairs of semicircular horizontal long-chain molecules stable to ~100 °C. At ≥ 150 °C, the corrals desorbed or reacted locally to imprint a halogen atom, X–Si, and an adjacent alkane residue, R–Si. The corral height profiles, together with the location of the imprinted X–Si resulting from thermal or electron-induced surface reaction, led to a picture of the molecular configurations in these haloalkane corrals, $(C_{12}H_{25}X)_2$, X = F, Cl, Br, and the dichloro corrals, 1,12-dichlorododecane, $(ClC_{12}H_{24}Cl)_2$.

1. Introduction

The interaction of organic molecules with silicon has been the subject of widespread study because of its fundamental interest and importance for building organosilicon nanodevices.^{1,2} Until now, *n*-alkanes were thought not to adsorb at Si(111)-7 × 7 surfaces at room temperature.^{3,4} Low-temperature (30–100 K) physisorption of methane and neopentane on the Si(111)-7 × 7 surface has, however, been studied by X-ray photoelectron spectroscopy (XPS) and high-resolution electron energy loss spectroscopy (HREELS).⁵

The adsorption of alkane chains terminated by carbon–carbon double bonds at the Si(111)-7 × 7 surface was studied by Manassen and co-workers employing room-temperature scanning tunneling microscopy (STM).^{4,6–8} The molecules studied by these workers were 1,13-tetradecadiene,⁶ 1,9-decadiene,⁶ 1,6-heptadiene, and 1,7-octadiene.⁸ All attached to the Si(111)-7 × 7 surface by opening their terminal double bonds and forming a total of four σ bonds with silicon rest atoms and adatoms. The length of the molecules made it possible to distinguish between the points of attachment, observed at a +2 V sample bias as darkened adatoms. The alkane chain between the points of attachment was reported to be visible as a variable light and dark line. The alkane chain was physisorbed at the surface, intact. The physisorption energy was greater on the unfaulted half of the unit cell than the faulted half.⁴

The most extensive STM studies of terminally substituted saturated long-chain hydrocarbons, of with chain lengths of 12–30, have been for physisorption on graphite under ambient conditions at a solid–liquid interface.^{9–14} Recently, this has been extended to haloalkanes distilled onto graphite in an ultrahigh vacuum (UHV).¹⁵ A terminal bromine exhibited increased brightness in the STM images, relative to the carbon atoms in the chain.

In a recent communication,¹⁶ we reported on a scanning tunneling spectroscopy (STS) study of chlorododecane at Si(111)-7 × 7 giving quantitative evidence of the “corralling” of

the enclosed Si adatom, from both experiment and theory. The concept of quantum corrals was first introduced by Crommie, Lutz, and Eigler.^{17,18} Their corrals were assembled one atom at a time at a 4 K metal surface. Silva and Leibsle¹⁹ reported self-assembled corral-like structures of random size made by ion implantation of nitrogen on Cu(111). The method employed here (see also ref 16) using haloalkanes as building blocks permits self-assembly of corrals with a defined molecular perimeter at semiconductor surfaces.

We report an STM study of the structure and reactivity (thermal and electron induced) of 1-haloalkanes, $C_{12}H_{25}X$, with X = F, Cl, Br, and a structural study of 1,12-dichlorododecane, $C_{12}H_{24}Cl_2$, at Si(111)-7 × 7. When these 1-haloalkane molecules, computed to be bent in the gas phase,¹⁶ are deposited on Si(111)-7 × 7 at room temperature, they physisorb to yield predominantly dimeric species, bent to form circular corral-like structures of ~1.5 nm diameter, in register with the surface below. These structures cover 5–6 adatoms, enclosing an adatom at the center, termed the “corralled” adatom, which is darkened in the STM image. The corralled adatom has been shown by STS to be the recipient of electron transfer induced by the surrounding corral.¹⁶ In a subsequent paper,²⁰ we reported on the adsorption of haloalkanes at reduced temperature and presented a model for the formation of the corrals by self-assembly.

2. Experimental Section

The apparatus has been described elsewhere.²¹ Briefly, the experiments were performed using an RHK-400 scanning tunneling microscope in an ultrahigh vacuum (UHV) chamber with a base pressure of 5.0×10^{-11} Torr. The UHV system consisted of a sample-preparation chamber and a second chamber housing the STM scanner. The chambers had separate ion pumps and were isolated from one another by a gate valve to minimize cross-contamination. An external gas manifold contained the adsorbates which were introduced into the preparation chamber through a variable leak valve. These molecular species were contained in glass bulbs that had been cleaned, baked, and degassed, to rid them of contaminants.

* Corresponding author. Phone: +1-416 978 3580. Fax: +1-416 978 7580. E-mail: jpolanyi@chem.utoronto.ca.

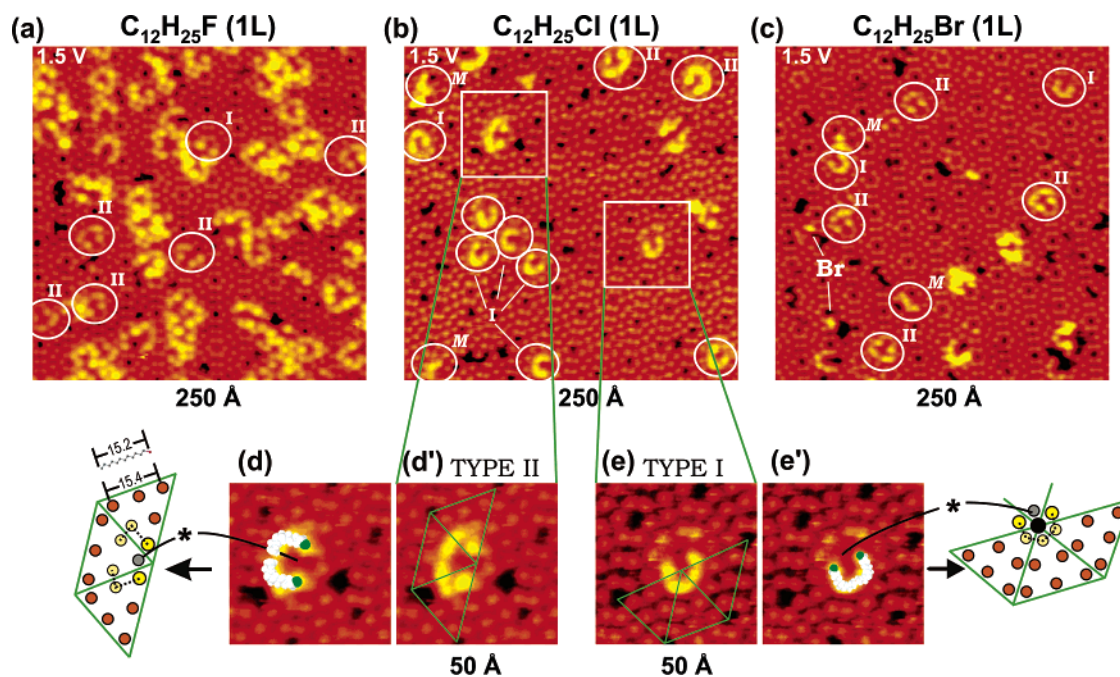


Figure 1. STM images of the Si(111)-7 \times 7 surface with adsorbed (a) 1-fluorododecane, (b) 1-chlorododecane, and (c) 1-bromododecane at room temperature, all at approx 1 L dosing, scanned at 1.5 V, 0.2 nA. The adsorbates have self-assembled to form mainly dimers. Several type I and II corrals have been labeled (white circles or squares) as well as monomers (labeled *M*; semicircular). The bright spots in part c labeled Br correspond to reaction product Br–Si. Panels d and e are the magnified STM images of type II and I, respectively, highlighted by squares in part b. The trapezium in parts d and e outlines the three half-unit cells covered by the corral structure. Panels d' and e' are the same STM images as those in parts d and e but with two chlorododecane molecules, drawn to scale, superimposed, with chlorine ends situated at the brighter ends of the corrals. Schematic representations of the type I and type II images are shown to the right of panel e' and left of panel d' with corral locations indicated by dashed lines. The asterisk marks the corralled adatom for each type of corral. The length of the chlorododecane molecule is 15.2 Å, as illustrated above the schematic to the left of part d'.

The UHV chamber was equipped with a quadrupole mass spectrometer (INFICON Quadrex-200) to check the pressure and purity of the chemicals from time to time during deposition. All reagents were purchased from Aldrich and further purified by freeze–pump–thaw cycles with liquid nitrogen, before being introduced into the UHV chamber for background dosing. Exposures are reported in langmuirs (1 L = 1×10^{-6} Torr s) measured at an uncorrected ion gauge, calibrated for N₂. The corrected doses would be ~ 10 times lower than the stated ones.²² In the experiments, the clean silicon surface was exposed to 1 L of halododecanes (uncorrected) by introducing the vapor into the STM chamber for 200 s at a pressure of 5×10^{-9} Torr.

The scanning tunneling microscope was operated in the constant-current mode. All measurements were made with a tunneling current of 0.2 nA unless otherwise stated. The STM tips were made by electrochemically etching tungsten wire. The Si(111) samples (2×9 mm²) were cut from n-type (phosphorus-doped) silicon wafers (250 ± 25 μ m in thickness) with a resistivity of 0.02–0.05 Ω cm (Virginia Semiconductor Inc). The samples were cleaned in an UHV by several cycles of direct current heating to 1240 K for ~ 1 min. Electrical contact was made by Ta foils of ~ 0.025 mm thickness attached to the bottom of the sample at either end; these foils were spot-welded to two tungsten posts (~ 0.5 mm thickness) inserted between the spring clips at the STM stage. The sample temperatures were measured by a C-type (tungsten/rhenium 5%–tungsten/rhenium 26%) thermocouple attached to the bottom surface of the sample. Temperatures were confirmed by optical pyrometry (Minolta, $\epsilon = 0.63$) in the applicable temperature range, > 600 $^{\circ}$ C. The STM images of the surface cleaned in this way showed a (7 \times 7) reconstruction and a small number of surface defects ($< 0.2\%$).

3. Results and Discussion

3.1. 1-Fluoro-, 1-Chloro-, and 1-Bromododecane; Types I and II Corrals. Figure 1a–c shows STM images of a Si(111)-7 \times 7 surface exposed to 1 L (uncorrected) of (a) 1-fluoro-, (b) 1-chloro-, and (c) 1-bromododecane molecules at room temperature. Upon adsorption from the gas phase, these adsorbates self-assembled to form mainly molecular dimers (plus occasionally monomers, circled and marked *M* in panels a and b) at the surface, giving rise to approximately circular structures (for monomers semicircular).

These molecular dimers, it has been proposed,¹⁶ are formed by diffusion of the molecules adsorbed on the surface in a mobile vertical, *v*, precursor state, which subsequently stabilizes by “lying down” on the surface (in the horizontal state, *h*), most often in pairs as a dimer. The mechanism of dimer formation ($2v \rightarrow 2h$ and $v + h \rightarrow 2h$) is discussed in greater detail in ref 20. Upon close observation, the dimeric structures can be seen to have a corralling effect on the Si atom at the center, which has been darkened by a process identified earlier as charge transfer to the corralled atom.¹⁶

The corrals appear as bright features in the STM images obtained at bias voltages from 0.5 to 3 V, of either polarity. Observation of bright features in both polarities has been found in a number of cases to be indicative of physisorption for aromatic and linear molecules on Si(111)-7 \times 7.^{23,24} This suggests that the corrals are physisorbed intact at the surface, as found for the saturated hydrocarbon chains of Manassen et al. which showed no C–C bond breaking.⁴

Though the corrals examined in this work are physisorbed, they show evidence of several (approximately six) points of contact with the underlying Si surface, that is, increased

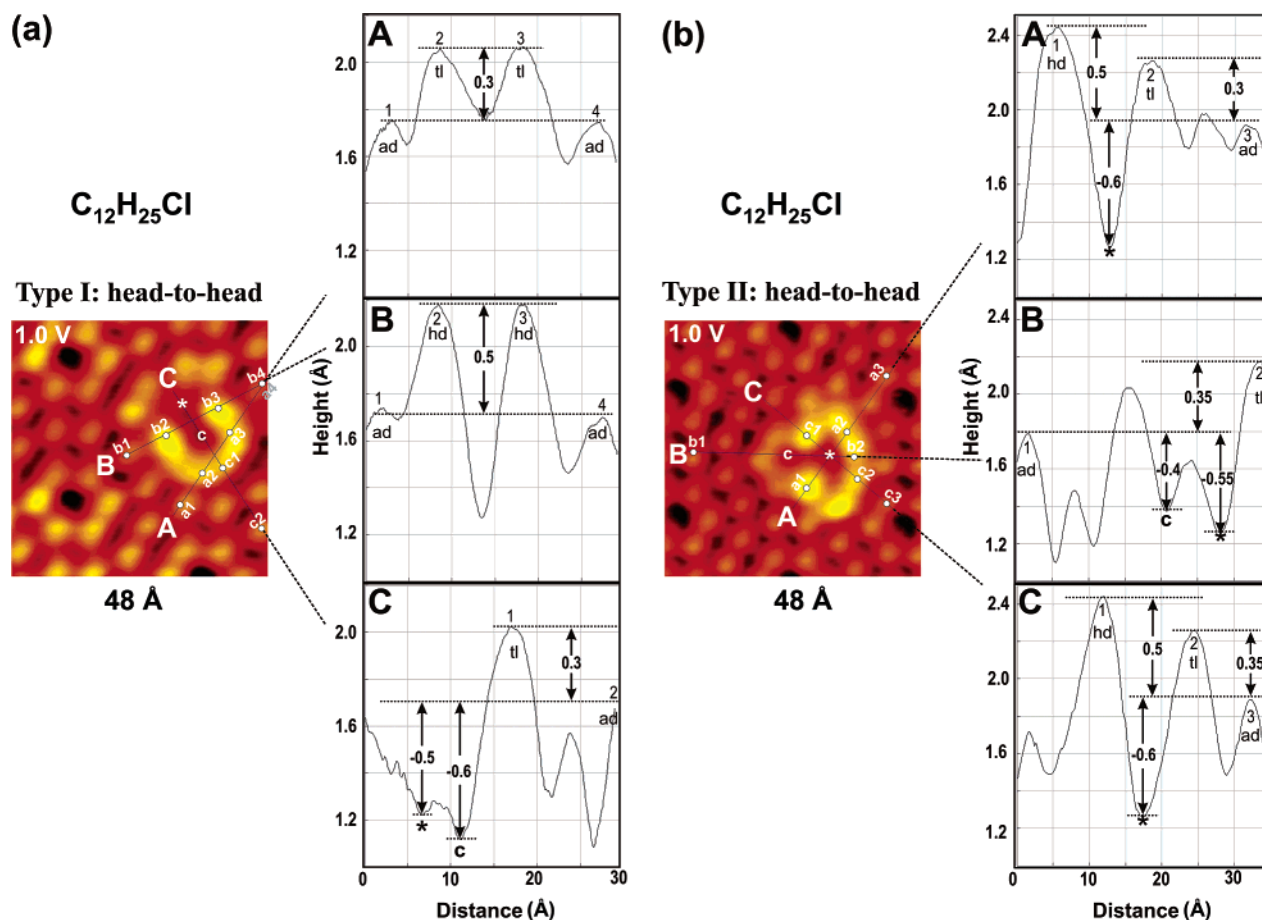


Figure 2. High-resolution STM image of the Si(111)- 7×7 surface together with (panel a) three height profiles for a type I chlorododecane corral and (panel b) three height profiles for a type II chlorododecane corral. The height profiles are along three surface directions, A, B and C, taken at 1.0 V, 0.2 nA. The maximum height of the corral is 0.5 Å above the clean adatom (labeled “ad” in the height profiles) seen in panel a at positions b2 and b3 for the type I corral and in panel b at positions a1 and c1 for the type II corral. These high points are the head location (labeled “hd”) of the $C_{12}H_{25}Cl$ molecule. Similarly, in panel a, the points a2 and a3, and in panel b, the points a2 and c2 are of equal heights of 0.3 Å, corresponding to the tail location (labeled “tl”). The point marked with an asterisk in both the STM images represents the location of the corralled adatom which exhibits a depth of -0.5 Å below the clean adatom, in panels a and b, respectively. The corner hole is marked by a “c” in the STM image of both the type I and II corrals as well as in their height profiles; it can be seen to be slightly deeper than the corralled adatom.

brightness of the Si adatoms.²⁵ The multiple points of contact render them stable at the surface, being immobile up to ~ 100 °C.

Lei et al., in their temperature-programmed desorption (TPD) study²⁶ of saturated hydrocarbon chains with a length of 3–12 carbon atoms, found that the measured physisorption energy increased linearly with chain length on many surfaces. The physisorption energy increased typically by ~ 0.25 eV per CH_2 group. In addition to $C_{12}H_{25}Cl$, we have performed preliminary experiments on $C_8H_{17}Cl$ (1-chlorooctane) and $C_6H_{13}Cl$ (1-chlorohexane) and have found a marked increase in sticking probability with increased chain length from C_6 to C_8 to C_{12} , indicating that physisorption at several CH_2 groups is effective in the adsorption process for these haloalkanes. Additional evidence for physisorption of the haloalkane adsorbates in the present work comes from the fact that the dimers (the corrals) and the monomers desorb at elevated temperature ($> \sim 150$ °C), leaving no residue at the surface, consistent with their being intact in the adsorbed state. A fraction of the adsorbate (as will be explained) shows evidence of carbon–halogen bond breaking at > 150 °C, leaving an imprint at the surface which is, however, readily distinguished from the intact room-temperature physisorbed state.

Comparison of the unextended length of 1-halododecane (~ 15 Å) with the distance between adjacent Si adatoms (6.7 or 7.7

Å) suggests that one molecule can cover up to three silicon adatoms, as shown schematically in the scale drawing of Figure 1d. This is in accord with the observation that a maximum of six Si adatoms appear brighter beneath a self-assembled corral (dimer). In general, one or the other end of each adsorbed haloalkane molecule was found to be brighter. We surmise that this brightening, more evident for the larger halogen atoms, is indicative of the presence of the X atom at that end of the chain, as found by the Flynn group.¹³ This interpretation is supported by the observed correlation between the location of the bright end of the intact adsorbate and the location of the halogen atom at the surface, that is, the location of X–Si, formed as a consequence of thermal or electron-impact-induced bond breaking; see sections 3.4 and 3.5.

In Figure 1d and e, we illustrate the two most common types of corral structures for the case of 1-chlorododecane, $C_{12}H_{25}Cl$, termed types I and II. Type I was formed around a corner hole, while type II was displaced by one atomic space (7.7 Å) to the side of the corner hole. Type I corrals cover five adatom sites (all of which are corner adatoms, see the schematic of Figure 1e), whereas type II cover six sites (two middle and one corner adatom for each half of the corral, see the schematic of Figure 1d). Type I and II corrals account for 80% of the total number of $C_{12}H_{25}Cl$ corrals. Other types of corrals were observed covering five or six adatom sites, but these were

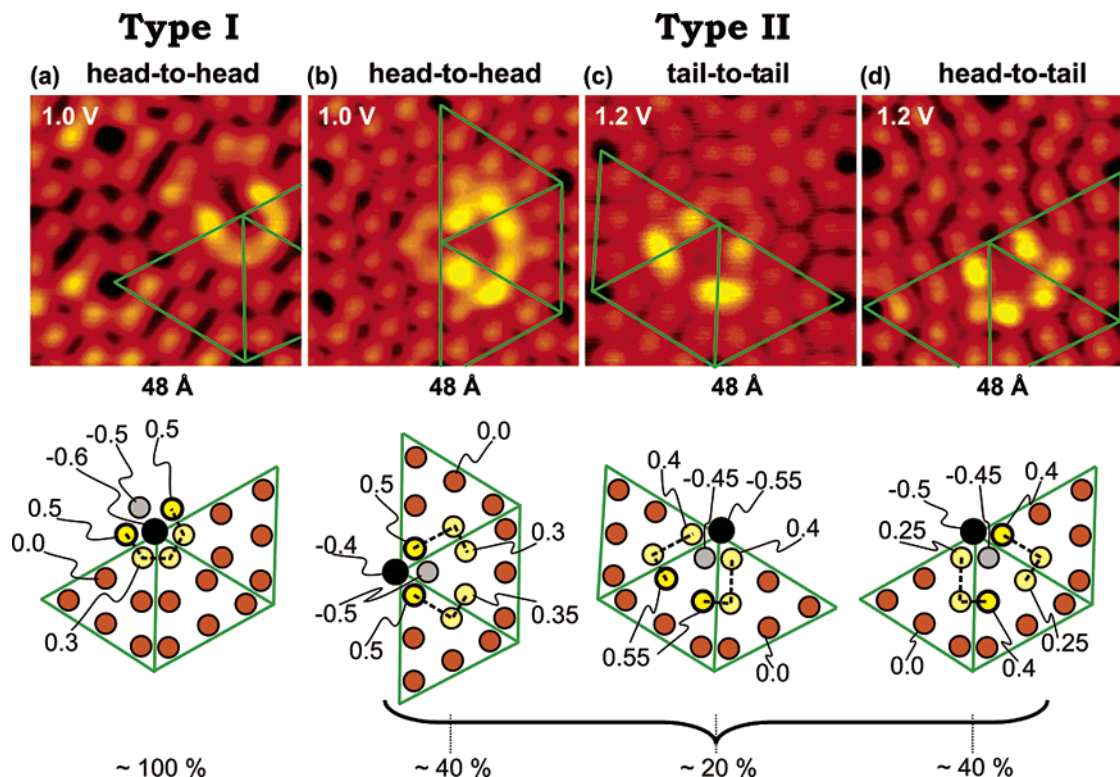


Figure 3. High-resolution STM images of the Si(111)- 7×7 surface with adsorbed 1-chlorododecane molecules at room temperature in various configurations. Panel a shows a type I corral, in a typical head-to-head configuration; panel b shows a type II corral, head-to-head; panel c shows a type II corral, tail-to-tail; and panel d shows a type II corral, head-to tail. Unit cells are outlined in the STM images showing the corral structures. A schematic is given below each image. Scanning voltages are indicated, top left of each image. The numbers shown in the schematics are heights in angstroms (negative values denote depth) compared to the clean adatom (clean adatoms being given the height zero). The positions of the molecules in each corral are shown in the schematic as a dashed line, with the chlorine ends indicated by two thick circles. Corralled adatoms are shown in light gray.

uncommon for 1-chloro- and 1-bromododecane. The variability in corral structure was greater for 1-fluorododecane, which was observed to have the highest sticking probability, as is evident from the panels in Figure 1a–c, all recorded at 1 L. In addition to forming corrals at room temperature, 1-bromododecane, $C_{12}H_{25}Br$, was unique in reacting at this temperature to a minor extent (approximately 10%). This molecule imprinted Br atoms as $Br-Si$ and also formed adjacent alkyl residue as $R-Si$ at the surface (see also section 3.4).

In this paper, we discuss the common type I and II corrals. A high-resolution STM image together with a schematic of a type II corral is shown in Figure 1d. At the open part of the corral are two bright spots which, as noted, we ascribe to the chlorine atoms of the component molecules of the dimer. The main body of the corral matches the dimension of two dodecane chains, as indicated. In the enclosed center of the corral, there is a dark feature $0.4\text{--}0.5\text{ \AA}$ lower than the other adatoms. (The z -piezoelectric (\AA V^{-1}) was calibrated by measuring a single step on a clean Si(111)- 7×7 surface with tunneling parameters of $+1.5\text{ V}$ and 150 pA .) The dark feature is the corralled adatom.

This feature could, in principle, be the result of a missing adatom. However, we can discount this possibility in view of the fact that when the corral desorbed or reacted at elevated temperature ($\sim 150\text{ }^\circ\text{C}$), the dark spot disappeared and the adatom reappeared. Furthermore, if a corral were to form only around naturally occurring defects, corral formation would “saturate” at $\sim 0.2\%$ coverage instead of continuing, as observed, up to high coverage. The presence of the dark spot shows, instead, that the electronic structure of the silicon adatom inside the corral is altered by the surrounding adsorbed molecules.¹⁶

3.2. Height Profiles of Types I and II Corrals. The STM images in Figure 2 show height profiles of type I and type II corrals. Type I surrounds a corner hole, whereas type II is displaced by one adatom from the corner hole. In what follows, we refer to the two brightest spots, namely, the halogen atoms, as the “heads” of the monomers and the remainder as the “tail”. The corrals of types I and II can be further subdivided by noting whether the heads of the monomers are (a) toward the corner hole (designated “head-to-head”), (b) away from the corner hole (“tail-to-tail”), or (c) one toward and one away from the corner hole (“head-to-tail”).

Figure 2a shows height profiles of a type I chlorododecane corral along three surface directions (A, B, and C). The points a2 and a3 on the corral along line A are of similar height, 0.3 \AA above the clean atoms (a1 and a4). The points b2 and b3 along line B are the brightest, being 0.5 \AA above the clean atoms b1 and b4. We associate points b2 and b3 with the two chlorine atoms (the heads), whereas points a2 and a3, of lower height, are the hydrocarbon-chain tails. Since the heads (Cl) are adjacent to the corner hole, we term this type I corral head-to-head.

The asterisk of profile C shows the depth of the dark spot, -0.5 \AA with respect to the clean-surface adatom, whereas point c of profile C gives the depth of the corner hole, -0.6 \AA . The corner holes associated with both types I and II corrals are shallower than other corner holes. This could be due to the fact that the STM tip scanning the corral cannot probe as deeply into a closely adjacent corner hole.

Figure 2b shows height profiles of a type II corral along three surface directions (A, B, and C). The bright points a1 and c1 of lines A and C are of similar height to one another, $\sim 0.5\text{ \AA}$ above the clean surface; this we attribute to the head, that is,

the Cl end, of the molecules. The average height of these bright head atoms was found to range from 0.4 to 0.6 Å above the clean adatom. The points a2, b2, and c2 of lines A, B, and C are also of similar height to one another, ~ 0.35 Å above the clean surface, but are lower than the head region a1 and c1; this we attribute to the tail. The corralled adatom marked with an asterisk is faintly visible in this high-resolution STM image. The lines A, B, and C give the comparative depth profile of this corralled adatom (-0.6 Å) and line B of the corner hole (-0.4 Å) marked by a "c".

As noted above, corrals can be formed in head-to-head, tail-to-tail, or head-to-tail configurations. Figure 3, which records heights rather than height profiles, shows types I and II chlorododecane corrals in their observed configurations. Figure 3a is the type I corral shown as a height profile in Figure 2a. The schematic representation of each corral configuration and its probability of formation are shown below the corresponding STM image. The numbers shown are heights in angstroms compared to the clean Si adatom. (The heights cannot be compared between images, which came from different experiments.) The heights of the molecules forming the corral vary from 0.2 for the tail to a maximum of 0.6 Å for the head. For the type I corral, $\sim 100\%$ were in the head-to-head configuration. For type II corrals, all three configurations were observed, as shown in Figure 3b–d. (i) In Figure 3b, both chlorine atoms are located at corner adatoms (separated by 11.5 Å), this being head-to-head. (ii) In Figure 3c, the tails are situated at corner adatoms (tail-to-tail). In Figure 3d, the chlorine atom of one molecule and the alkyl end of the other are located at corner adatoms (head-to-tail). The head-to-head (40%) and head-to-tail (40%) configurations form in total about 80% of the observed type II corrals. The decreased heights observed in Figure 3 for the corralled adatoms are not due to missing atoms but due to the altered electronic property of the corralled atom.¹⁶

3.3. 1,12-Dichlorododecane Corrals. The increase in the number of terminal chlorine atoms in going from 1-chloro- to 1,12-dichlorododecane significantly altered the shape of the corral. Figure 4 shows an STM image of a Si(111)- 7×7 surface exposed to 1 L (uncorrected) of 1,12-dichlorododecane at room temperature. The size of the corral formed by 1,12-dichlorododecane was less than the size of the corral formed from 1-chlorododecane, despite the fact that both molecules have approximately the same length. Only four silicon adatoms were covered in the case of 1,12-dichlorododecane, rather than five silicon adatoms for type I and six for type II. Each corral formed from 1,12-dichlorododecane showed four prominent bright spots—which we interpret as one for each chlorine atom—in contrast to the 1-chlorododecane dimer for which each corral had only two prominent bright spots (again, one per chlorine atom).

In an earlier communication,¹⁶ ab initio calculation of the interaction of 1-chlorododecane with Si(111) showed evidence of the preferred (physisorption) attachment of the terminal chlorine atom to Si-adatom dangling bonds. In light of this earlier finding, and the foregoing discussion, we conclude that the Cl \cdots Si attachment in the present example has caused the alkane chains to be bent approximately as pictured in the ball-and-stick models of Figure 4, bringing the four terminal Cl atoms over four Si. The fact that only the four points of Cl \cdots Si physisorptive attachment are visible in the STM image, rather than the five or six brightened Si adatoms invariably found for the monochloride dimers, suggests that the curved alkane chain for the dichloride dimers, rather than lying flat on the surface may be in a plane more nearly perpendicular to the surface. As a result,

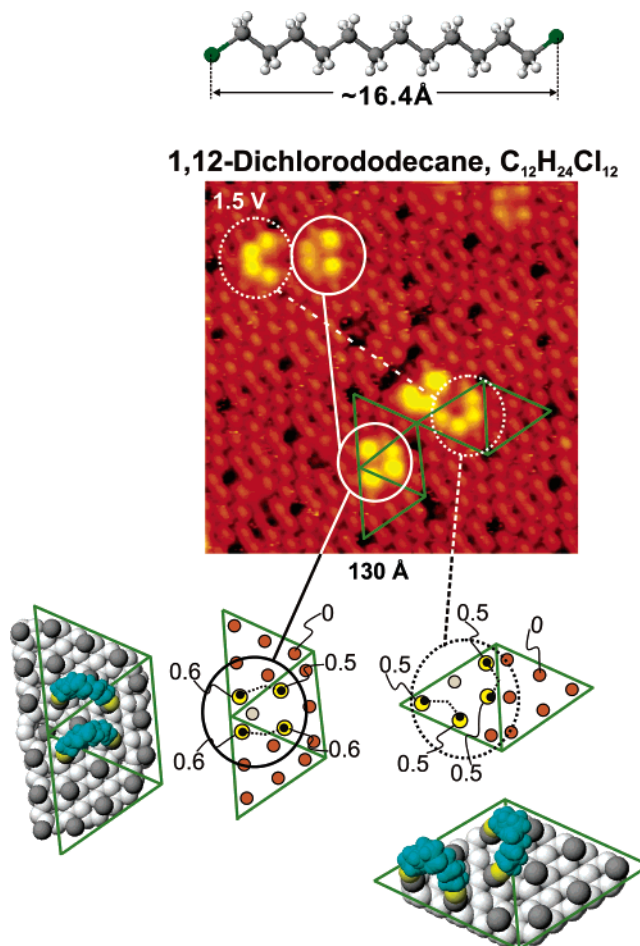


Figure 4. STM images of a Si(111)- 7×7 surface with adsorbed 1,12-dichlorododecane, at room temperature. Two locations for the corral structures are illustrated, with one type highlighted with white circles and the other with broken circles. Unit cells are outlined in the STM image for each type. The corresponding schematics are shown below each image. Four silicon adatoms appear as prominent bright spots, one for each chlorine atom. The numbers shown in the schematics below are heights in angstroms (negative values denote depth) compared to the clean adatom. The corralled adatom is shaded in the schematic. The ball-and-stick models of 1,12-dichlorododecane molecules, drawn to scale, are superimposed at the expected positions in both schematics. The length of the molecule is 15.8 Å (illustrated at the top of the image).

it fails to enhance charge conductance between tip and surface at any Si atoms other than the four covered by the Cl atoms in the corral dimer.

3.4. Thermal Reaction of 1-Chloro- and 1-Bromododecane. The corrals formed at room temperature can survive heating to ~ 100 °C without change in shape, or migration. At 100 °C and above, reaction of the corrals to form X–Si (X = Cl, Br) and adjacent organic residue, R–Si, where R is C₁₂H₂₅, proceeded at a measurable rate. At positive sample bias, the chemisorbed halogen atom formed as a result of reaction appeared as a bright spot in the STM image at 2–3 V, whereas the organic residue covalently attached through a carbon–silicon bond appeared as an adjacent dark feature indicative of its point of attachment to Si. Such darkening upon attachment of carbon to silicon has been previously reported.^{8,21} A similar reaction mechanism to give X–Si and R–Si for 1-haloalkanes at silicon has been postulated at the liquid–solid interface on the basis of XPS and secondary-ion mass spectrometry (SIMS).²⁷

To observe the dynamics of thermal reaction, we deposited 1-bromo- and 1-chlorododecane at 100 °C in separate experiments and then scanned the same area of the surface at irregular

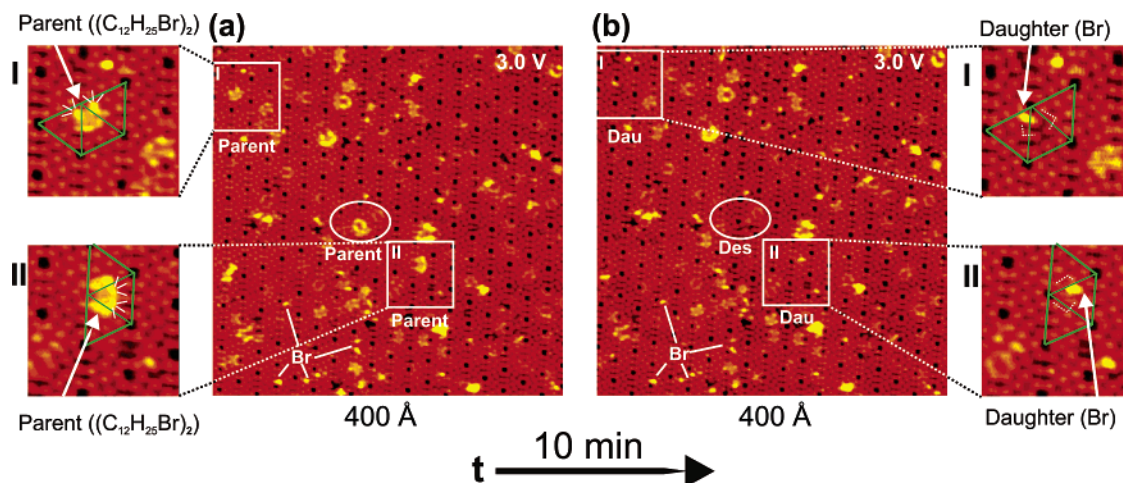


Figure 5. STM images of the Si(111)- 7×7 surface with adsorbed 1-bromododecane molecules deposited at 100 °C (a) 15 min after deposition and (b) 25 min after deposition; both images were recorded at 100 °C. The white squares marked I and II in panel a labeled “Parent” are two examples of a parent bromododecane corral, $(C_{12}H_{25}Br)_2$, (both type II), magnified at the left. The white squares I and II in panel b labeled “Dau” and the corresponding magnified images at the right show the product of thermal reaction, daughter Br–Si. A desorption event is circled white for a type I corral (a) showing the corral before desorption (the parent) and (b) after desorption (“Des”). The trapeziums in the magnified images I and II outline the three half-unit cells embodying the parent corral (left side) and daughter Br (at the right). The bright spots associated with Br in the parent molecule are highlighted by white markers in the magnified images I and II at the left (“Parent”). The single bright spots in parts a and b labeled “Br” correspond to reaction product, Br–Si, already formed at the time of the first image. Both images were scanned at 3 V.

time intervals of 5–10 min. Some 50 corrals were observed reacting with the passage of time. The location of the halogen atom in the corral was assigned from the position of the X–Si formed subsequently at the surface, assuming that the preferred reaction path involved a closely adjacent Si dangling bond, that is, localized reaction.^{21,28,29}

Figure 5 shows two type II bromododecane corrals before and after reaction. The first STM image, Figure 5a, was taken approximately 15 min after deposition with the temperature maintained at 100 °C. The second image, Figure 5b, was taken 10 min after the first one. The figure shows that these two parent corrals have reacted thermally, each giving rise to an adjacent bright spot that we designate as “daughter” Br–Si. In example I, before reaction, the bright locations which we associated with Br in the parent molecule were at the top left of the corral, as highlighted. After reaction, the bright spot corresponding to the daughter Br–Si was once more located at the top left of the (previous) corral location. The remainder of the corral has desorbed. Similarly, for example II, in the same trace, for which the Br atom in the parent molecule could be seen to be at the right (as highlighted), after reaction the daughter Br–Si was also at the right of the corral location. The remainder of the corral, once again, has desorbed.

Both examples support the idea that the bright feature in the intact parent corral corresponds to the location of the Br atom. The adjacent dark feature in the product of reaction, R–Si, is barely visible at the 3 V scanning voltage used for Figure 5 but clearly evident at 1–2 V. It should be noted that in each case after reaction (i.e., following C–Br bond scission) the second molecule in the corral desorbed from the surface. Evidently, it owes its stability at the surface in part to the presence of the first molecule. Additionally, the corralled adatom ceases to be dark, proving that the darkening was not due to a surface defect but to the corral.¹⁶

In addition to the two reactive events, I and II, desorption was also observed; this is the event circled in white in the STM image of Figure 5. Desorption was comparable in probability to reaction. It is noteworthy that in the substantial number of desorption events recorded (see below) in no case was only one-half of a corral seen to desorb. This is strong evidence that the

corral (dimer) gains stability from the proximity of its two component monomers, as suggested above on the basis of the desorption that followed reaction.

At our initial time of observation, represented by panel a of Figure 5, in addition to the corrals and half-corrals from the 100 °C deposition, a roughly equal number of single bright spots characteristic of Br–Si were observed. Some of these Br–Si were due to slow reaction during the 15 min time lapse (in this experiment) between dosing and recording the image of Figure 5a. This is the same process that we have described as occurring in the subsequent time periods (part b compared with part a of Figure 5). We term the reaction dynamics of this gradual surface halogenation with the passage of time, shown in Figure 5, parent-mediated, since, as noted, we have observed adsorbed parent prior to reaction.^{21,30}

However, from the fact that a significant yield of Br–Si was obtained even at room temperature and at the shortest observation times used, we conclude that there is, in addition, a second (instantaneous) type of reaction dynamics leading to surface bromination. We interpret this additional pathway (as in previous studies^{21,30}) to be “daughter-mediated” reaction, in which the 1-haloalkane approaches the surface with its halogen atom pointing down, and halogen-atom transfer to the surface ensues directly during the initial encounter with the surface. These alternative pathways, parent- and daughter-mediated, will be explored in greater detail in the following paper.²⁰

To observe the parent-mediated reaction largely in the absence of the daughter-mediated one, we have made a study of chlorododecane at a 100 °C Si surface. The stronger C–Cl bond than C–Br markedly diminished the contribution from daughter-mediated reaction for chlorododecane, rendering it unobservable at room temperature. The simplest case in which to compare the location of the parent molecule in parent-mediated reaction with the location of the subsequent X–Si is for type I corrals. For these corrals, we know (see section 3.2) that the head, that is, the bright feature in the corral, is at the open end. In the present study, the scan speed was generally too fast for observation of the bright feature in each individual parent molecule, so we rely on our knowledge of its invariable position for type I corrals. In 14 out of 18 type I corrals whose reaction

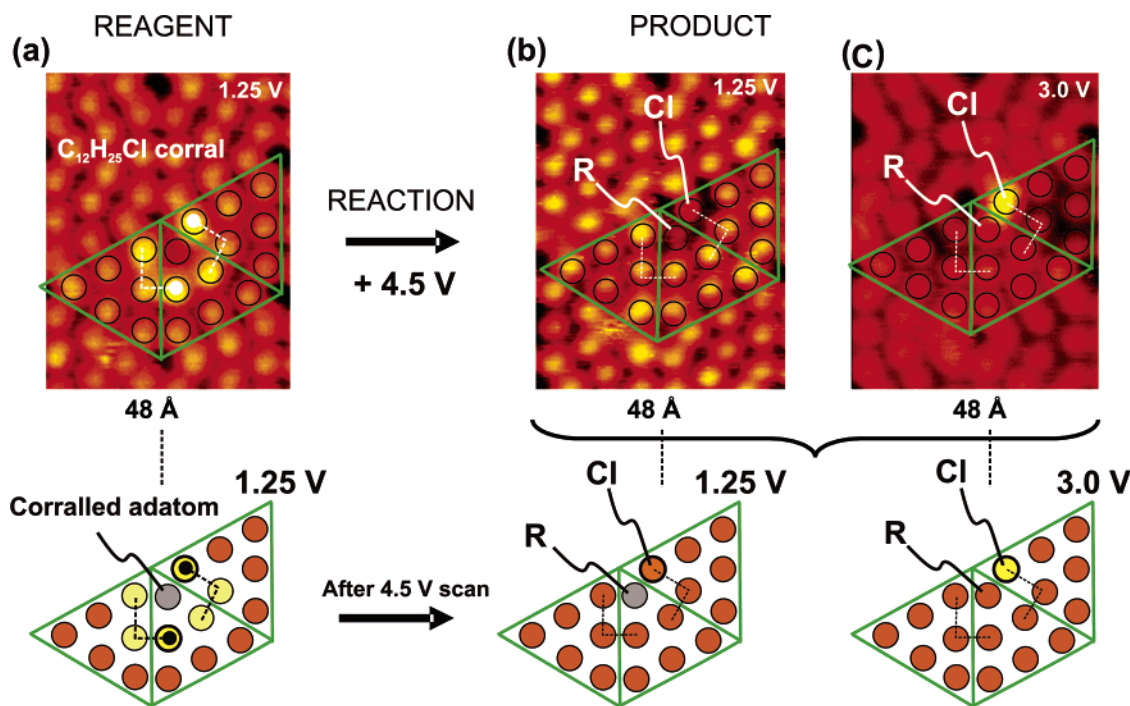


Figure 6. STM images of a type II chlorododecane corral (the example given is head-to-tail) (a) before and (b and c) after electron-induced reaction by scanning at +4.5 V_s, 0.2 nA. Three half-unit cells are outlined in each image, with schematics below. The corralled adatom is shaded in the schematic of part a. The positions of the individual molecules of this corral are indicated by dotted lines in the STM image as well as in the schematics. The heavy circles denote the location of the chlorine end of each of the component molecules of the corral, corresponding to the highest points in the height profiles. Images b and c are of the same area of the surface as part a, taken in the 1.25 V/3.0 V dual-bias voltage mode. The dark spots in part b are due to organic residue, R (present as R–Si), and Cl imprinted by induced surface reaction (i.e., Cl–Si). In image c, at 3 V, the imprinted Cl appears bright as compared with image b, and the organic residue, R, has become indistinguishable from the other adatoms.

was followed at 100 °C, the chlorine atom product, Cl–Si, appeared at the identical adatom to the head of the type I corral. In two additional cases, the Cl atom was found to be directly adjacent to this head atom of the corral. For the remaining two cases, the Cl atom was in one case on the tail adatom and in the other directly adjacent to the head. In sum, in 14 out of 18 cases, the bright feature at the head of the type I corral gave evidence of being the source of the Cl thermally imprinted in localized reaction at the surface.

For other corral configurations than type I, we followed the reaction in a total of 28 cases. Since once again these STM images were not obtained at the highest resolution, we could not locate the bright features within the parent corral. We know, however, from high-resolution studies that these features are to be found at one or the other end of the monomer components (section 3.2). Comparing the parent configuration with the location of the imprinted Cl atom following reaction, we found that in 86% of the cases (24 out of 28) the Cl–Si appeared on an end atom of a 1-chloroalkane molecule. Of the four anomalous cases, three product Cl–Si's appeared in a location that had previously been midchain and one appeared at an adatom directly adjacent to a chain end (rather than on the chain end). Once again, this supports the contention that the bright feature in the corral is the halogen atom (Cl, in the present instance).

It is instructive to compare the number of reactive events—a total of 46 in the above discussion—with the accompanying desorption events. In “desorption” (see Figure 5), a corral dimer was observed to vanish from the surface at 100 °C, without leaving an X–Si or R–Si imprint. In the same scanned area as the 46 reactive events, we noted 70 such desorptions. It appears that desorption is almost twice as probable as reaction at 100 °C. As already noted for some isolated cases, in every case that desorption was observed, it involved the complete corral; in no

case was a monomer residue left at the surface. This substantiates the conclusion that a corral “dimer” owes a significant fraction of its stability to monomer–monomer interaction, so that desorption of one monomeric component destabilized the other.

3.5. Electron-Induced Reaction of 1-Chlorododecane. As noted in earlier work, the carbon–halogen bond can be severed, and surface halogenation induced, not only thermally but also by incident electrons from the STM tip at room temperature.^{21,28,31} The STM images shown in Figure 6 illustrate reaction of a corral caused by electron impact at 4.5 eV. The electron impact led to the localized reaction of a halogen atom in the majority of cases, consistent with the case of thermal reaction described above and consistent with earlier findings.^{21,28,31}

Figure 6a shows a type II corral with head-to-tail configuration (as also illustrated for a different example in Figure 3d). The dimer (corral) is of 1-chlorododecane and is imaged at $V_s = 1.25$ V. The two panels labeled Figure 6b and c show the effect of scanning over area (a) at 4.5 V, 0.2 nA, so as to induce reaction (not observed below approximately 3.5 V). The chemical reaction, that is, C–Cl bond scission followed by formation of Cl–Si and R–Si, is thought to be induced by electrons from the tip entering the antibonding orbital of C–Cl.^{28,31–35} After performing the +4.5 V scan to induce reaction, dual-bias voltage STM images (+1.25 and +3 V) of the same area of the surface were taken, as shown in Figure 6b and c. From the images in Figure 6b and c, it is evident that the C–Cl bond at the head of the right-hand molecule in the corral was severed during the +4.5 V scan. We infer this from the fact that a new Cl–Si bond has been formed at the identical corner Si adatom, marked Cl in Figure 6b and c, where the right-hand chlorine of the corral was located prior to reaction. The Cl–Si in Figure 6b and c is identified as such by the characteristic brightening between 1.25 and 3 V.^{28,36}

The presence of R–Si directly adjacent to the Cl–Si is evident from the darkened adatom in Figure 6b at 1.25 V (no longer evident in the 3 V image of Figure 6c).^{21,37} Reaction to form R–Si is localized to within one adatom site of the Cl end of the undissociated corral. A similar localized atomic reaction (termed LAR) was observed in our previous studies involving aromatic molecules at silicon surfaces in which the parent molecule and its R–Si imprint were found to be closely adjacent.^{21,28,37}

As noted in the previous section, the stability of the corral is lost following reaction, as evidenced by the fact that the second molecule comprising the corral desorbs, leaving behind a clean surface (Figure 6c and its schematic). This would be expected if monomer–monomer interaction contributed to the dimer (the corral) stability at the surface. It is remarkable that complete loss of a corral to desorption occurred even at the room-temperature surface, following electron-impact dissociation of one of its monomeric components.

4. Conclusions

We report a study of self-assembled physisorbed “corrals” of 1-monohalide alkane dimers at Si(111)-7 × 7. We found decreased sticking probability and also decreased variety in the structure of the self-assembled corrals, as we proceeded down the series of monohalide dodecanes, C₁₂H₂₅X, from 1-fluoro- to 1-chloro- to 1-bromododecane. For chlorododecane, the corral structure at room temperature divided largely into types I and II, that is, those that assembled on five adatom sites around a corner hole (type I) and those that were displaced by one atomic space to the side of a corner hole and covered six adatom sites (type II). Preliminary experiments with C₆H₁₃Cl and C₈H₁₇Cl as compared with C₁₂H₂₅Cl showed a systematic increase in sticking probability with increased alkane chain length, indicating that several CH₂ groups of the alkane chain interacted with the underlying silicon atoms, contributing to the physisorption binding.

Type I corrals of 1-chlorododecane (which represented 50% of the total, at room temperature) had the simplest internal structure, with bright features evident in their height profiles at their open ends, corresponding to the two chlorine atoms, the so-called heads of the chain. Type I corrals were therefore exclusively head-to-head. Type II corrals (an additional 30% of those observed) were interpreted, from their bright-feature locations and height profiles, as being mainly of two types; head-to-head with the Cl's both adjacent to a corner hole and (with equal probability) head-to-tail with a head and tail adjacent to the corner hole. Additionally, a small fraction (20%) of type II were in the tail-to-tail configuration.

All corrals of both types enclosed a darkened adatom, termed the corralled atom. This was typically lower in height than a normal adatom by 0.4–0.5 Å. For type II, this effect has been ascribed, in previous STS experiments and with the aid of theory, to charge transfer from the corral to the darkened adatom.¹⁶

Both thermal and electron-induced reaction were studied, the former for 1-chloro- and 1-bromododecane at 100 °C and the latter for 1-chlorododecane at room temperature. Parent-mediated reaction, in which molecular adsorption occurs prior to reaction so that the corral can be seen at the surface with subsequent reactive C–X bond breaking plus R–Si bond formation, leads most often to X–Si being formed at the head of a XC₁₂ monomer that makes up the corral. This confirms the identification of the bright features in the corrals as being due to X atoms.

Thermal reaction of chlorododecane corrals deposited at 100 °C was accompanied by approximately double the amount of desorption as compared with reaction. It was found that either reaction of a monomer of a corral (to give X–Si) or its desorption resulted in the accompanying desorption of the second monomer of the corral. This indicated that monomer–monomer interaction played a significant role in stabilizing the corral. Desorption of the second monomer of a dimeric corral following surface reaction of the first was observed even when the reaction of the component C₁₂H₂₅Cl to yield Cl–Si was induced at room temperature by electron impact.

A few experiments were performed with 1,12-dichlorododecane rather than monochlorododecane. As might have been expected from the earlier theoretical finding that the Cl “headgroup” is attracted to adatom dangling bonds, the corrals formed with their four terminal Cl's exhibiting the same number of bright features at the surface, indicative of Cl attachment to four adjacent adatoms. There was no corralled Si adatom within this smaller structure. The fact that a chain of approximately the same length as before affected only four adatoms instead of five or six suggested that the alkane portion of the dihaloalkane, comprising a total of 24 CH₂ groups, was not in close contact with the surface in this instance.

Acknowledgment. The authors are indebted to the Natural Sciences and Engineering Research Council of Canada (NSERC), Photonics Research Ontario (PRO), an Ontario Centre of Excellence, the Canadian Institute of Photonic Innovation (CIPI), and the Canadian Institute for Advanced Research (CIAR) for support of this work.

References and Notes

- (1) Wolkow, R. A. *Annu. Rev. Phys. Chem.* **1999**, *50*, 413.
- (2) Hamers, R. J.; Wang, Y. *Chem. Rev.* **1996**, *96*, 1261.
- (3) Waltenburg, H. N.; John T.; Yates, J. *Chem. Rev.* **1995**, *95*, 1589–1673.
- (4) Shachal, D.; Manassen, Y. *Appl. Phys. A* **1998**, *66*, S1229–S1231.
- (5) Simons, J. K.; Frigo, S. P.; Taylor, J. W.; Rosenberg, R. A. *Surf. Sci.* **1996**, *346*, 21–30.
- (6) Shachal, D.; Manassen, Y. *J. Vac. Sci. Technol., B* **1997**, *15*, 1310–1312.
- (7) Shachal, D.; Manassen, Y. *Chem. Phys. Lett.* **1997**, *271*, 107–112.
- (8) Shachal, D.; Manassen, Y.; Ter-Ovanesyan, E. *Phys. Rev. B* **1997**, *55*, 9367–9370.
- (9) Cyr, D. M.; Venkataraman, B.; Flynn, G. W. *Chem. Mater.* **1996**, *8*, 1600–1615.
- (10) Giancarlo, L. C.; Flynn, G. W. *Annu. Rev. Phys. Chem.* **1998**, *49*, 297–336.
- (11) Giancarlo, L. C.; Flynn, G. W. *Acc. Chem. Res.* **2000**, *33*, 491–501.
- (12) Giancarlo, L.; Cyr, D.; Muyskens, K.; Flynn, G. W. *Langmuir* **1998**, *14*, 1465–1471.
- (13) Cyr, D. M.; Venkataraman, B.; Flynn, G. W. *J. Phys. Chem.* **1996**, *100*, 13747–13759.
- (14) Venkataraman, B.; Flynn, G. W. *J. Phys. Chem.* **1995**, *99*, 8684–8689.
- (15) Muller, T.; Werblowsky, T. L.; Florio, G. M.; Berne, B. J.; Flynn, G. W. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 5315.
- (16) Dobrin, S.; Harikumar, K. R.; Jones, R. V.; Li, N.; McNab, I. R.; Polanyi, J. C.; Sloan, P. A.; Waqar, Z.; Yang, (S. Y.) J.; Ayissi, S.; Hofer, W. A. *Surf. Sci.* **2006**, *600*, L43.
- (17) Crommie, M. F.; Lutz, C. P.; Eigler, D. M. *Nature* **1993**, *363*, 524.
- (18) Crommie, M. F.; Lutz, C. P.; Eigler, D. M. *Science* **1993**, *262*, 218.
- (19) Silva, S. L.; Leibsle, F. M. *Surf. Sci.* **1999**, *441*, L904.
- (20) Dobrin, S.; Harikumar, K. R.; McNab, I. R.; Polanyi, J. C.; Waqar, Z.; Yang, J. Manuscript in preparation.
- (21) Dobrin, S.; Harikumar, K. R.; Polanyi, J. C. *Surf. Sci.* **2004**, *561*, 11.
- (22) Nakao, F. *Vacuum* **1975**, *25*, 431.
- (23) Brown, D. E.; Moffat, D. J.; Wolkow, R. A. *Science* **1998**, *279*, 542.

- (24) Dobrin, S.; Lu, X.; Naumkin, F. Y.; Polanyi, J. C.; Yang, J. *Surf. Sci.* **2004**, *573*, L363.
- (25) Dubois, M.; Delerue, C.; Allan, G. *Phys. Rev. B* **2005**, *71*, 165435.
- (26) Lei, R. Z.; Gellman, A. J.; Koel, B. E. *Surf. Sci.* **2004**, *554*, 125–140.
- (27) Lua, Y.-Y.; Niederhauser, T. L.; Matheson, R.; Bristol, C.; Mowat, I. A.; Asplund, M. C.; Linford, M. R. *Langmuir* **2002**, *18*, 4840.
- (28) Lu, P. H.; Polanyi, J. C.; Rogers, D. *J. Chem. Phys.* **1999**, *111*, 9905.
- (29) Matta, C. F.; Polanyi, J. C. *Philos. Trans. R. Soc. London, Ser. A* **2004**, *362*, 1185.
- (30) Harikumar, K. R.; Petsalakis, I. D.; Polanyi, J. C.; Theodorakopoulos, G. *Surf. Sci.* **2004**, *572*, 162.
- (31) Sloan, P. A.; Hedouin, M. F. G.; Palmer, R. E.; Persson, M. *Phys. Rev. Lett.* **2003**, *91*, 118301.
- (32) Zhou, X. L.; White, J. M. *J. Chem. Phys.* **1990**, *92*, 5612.
- (33) Rowntree, P.; Sanche, L.; Parenteau, L.; Meinke, M.; Weik, F.; Illenberger, E. *J. Chem. Phys.* **1994**, *101*, 4248.
- (34) Stipe, B. C.; Rezaei, M. A.; Ho, W.; Gao, S.; Persson, M.; Lundqvist, B. I. *Phys. Rev. Lett.* **1997**, *78*, 4410.
- (35) Ho, W. *Acc. Chem. Res.* **1998**, *31*, 567.
- (36) Boland, J. J.; Villarubia, J. S. *Phys. Rev. B* **1990**, *41*, 9865.
- (37) Dobrin, S.; Harikumar, K. R.; Matta, C. F.; Polanyi, J. C. *Surf. Sci.* **2005**, *580*, 39.