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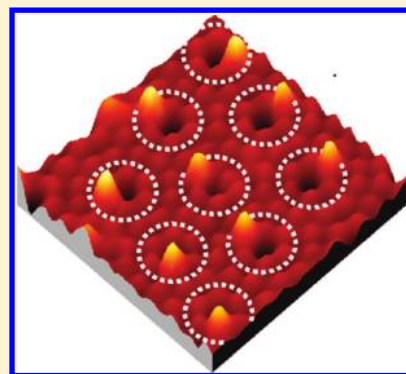
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## Facile Charge-Displacement at Silicon Gives Spaced-out Reaction

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S Supporting Information

**ABSTRACT:** Adsorbates on metals, but not previously on semiconductors, have been observed to display long-range repulsive interactions. On metals, due to efficient dissipation, the repulsions are weak, typically on the order of 5 meV at 10 Å. On the 7×7 reconstruction of the Si(111) surface, charge transport through the surface has been demonstrated by others using charge injection by STM tips. Here we show that for both physisorbed brominated molecules, and for chemisorbed Br-atoms, induced charge-transfer in the Si(111)-7×7 surface can lead to a strong repulsive interaction between adsorbates, calculated as 200 meV at 13.4 Å. This large repulsive interaction must be channeled through the surface since it causes widely spaced “one-per-corner-hole” patterns of physisorption (three cases—directly observed here) and subsequent chemisorption (four cases observed). The patterns were observed by ultrahigh vacuum scanning tunneling microscopy for four different brominated hydrocarbon adsorbates; 1,2-dibromoethane, 1-bromopropane, 1-bromopentane, and bromobenzene, deposited individually on the surface. In every case, adsorbates were overwhelmingly more likely to be found singly than multiply adjacent to a corner-hole, constituting a distinctive pattern having a probability  $p = 7 \times 10^{-5}$  compared to a random distribution.



## 1. INTRODUCTION

Weak long-range repulsive interactions between adsorbates have frequently been observed on metal surfaces<sup>1–14</sup> and on a metal-supported surfaces,<sup>15</sup> but repulsions have not previously been observed on semiconductors. On metals, weak repulsions ( $\sim 5$  meV at 10 Å) are transmitted by standing waves of the electron gas at the surface. More substantial repulsions ( $\sim 70$  meV at 10 Å<sup>11</sup>) on metals are due to electrostatic interaction between molecules that have acquired charge by electron-transfer to or from the surface.<sup>11,12,15</sup> For dipolar molecules on metal surfaces, repulsive interactions have been observed which depend upon dipole–dipole interactions ( $\sim 20$  meV at 15 Å);<sup>10</sup> the interaction strengths being enhanced by image dipoles within the metal,  $\sim 2$  times greater than gas-phase dipole–dipole interaction at the same distance.

In this work, we demonstrate long-range repulsion between adsorbates at a Si(111)-(7×7) surface. The maximum range of repulsion was between two corner silicon-adatoms opposite one another at a corner-hole, a distance of 13.4 Å. For a representative system, we calculated *ab initio* that the magnitude of the repulsion was 200 meV, which is  $\sim 10\times$  greater than on metals over a similar distance. To our knowledge, this is the first demonstration of a long-range repulsion at a semiconductor surface.

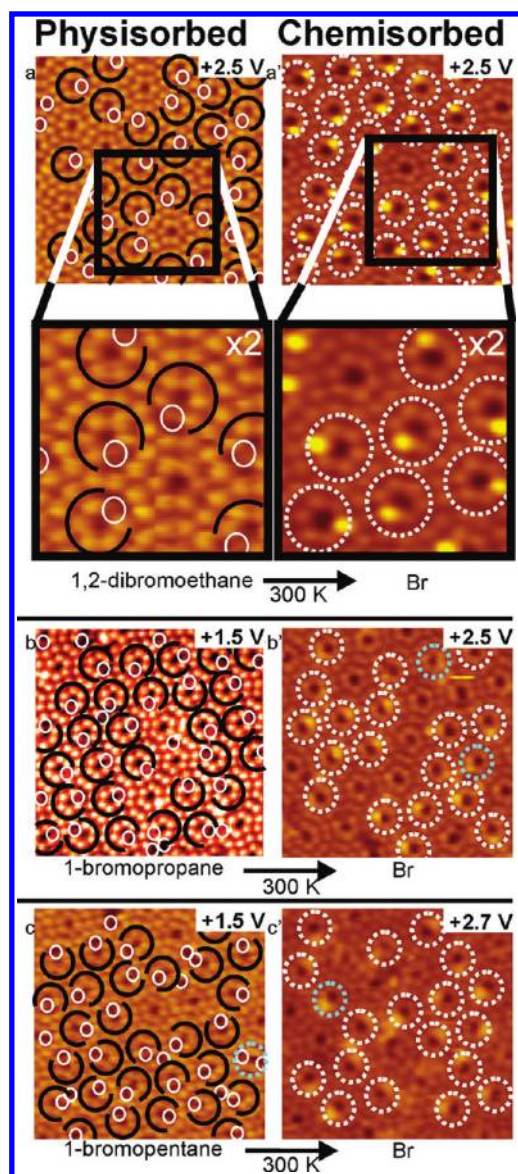
The repulsion reported here originated from a lateral flow of charge in the surface, induced by either physisorbed or chemisorbed species. Work by others recently demonstrated lateral charge flows through silicon surfaces induced by charge injection

from an STM tip. Electron injection was shown to result in “hopping” of chlorine atoms on Si(111)-(7×7),<sup>16</sup> or nonlocal removal of molecularly adsorbed chlorobenzene on Si(111)-(7×7).<sup>17</sup> Hole injection can result in nonlocal activation of a bistable H-atom on Si(100)-(2×1):H.<sup>18</sup>

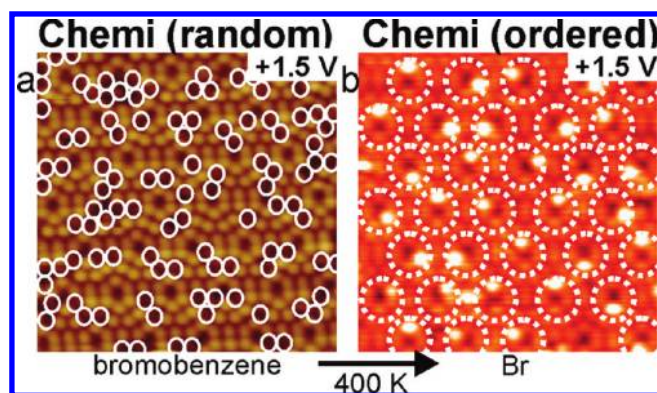
In the present work, the repulsion was induced by adsorbates, resulting in self-assembly of both physisorbed and chemisorbed species in a previously unobserved but characteristic widely spaced pattern that we shall term as “one-per-corner-hole” (OPCH). We use the designation OPCH to describe widely separated physisorbed species, chemisorbed species and mixtures of both. The OPCH pattern is shown for 1,2-dibromoethane, 1-bromopropane, 1-bromopentane in Figure 1, and for bromobenzene in Figure 2. The four molecules studied all gave rise to OPCH bromination, evidencing repulsion between the physisorbed precursors to bromination as well as (it will be shown) repulsion between chemisorbed Br-atoms and physisorbed precursors. In the first three cases, the physisorbed OPCH precursors were directly observable by STM, separated by their mutual repulsion. The ability, demonstrated here, to introduce regular separations between adsorbates, and thereby between their reaction products at a surface, should be of value in achieving an even distribution of dopant in nanocircuitry.

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**Figure 1.** STM topographs ( $140 \times 140 \text{ \AA}^2$ ,  $I_t = 0.2 \text{ nA}$ , constant current, bias given in each panel) showing initial physisorbed molecular arrangements (left-hand column) and their corresponding chemisorbed Br-atoms (right-hand column), both forming characteristic “one-per-corner-hole” (OPCH) patterns on Si(111)- $7 \times 7$ . (Images shown at left and right are of different areas of the surface). The physisorbed molecules image dark compared to silicon-adatoms. To guide the eye, physisorbed molecules are highlighted with white circles enclosed by larger black circles surrounding the adjacent corner silicon ad-atoms. Chemisorbed Br-atoms image bright compared to the silicon ad-atoms. White dashed circles are drawn around the corner silicon ad-atoms. Exceptional cases of more than one adsorbate at a single corner-hole have been circled with dashed blue lines. Individual panels show (a) physisorbed 1,2-dibromoethane dosed at 110 K, distributed OPCH in wide area (top) and close-up (below) and (a') corresponding chemisorbed Br-atoms, OPCH, arising from 1,2-dibromoethane dosed at 300 K in wide area (top) and close-up (below). (b) Physisorbed 1-bromopropane dosed at 50 K, distributed OPCH and (b') corresponding chemisorbed Br-atoms, OPCH, arising from 1-bromopropane dosed at 300 K. (c) Physisorbed 1-bromopentane dosed at 100 K, distributed OPCH and (c') corresponding chemisorbed Br-atoms, OPCH, arising from 1-bromopentane dosed at 300 K.



**Figure 2.** STM topographs ( $140 \times 140 \text{ \AA}^2$ ,  $I_t = 0.2 \text{ nA}$ , constant current, bias given in each panel) showing initial random molecularly adsorbed arrangements (a) and their corresponding chemisorbed Br-atoms arrangement (b), in a highly ordered “one-per-corner-hole” (OPCH) pattern on Si(111)- $7 \times 7$  (Different areas). (a) Bromobenzene dosed at 300 K chemisorbs molecularly in a random pattern by forming two  $\sigma$ -bonds with the surface, (b) corresponding chemisorbed Br-atoms, in an ordered OPCH pattern, arising from chemisorbed bromobenzene after an anneal to 400 K.

## 2. METHODS

**2.1. Experiment.** Experiments employed two separate ultrahigh vacuum scanning tunneling microscopes (Omicron VT-STM, RHK300) both with base pressures less than  $8 \times 10^{-11}$  Torr. Samples of Si(111) [ $10 \times 2 \times 0.3 \text{ mm}^3$ ,  $n$ -type phosphorus-doped Si(111) single side polished wafers with resistivity  $0.02\text{--}0.05 \text{ } \Omega \text{ cm}$ ] were degassed at  $\sim 900 \text{ K}$  for a few hours before eight cycles of direct-current heating at  $1550 \text{ K}$  to produce the  $7 \times 7$  reconstruction ( $<0.2\%$  defects). Tungsten STM tips were made by a  $9 \text{ V}$  direct-current etch in  $3 \text{ M NaOH}$  solution. Imaging at reduced temperatures was achieved by cryogenic cooling using either liquid nitrogen or liquid helium, together with offset heating for fine temperature control. The STM images were processed with XPMPPro 2.0.0.0 or WSxM 4.0.<sup>19</sup>

**2.2. Theory.** Density Functional Theory (DFT) calculations, and also semiempirical DFT-D calculations that included van der Waals interactions, were made with the Vienna Ab-initio Simulation Package (VASP 5.2.8),<sup>20,21</sup> installed at the SciNet supercomputer.<sup>22</sup> DFT calculations were made using Plane Augmented Wave potentials and the PBE parameterization<sup>23</sup> of the exchange-correlation potential (PAW PBE potentials). Simulations of the relaxed geometry were restricted to one  $k$ -point at the center of the surface Brillouin zone, using a cutoff energy of  $450 \text{ eV}$ . Final calculations were made with the DFT-D method,<sup>24</sup> in which dispersion effects are taken into account via a semiempirical approach; this method allows ionic relaxations that take van der Waals forces into account, and the final geometries of the adsorption structures should be more accurate than those from the standard DFT calculations.

## 3. RESULTS

**3.1. Experiment.** In Figure 1 (left column), we show physisorbed molecules, RBr (RBr = 1,2-dibromoethane, 1-bromopropane and 1-bromopentane), in OPCH patterns and (right column) the corresponding chemisorbed Br-atoms in OPCH patterns that result from thermally induced chemical reaction. The physisorbed molecules in each case attached preferentially at one of the Si-adatoms that surrounded a corner-hole of the Si(111)-( $7 \times 7$ ) surface. In general, no more than one molecule



attached to the adatoms of a corner-hole, but in exceptional cases double-occupancy was observed at a corner-hole (see below).

For the single case of bromobenzene, physisorbed precursors were not observable by STM in our range of surface temperatures; instead, randomly distributed molecular chemisorption was observed (Figure 2a, left column) due to the well-known reactivity of the phenyl group at Si(111)-(7×7). The binding energy of the phenyl to the silicon surface, through two strained sigma bonds, is  $\sim 1$  eV.<sup>25</sup> On heating to  $\sim 400$  K, these adsorbates reacted to give the observed OPCH bromination of the surface. The evidence for a mobile precursor is indirect in this case, but its existence is clear from the highly ordered nature of the subsequent OPCH chemisorptions (Figure 2b, right-hand column).

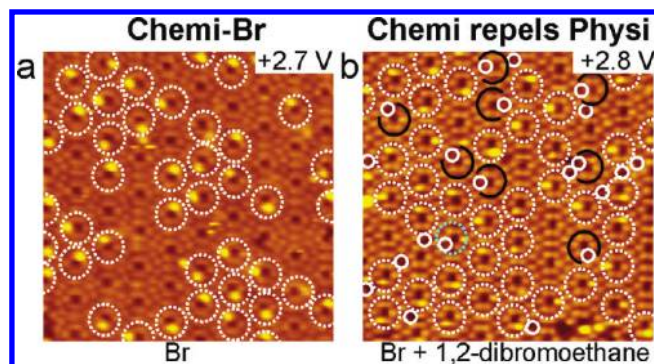
In none of the four cases of OPCH bromine chemisorption thermally induced at Si(111)-(7×7) did we find evidence of attachment of the hydrocarbon radicals to the surface. This implies that the transition state geometries all favored ejection of the hydrocarbon residue away from the surface. The same reaction dynamics were found previously for methyl bromide at Si(111)-(7×7) ejecting  $\text{CH}_3$ .<sup>26</sup>

The observed OPCH patterns were highly site-selective in two ways. First, adsorption or reaction occurred almost exclusively at corner silicon-adatoms adjacent to a corner-hole, rather than on middle silicon-adatoms. Typically, the ratio of occupied corner silicon-adatoms to middle silicon-adatoms was greater than  $\sim 13$ . In no case was a statistically significant difference in site-selectivity found between faulted and unfaulted half unit-cells.<sup>27</sup> Second, for both physisorption and chemisorption, once one of the six available silicon-adatoms around one corner-hole site was occupied, further adsorption rarely occurred at any of the remaining five corner adatoms, as quantified below.

The furthest distance between two silicon corner-adatoms at a single corner-hole is  $13.4 \text{ \AA}$ . The observed distributions indicated that repulsion must operate over at least  $13.4 \text{ \AA}$  for the three physisorbed and four chemisorbed OPCH patterns examined. In all cases, single occupancy at a corner-hole was favored by a factor  $>25$  as compared with two or more adsorbates appearing at the same corner-hole. This distribution is highly statistically significant,  $p \approx 7 \times 10^{-5}$ , compared with the same results arising from random events.<sup>27</sup>

The OPCH pattern is also discernible, in light of the present observations, in the chlorination of the Si(111)-7×7 surface by trichloroethylene in the STM work of the Patitsas group.<sup>28,29</sup> The exposure was insufficient to reveal the OPCH pattern, but a preference for reaction at corner adatoms leading to a product separation of  $30 \text{ \AA}$ , was observed. The indication from all five chemically different adsorbates (trichloroethylene<sup>28,29</sup> and the four molecules examined here) is that the molecular physisorption of organic halides on Si(111)-7×7 gives a strong preference for OPCH physisorption and hence, subsequently, OPCH surface-halogenation.

For the three cases of 1,2-dibromoethane, 1-bromopropane, and 1-bromopentane, both the physisorbed and the resultant chemisorbed OPCH patterns were imaged. Extensive measurements for 1,2-dibromoethane showed that physisorption and subsequent chemisorption coverage was linear with dose until saturation at  $\sim 80\%$  OPCH, after which no further molecules physisorbed.<sup>27</sup> It appears that beyond this coverage, repulsive interactions between OPCH-physisorbed 1,2-dibromoethane at adjacent occupied corner-holes (not adjacent corner adatoms, as described above) prevented further attachment at the adatoms of remaining unoccupied corner-holes.



**Figure 3.** Chemisorbed Br–Si (one-per-corner-hole) repels physisorbed 1,2-dibromoethane(ad). (a) 300 K STM image ( $\sim 210 \times 210 \text{ \AA}^2$ ,  $V_s = +2.7 \text{ V}$ ,  $I_t = 0.2 \text{ nA}$ ) showing chemisorbed Br one-per-corner-hole, OPCH, coloring as Figure 1. After cooling to 110 K and further exposure to  $\sim 0.4 \text{ L}$  1,2-dibromoethane(g), the surface was re-imaged: (b) different area 110 K STM image ( $\sim 210 \times 210 \text{ \AA}^2$  in size,  $V_s = +2.8 \text{ V}$ ,  $I_t = 0.2 \text{ nA}$ ). In addition to brominated corner-hole adatoms we now also see physisorbed 1,2-dibromoethane(ad) (dim spots, circled by small solid white lines) in OPCH adsorption (outlined with dotted black lines) and also on middle adatoms. Only in one exceptional case, circled by a dotted blue line, did 1,2-dibromoethane(ad) and Br adsorb around the same corner-hole on corner Si-adatoms. 1,2-dibromoethane(ad) prefers to adsorb at corner-holes that did not previously contain Br-adatoms.

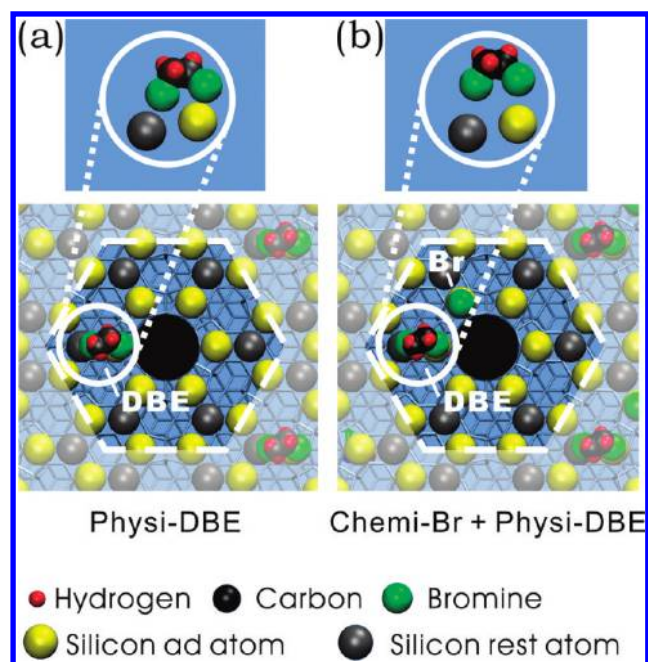
The overwhelming preference for OPCH patterns of physisorption (Figure 1a–c) and chemisorption of Br-atoms (Figure 1a', b', c' and 2b) implies a mobile physisorbed precursor.<sup>27</sup> Mobile precursors were first directly imaged by Brown, Moffatt, and Wolkow, for benzene on Si(111)-(7×7) at 78 K.<sup>30</sup> Adsorption in the absence of a mobile state would have resulted in random patterns of attachment as shown for chemisorbed bromobenzene (Figure 2a), rather than OPCH (Figure 1a–c).

Figure 1 shows the same patterns of physisorption and chemisorption consistent with “localized atomic reaction”, previously reported for halides reacting with silicon. A theoretical analysis<sup>26</sup> attributed this to concurrent breaking of an old bond and formation of a new bond.<sup>31,32</sup> Such “concerted” reaction can only occur locally.

Mobile physisorbed precursors react locally at different corner holes to yield chemisorbed Br-atoms. Further physisorbed molecules arriving at the same corner-hole are repelled by previously physisorbed molecules as evidenced in Figure 1a–c or, as will now be shown, by a reacted Br-atom.

For the case of 1,2-dibromoethane, we show directly that chemisorbed Br-atoms repel physisorbed molecules (Figure 3). A silicon surface was partially brominated with Br-atoms distributed OPCH, using a moderate dose of 1,2-dibromoethane (Figure 3a). The surface was then cooled to 110 K, and further dosed with 1,2-dibromoethane which physisorbed. The OPCH pattern was thereupon simultaneously observed for both chemisorbed Br-atoms and physisorbed 1,2-dibromoethane molecules, coexistent at the surface (Figure 3b). (Thermal bromination by 1,2-dibromoethane would confuse this picture, but the thermal rate of reaction was negligible at  $110 \text{ K}$ .<sup>27</sup>)

In this dual adsorbate experiment it was found exceptionally that some corner Si-adatom sites were occupied by both chemically attached Br-atoms and physisorbed 1,2-dibromoethane molecules. However, single occupancy was overwhelming ( $93 \pm 8\%$ ,  $N = 165$ ) compared with multiple occupancy ( $7 \pm 2\%$ ,  $N = 165$ ).<sup>27</sup>



**Figure 4.** Chemisorbed Br repels 1,2-dibromoethane (DBE) at a single corner-hole of Si(111)- $7\times 7$ . Physisorbed 1,2-dibromoethane (a) in the absence of a coadsorbed Br-atom and (b) in the presence of a coadsorbed Br-atom. Top panels show side-views, bottom panels show top-views. In both cases, 1,2-dibromoethane is physisorbed above a corner silicon-adatom (yellow), and a silicon-restatom (gray) pair as is particularly evident in the side-view above. The physisorbed 1,2-dibromoethane is repelled from the surface by a Br-atom (green) chemisorbed on an adatom of the same corner-hole (as shown, positioned at the top-left corner adatom). In the presence of a chemisorbed Br-atom the physisorbed 1,2-dibromoethane moves almost 1.0 Å further from the surface. The silicon substructure is shown in wire-frame and the corner-hole is shown as a black disk. A hexagonal unit-cell of the Si(111)- $7\times 7$  surface is outlined with a white dashed line that passes through the centers of all Middle adatoms.

This evidenced a substantial repulsion between chemisorbed Br-atom and mobile 1,2-dibromoethane(ad) at the same corner-hole.

We have used the Arrhenius expressions to estimate the differences in activation energies required to reproduce the observed ratios of occurrences of single and much less probable multiple adsorption.<sup>27</sup> The activation energy for the second physisorption at a corner-hole with a previous physisorbed molecule or chemisorbed Br-atom was calculated to be  $\Delta E = 15\text{--}30$  meV greater than for the first physisorption, depending on the nature of the physisorbed halide<sup>27</sup> (1,2-dibromoethane, 1-bromopropane or 1-bromopentane).

**3.2. Theory.** Calculations were made for our principal exemplar, 1,2-dibromoethane. In the gas phase, 1,2-dibromoethane exists as both *gauche* and *trans* rotational isomers; *gauche*-1,2-dibromoethane is 10% of the total population, and is excited by  $73 \pm 5$  meV relative to *trans*-1,2-dibromoethane.<sup>33</sup> This energy difference, together with our calculated (DFT-D) physisorption energies for *gauche*-1,2-dibromoethane ( $-392$  meV) and *trans*-1,2-dibromoethane ( $-256$  meV) allowed us to calculate that at 300 K in equilibrium at the Si(111)-( $7\times 7$ ) surface *gauche*-1,2-dibromoethane was 96% of the total physisorbed population, which increased to 99.9% at 110 K; all further analysis assumed that the only rotational isomer present at the silicon surface was *gauche*-1,2-dibromoethane.



**Figure 5.** Isodensity charge difference contours around the corner-hole (black disk) of Si(111)- $7\times 7$  occupied by a single Br located on a corner adatom. The difference in charge distributions is for a clean silicon surface, and a silicon surface with a chemisorbed Br-atom. Isosurfaces contours of electron density differences are drawn at  $\pm 5 \times 10^{-4} \text{ e}/\text{\AA}^3$ , using cyan for electron density gain, and magenta for electron density loss. The Br-atom (green) is positioned at the top-left corner-adatom and draws charge from all the corner-hole adatoms and neighboring rest-atoms. Surface silicon atoms are shown with van der Waals radii. Silicon-adatoms are shown in yellow, all other Si-atoms are shown in gray. The position of the Br-atom within the electron-gain isosurface is indicated with a green disk. One hexagonal unit-cell of the surface is outlined with a hexagonal white dashed line passing through the centers of all Middle adatoms, the white dashed circles corresponds to the dashed circles shown on the STM images of Figures 1, 2, and 3.

The ab initio physisorption configurations for 1,2-dibromoethane at Si(111)- $7\times 7$  was determined by placing the C–C bond of 1,2-dibromoethane 3 Å above, and parallel to both a clean silicon surface, and a prebrominated surface, at the position determined from STM imaging.<sup>27</sup> The molecule, three surface silicon layers (ad-atoms, rest-atoms, and the first half bilayer beneath) and Br (when present) were then relaxed until the forces on individual ions were below 0.02 eV/Å. The resulting geometries are shown in Figure 4.

We also simulated, ab initio, coexisting chemically attached Br-atoms and physisorbed 1,2-dibromoethane molecules at a single corner-hole of the Si(111)-( $7\times 7$ ) surface. The physisorption energies in the presence and absence of a chemisorbed Br-atom were calculated at the smallest and greatest separations between adatoms at a corner-hole (see below).

The physisorption geometry of the more stable *gauche*-1,2-dibromoethane (rather than *trans*-1,2-dibromoethane, see Methods: Theory and ref 27) was obtained from an analysis of height profiles averaged from multiple STM images obtained at 110 K.<sup>27</sup> The measured configuration has one Br-atom above a corner silicon-adatom and the other Br-atom above the adjacent silicon rest-atom. It agrees with that calculated ab initio (see Figure 4).

Initial DFT calculations with a six-layer supercell (200 Si-atoms) found no effect greater than the expected error of integration ( $\sim 10$  meV). We needed a Si(111)-( $7\times 7$ ) unit-cell of eight silicon layers thickness (298 Si-atoms),<sup>27</sup> in order to reproduce the experimentally observed long-range repulsion. For *gauche*-1,2-dibromoethane adjacent to a chemically attached Br-atom, the calculated physisorption energy decreased (DFT with van der Waals) by some 200 meV, a measure of the interadsorbate repulsion, in the presence of the chemisorbed Br. At the same



time, the 1,2-dibromoethane, was lifted by almost 1.0 Å from its unperturbed physisorbed height over the surface. This is shown in Figure 4, in which a hexagonal unit-cell of the Si(111)-(7×7) is highlighted, and the 1,2-dibromoethane shown in top and side-views. (The relationship between the coordinates of the hexagonal unit-cell and the more usually pictured rhombohedral unit-cell were given by Tong et al., Figure S5;<sup>34</sup> see ref 27).

To analyze the nature of the repulsive interaction, we calculated the energy, charge distribution, and projected partial-densities of states (p-DOS) for physisorbed 1,2-dibromoethane at the surface, and then added a Br-atom to the surface to observe the resultant changes in these quantities. A Bader charge-analysis<sup>35,36</sup> showed that the major effect of the chemisorbed Br was to withdraw electron-charge from the surface, by removing it from all of the adatoms around the corner-hole. The electron-charge flow that results from a chemisorbed Br-atom is shown in Figure 5 (a, electron density gain and b, electron density loss). A p-DOS analysis further showed that the charge redistribution caused by chemisorbed Br prevented the hybridization of the surface with the 1,2-dibromoethane. Such lateral charge transfer was occasionally imaged directly when we had a special tip-state [See Supporting Information, Figure S6].

The decrease in physisorption energy of 1,2-dibromoethane due to a chemisorbed bromine atom at the same corner-hole as the 1,2-dibromoethane was calculated at ~200 meV irrespective of relative position (at adjacent corner adatoms or opposed corner adatoms) provided only that the interaction occurred at a single corner-hole. This decreased physisorption energy for the second adsorbate at a corner-hole correlates with the increased activation barrier to adsorption ( $\Delta E = 15$  meV) obtained, above, from the Arrhenius expression.

#### 4. CONCLUSIONS

Our experiments give evidence of repulsion between physisorbed brominated hydrocarbons at Si(111)-(7×7) and also between chemisorbed Br and these physisorbed species. This repulsion acted over at least the 13.4 Å that separates the corner adatoms at opposite sides of the same corner-hole. It was calculated ab initio for the case of a Br-atom repelling physisorbed 1,2-dibromoethane at the same corner-hole, to be ~200 meV in magnitude.

The result of long-range repulsive interaction was a preference for physisorption and subsequent chemisorption of bromine-containing organic molecules in a spaced out “one-per-corner-hole” pattern on Si(111)-(7×7). The statistical significance of the observed OPCH patterns was extremely high, the probability of obtaining the same pattern randomly was  $p \approx 7 \times 10^{-5}$ .

Theoretical analysis showed that the OPCH patterns resulted from charge flow between the adatoms at a corner-hole of Si(111)-(7×7). This previously unremarked repulsive interaction, due to charge flow across the surface, is likely to be a general property of halogenation at a Si(111)-(7×7) surface.

The ability to achieve regular separation between adsorbates should be of value in molecular beam epitaxy, en route to controlling doping in solids. If dopant levels are one per billion and the device has features that are only 1 billion atoms in extent, then there is a 50% chance that a component is dopant-free. There is, therefore, applied interest in the regular spacing of potential dopant molecules in layer-by-layer construction of nanodevices.

#### ■ ASSOCIATED CONTENT

**S Supporting Information.** Site-selective adsorption, relationship between OPCH coverage and exposure, evidence that OPCH chemisorption is precursor-mediated, limits for activation energies for bromination and desorption of 1,2-dibromoethane (ad), statistical analysis of pattern probabilities, differences in activation energies for the observed OPCH distributions, assignment of physisorption geometry on the basis of height profiles, STM images visualizing the lateral charge transfer, calculated energetics of physisorption, partial projected densities of states analysis of charge flow, atomic coordinates of Si(111)-7×7 unit cell geometries developed for this work, and complete ref 22. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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