

# Effect of Alkyl Chain-Length on Dissociative Attachment: 1-Bromoalkanes on Si(100)-c(4×2)

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## Supporting Information

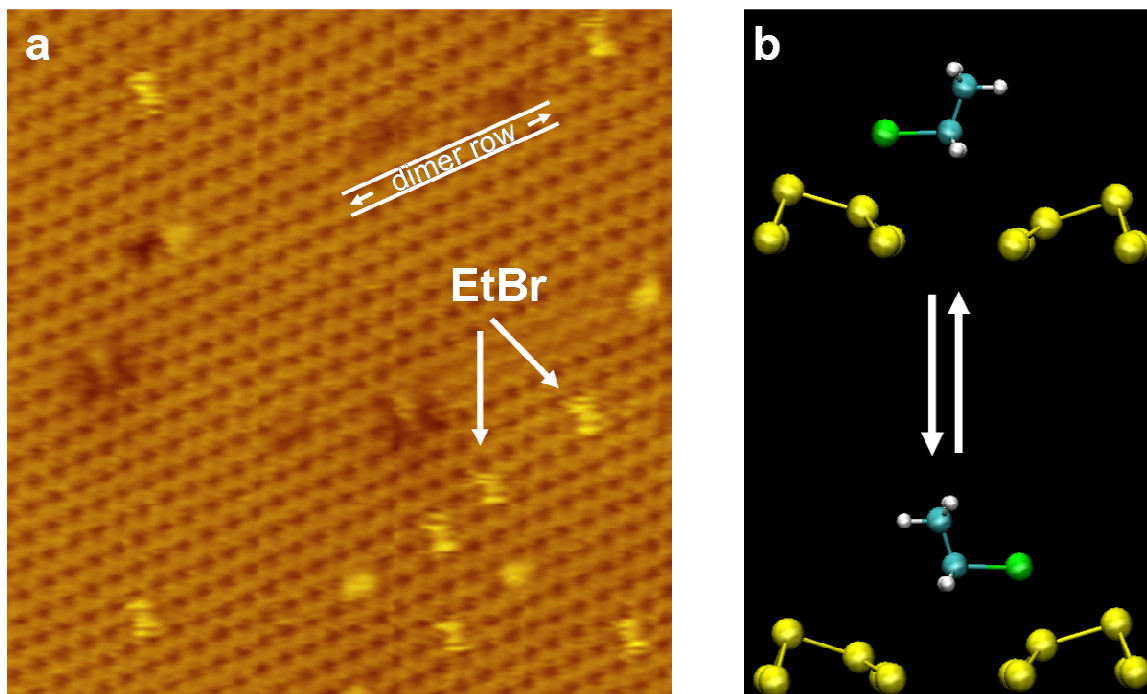
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## SI 1 STM Imaging behaviors of physisorbed 1-bromoalkanes on Si(100)-c(4×2)

We note that in all three cases the physisorbed molecules were only observable in our empty-state (positive surface bias) images. In filled-state images (negative surface bias) the molecules are invisible. This is understandable for the case of EtBr on Si(100)-c(4×2), in light of the early UPS study.<sup>1</sup> According to this early study, all electronic bonding states that originate from EtBr are more than 4 eV below the Fermi level, and are therefore inaccessible over the typical bias range used in STM imaging of silicon ( $V_{\text{sample}} = -0.6$  V to  $-3.0$  V). It is reasonable to suppose that the invisibility of PrBr and BuBr in our filled-state images indicates that they also have no accessible states within  $-3$  V of the Fermi level. Similar imaging behavior as seen by STM was also reported for 1,4-cyclohexadiene on Si(100)-c(4×2) at 80 K.<sup>2</sup>

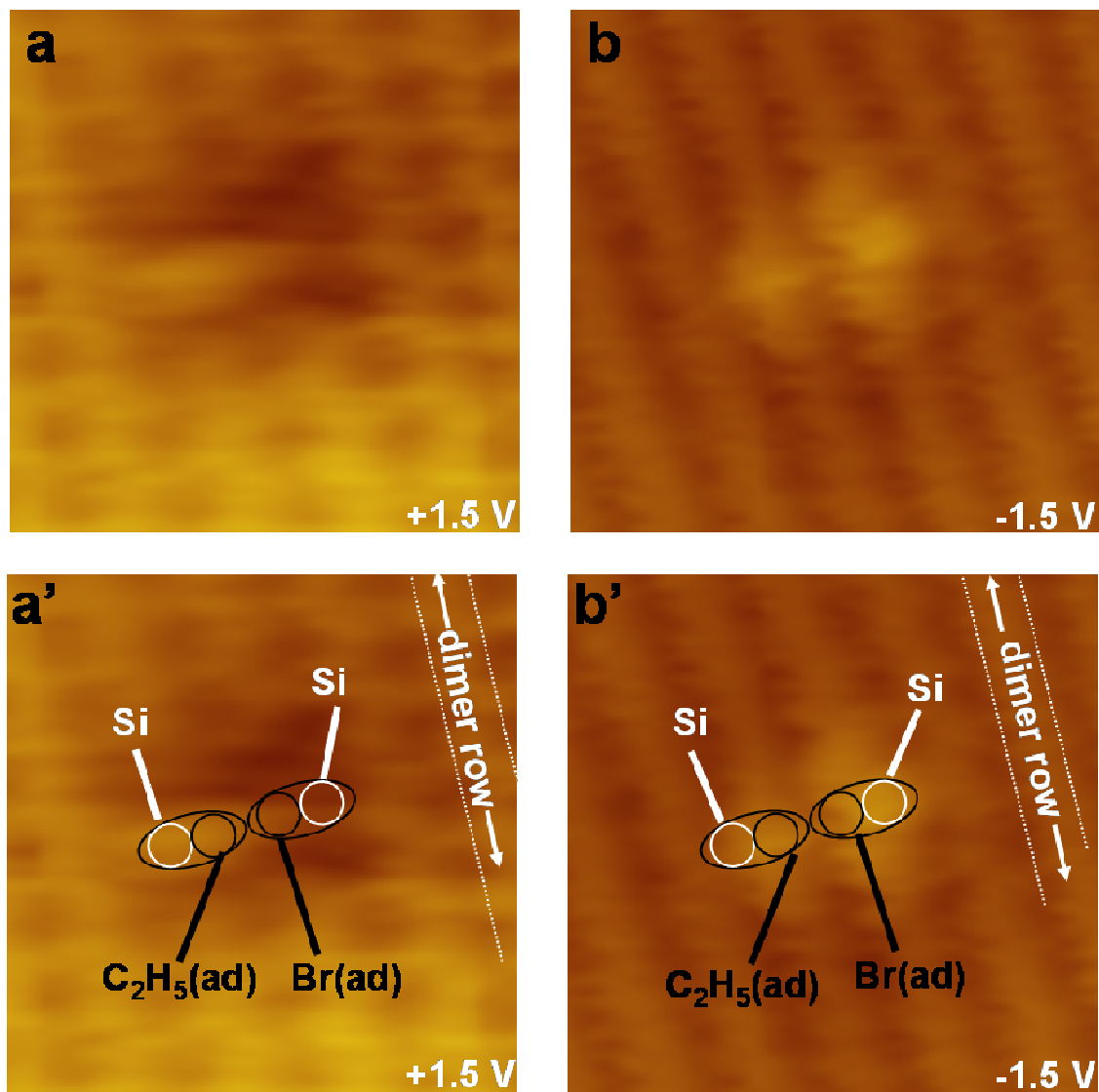


**Figure S1** (a) an STM image (size of  $\sim 207 \times 215 \text{ \AA}^2$ ,  $V_{\text{sample}} = +1.1$  V,  $I = 0.2$  nA; a small drift at the top left is not corrected) taken after an exposure of bromoethane (EtBr) at 100 K. In (a), physisorbed EtBr molecules were imaged as bright fuzzy features that may associate to a reversible switching process as shown in (b).

Physisorbed 1-bromoalkanes on Si(100)-c(4×2) at low temperatures were captured in our empty-state STM images as bright features, symmetric both along and across Si dimer row direction. In our measurements at a very quiet condition, we observed fuzziness associating with these bright physisorption features, as shown in Figure S1(a) for the case of EtBr. This fuzziness is usually interpreted as an adsorbate motion of comparable rate as our imaging speed (~10 ms per scan line, that is ~200 nm/s).

This observed fuzziness may explain a discrepancy regarding the physisorption state of 1-bromoalkane between experiment and theory. Whereas STM imaged the physisorption state as symmetric bright features, ab initio calculations consistently gave the most stable configuration asymmetric across the dimer row direction, e.g. bromine at left and alkyl at right in Figure 4 of the main manuscript, first column. We speculate that this discrepancy is due to a reversible switching process, as indicated by the observed fuzziness in our STM images. As shown in Figure S1(b), such a fast switching motion (likely a rotation) between two equivalent physisorption geometry could give the apparent symmetric (fuzzy) appearance in our STM measurement. Assuming an Arrhenius (thermal) behavior and a prefactor of  $10^{13} \text{ s}^{-1}$ ,<sup>3</sup> we could estimate the switching barrier as ~200 meV. The assumed thermal nature of this process is pending on a more careful examination on the dependence of switching rate on temperature, sample voltage, tunneling current and tip height. The same fast reversible switching motion was argued to explain the symmetry discrepancy between STM imaging and UPS spectra in studying 1,4-cyclohexadiene on Si(100)-c(4×2).<sup>2</sup>

## **SI 2 Product fragment assignment**



**Figure S2** High resolution images of reaction products from bromoethane on Si(100)-c(4×2) at 100 K. Images are  $\sim 50 \times 50 \text{ \AA}^2$  in size. Imaging parameters are as following: (a)  $V_{\text{sample}} = +1.5 \text{ V}$ ,  $I_t = 0.1 \text{ nA}$ ; (b)  $V_{\text{sample}} = -1.5 \text{ V}$ ,  $I_t = 0.6 \text{ nA}$ . (a') and (b') are duplicates of (a) and (b), with labels to locate the involved two Si-dimers and individual surface fragments. In (a'), the left Si-atom (adjacent to  $\text{C}_2\text{H}_5$ ) is bright, while the right Si-atom (adjacent to Br) is dark; in (b') the right Si is brighter than the left Si-atom.

Our assignment of the product fragment is based on a careful comparison of the buckling direction of the reacted Si-dimers between our STM images and ab initio calculations, see below.

Figure S2 are a set of high resolution STM images of the reaction products following the dissociation of EtBr. As shown in the empty-stage image as in Figure S2(a) and (a'), the unbonded Si atom adjacent to the bright product fragment is visible, suggesting that the buckling direction of this Si dimer is reversed; by contrast, the buckling direction of the other Si-dimer is preserved, evidencing in the invisible appearance of unbonded Si atom adjacent to the dark product fragment.

In our computation of the final products of DA, such a reversed buckling direction was only observed for the dimer that alkyls attach; the buckling direction was kept for the dimers that Br-atoms attach, see Figure 4 of the main manuscript. This is remarkable as the two bonded Si atoms began as down Si atoms before structure relaxation in all of our trial configurations. Hence, we assign the bright and dark fragment in our empty state images as alkyl and bromine, respectively. On the same Si(100) surface, the reverse of buckling direction of Si dimers was also reported for the Si-dimers to which CH<sub>3</sub> groups attach.<sup>4,5</sup>

This assignment is also supported by our filled-state images. At a sample bias of -1.5 V, as shown in Figure S2(b) and (b'), the unbonded Si atom images brighter adjacent to Br-atom than adjacent to alkyl. As the Si adjacent to Br-atom stays as an up Si-atom, it is expected to be higher than the Si adjacent to alkyl. This is in line with the typical filled-state STM images from our laboratory following the DA of CH<sub>3</sub>Cl<sup>4</sup> and CH<sub>3</sub>Br<sup>5</sup> on Si(100). It was also found that the Si-atom adjoining surface halogen atom appeared brighter than the Si-atom beside methyl.

### **SI 3 Evidence of negligible tip-induced effect in measuring barrier height**

A known problem in determining rates by STM is that reactions may be caused by the process of observation: that is by the STM tip itself, either by electron-induced or field-induced processes.<sup>6</sup> For the present measurements we were able to conclude that the influence of the measurements was negligible, on the basis of the following two arguments.

First, we used a self-consistency check; using the measured rate of reaction and the final number of reacted molecules, we back-calculated to determine the original physisorbed population at the start of the measurement. If a measurement effect existed then the measured rates would be increased hence back-extrapolation from the final measurement, using the measured rate of reaction would give a markedly different calculated total number of initial physisorbed molecules. No such discrepancy was found within the statistical uncertainties.

Second, we checked for a possible tip-induced effect directly at lower temperatures where thermal reaction was negligible. Tip-induced reactions, as determined by the nature of electronic excitation or electric field, are expected to be insensitive to temperature. If there was a tip effect in our thermal rate measurements, we would observe the dissociations at any temperatures by using the same scanning parameters. However, no detectable reactions were observed in our preliminary tests of EtBr at 50 K (rather than 100 K in thermal rate measurement), and PrBr at 100 K (rather than 123 K in thermal rate measurement). It follows again that the tip-induced effect is negligible in our thermal rate measurements.

#### **SI 4 DFT and DFT-D calculation details**

Compared with the results by DFT-D method as presented in the main manuscript, standard DFT calculations gave similar geometries for initial physisorption state, transition state and final chemisorbed states, with alkyl chain slightly further from the surface plane. The relevant energies by our standard DFT calculations are given in Table S1 to compare with values from DFT-D and experiments.

**Table S1 Energetics**

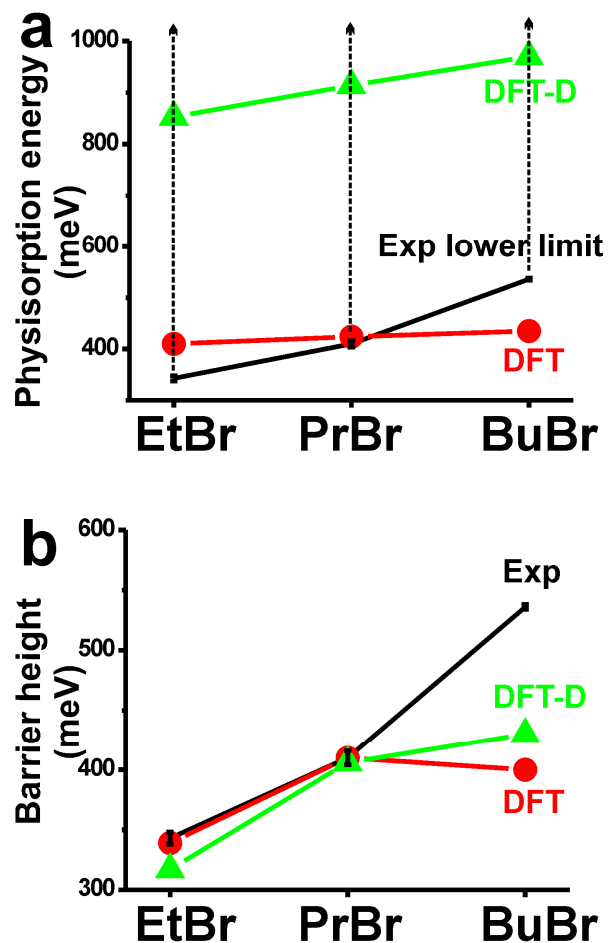
		EtBr	PrBr	BuBr
Physisorption energy (in meV)	Experiment	$>343\pm5$	$>410\pm6$	$>536\pm2$
	DFT	410	424	435
	DFT-D	853	914	970
Barrier (in meV)	Experiment	$343\pm5$	$410\pm6$	$536\pm2$
	DFT	339	410	400
	DFT-D	317	406	430
Chemisorption energy (in eV)	DFT	2.306	2.338	2.341
	DFT-D	2.802	2.856	2.874

The physisorption energies computed using standard DFT and DFT-D methods are quite different. As expected, the DFT-D method gives significantly greater physisorption energies. In Figure S3(a) the computed energies are compared with *lower limits* to the physisorption energies derived from experiment. The DFT-D energies are within the experimental range for all molecules, while DFT energies badly underestimate the physisorption energy for BuBr. Standard DFT gave physisorption energies of 424 meV for PrBr and 435 meV for BuBr, which are too close to the corresponding DA barriers of 410 meV for PrBr and 435 meV for BuBr. Such similar values for

physisorption energy and reaction barrier would lead to comparable rates for desorption and reaction, in contradiction to experiment. The computed physisorption energy by DFT of 435 meV for BuBr was even smaller by 101 meV than the lower limit of  $536 \pm 2$  meV from experiment. Also, standard DFT did not give the anticipated difference in physisorption energies along the 1-bromoalkane series. Within the integration uncertainty of  $\sim 10$  meV, the physisorption energies calculated by DFT were identical for all three 1-bromoalkanes: 410 meV for EtBr, 424 meV for PrBr and 435 meV for BuBr. This is in contradiction with our anticipation on the basis of a number of previous studies that measured the heat of adsorption as a function of alkyl chain-length and all found an increase of 50~100 meV per  $\text{CH}_2$  group for 1-bromoalkanes on Cu(111),<sup>7</sup> 1-bromoalkanes on GaAs(110),<sup>8</sup> alkanes on Cu(111),<sup>9</sup> alkanes on Pt(111),<sup>9</sup> alkanes on  $\text{TiO}_2(110)$ ,<sup>10</sup> 1-alcohols on Ag(110),<sup>11</sup> and 1-alcohols on  $\text{TiO}_2(110)$ .<sup>12</sup>

The trend in increasing activation energies with alkyl-chain length is better matched by DFT-D as shown in Figure S3(b), which appears to do slightly better for activation energies, and much better for physisorption energies, as might have been anticipated.





**Figure S3** (a) Computed physisorption energies by both DFT and DFT-D methods for EtBr, PrBr and BuBr on Si(100)-c(4×2) are compared with experimentally derived lower limits; (b) Computed barrier heights by both DFT and DFT-D methods are compared with experimentally measured values. For both panels, only relative uncertainties from fitting into the Arrhenius formula assuming a common prefactor of  $10^{13}$  Hz are given for experimentally derived values. The absolute uncertainty is estimated as 50 meV, using a wider range of  $10^{13\pm2}$  s<sup>-1</sup> for the prefactor; but such an uncertainty should be the same for all three cases and hence does not affect the relative energies that are the main interest of this paper. See main text for details.

### SI 5 Quantum zero-point energy effect on computed barrier height

In our DFT calculations, we also investigated the effects of quantum zero-point energies on computed barrier heights, using the Dynamical Matrix method of Henkelman et al.<sup>13</sup> We found that the zero-point energy corrections only slightly reduced the thermal barriers of DA by 49 meV for EtBr, 43 meV for PrBr, and 38 meV for BuBr – an

identical shift within the expected integration errors. The zero-point energy shifts do not affect the calculated barrier differences that are the main interest of this work.

We were limited by the high cost and code-compiling issues to perform such computations for the quantum zero-energy effect with DFT-D method. However, similar to the geometries by DFT, our DFT-D calculations revealed that all three 1-bromoalkanes share identical geometries of the four-atom reactive center, Si-Br-C-Si, for both initial physisorbed states and transition states. This should also lead to similar zero-point energy corrections for the DA barriers of all three 1-bromoalkanes; and the calculated barrier differences in our DFT-D calculations should not be affected.

**SI 6 Complete author lists for refs 32 and 52.**

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