

# A New Mechanism of Atomic Manipulation: Bond-Selective Molecular Dissociation *via* Thermally Activated Electron Attachment

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**ABSTRACT** We report a new mechanism of (bond-selective) atomic manipulation in the scanning tunneling microscope (STM). We demonstrate a channel for one-electron-induced C–Cl bond dissociation in chlorobenzene molecules chemisorbed on the Si(111)-7 × 7 surface, at room temperature and above, which is thermally activated. We find an Arrhenius thermal energy barrier to one-electron dissociation of  $0.8 \pm 0.2$  eV, which we correlate explicitly with the barrier between chemisorbed and physisorbed precursor states of the molecule. Thermal excitation promotes the target molecule from a state where one-electron dissociation is suppressed to a transient state where efficient one-electron dissociation, analogous to the gas-phase negative-ion resonance process, occurs. We expect the mechanism will be obtained in many surface systems, and not just in STM manipulation, but in photon and electron beam stimulated (selective) chemistry.

**KEYWORDS:** scanning tunneling microscopy · atomic manipulation · negative-ion resonance · electron attachment · thermal excitations

How to overcome the unselective nature of thermal chemistry is one of the major themes of physical science in the last 30 years<sup>1–3</sup> and is likely relevant to the clean green chemistry agenda.<sup>4</sup> Typically state-specific electronic (or vibrational) excitation of the molecule, induced for example by laser irradiation, is set in tension against the thermalization that spreads the energy among the molecular states, desired and undesired.<sup>5–7</sup> But what if thermal excitation and electronic could work together to drive bond-selective chemistry? Atomic manipulation experiments in the STM<sup>8–11</sup> are not just the ultimate limit of nanotechnology—they provide a highly sensitive approach to the elucidation of molecular dynamic processes. To date, such manipulation experiments have been largely confined to set point temperatures, often in the cryogenic regime,<sup>12–15</sup> sometimes at room temperature.<sup>16,17</sup> Here we demonstrate, *via* STM manipulation experiments at variable, elevated temperatures, a new mechanism of atomic manipulation in which thermal

excitation prepares a molecular state for efficient bond-selective cleaving induced by electron attachment. Specifically, we demonstrate a one-electron dissociation process for the C–Cl bond in chlorobenzene molecules chemisorbed on the Si(111)-7 × 7 surface, which shows an exponential dependence on temperature, and associate the measured thermal activation energy with the energy barrier between chemisorbed and physisorbed molecular states at the surface. Electron attachment to this (transient) physisorbed species is believed to lead to efficient production of Cl<sup>−</sup> ions *via* a negative-ion resonance state (*i.e.*, dissociative electron attachment).<sup>18</sup> We therefore have a mechanism whereby the molecule is promoted from its strongly bound chemisorbed state to a more weakly bound physisorbed state, and in this weakly bound state the STM can induce a one-electron, gas-phase-like, dissociative electron attachment event. This one-electron mechanism complements our previously proposed two-electron process whereby the first electron excites the molecule and a second electron causes C–Cl dissociation.<sup>16</sup> It seems that the thermally activated one-electron mechanism proposed here may be quite general and, moreover, applicable beyond the atomic manipulation regime (*e.g.*, in photo- and electron-beam-stimulated reaction schemes).

## RESULTS AND DISCUSSION

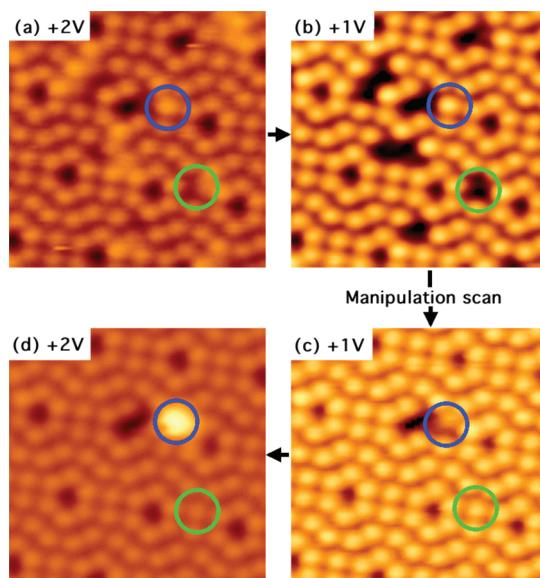
Figure 1 shows a series of STM images of a Si(111)-7 × 7 surface with the typical coverage (0.8 molecules per unit cell) of chlorobenzene molecules (large-scale STM images can be seen in Supporting Information). Images in panels a and b of Figure 1

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**Figure 1.** Sequential STM images ( $80 \text{ \AA} \times 80 \text{ \AA}$ ) demonstrating dissociation of a chlorobenzene molecule on Si(111)- $7 \times 7$ . STM images before manipulation at a surface bias voltage of (a) +2 V and (b) +1 V and afterward at (c) +1 V and (d) +2 V (tunnel current 100 pA). The green circle indicates the adsorption sites of a chlorobenzene molecule, which images dark at +1 V and as a slight protrusion at +2 V and desorbed or dissociated during the manipulation (+3.5 V, 100 pA) scan (not shown). The blue circle indicates the adsorption site of a chlorine atom, dark at +1 V (c) and bright at +2 V (d), that is liberated from a chlorobenzene molecule.

were recorded at surface bias voltages of +2 V and +1 V, respectively, before a scan at +3.5 V that induced both molecular desorption and C–Cl bond dissociation events. Chlorobenzene molecules image as dark features with respect to the silicon adatoms at both +1 V and +2 V.<sup>17</sup> One such molecule is circled in green in Figure 1a,b. Panels c and d of Figure 1 were obtained after the manipulation scan and demonstrate the appearance of a chlorine atom (circled in blue), identified as a dark spot at +1 V (Figure 1c) and a bright spot at +2 V (Figure 1d).<sup>19</sup> From such sets of STM images, taken on a larger scale, we measure the number of chlorine atoms generated, that is, dissociation events,  $N_{\text{diss}}$ , from the difference between the number of bright spots in the images at +2 V before and after manipulation. Similarly, the number of molecules desorbed,  $N_{\text{des}}$ , is found by comparing the number of dark spots in images at +1 V before and after manipulation. Images taken at +1 V were processed using automated software to give the total number of molecules and the total number of adatoms in each image.<sup>20</sup>

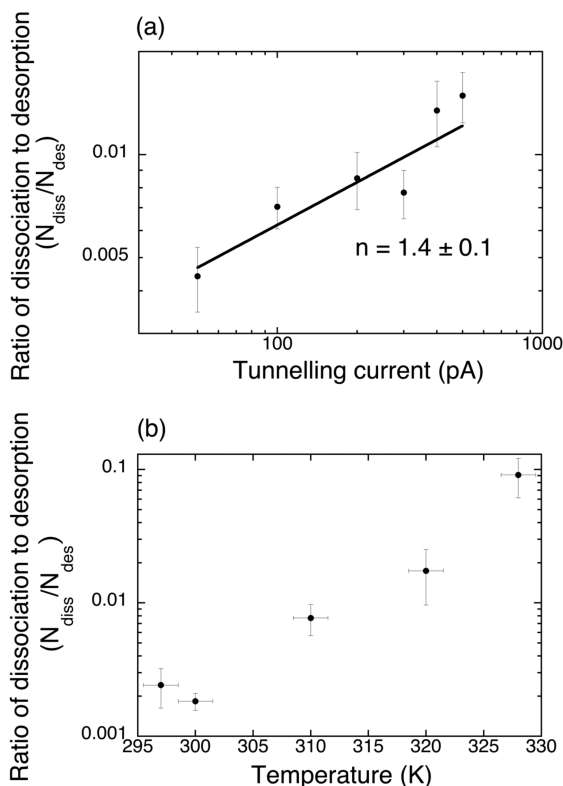
The rate of molecular dissociation on the surface depends on the rate of desorption since the latter depletes the number of chlorobenzene molecules available. Thus we adopt an analytical framework that takes into account both these processes. The rate of dissociation can be written as

$$dN_{\text{diss}}/dt = k_{\text{diss}}N_a(I/e)^n \quad (1)$$

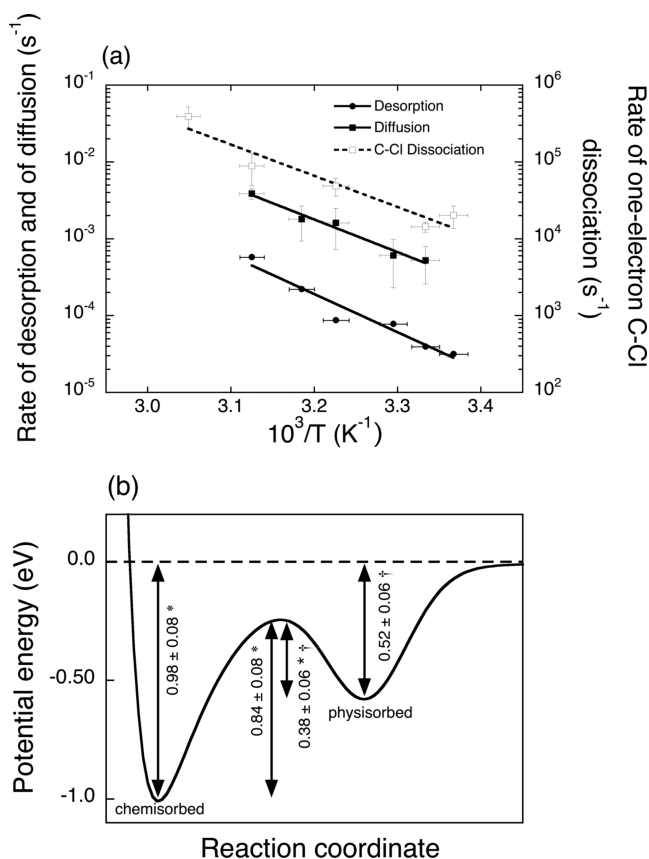
where  $N_{\text{diss}}$  is the number of dissociation events,  $k_{\text{diss}}$  is the dissociation rate,  $N_a$  is the population of chlorobenzene molecules at a given time,  $I$  is the tunneling current during STM manipulation,  $e$  is the electron charge, and  $n$  is the number of electrons required to break a C–Cl bond. Similarly, the rate of desorption, a one-electron process,<sup>21</sup> can be written  $dN_{\text{des}}/dt = k_{\text{des}}N_a(I/e)$ , where  $N_{\text{des}}$  is the number of desorption events and  $k_{\text{des}}$  is the desorption rate. At room temperature, the rate of STM electron-induced desorption for chlorobenzene is  $\sim 10^7$  times higher than the rate of thermal desorption; therefore, we neglect thermal desorption in this particular calculation.<sup>20,21</sup> By integrating the ratio of the rates of dissociation and desorption and taking natural logs, we obtain

$$\ln\left(\frac{N_{\text{diss}}}{N_{\text{des}}}\right) = \ln\left(\frac{k_{\text{diss}}}{k_{\text{des}}}\right) + (n-1)\ln\left(\frac{I}{e}\right) \quad (2)$$

Plotting the left-hand side as a function of tunneling current (at the manipulation bias voltage of +3.5 V), Figure 2a, we find that the number of electrons required for C–Cl bond breaking,  $n$ , is  $1.4 \pm 0.1$ . This result compares with the previously reported value of  $n = 1.8 \pm 0.3$  (i.e., approximately 2), where the analysis did not take into account desorption.<sup>16</sup> Crucially, the value of  $n = 1.4$  means that the measured dissociation events



**Figure 2.** (a) Ratio of dissociation to desorption as a function of the tunneling current at room temperature for a manipulation voltage of +3.5 V. The average number of electrons required to break the C–Cl bond is  $1.4 \pm 0.1$ , from eq 2. (b) Temperature dependence (log plot) of the ratio of dissociation to desorption at +3.4 V, showing an exponential increase.



**Figure 3.** (a) Arrhenius plot (log scale) with fits of the rates of thermal desorption,  $E_{\text{des}} = 0.98 \pm 0.08$  eV,  $A = 10^{12.7 \pm 1.4} \text{ s}^{-1}$ ; of thermal diffusion,  $E_{\text{diff}} = 0.84 \pm 0.08$  eV,  $A = 10^{10.8 \pm 1.3} \text{ s}^{-1}$ ; and of one-electron C–Cl dissociation,  $E_{\text{Act}} = 0.8 \pm 0.2$  eV. (b) Schematic potential energy diagram of chlorobenzene on Si(111)-7 × 7 showing both chemisorbed and physisorbed states with experimental energy barriers from this work (\*) and from ref 24 (†).

are a mixture of a one-electron and a two-electron C–Cl dissociation process. Therefore, our focus is now to establish the nature of the one-electron dissociation channel. Figure 2b demonstrates that the rate of one-electron dissociation depends on the temperature.

On the assumption that the rate of two-electron dissociation is independent of temperature (see below), also consistent with the proposed vibronic coupling mechanism,<sup>16</sup> the temperature dependence of the chlorine production rate Figure 2b shows that the one-electron process is coupled to the thermal excitation. Figure 2b plots the ratio of STM dissociation to desorption, but the STM desorption rate is very weakly temperature-dependent.<sup>20</sup> Moreover, Figure 2b is a log plot, so the STM temperature dependence of one-electron STM dissociation is approximately exponential, consistent with a thermally activated, Arrhenius-type mechanism.

To extract quantitative parameters from Figure 2b, we need to separate the temperature-dependent one-electron process and the temperature-independent two-electron process in the description of the kinetics of dissociation. Thus, we rewrite eq 1 as

$$\frac{dN_{\text{diss}}}{dt} = k_{\text{diss}}^{1e} N_a \left(\frac{l}{e}\right) \exp\left(\frac{-E_{\text{Act}}}{k_B T}\right) + k_{\text{diss}}^{2e} N_a \left(\frac{l}{e}\right)^2 \quad (3)$$

where  $E_{\text{Act}}$  is the energy barrier that must be overcome thermally to activate one-electron dissociation,  $k_B$  is Boltzmann's constant,  $T$  is the temperature of the substrate,  $k_{\text{diss}}^{1e}$  is the dissociation rate for the one-electron process,  $k_{\text{diss}}^{2e}$  is the dissociation rate for the two-electron process, and  $N_a$ ,  $l$ , and  $e$  are as described above. At elevated temperatures, the rate of desorption term also has to include thermal processes. Therefore, we write  $dN_{\text{des}}/dt = k_{\text{des}} N_a (l/e) + AN_a \exp(-E_{\text{des}}/k_B T)$ , where  $A$  is the pre-exponential factor and  $E_{\text{des}}$  is the energy barrier to desorption. The key to determine the physical cause of the one-electron thermally activated C–Cl dissociation lies in the  $E_{\text{Act}}$  energy barrier. Taking the ratio of the rates of dissociation to desorption, integrating and rearranging gives the rate of one-electron dissociation as

$$k_{\text{diss}}^{1e} \left(\frac{l}{e}\right) \exp\left(\frac{-E_{\text{Act}}}{k_B T}\right) = \frac{N_{\text{diss}}}{N_{\text{des}}} \left[ k_{\text{des}} \left(\frac{l}{e}\right) + A \exp\left(\frac{-E_{\text{des}}}{k_B T}\right) - k_{\text{diss}}^{2e} \left(\frac{l}{e}\right)^2 \right] \quad (4)$$

This expression provides a route to translate the data of Figure 2b into a value for  $E_{\text{Act}}$ . We recently reported the temperature dependence of  $k_{\text{des}}$ , the STM desorption rate, and found that it decreases (only) slightly with increasing temperature.<sup>20</sup> In order to determine  $E_{\text{Act}}$ , we therefore have to find  $A$  and  $E_{\text{des}}$ , the parameters governing pure thermal desorption.

We thus measured the surface coverage as a function of time at seven temperatures from 289 to 320 K using scanning parameters that are strictly passive (+1 V, 100 pA).<sup>20</sup> As expected, the number of molecules decreases with time and the rate of desorption increases with increasing temperature. Figure 3a shows an Arrhenius plot of the rate of desorption with exponential fit giving an energy barrier to desorption of  $0.98 \pm 0.08$  eV and a pre-exponential factor of  $10^{12.7 \pm 1.4} \text{ s}^{-1}$ . This is in excellent agreement with temperature-programmed desorption (TPD) experiments that gave  $E_{\text{des}}$  as  $1.01 \pm 0.09$  eV (although this relied on the usual assumption of  $10^{13}$  for the pre-exponential factor).<sup>22</sup>

We are now in a position to determine the activation energy of one-electron dissociation. Figure 3a also shows the rate of one-electron dissociation, extracted from Figure 2b according to eq 4 and using the values of  $E_{\text{des}}$  above. The one-electron dissociation rate is shown as an Arrhenius plot, and the exponential fit gives an energy barrier for thermally activated one-electron dissociation of  $E_{\text{Act}} = 0.8 \pm 0.2$  eV. This activation energy is much lower than the C–Cl bond energy of chemisorbed chlorobenzene of 1.9 eV<sup>23</sup> and significantly higher than the vibrational energies of the molecule (40–374 meV). The goodness of fit is also consis-

tent with our assumption that the two-electron dissociation process is temperature-independent. Note that the two-electron dissociation model proposal<sup>16</sup> involved electron-induced excitation of the C–Cl wag mode at 60 meV<sup>22</sup> followed by resonant attachment of the (second) electron to the excited molecule.<sup>18</sup> If this model is correct, it is therefore clear that the thermally activated one-electron process is different because the activation energy is 0.8 eV (not 60 meV). The key question is what process does the energy barrier of  $0.8 \pm 0.2$  eV correspond to?

Chlorobenzene chemisorbs to the Si(111)-7 × 7 surface *via* a physisorbed precursor state.<sup>17</sup> This state is not stable at room temperature, whereas it can be observed in STM at cryogenic temperatures.<sup>24</sup> Could thermal excitation to this physisorbed precursor create a short-lived state sufficiently decoupled from the surface to enable one-electron dissociation to occur, by analogy with the free molecule?<sup>18</sup> If so, the thermal energy barrier to one-electron C–Cl bond dissociation should reflect the energy barrier between the chemisorbed and physisorbed states of chlorobenzene on Si(111)-7 × 7.

To measure the barrier between chemisorbed and physisorbed chlorobenzene, we examined the rate of thermally excited molecular diffusion as a function of temperature, which in the case for benzene on the Si(111)-7 × 7 surface is known to proceed *via* the physisorbed state.<sup>25</sup> Since benzene and chlorobenzene have similar (di-σ) chemisorption configurations, physisorbed precursor states and nearly identical binding energies for both chemisorbed (benzene =  $0.98 \pm 0.06$  eV,<sup>26,27</sup> chlorobenzene =  $0.98 \pm 0.08$  eV) and physisorbed (benzene =  $0.46 \pm 0.01$  eV,<sup>27,28</sup> chlorobenzene =  $0.52 \pm 0.06$  eV<sup>22</sup>) species, it seems reasonable that chlorobenzene molecules also diffuse across the surface *via* thermal excitation to the physisorbed state. The diffusion rate was obtained by comparing a sequence of STM images of precisely the same surface area (as used above to determine the desorption barrier). Sites originally empty before but filled after a time interval were attributed to a thermally induced diffusion event. Figure 3a includes an Arrhenius plot of the rate of thermally excited molecular diffusion as a function of temperature, from which an energy barrier of  $0.84 \pm 0.08$  eV and a pre-exponential factor of  $10^{10.8 \pm 1.3}$  s<sup>-1</sup> are derived. It is evident that this energy barrier for

thermal diffusion, which we assign to the barrier from chemisorbed to physisorbed state, is very close to our measured activation energy for thermally activated one-electron dissociation,  $0.8 \pm 0.2$  eV.

Figure 3b draws our data together and presents a schematic representation of a (one-dimensional) potential energy curve for chlorobenzene on Si(111)-7 × 7, which includes both chemisorbed and physisorbed states. By coupling our measurements here with TPD experiments,<sup>22</sup> we also deduce the barrier from physisorbed to chemisorbed of  $0.38 \pm 0.13$  eV, which is comparable with that directly measured for benzene on Si(111)-7 × 7 of  $0.30 \pm 0.03$  eV.<sup>24</sup> The thermal activation of the one-electron C–Cl dissociation channel naturally correlates with the molecular transition from chemisorbed to physisorbed states. This interpretation also implies that STM dissociation of the stabilized physisorbed species at cryogenic temperatures should be an efficient one-electron process, and there is some evidence in the literature that this is the case.<sup>29</sup>

## CONCLUSIONS

In summary, we have conducted a close examination of the possible outcomes of both thermal and STM current-induced excitations of chemisorbed chlorobenzene on the Si(111)-7 × 7 surface and thus identified a new mechanism of atomic manipulation in the STM. Thermally activated one-electron dissociation of the C–Cl bond is observed at room temperature and above. The energy barrier of  $0.8 \pm 0.2$  eV for this process matches that from the chemisorbed to the physisorbed state, as measured in thermal diffusion experiments with the STM. We propose that the lifetime of the negative-ion resonance state<sup>30,31</sup> of the physisorbed species is enhanced with respect to the chemisorbed state, allowing the one-electron process characteristic of the free molecule to occur. The generality of the scheme proposed here, and its application beyond atomic manipulation in, for example, electron, photon, and possibly plasma-driven processes, remains to be established by future experimental and theoretical study. However, the concept of weakly bound (physisorbed) precursor states has a good pedigree,<sup>32,33</sup> and the same is true of dissociative electron attachment/negative-ion resonance states,<sup>34</sup> so the prospects of harnessing our mechanism more generally for selective chemistry seem rather strong.

## METHODS

The experiments were performed with an (RHK 400) STM housed in an ultrahigh vacuum chamber with a base pressure below  $1 \times 10^{-10}$  Torr. Tungsten tips were etched by the drop-off technique using a circular gold anode in 2 M NaOH solution with a bias of 9 V. Tungsten oxide was removed by resistive heating in high vacuum.<sup>35</sup> Silicon samples were cut from phosphorus-doped n-type (1–30 Ω cm) wafers of Si(111), degassed at ~600 °C in the UHV chamber for a few

hours before “flashing”, typically for 10 s, to temperatures increasing until 1250 °C. A computer-controlled leak-valve was used to ensure accurate and reproducible dose of the chlorobenzene molecules. A typical dose of 0.3 L onto a room temperature sample produced a coverage of 0.8 molecules per unit cell. The sticking coefficient drops above room temperature,<sup>36</sup> and therefore a larger dose was required at higher temperatures to generate the same final coverage (e.g., 6 L at 310 K).



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**Supporting Information Available:** Example of a set of large-scale STM images showing the dissociation of chlorobenzene molecules. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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