Concerted Thermal-plus-Electronic Non-local Desorption of Chlorobenzene from Si(111)-7×7 in the STM

Tianluo Pan[1], Peter A. Sloan[1, 2] and Richard E. Palmer[1*]

[1]Nanoscale Physics Research Laboratory, School of Physics and Astronomy, University of Birmingham, Birmingham, B15 2TT, U.K.

[2]Department of Physics, University of Bath, Bath, BA2 7AY, U.K.

Corresponding author: R. E. Palmer:

E-mail: [*]r.e.palmer@bham.ac.uk

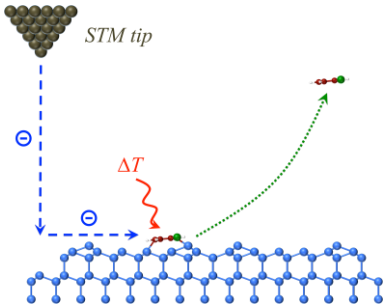
Tel: 0121 414 4653

Fax: 0121 414 7327

Abstract:

The rate of desorption of chemisorbed chlorobenzene molecules from the Si(111)-7×7 surface, induced by non-local charge injection from an STM tip, depends on the surface temperature. Between 260 K and 313 K we find an Arrhenius thermal activation energy of 450 ± 170 meV, consistent with the binding energy of physisorbed chlorobenzene on the same surface. Injected electrons excite the chlorobenzene molecule from the chemisorption state to an intermediate physisorption state, followed by thermal desorption. We find a second thermal activation energy of 21 ± 4 meV in the lower temperature region between 77 K and

260 K, assigned to surface phonon excitation.



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Atomic manipulation in the scanning tunnelling microscope (STM) provides the potential to create and control nanoscale architectures. A thorough knowledge of the manipulation mechanisms at play is essential to realizing this potential. Recently a set of "non-local" reactions has been achieved on various surfaces;[1-13] they are non-local in the sense that molecules far from the tip respond. The chlorobenzene/Si(111)-7×7 system has been used for the elucidation of atomic manipulation mechanisms by both our group and others.[4, 11, 14-21] Here we demonstrate that non-local desorption of the molecules by electron injection depends on the surface temperature. The emerging picture is of "concerted" (i.e., thermal plus electronic) desorption, via electronic excitation of the chemisorbed chlorobenzene molecule to an intermediate physisorbed state from which thermal desorption occurs. This is the inverse of the mechanism of one-electron-induced C-Cl bond dissociation in the same molecule, wherein thermal excitation to the intermediate physisorbed state is followed by electron-induced bond dissociation.[4, 22-23] Moreover, the non-local behaviour in our new mechanism couples quantum charge transport to the concerted molecular dynamics.

Upon adsorption on the Si(111)-7×7 surface, the chlorobenzene molecule will either reside in a physisorption state or a chemisorption state. For the physisorbed chlorobenzene, simulations[24] indicate almost no change in structure compared with that of the free chlorobenzene The distance between the lowest carbon atom of the phenyl ring and the plane formed by the adatoms in the physisorbed state is ~2.2 Å. When the chlorobenzene is deposited onto the surface at room temperature, it chemisorbs onto the Si(111)-7×7 surface surface, forming a 2, 5 di-σ butterfly-like structure, where two opposite carbon atoms of the phenyl ring form covalent bonds with an adatom-rest atom pair.[25-26] The experiments at room temperature and above were conducted with a Beetle-type STM (RHK-400) in an ultrahigh vacuum chamber with base pressure of 8×10^{-11} Torr, while the experiments at low temperature were conducted with a low temperature STM (Omicron LT STM) in a different chamber with base pressure of 2×10^{-11} mbar. The silicon samples were cut from a boron-doped p-type (0.01~0.02 Ω·cm) Si(111) wafer (from Siltronix). Surface preparation and gas dosing proceeded as per Ref. 11 and Ref. 27. The electron injection experiments were performed at a surface bias voltage of +2.7 V. STM images taken under passive condition (+1.0 V, 300 pA) before and after the injection were compared and analyzed. The drift was corrected in the data analysis by the program.

Figure 1 shows some examples of images taken before and after electron injection at two different temperatures, 77 K and 260 K. The corner hole site was chosen as the

injection site (indicated by the white cross), since the probability of non-local desorption is maximized for this site.[11] To avoid thermal drift, the injection time was confined to 8 seconds for the experiments conducted above 293 K. In the lower yield region below 293 K, the injection time was increased to 80 seconds in line with the lower cross-section and reduced thermal drift at lower temperatures. In the STM image, the silicon adatoms image as white spots. The chemisorbed chlorobenzene molecules image as missing adatoms on the surface; after the electron injection, the "clean" Si(111)-7×7 surface is revealed around the injection site, Figure 1. Comparing the images taken before and after the injection at different temperatures, as illustrated in Figure 1, shows that the range and efficiency of the chlorobenzene desorption are both increased dramatically as the temperature is increased. At 77 K most of the chlorobenzene desorption is confined to a radius of ~6 nm, while at 260 K the desorption observed can extend to ~20 nm.

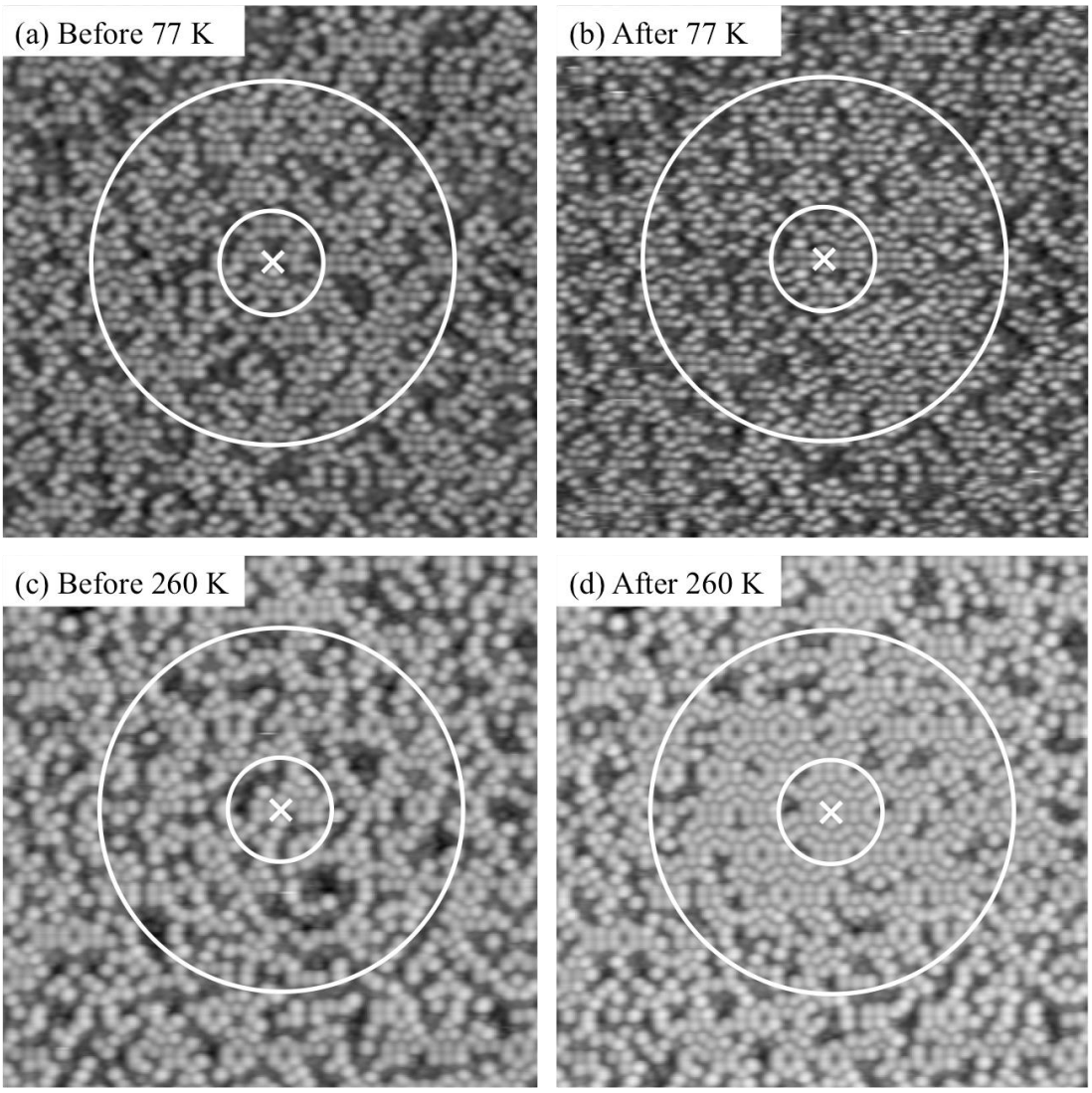

Figure 1. STM images before (a) and after (b) electron injection at 77 K; (c) and (d) similarly for 260 K. Images were taken at +1.0 V, 100 pA; size 30 nm × 30 nm. The electron injections were performed at +2.7 V, 800 pA, for 80 seconds. The white circles indicate the area between 50 Å and 175 Å. The silicon adatoms image as white spots, while chemisorbed chlorobenzene molecules image as missing adatoms. The chosen corner hole sites for the injection sites are marked with white crosses. The concentric white circles have radii of 2.7 nm and 10.8 nm, respectively.

To analyze in detail the temperature-dependent non-local desorption process observed,

images obtained before and after manipulation were processed and compared numerically. Figure 2 is a plot of the non-local desorption ratio, $R(T) = \Delta N/N_{0,}$ as a function of surface temperature for five different temperatures. Here R(T) is the ratio of the number of desorbed molecules ΔN to the total number of molecules N_0. The injection current is 800 pA, for 8 seconds at temperature above 293 K and for 80 seconds below 293 K (where the yields were lower). The R(T) is normalized to the injected charge. For each set of experiments at different temperatures, ~10 injection experiments were performed and averaged. We only plot R(T) between 50 Å and 175 Å, as indicated in Figure 1, due to the presence of the suppression region at small radius. Below 50 Å desorption is suppressed by the tip itself; this will be the subject of a future paper. It is evident for Figure 2 that the non-local desorption ratio increases as the temperature increases. The change in decay length of the non-local desorption with temperature, which relates to the charge transport process, is beyond the scope of this work and will be discussed in a future paper.

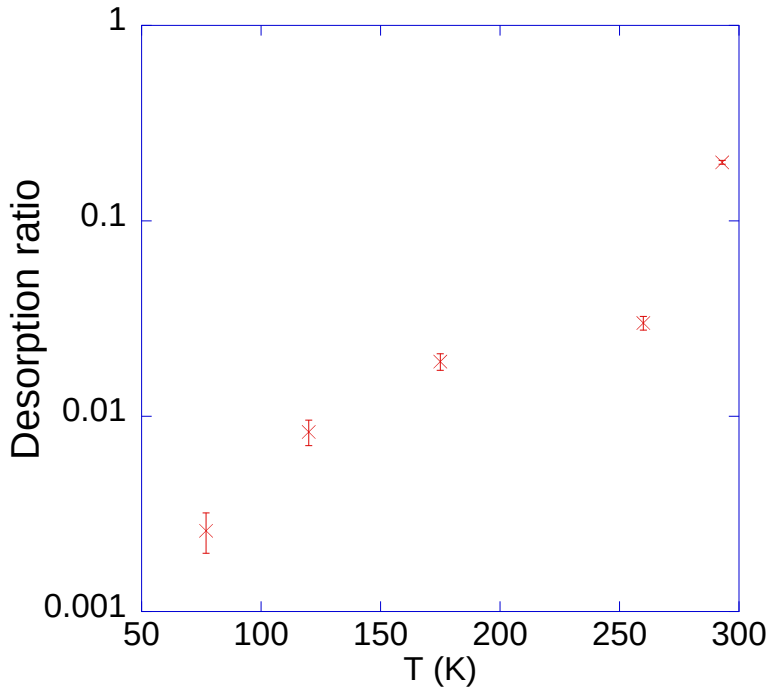

Figure 2. Non-local desorption ratio (logarithmic scale) as a function of surface temperature for five different temperatures. Electron injection was performed at +2.7 V, 800 pA, 8 seconds (for 293 K) and 80 seconds (for 77 K, 120 K, 175 K and 260 K).

Since there is a clear temperature dependence of the non-local desorption process in Figure 2, we present in Figure 3 an Arrhenius plot of the desorption data from Figure 2 (and other temperatures), integrated across the radial range up to 200 Å. The data in Figure 3 naturally falls into two regions: the blue line is an exponential fit to the data at low temperature (77 K, 95 K, 120 K, 175 K, 230 K and 260 K), the red line is an exponential fit to the data at high temperature (260 K, 293 K and 313 K). The green line is the sum of these two exponential fits. The corresponding activation energies obtained from the exponential fits (red dash line and blue dash line) are 450 ± 170 meV and 21 ± 4 meV.

In the higher temperature region, the activation energy E_a = 450 ± 170 meV is similar to the reported binding energy (0.52 ± 0.06 eV)[25, 28] of physisorbed chlorobenzene on Si(111)-7×7. This leads us to propose a new mechanism of concerted "thermal-plus-electronic" non-local desorption. Here the molecule is first excited by electron attachment from the initial chemisorbed state to an intermediate physisorbed state, before thermally activated desorption from this intermediate state occurs (corresponding to the activation energy of the Arrhenius plot). This new mechanism can be compared and contrasted with the previously reported thermally enhanced electron-induced bond *dissociation* process for the PhCl/Si(111)-7×7 system in the STM.[4] In that scheme the molecule is first excited thermally to the intermediate physisorption state from the chemisorbed state, then C-Cl bond cleavage in the physisorbed state is induced by the captured electron. The principle difference between the two electron-driven processes, i.e., thermally assisted desorption and thermally assisted dissociation, is which stage is thermally activated and which is induced by electron capture, thus leading to the quite different thermal activation energies. Moreover we deduce that electron attachment to the proposed intermediate physisorbed state does not couple efficiently to the desorption channel, so that desorption requires the thermal excitation step identified here, whereas dissociative electron attachment to physisorbed molecules is well established in the literature.[29-30] Detailed mechanistic studies of the physisorbed species stabilized at very low temperature would be instructive. Theoretical treatments of the non-adiabatic dynamics of the PhCl molecule in both the physisorbed and chemisorbed state on

Si(111)-7×7 would also be illuminating, building on the recent treatment of the bonding energies.[24]

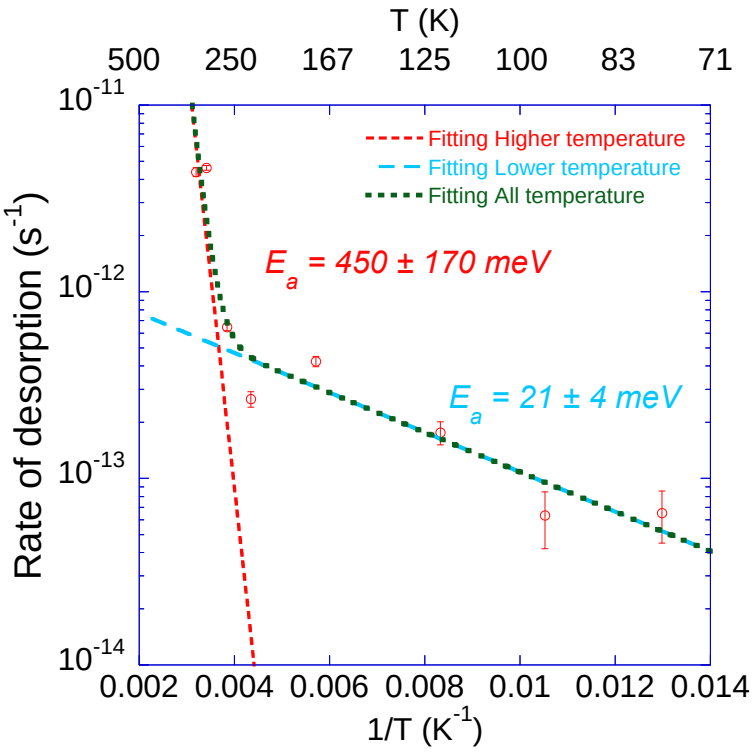

Figure 3. Arrhenius plot of the non-local chlorobenzene desorption data. The red circles represent the measurements performed at 77 K, 95 K, 120 K, 175 K, 230 K, 260 K, 293 K and 313 K. The various line fits plotted are explained in the text (activation energies are marked).

In the lower temperature region (77 K to 260 K), the rate of non-local desorption increases rather slowly as the temperature increases, exhibiting a small activation energy of 21 ± 4 meV. This energy is much lower than the binding energy of the chemisorbed chlorobenzene molecule (~980 meV).[4] However, it is quite close to the energy of surface phonons at adatom sites on the clean surface, which lie between 24

and 41 meV.[31] Since the chlorobenzene molecule is bonded to the surface via adatom and rest atom sites, we tentatively propose that the non-local desorption process is assisted by surface phonon excitation.

In summary, we have reported a systematic study of STM-induced non-local desorption of chlorobenzene from the Si(111)-7×7 surface as a function of surface temperature, which identifies two thermal activation energies. The value of one, at high temperature, 450 ± 170 meV, is in line with the binding energy of the physisorbed molecule state, while the other, at 21 ± 4 meV, lies in the surface phonon region. We propose that in the higher temperature region, non-local desorption occurs via an intermediate physisorbed state, to which the molecule is excited by electron attachment, and from which thermal desorption occurs. This significant thermal enhancement of a molecular process, stimulated and guided by charge injection, substantially increases the efficiency of atomic manipulation by the harnessing of the freely available resources of thermal energy. Much of the work in atomic manipulation has been confined to the low temperature regime. It may be that thermal enhancement of charge-induced manipulation may turn out to be ubiquitous at more elevated temperatures.

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