

Mechanisms of Molecular Manipulation with the Scanning Tunneling Microscope at Room Temperature: Chlorobenzene/Si(111)-(7 × 7)

P. A. Sloan, M. F. G. Hedouin, and R. E. Palmer*

Nanoscale Physics Research Laboratory, School of Physics and Astronomy, The University of Birmingham, Birmingham B15 2TT, United Kingdom

M. Persson

Department of Applied Physics, Chalmers/Göteborg University, S-412 96 Göteborg, Sweden

(Received 9 December 2002; published 9 September 2003)

We report a systematic experimental investigation of the mechanism of desorption of chlorobenzene molecules from the Si(111) – (7 × 7) surface induced by the STM at room temperature. We measure the desorption probability as a function of both tunneling current and a wide range of sample bias voltages between –3 V and +4 V. The results exclude field desorption, thermally induced desorption, and mechanical tip-surface effects. They indicate that desorption is driven by the population of negative (or positive) ion resonances of the chemisorbed molecule by the tunneling electrons (or holes). Density functional calculations suggest that these resonant states are associated with the π orbitals of the benzene ring.

DOI: 10.1103/PhysRevLett.91.118301

PACS numbers: 82.37.Gk, 34.80.Ht, 68.37.Ef, 68.43.Rs

The manipulation of individual atoms and molecules with the STM is one of the great scientific achievements of the last 20 years. Beginning with the lateral manipulation of physisorbed Xe atoms on the Ni(110) surface at cryogenic temperatures [1], Eigler and colleagues have demonstrated how to assemble predesigned, nanometer-scale structures which can be employed to trap electrons in “textbook” quantum boxes [2], or to perform logic operations by sequential electromechanical molecular manipulation [3]. While the extension of such methods to room temperature systems is far from trivial, significant progress has been reported, especially in relation to vertical manipulation, i.e., the STM-induced desorption of surface or adsorbed atoms [4–7]. Underpinning all these examples is the question of the mechanism of atomic manipulation [8,9], not always evident from the experiments and sometimes the subject of controversy [10,11].

In this Letter we bring a combination of systematic experimental investigations and density functional calculations to bear on the problem of the mechanism of desorption of chemisorbed chlorobenzene (C_6H_5Cl) molecules from the reconstructed Si(111)-(7 × 7) surface at room temperature. This model system is also relevant to the interface between molecular electronics and conventional silicon devices [12]. Measurements of the desorption probability over an unusually wide range of both positive and negative sample bias voltages (from –3 V to +4 V) establish asymmetric threshold voltages for desorption. Measurements as a function of tunneling current rule out vibrational heating, electric field, and mechanical (i.e., tip-surface force) mechanisms. We deduce that desorption is driven by the population of negative (or positive) ion resonance states of the chemisorbed

chlorobenzene molecule. Comparison with the density of states (DOS) calculated from density functional theory leads us to propose further that these resonance states are associated with the π orbitals of the molecular benzene ring.

The room temperature STM was housed in a UHV chamber [13] with a base pressure of 1×10^{-10} Torr. The silicon (111) samples, cut from *n*-type and *p*-type wafers 0.38 mm thick, had resistivities of 1–30 Ω cm. To create extremely large (10 000 Å) and almost defect-free terraces, the samples were initially degassed overnight at 700 °C and subsequently flashed for 30 s to temperatures increasing to 1300 °C (by resistive heating). The final step was a flash to 1300 °C for 30 s followed by quick cooling to 960 °C and further cooling ($1 \text{ }^\circ\text{C s}^{-1}$) to room temperature. The STM tips, produced by electrochemical etching (2 M NaOH) of polycrystalline tungsten wire, before electron bombardment in the UHV chamber, were characterized by their field emission properties. Thus electron bombardment was stopped after oxide removal but before the tip apex began to melt appreciably. Chlorobenzene was subject to repeated freeze-pump-thaw cycles before dosing into the vacuum chamber by means of a leak valve. The typical dosage was $50 \text{ s} \times 2 \times 10^{-8}$ Torr (i.e., 1 Langmuir), corresponding to about 0.05 monolayer (ML)—1 ML corresponds to one molecule per 1×1 unreconstructed unit cell of the Si(111) surface [14].

Previous experiments [15] have demonstrated that chlorobenzene can be dissociated on the Si(111)-(7 × 7) surface under an STM tip by the application of (+4 V) voltage pulses to the sample, thereby generating chemisorbed chlorine atoms. We find that the dominant channel of STM manipulation, i.e., desorption versus dissociation,

depends on the condition of the tip, manifest in the imaging of chlorobenzene. A tip which induces dissociation images the molecule as a depression at sample bias voltages of both +1 V and +2 V, whereas a tip which induces desorption sees the molecule as a protrusion at +2 V. It seems possible that one type of tip is itself terminated by an adsorbed atom or molecule [16]. Thus the STM tips were repeatedly pulsed, as required, until the desired imaging characteristics were obtained.

Figure 1 shows a pair of STM images ($100 \times 100 \text{ \AA}$) obtained with tunneling parameters which do not disturb the system (sample bias +1 V, tunneling current 50 pA). These images were taken (a) before and (b) after scanning the same area under conditions which lead to some desorption of the chlorobenzene molecules (in this case, the manipulation parameters were a sample bias voltage of +2.2 V, a tunneling current of 50 pA, and a tip speed of 280 nm s^{-1}). It is evident that the number of chemisorbed chlorobenzene molecules, which appear like missing adatoms, is reduced in Fig. 1(b) compared with Fig. 1(a), as illustrated by the sites circled in the figures. The acquisition of numerous similar image pairs (typically over an area of $500 \times 500 \text{ \AA}$) for a wide range of manipulation parameters allows us to count the number of desorbed molecules and thus to plot the desorption probability [17] as a function of both current and voltage. Care

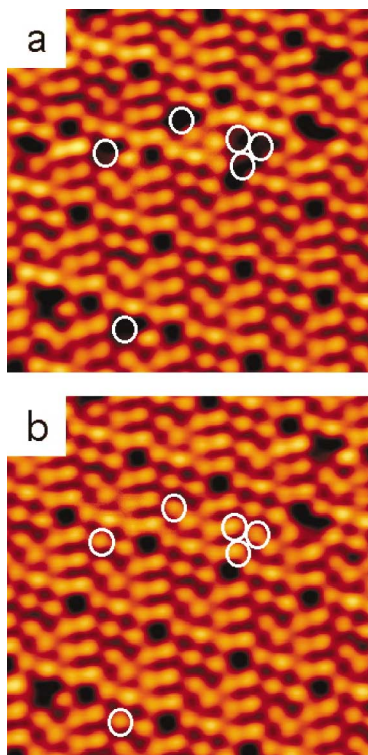


FIG. 1 (color). STM images ($100 \times 100 \text{ \AA}$) of $\text{C}_6\text{H}_5\text{Cl}$ molecules on Si(111)-(7 \times 7) before (a) and after (b) a desorption scan. Image (desorption) scan parameters; sample bias +1 V (+2.2 V), tunneling current 50 pA (50 pA). The white circles mark the locations of chlorobenzene molecules which desorb in this case.

is taken to exclude the small number of molecules which are readsorbed on the surface following desorption as well as any surface contamination.

Measurement of the STM-induced desorption rate as a function of tunneling current yields a result that is both simple and telling, as shown in Fig. 2(a) (sample bias voltages +3 V and -2 V). In particular, the dependence on current is linear for both voltage polarities and yields a slope in the log-log plot of 0.88 ± 0.09 (+3 V) and 0.89 ± 0.04 (-2 V). The value of the slope immediately rules out a nonlinear “vibrational heating” mechanism, indicating instead that the desorption process involves only one electron (or hole) per desorption event [18,19]. Moreover, the wide range of tunneling currents probed in each case (from 5 to 100 pA at +3 V and 10 pA to 1 nA

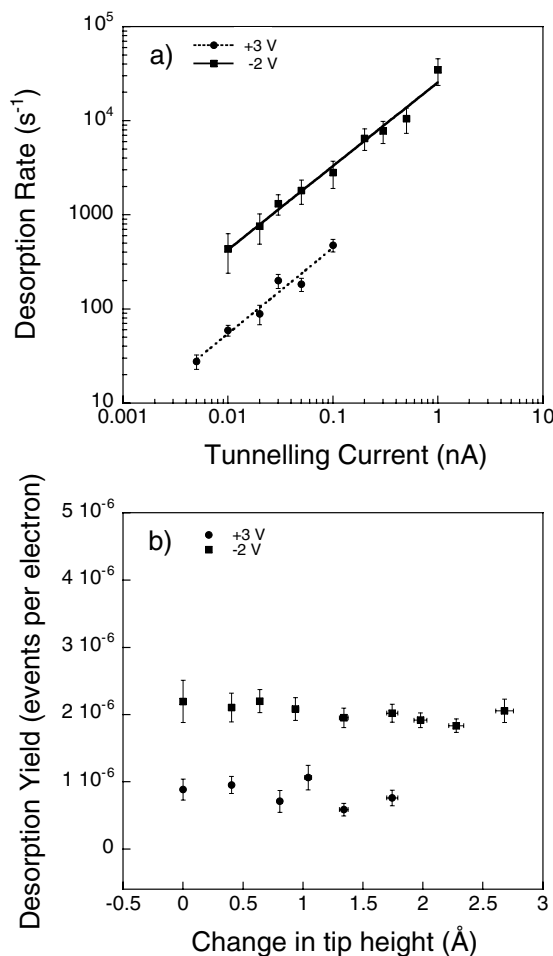


FIG. 2. (a) Rate of desorption of $\text{C}_6\text{H}_5\text{Cl}$ molecules from the Si(111)-(7 \times 7) surface as a function of the tunneling current in the STM (log-log plot with straight line fit); sample bias voltage +3 V (filled circles) and -2 V (filled squares). For ease of viewing the -2 V data have been shifted up by an order of magnitude. (b) The same basic data plotted in terms of the change in tip-surface distance (positive value, tip moves towards the surface) which occurs when the current is altered. The reference set points are +3 V, 5 pA (filled circles) and -2 V, 10 pA (filled squares). Again, for viewing clarity the -2 V data have been shifted up by a factor of 2.

at -2 V) corresponds to a substantial change in tip height (-1.74 ± 0.05 Å and 2.68 ± 0.07 Å, respectively). Plotting the same data for the desorption yield in terms of the change in tip height, Fig. 2(b), clearly shows that the desorption yield is independent of the tip height in the range considered for both voltage polarities [20]. As a consequence we can exclude the possibility that a mechanical interaction between the tip and adsorbate plays an active role in the desorption mechanism. The same argument from Fig. 2(b) also rules out an electric field mechanism (since the voltage is constant while the tip-surface height is varying substantially). So what is the mechanism of the STM-induced desorption?

Figure 3 presents the most significant results obtained in this work. It shows the chlorobenzene desorption yield from Si(111)-(7 × 7) as a function of sample bias over a wide range of both positive and negative voltage values, averaged over 16 different STM experiments (i.e., tips). Such a comprehensive, wide ranging data set has not previously been reported, to the best of our knowledge, in STM manipulation experiments. Detailed experiments have largely been restricted to voltages of one polarity [5,6,17,21]. The data plotted in Fig. 3 show two clear thresholds for the onset of chlorobenzene desorption at $+2.5$ V and -1.5 V. No significant change was observed when *p*-type silicon replaced *n*-type, consistent with pinning of the Fermi level near midgap by the surface states. We also explored the desorption yield as a function of the molecular adsorption site within the surface unit cell. No

significant differences were observed between corner or center sites or between the faulted and unfaulted halves of the unit cell. Thus the desorption mechanism is independent of the surface site.

The asymmetry of the desorption probability with respect to bias voltage is relevant to the interpretation of the desorption mechanism. For example, a current-driven thermal process should depend only on the power input, i.e., the modulus of the applied voltage [22]. Thus, from the experimental data presented so far, we can rule out a whole raft of possible mechanisms: field desorption, mechanical (tip-sample) interaction, vibrational heating, and thermal dissipation. What is left as the likely candidate for the desorption mechanism is an “electronic mechanism,” i.e., the formation of an excited electronic state of the molecule-surface system which couples strongly to the nuclear motion (desorption) of the molecule, specifically, excitation of the molecule-substrate bond.

Previous work has suggested that the π states of small organic molecules [23] play a key role in regulating the STM-induced desorption process [24]. In the context of a proposed electronic mechanism, the fact that STM-induced desorption of C_6H_5Cl from the Si(111)-(7 × 7) takes place at both positive and negative bias voltages implies that both electron and hole attachment to the molecule occur, i.e., both the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) must be accessible to the tunneling electrons. It has been suggested from experiments [25] that the chlorobenzene is di- σ bonded through two of the carbon atoms of the ring, like benzene/Si(001) [26], where the HOMO and LUMO (both π in character) lie within a few eV of the Fermi level. It seems likely that this is true of C_6H_5Cl /Si(111)-(7 × 7) as well.

In order to cast more light on which electronic states drive the STM-induced desorption of chlorobenzene from the Si(111)-(7 × 7) surface, we have carried out electronic structure calculations of a mimic system via density functional theory (DFT). For practical computation we have used a 2×2 mimic surface, which displays the key electronic and structural features of the 7×7 surface [27]. The supercell consisted of a slab of silicon, five double atom layers thick. The dangling bonds were passivated with hydrogen atoms unless bonded to a chlorobenzene molecule. The supercell incorporated four 2×2 unit cells, each with added silicon atoms to represent the adatoms of the 7×7 surface, leading to a total of 176 atoms per supercell [27]. The VASP code [28,29] employed ultrasoft pseudopotentials [30] and the generalized gradient approximation to the exchange correlation [31].

The geometry of chemisorbed chlorobenzene was optimized in the calculations, which confirmed the di- σ bonding configuration, while the calculated binding energy of 1.2 eV (faulted half of the unit cell) compares well with thermal desorption experiments (1.0 eV) [25]. In the lowest energy configuration, the Cl atom does not

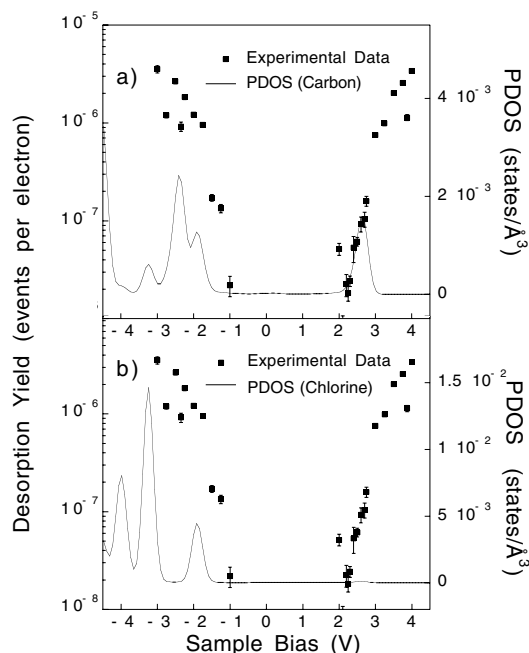


FIG. 3. Experimental desorption yield per electron of C_6H_5Cl molecules from the Si(111)-(7 × 7) surface as a function of the sample bias voltage in the STM (black squares), compared with (solid lines) calculated partial density of *p* states at (a) the carbon atom in the ring and (b) the chlorine atom (for details see text).

participate in bonding to the surface, consistent with vibrational spectra [25].

Although DFT is best suited for ground state calculations, the Kohn-Sham (KS) states provide a useful starting point for describing electron and hole attachment. A more quantitative description of these excited states requires a theory such as the *GW* approximation [32], whose application to this large system is currently out of reach. Comparison between the calculated partial densities of KS states, centered at the atomic sites of the adsorbed molecule, and the measured desorption yield as a function of voltage may then shed some light on which states drive the desorption process. Thus, in addition to the experimental desorption probability, Fig. 3 also plots examples of the partial density of *p* states at two different sites: (a) the carbon atoms of the phenyl ring that are not involved in either the bonding to the Cl or the surface and (b) the Cl atom. The DOS in (a) then reflects the DOS of the π orbitals of the carbon ring, while the DOS in (b) reflects the DOS of the C-Cl σ orbitals. The measured, asymmetric thresholds for desorption correlate nicely with the density of states for the ring orbital, and not at all well with the Cl orbital. Thus, despite the large cross sections for low energy electron scattering by halogen atoms [33], electron attachment to the Cl atom does not seem to be the mechanism of desorption (presumably because the $2p$ orbitals of the Cl atom are partially filled). In contrast, the calculations are consistent with electron attachment to the π states of the benzene ring (for positive sample bias, or hole attachment for negative sample bias).

In summary, we have reported comprehensive experimental measurements of the desorption yield of chlorobenzene molecules from the Si(111)-(7 × 7) surface as a function of the tunneling current and the sample bias voltage (both polarities), as well as complementary density functional calculations, which enable us to identify the mechanism of STM manipulation at room temperature in this model system. In the future, it would be interesting to explore whether the mechanism of single molecule dissociation (C-Cl bond fission) is the same as the desorption mechanism, or not, and to establish the means by which the state of the STM tip selects between the competing dynamical channels (desorption, dissociation) in the system.

We thank Dr. K. Svensson for useful discussions and acknowledge financial support from the EPSRC, the European Union, the Swedish Science Research Council, and ATOMICS.

*Electronic address: r.e.palmer@bham.ac.uk

[1] D. M. Eigler and E. K. Schweizer, *Nature (London)* **344**, 524 (1990).

- [2] M. F. Crommie, C. P. Lutz, and D. M. Eigler, *Science* **262**, 218 (1993).
- [3] A. J. Heinrich, C. P. Lutz, J. A. Gupta, and D. M. Eigler, *Science* **298**, 1381 (2002).
- [4] D. M. Eigler, C. P. Lutz, and W. E. Rudge, *Nature (London)* **352**, 600 (1991).
- [5] K. Stokbro, C. Thirstrup, M. Sakurai, U. Quaade, B. Y.-K. Hu, F. Perez-Murano, and F. Grey, *Phys. Rev. Lett.* **80**, 2618 (1998).
- [6] G. Dujardin, A. Mayne, O. Robert, F. Rose, C. Joachim, and H. Tang, *Phys. Rev. Lett.* **80**, 3085 (1998).
- [7] M. A. Rezaei, B. C. Stipe, and W. Ho, *J. Chem. Phys.* **110**, 4891 (1999).
- [8] W. Ho, *Acc. Chem. Res.* **31**, 567 (1998).
- [9] L. Bartels, G. Meyer, and K.-H. Rieder, *Phys. Rev. Lett.* **79**, 697 (1997).
- [10] Aeschlimann *et al.*, *Discuss. Faraday Soc.* **117**, 257 (2000).
- [11] Ph. Avouris *et al.*, *Chem. Phys. Lett.* **257**, 148 (1996).
- [12] R. A. Wolkow, *Annu. Rev. Phys. Chem.* **50**, 413 (1999).
- [13] P. J. Durston and R. E. Palmer, *Surf. Sci.* **400**, 277 (1998).
- [14] X. H. Chen, Q. Kong, J. C. Polanyi, D. Rogers, and S. So, *Surf. Sci.* **340**, 224 (1995).
- [15] P. H. Lu, J. C. Polanyi, and D. Rogers, *J. Chem. Phys.* **111**, 9905 (1999).
- [16] L. Bartels, G. Meyer, and K.-H. Rieder, *Appl. Phys. Lett.* **71**, 213 (1997).
- [17] S. Alavi, R. Rousseau, S. N. Patitsas, G. P. Lopinski, R. A. Wolkow, and T. Seideman, *Phys. Rev. Lett.* **85**, 5372 (2000).
- [18] B. C. Stipe, M. A. Rezaei, W. Ho, S. Gao, M. Persson, and B. I. Lundqvist, *Phys. Rev. Lett.* **78**, 4410 (1997).
- [19] G. P. Salam, M. Persson, and R. E. Palmer, *Phys. Rev. B* **49**, 10 655 (1994).
- [20] The slight decrease in desorption yield as the tip approaches the surface is ascribed to molecular readsorption onto the parent surface site.
- [21] T.-C. Shen *et al.*, *Science* **268**, 1590 (1995).
- [22] Ph. Avouris, *Acc. Chem. Res.* **28**, 95 (1995).
- [23] S. Hla, L. Bartels, G. Meyer, and K.-H. Rieder, *Phys. Rev. Lett.* **85**, 2777 (2000).
- [24] S. N. Patitsas, G. P. Lopinski, O. Hul'ko, D. J. Moffatt, and R. A. Wolkow, *Surf. Sci.* **457**, L425 (2000).
- [25] Y. Cao, J. F. Deng, and G. Q. Xu, *J. Chem. Phys.* **112**, 4759 (2000).
- [26] S. Gokhale *et al.*, *J. Chem. Phys.* **108**, 5554 (1998).
- [27] R. D. Meade and D. Vanderbilt, *Phys. Rev. B* **40**, 3905 (1989).
- [28] G. Kresse and J. Hafner, *Phys. Rev. B* **47**, 558 (1993).
- [29] G. Kresse and J. Furthmuller, *Comput. Mater. Sci.* **6**, 15 (1996).
- [30] Plane wave cutoff energy 300 eV, surface Brillouin zone sampled by 3 × 3 *k* points.
- [31] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, *Phys. Rev. B* **46**, 6671 (1992).
- [32] G.-M. Rignanse, X. Blase, and S. G. Louie, *Phys. Rev. Lett.* **86**, 2110 (2001).
- [33] A. Mann and F. Linder, *J. Phys. B* **25**, 1621 (1992).