Atomic manipulation by electron injection

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Atomic manipulation is the extreme limit of nanotechnology. I will discuss the manipulation (specifically, desorption, dissociation and re-configuration) of polyatomic molecules – chlorobenzene (C_6H_5Cl or PhCl) and polychlorinated biphenyls (PCBs) – anchored to a silicon surface at room temperature (and above), with a focus on new mechanisms [1] for atomic manipulation via electron injection. Such mechanisms may (eventually) be relevant to chip-scale molecular manufacturing.

(i) Site-specific non-local atomic manipulation (leading to molecular desorption) of PhCl [2]: effectively this is 'remote control' of molecular manipulation, and occurs via (a) the injection of charge far away from the molecule at a specific surface atomic site followed by (b) charge transport across the Si(111)-7x7 surface to the target molecule. This non-local mechanism also calls into question a body of published cross-sections and may also have implications, ultimately (!), for solar energy harvesting.

(ii) Thermally activated C-Cl bond dissociation in PhCl (one electron mechanism) [3]: we find an Arrhenius energy barrier to one-electron dissociation of 0.8 ± 0.2 eV, which we correlate experimentally with the barrier between the 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. The mechanism may apply in many surface systems and not just in STM manipulation but also in photon and electron beam stimulated processes.

(iii) Intramolecular site- and energy-selective manipulation of PCB molecules [4]: the two benzene rings of the molecule bond in different fashions to the surface. Several competing manipulation outcomes are identified, notably molecular desorption via electron injection into the strongly bonded ring and re-configuration of the molecule via injection into the weakly bonded ring, each with different energy thresholds which align with STS measurements.

1. P.A. Sloan and R.E. Palmer, Nature **434** 367 (2005).
2. P.A. Sloan, S. Sakulsermsuk and R.E. Palmer, Phys. Rev. Lett. **105** 048301 (2010); *see also* “Electron 'submarines' help push atoms around”, *E.S. Reich,* New Scientist**,** 31 July 2010, p. 11.
3. S. Sakulsermsuk, P.A. Sloan and R.E. Palmer, ACS Nano **4** 7344 (2010); *see also* "Physisorbed molecules take the heat", In Nano, ACS Nano **4** 7040 (2010).
4. T. Pan, S. Sakulsermsuk, P.A. Sloan and R.E. Palmer, J. Am. Chem. Soc. (Communications) **133** 11834-11836 (2011).

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