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SMR 1564 - 8

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**SPRING COLLEGE ON SCIENCE AT THE NANOSCALE**  
**(24 May - 11 June 2004)**

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**STM of molecules and silicon - Part II**

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*These are preliminary lecture notes, intended only for distribution to participants.*

- Molecules are prefabricated units, with unique size, shape, flexibility, chemical and physical affinities, electronic signatures, thermal conductivity, and more.
- Because we now have (or can foresee having) the ability to configure these complex units, it becomes possible to imagine making functional molecular entities.

- We know that molecular assemblies can achieve extraordinary computational feats - our brains allow us to recognize a face, even the gender, age and mood of a person after just a glance - something no other computer can do.
- So the question isn't, can molecules perform computations? The question is, how do we fit a harness onto molecules?

- To achieve competitive computational capacity we will need systems of very substantial complexity.
- Such systems are well out of reach now.
- An intermediate goal - concepts for detectors, possibly medical diagnostic devices. En route, learn to position, configure and communicate with molecules.
- Then, prepared to explore more complex structures, relevant for computation.

- We take as a starting point, hybrid molecule-silicon assemblies.
  - Controlled Molecular Adsorption on Si: Laying a Foundation for Molecular Devices, R.A. Wolkow, Annual Review of Physical Chemistry, volume 50, 413-41, 1999
- By adapting the sophisticated capabilities of Si-technology we will establish methods for controllably positioning and addressing molecular entities.
- By marrying organics and silicon, we aim to underpin a new array of devices, capable of interfacing and interacting with the local environment.

dotted lines and pictured as forming a continuous conducting path. The separations between such filamentary conducting paths might vary between a few angstroms as in some NiAs-type structures to hundreds of angstroms. While a suitable material cannot be pointed to at this time these materials would seem to be an area of considerable potential use.

For example, two layers of semiconducting components might be positioned on opposite sides of such a modulated insulator so that the conducting filaments might electrically link the two sides. As suggested in Fig. 5(a), conducting pads might overlap more than one filament enhancing conductivity and easing the problem of registration. By coating one side of the modulated material with a conducting film one might electrochemically form a regular array of active sites on the opposite side for the disposition of metal pads or a specific reagent leading to the preparation of molecular wires. Of course, the conducting film could be removed later and another pattern formed.

#### IV. ELECTRON TUNNELLING AS AN MED SWITCH

In order to achieve logical operations at the individual molecular level, that is, to achieve molecular addressability, one needs not only a direct line of communication as is suggested in Fig. 2 but also a corresponding set of switches to differentiate between functional units. In this and the next section three different phenomena operating at the molecular level are discussed as switches. These phenomena are (1) electron tunnelling through short periodic arrays, (2) soliton switching, and (3) soliton valving.

Electron tunnel switches are based on the early quasiclassical results of Pschenichnov.<sup>14</sup> He suggested that the trans-

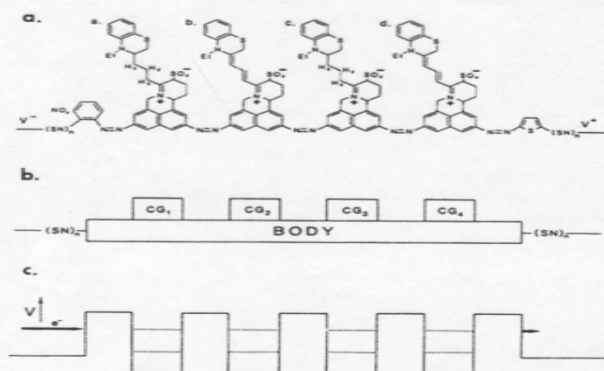
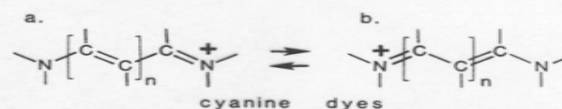


FIG. 6. (a) Molecular analogue of a NAND gate with two dummy (a and c) and two cyanine dyelike control groups (b and d) is shown. By changing the conjugation in b and d different optical frequencies can be used as inputs. Figures 6(b) and 6(c) define body and the relationship of control groups to the periodic wells and barriers.

mission coefficient of an electron approaching a finite series of periodic barriers would be unity if the electron energy matched exactly a pseudostationary energy level of the barriers. This is illustrated in Fig. 6(c) where the energy of the electron approaching the barriers from the left matches the upper resonant level of the wells. The tunnel switch can be turned off by either changing a barrier height or the depth of a potential well so that the associated pseudostationary energy level no longer matches the other levels and the energy of the incoming electron. Figure 6(b) illustrates schematically four control groups (CG<sub>1</sub>) on the body of a tunnel switch that are positioned to control the depth of the potential wells. In comparing Fig. 6(a) and 6(b) we note that the potential well is associated with the quaternary nitrogen = N<sup>+</sup> =. Of these four control groups in CG<sub>1</sub> and CG<sub>3</sub> the quaternary nitrogen charges are stationary. However, in control groups CG<sub>2</sub> and CG<sub>4</sub> the positive charges can move away from the tunnel body as indicated for the cyanine dyes below:



In Fig. 6(a) if the charge is moved to the upper nitrogen in either the second (b) or the fourth (d) control group then the associated electric field (dipole) is dramatically changed and any electron tunnelling through the body would be switched off. By having different amounts of conjugation in the control groups of Fig. 6(a), that is by varying  $n$  (as in the cyanine dye example above) the charge of different CGs can be shifted by photons of different energy. Thus Fig. 6(a) would be a molecular NAND gate analogue with optical inputs. Alternatively the charges could be shifted by the motion of a nearby charged soliton as suggested by the author recently (WMED2).<sup>15</sup>

Finally we note that a variety of molecular analogue gates have been proposed,<sup>1(a),1(b),16</sup> and Pschenichnov's quasiclassical solution has been supported by an exact analytical solution for square well potentials.<sup>16</sup> Recently the predicted switching action was computationally verified (WMED2).<sup>15,17,18</sup> However, Barker *et al.* noted that long delays could be produced in the transport of the electrons through the body by trapping them between wells.<sup>17</sup> This effect may be an artifact of the rectangular walls of the square well model.

#### V. SOLITON SWITCHING

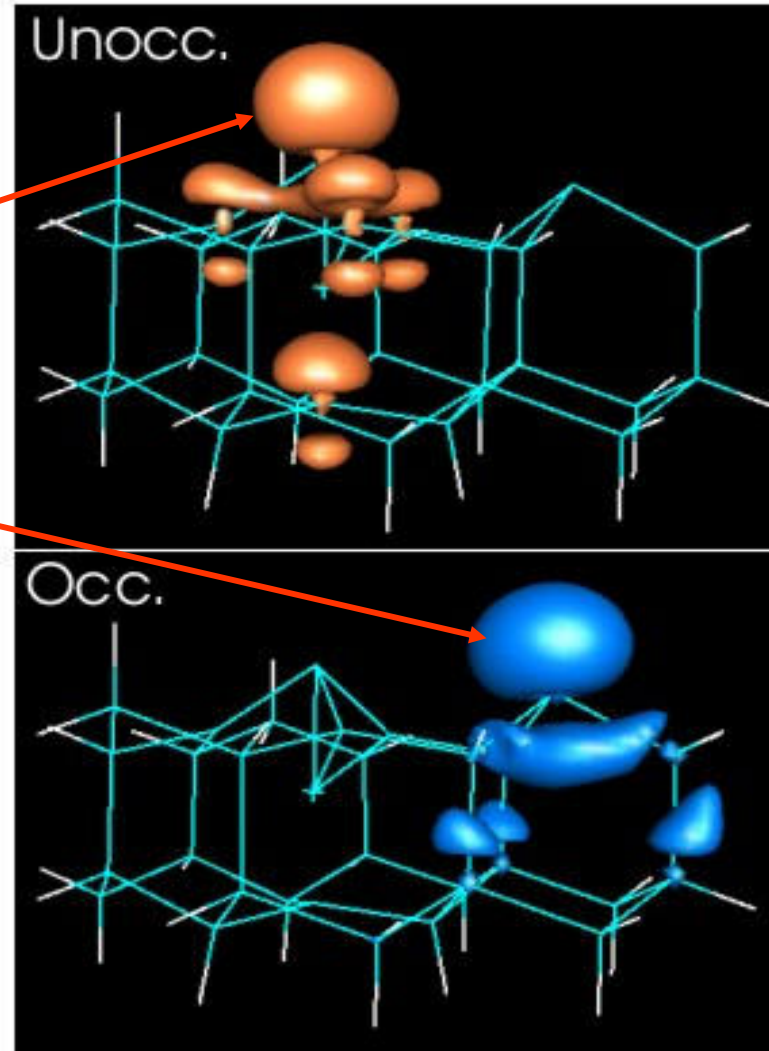
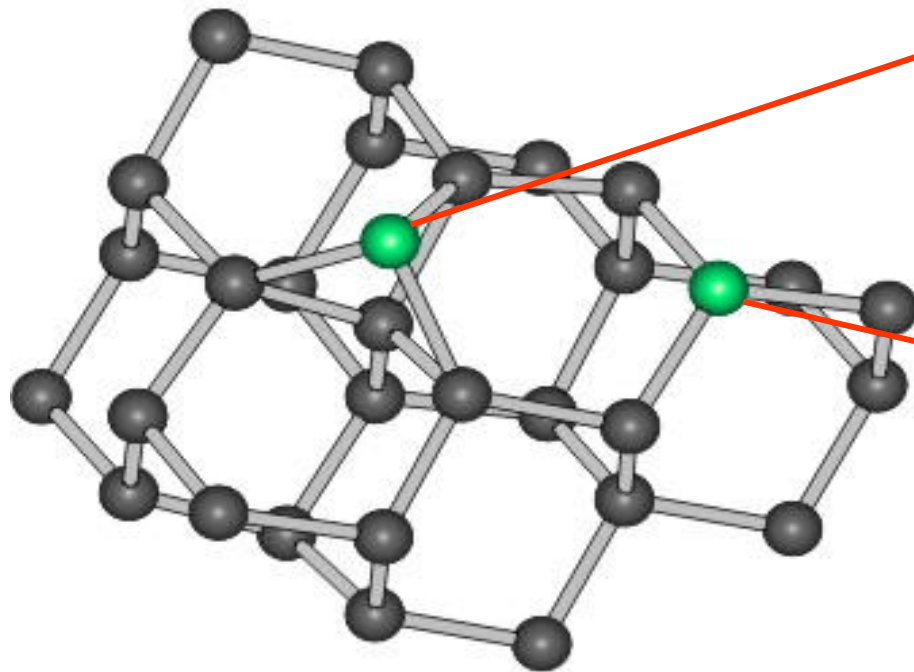
While conformational changes, that is changes in bond angles and distances, are significant in electron tunnel switches they are of fundamental importance in both soliton switching and soliton valving.

The soliton is a nonlinear disturbance which behaves like a pseudoparticle and travels in a dispersive medium but without being dispersed. The soliton of special interest here is primarily an excited electronic state associated with zero, one, or two electrons occupying a  $p$ - $\pi$  orbital in a conjugated system with the associated soliton charge of +, 0, or - and of spin 0,  $\pm 1/2$ , 0, respectively.<sup>19</sup>

Now, figuring out the fussy details

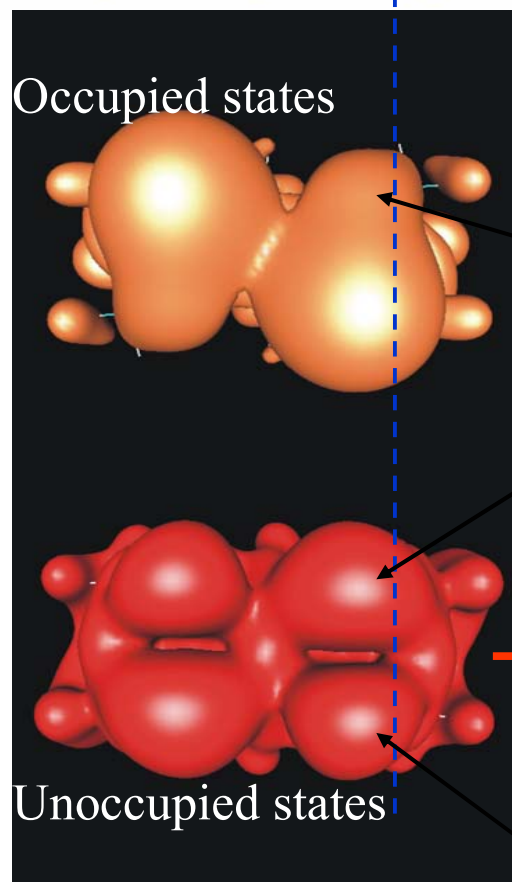
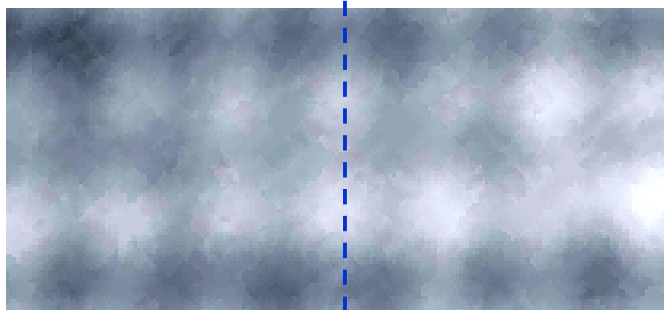
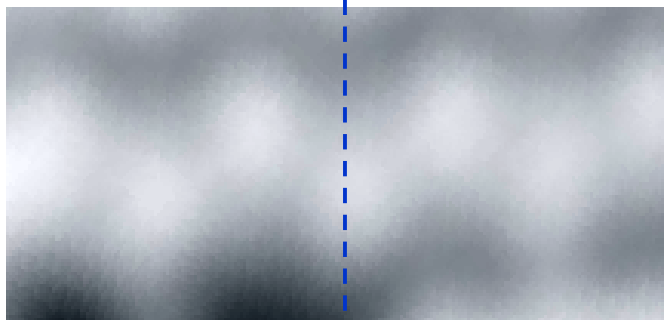
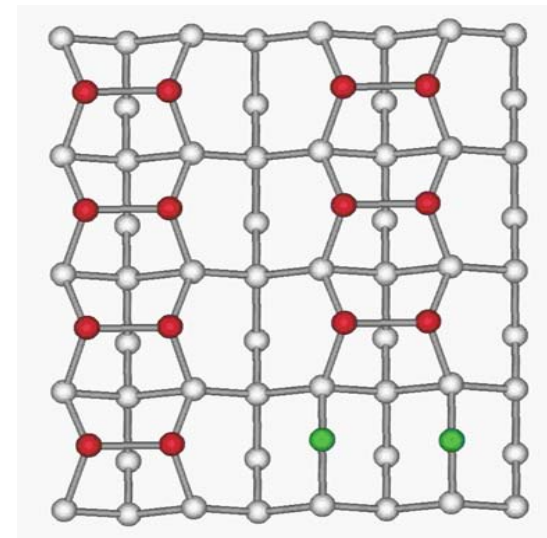
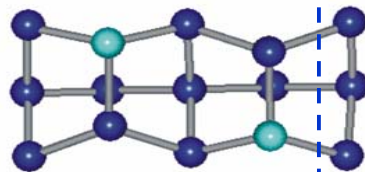
- an experimentalist doing “theory”(modeling)
- careful comparison to experiment
- building up understanding step-by-step
- finally, solve complex structures that were out of reach previously

# Electronic Structure of Si(111)- 7x7





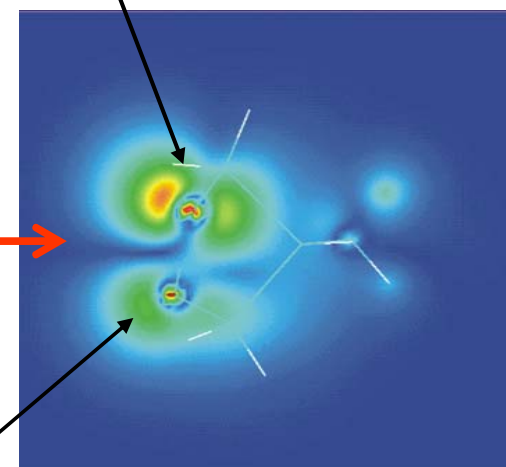
*Si(100)*

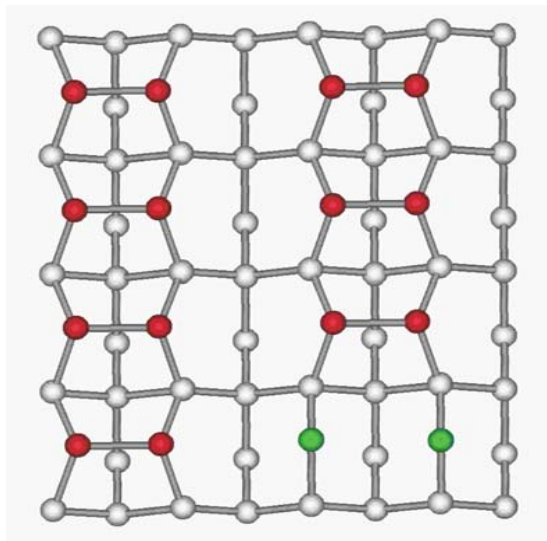


“down” atom

Cross  
section

“up” atom

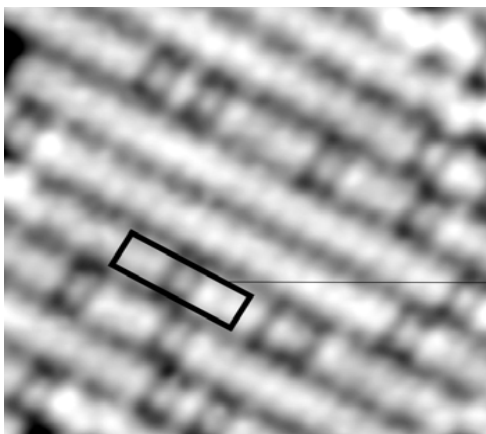




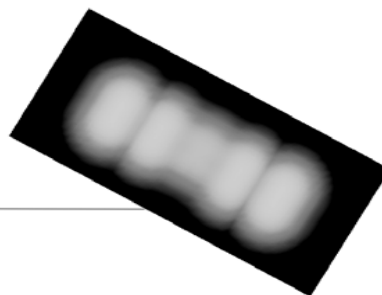
Si(100)

## Ethylene ( $\text{C}_2\text{H}_4$ ) on Si(100)

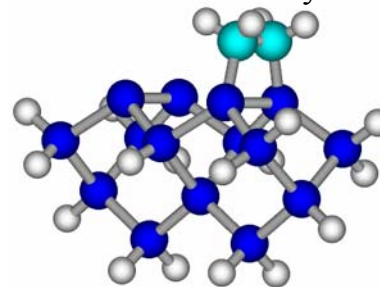
Occupied states -2V



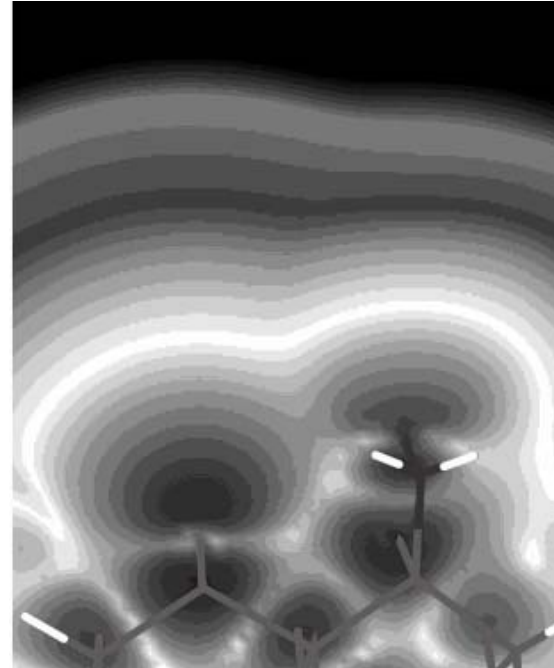
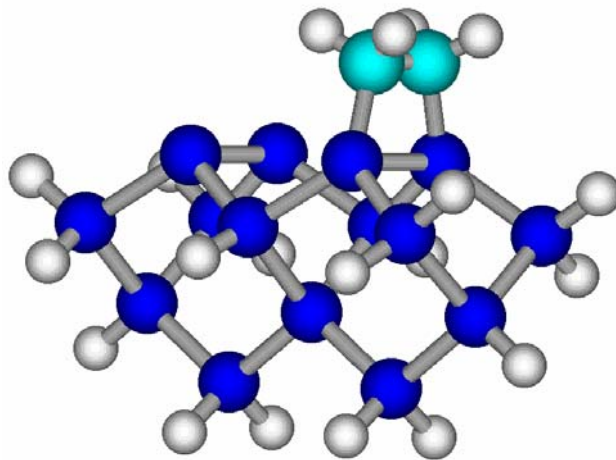
Simulation  
5 dimers + ethylene



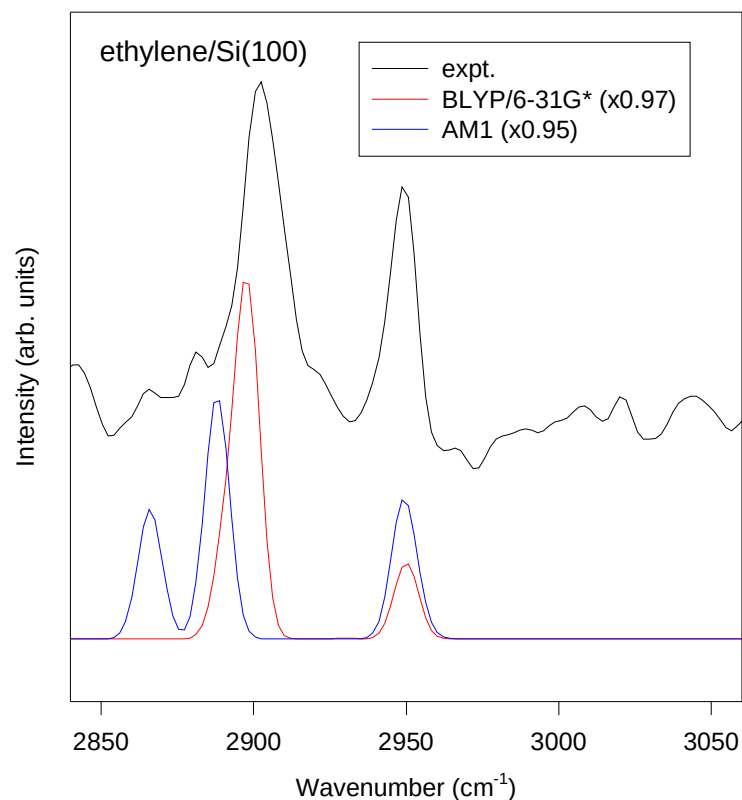
2 dimers + ethylene



near-Fermi level iso-charge density  
surfaces simulate STM contours



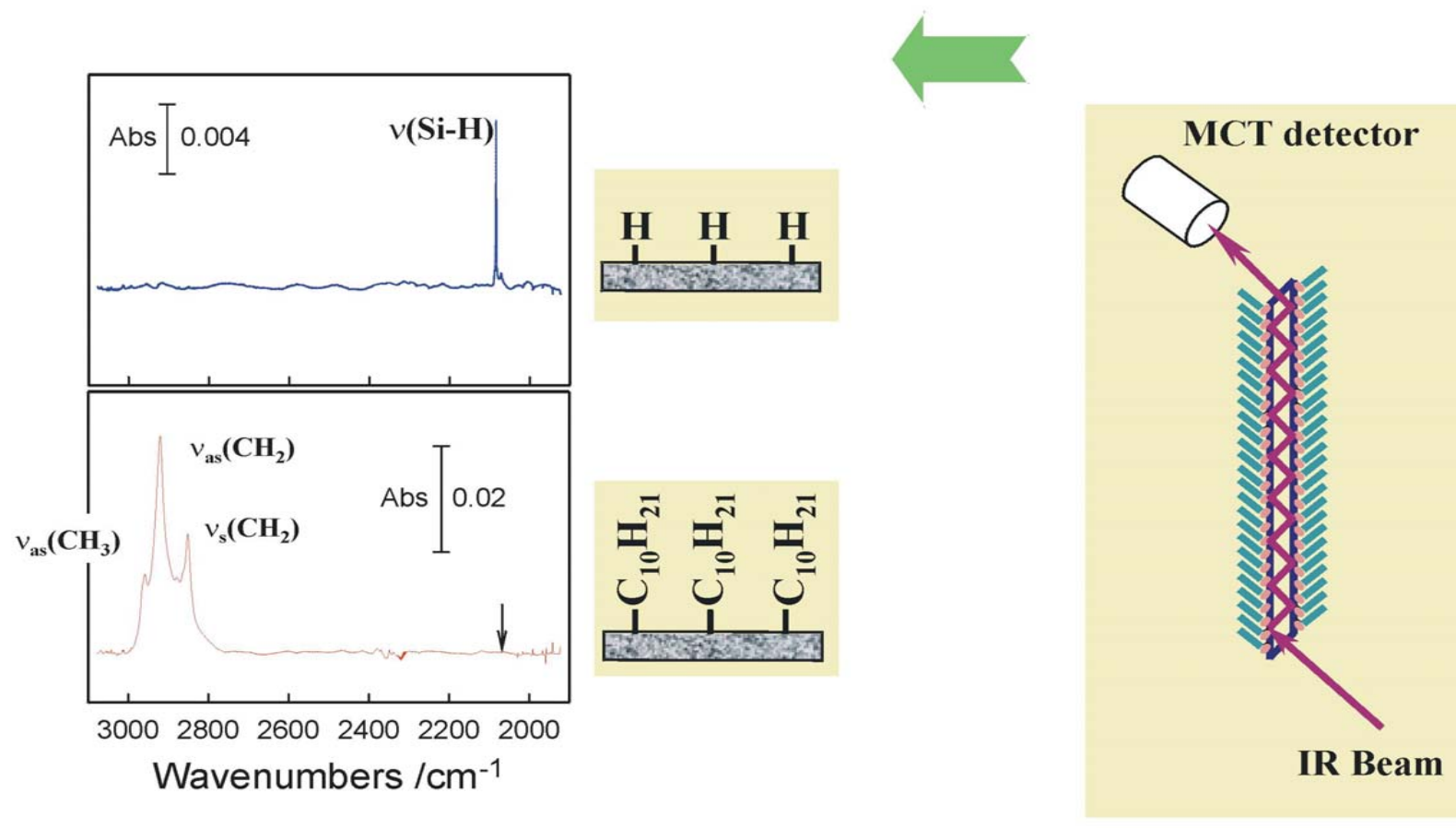
## Vibrational Spectrum of ethylene/Si(100)



- C-H stretch frequencies shifted below 3000cm<sup>-1</sup>, indicating sp<sup>3</sup> hybridization.
- **AM-1** level calculations give fair agreement with experiment, **BLYP/6-31G\*** in excellent agreement.

A Step Toward Making and Wiring-up  
Molecular-Scale Devices, R.A. Wolkow,  
Japanese Journal of Applied Physics, 2001.

# ATR-FTIR Spectra of Modified Si(111)

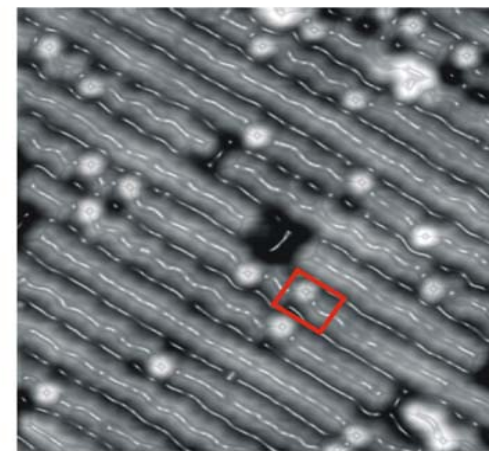
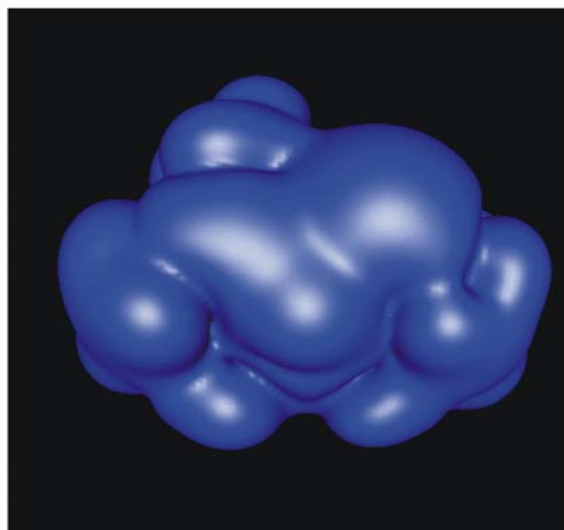
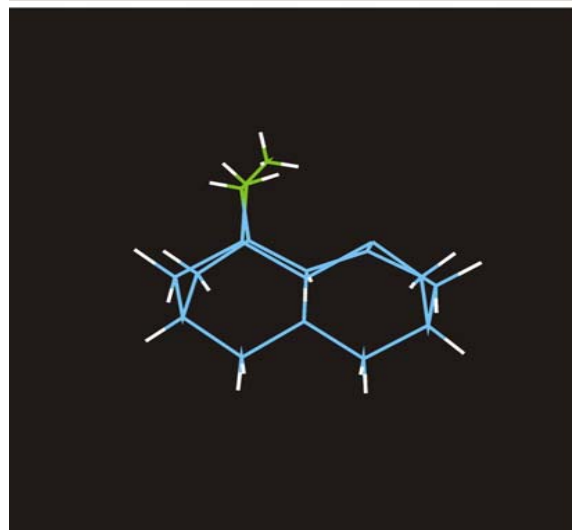
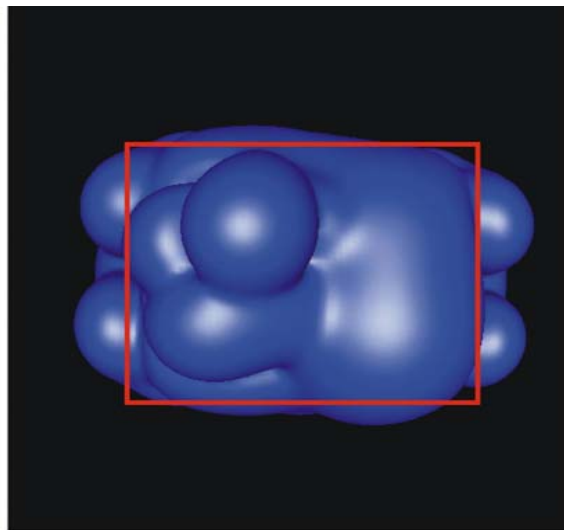
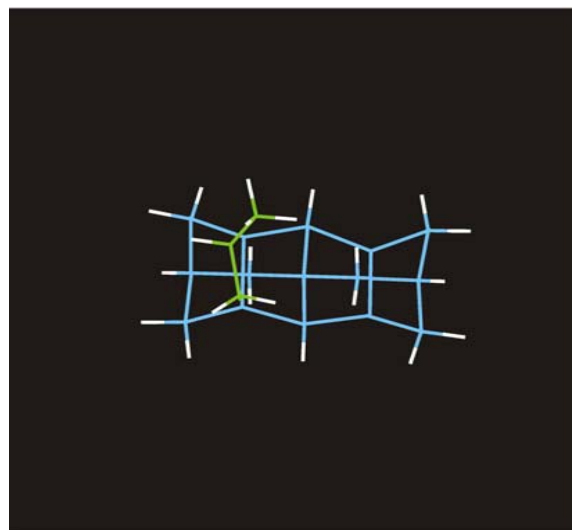
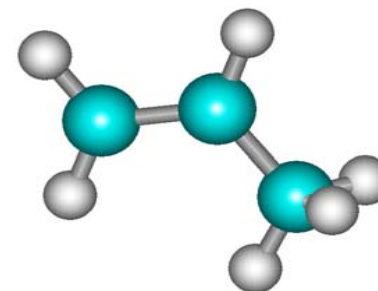


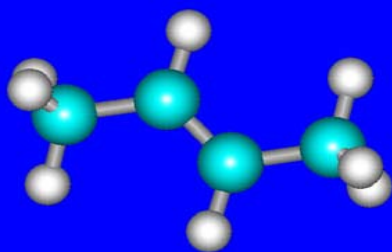
Organic modification of hydrogen terminated silicon surfaces, Danial D. M. Wayner and Robert A. Wolkow, J. Chem. Soc., Perkin Trans. 2, 23-34 (2002).

Soon, high resolution electron energy loss spectroscopy combined with STM

- ~100x more sensitive
- Can do (must do) in vacuum
- combined with STM will allow “white bumps” to be identified

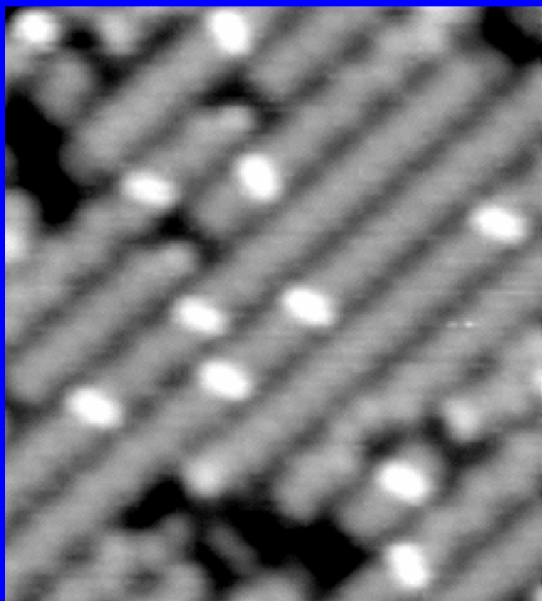
# Propylene on Si(100)



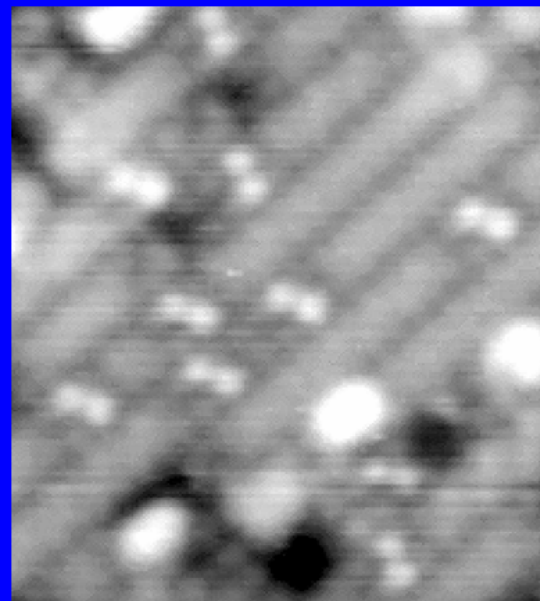


*trans*-2-butene on Si(100)

Occupied states (-2V)



Unoccupied states (+2V)



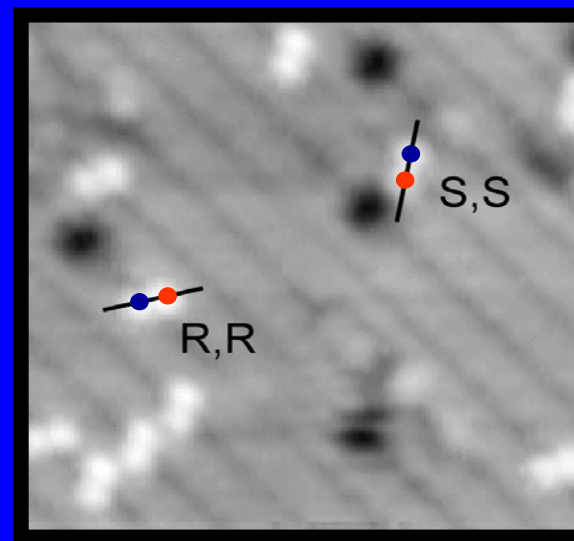
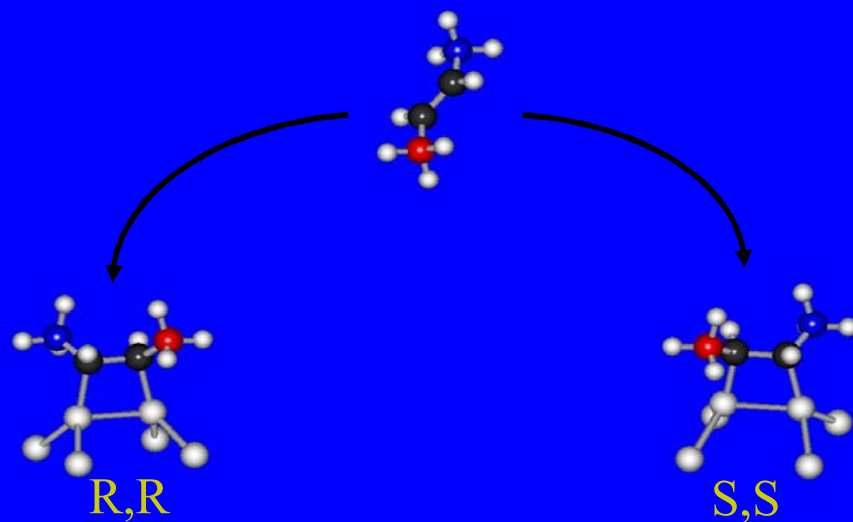


unoccupied

occupied



## Determination of absolute chirality

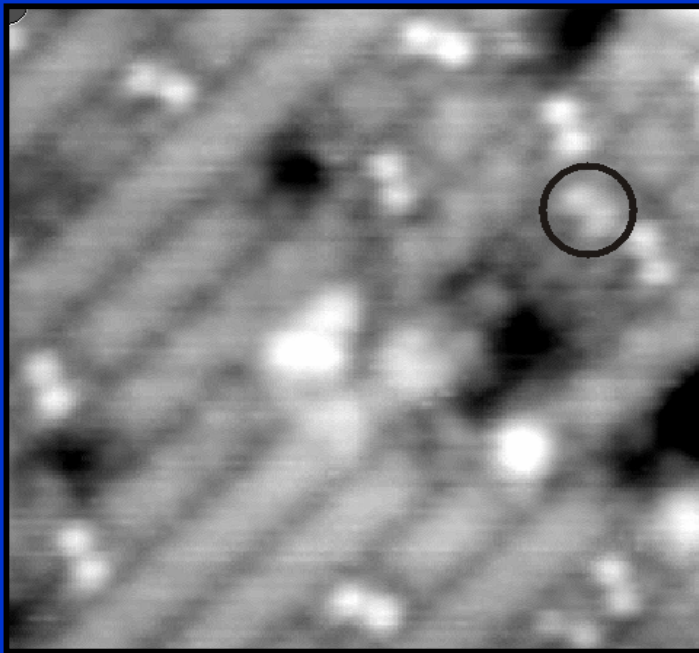


1. the molecule *trans*-2-butene has 2 “faces”
2. reaction at these results in products with different chirality.
3. the two enantiomers formed, though spectroscopically indistinguishable are clearly identified in the STM image.
4. Since reaction at the 2 faces is equally likely, equal numbers of the two enantiomers are formed - resulting in an achiral surface

Lopinski, Moffatt, Wayner and Wolkow,  
*Nature*, **392**, 909 (1998)

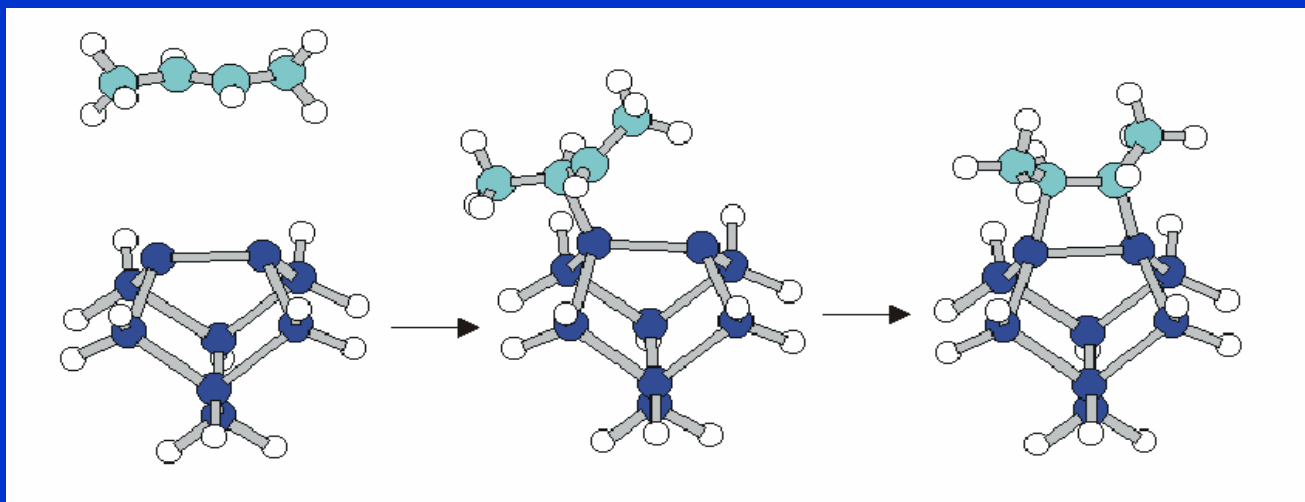
## Observation of isomerization in 2-butene addition

Si(100) dosed with *trans*-2-butene



- Small fraction of molecules undergo isomerization upon addition to the surface at 295K.
  - 2.1 $\pm$ 0.7% *cis* in *trans*
  - 2.6 $\pm$ 0.6% *trans* in *cis*
- Gases are isomerically pure to 99.8% as determined by NMR, FTIR and chromatography.
- Similar probability of isomerization at 350K.
  - 2.1 $\pm$ 0.5% *trans* in *cis*

## Stepwise reaction of 2-butenes to Si(100)



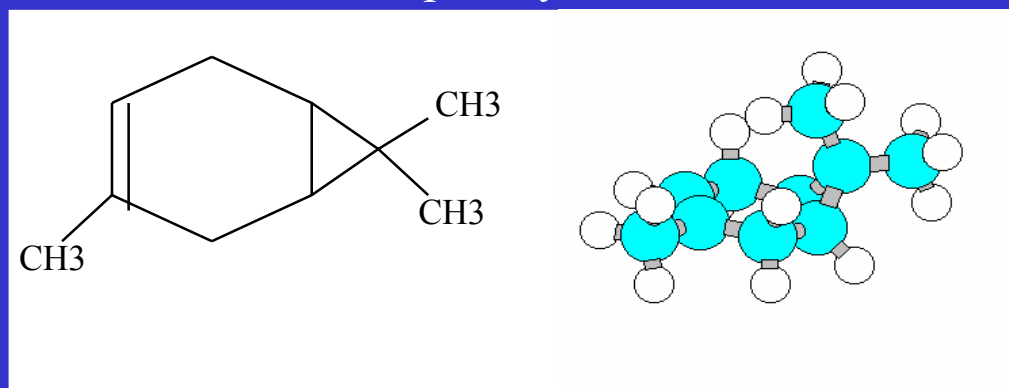
- 1) Some isomerization is observed, indicating sequential, but rapid formation of second Si-C bond.
- 2) Only a small probability of rotation about the C-C single bond. *For rotational barrier of 4 kcal this timescale is 2 ps.*
- 3) Weak temperature dependence suggests three scenarios;
  - *small barrier to rotation (<1 kcal).*
  - *barrier to formation of second Si-C bond.*
  - *energy of adsorption leaves molecule rotationally hot*

How stereoselective are alkene addition reactions on Si(100)?, G.P. Lopinski, D.J. Moffatt, D.D.M. Wayner and R.A. Wolkow, J. Am. Chem. Soc. **122**, 3548-3549 (2000).

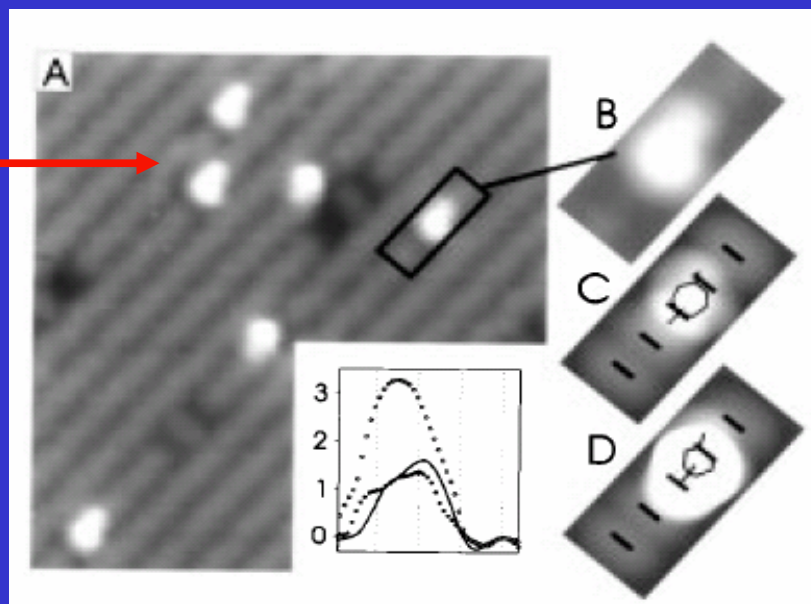
Carene, reaction at one face is blocked

An enantiospecific reaction (“asymmetric induction”) results

Formation of a macroscopically chiral surface.



Wrong  
Enantiomer ?

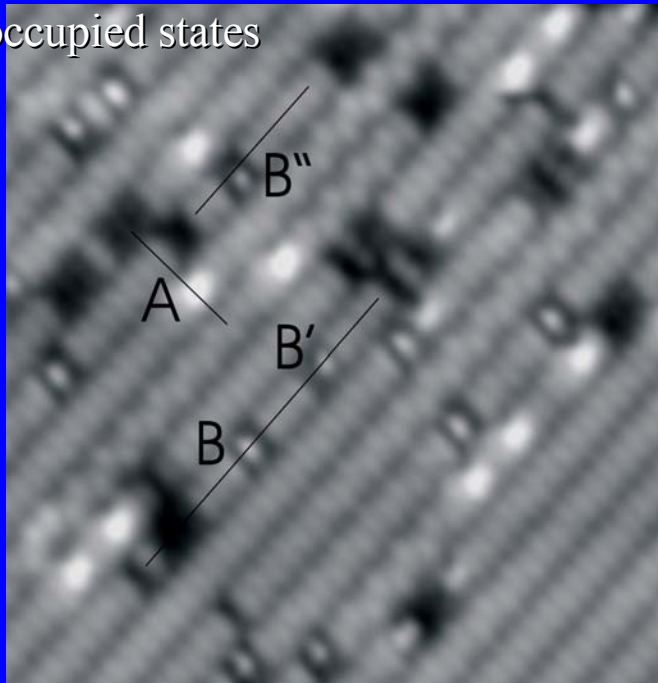


Asymmetric Induction at a Silicon Surface, G.P. Lopinski, D.J. Moffatt, D.D.M. Wayner, M. Z. Zgierski and R.A. Wolkow, *J. Am. Chem. Soc. communication*, **121**, 4532-4 (1999).

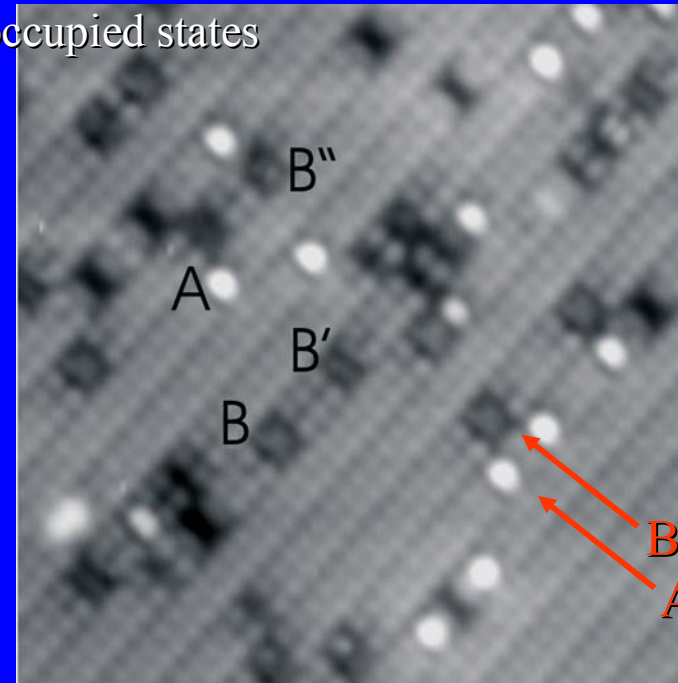
## Benzene adsorbed on Si(100)



occupied states

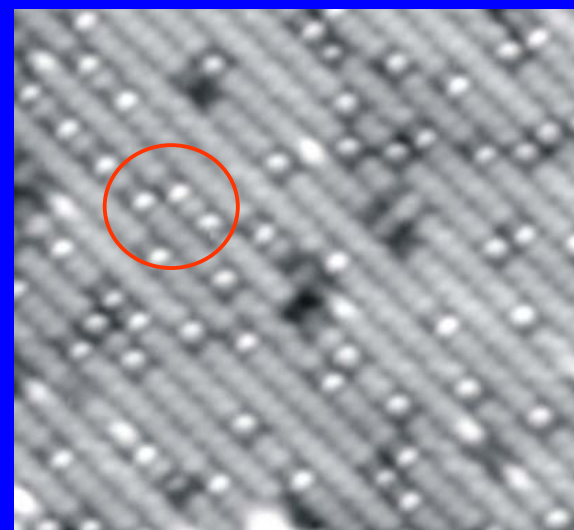
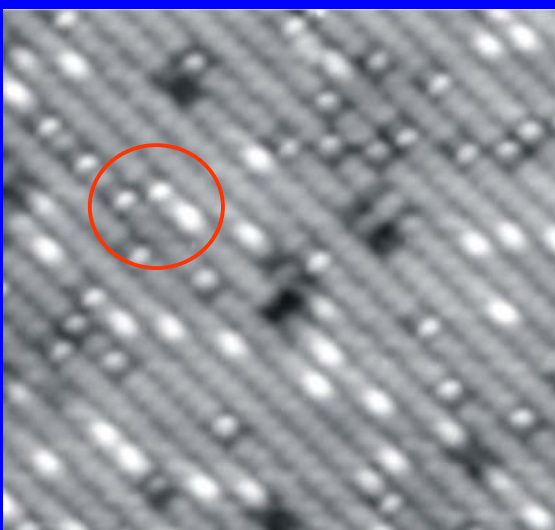
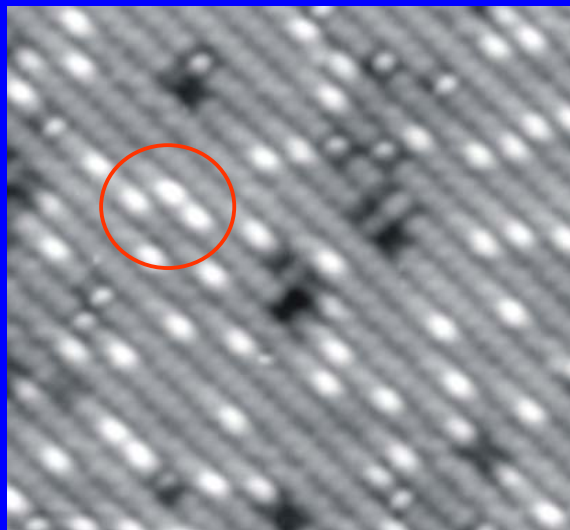


occupied states

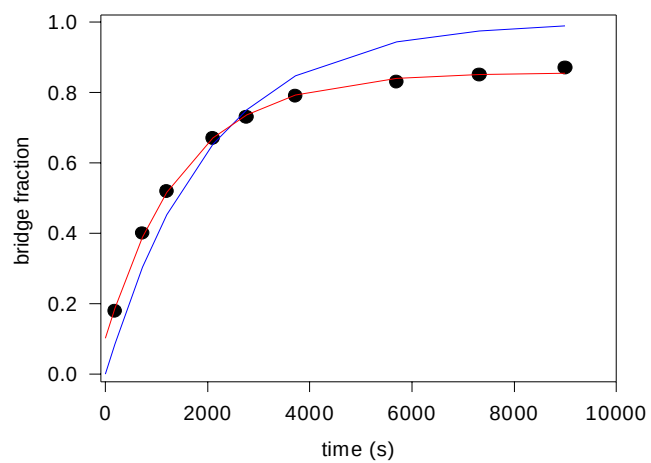


- don't see C or H atoms - only blobs
- more than one configuration evident – very diff. appearances
- can't solve this structure

Adsorbed benzene shows  
changes with time



Barrier 0.95 eV, assuming pre-exponential of  $10^{13}$



# Benzene/Si(100) Calculated Bonding Geometries

Single dimer

1,2

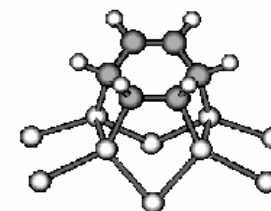
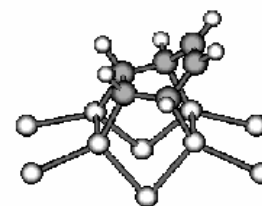
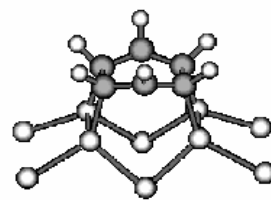
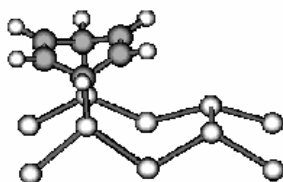
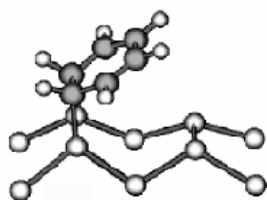
1,4

symmetric

bridge

tight

twist

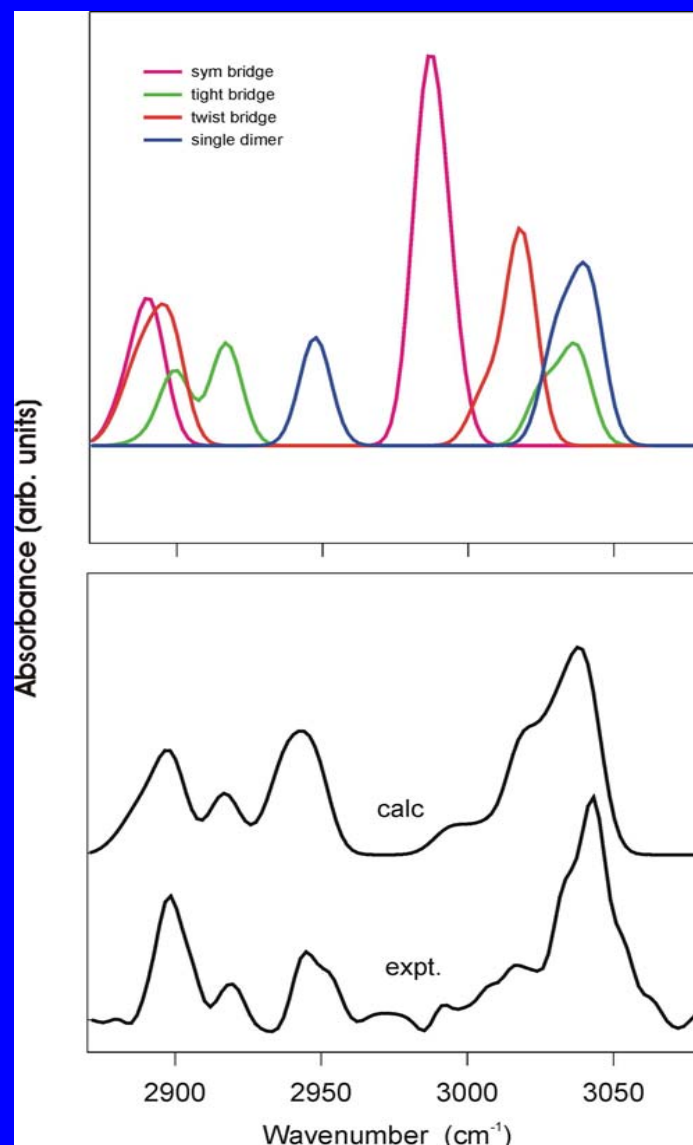


|     |        |        |        |        |        |
|-----|--------|--------|--------|--------|--------|
| AM1 | 1.07eV | 1.02eV | 1.58eV | 1.64eV | 1.74eV |
|-----|--------|--------|--------|--------|--------|

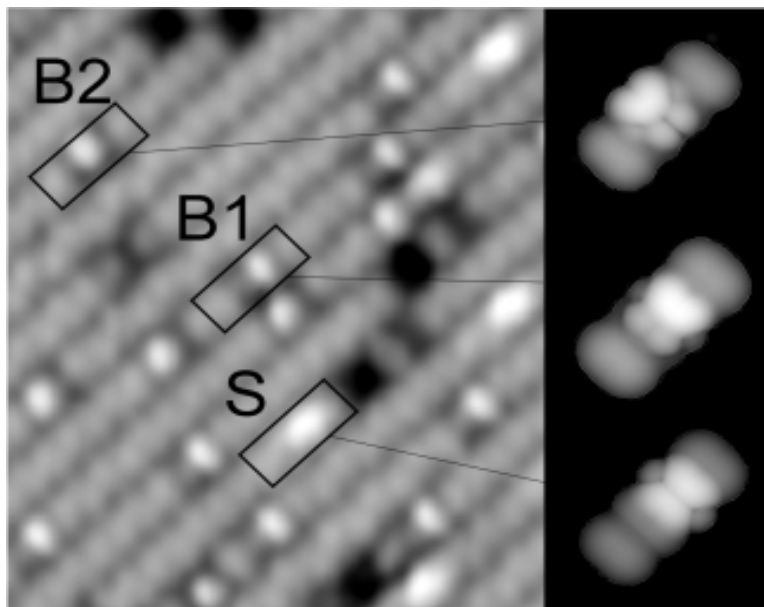
|                |        |        |   |        |        |
|----------------|--------|--------|---|--------|--------|
| DFT            | 0.17eV | 0.88eV | x | 1.49eV | 0.91eV |
| (B3LYP/6-31G*) |        |        |   |        |        |



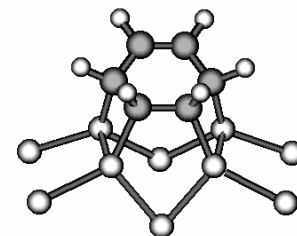
## Benzene/Si(100): Calculated Vibrational Spectrum



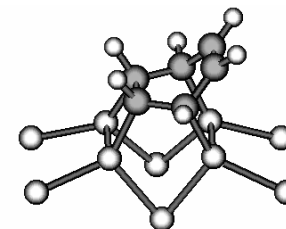
- Can assign all the observed modes to either single dimer, tight or twist bridge bonding geometries.
- Symmetric bridge can be ruled out, consistent with calculated adsorption energy



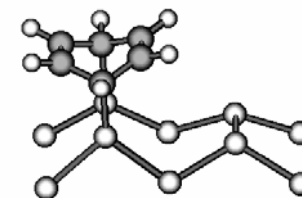
Twist  
bridge



Tight  
bridge



Single  
dimer



Resolving Organic Molecule-Silicon Scanning Tunneling  
Microscopy Features with Molecular Orbital Methods, R.A.  
Wolkow, G.P. Lopinski and D.J. Moffatt, *Surf. Sci.*, **416**,  
L1107-1113 (1998).

# Adsorption of benzene on Si(100)-(2×1): Adsorption energies and STM image analysis by *ab initio* methods

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(Received 19 April 2000; revised manuscript received 10 July 2000; published 6 February 2001)

We model the adsorption and STM imaging of benzene on Si(100) by using first principles density functional methods and a perturbation approach for the tunneling current. The simulations are well in accordance with experimental data and reproduce the adsorption energies and the energy differences between adsorption sites remarkably well. We were able to simulate images and line scans of the two principal adsorption geometries and to show that they reproduce the actual measurements. The chemical nature of the tip in measurements is discussed and it is shown that a tip structure protruding several layers from the crystal face and terminated by a tungsten atom gives the best agreement with measurements. The results confirm the view that tunneling is dominated by a single tip atom.

DOI: 10.1103/PhysRevB.63.085314

PACS number(s): 73.20.-r, 68.37.Ef

## ADSORPTION OF BENZENE ON Si(100)-(2×1): ...

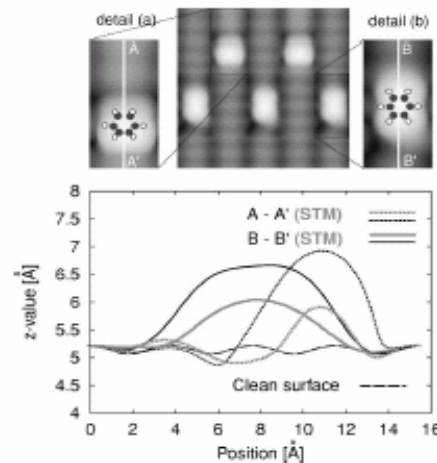
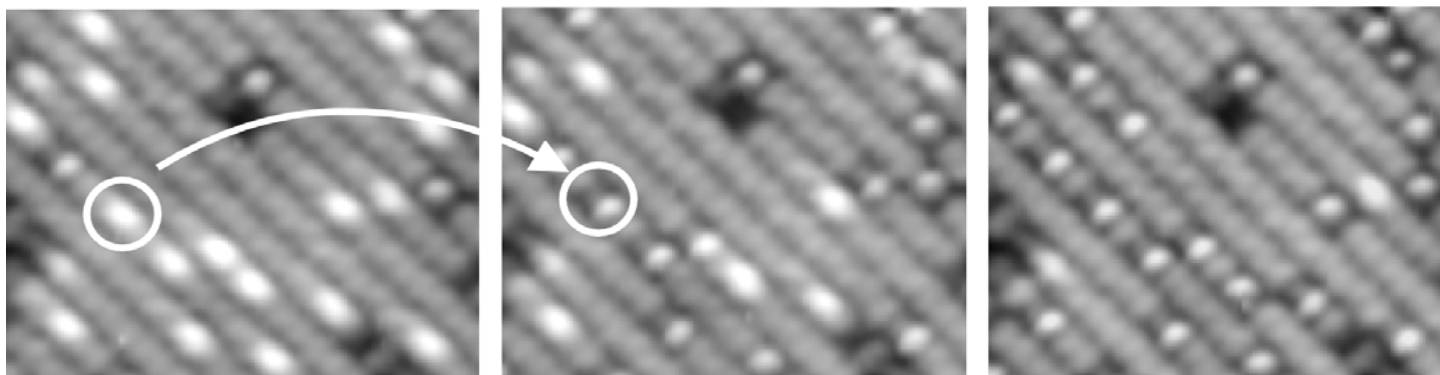
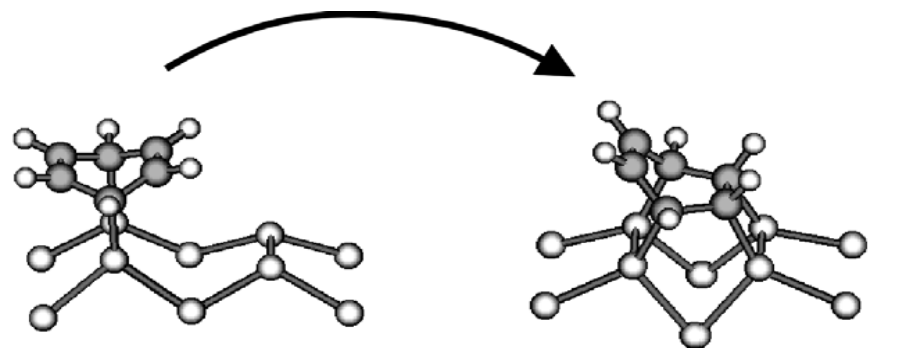
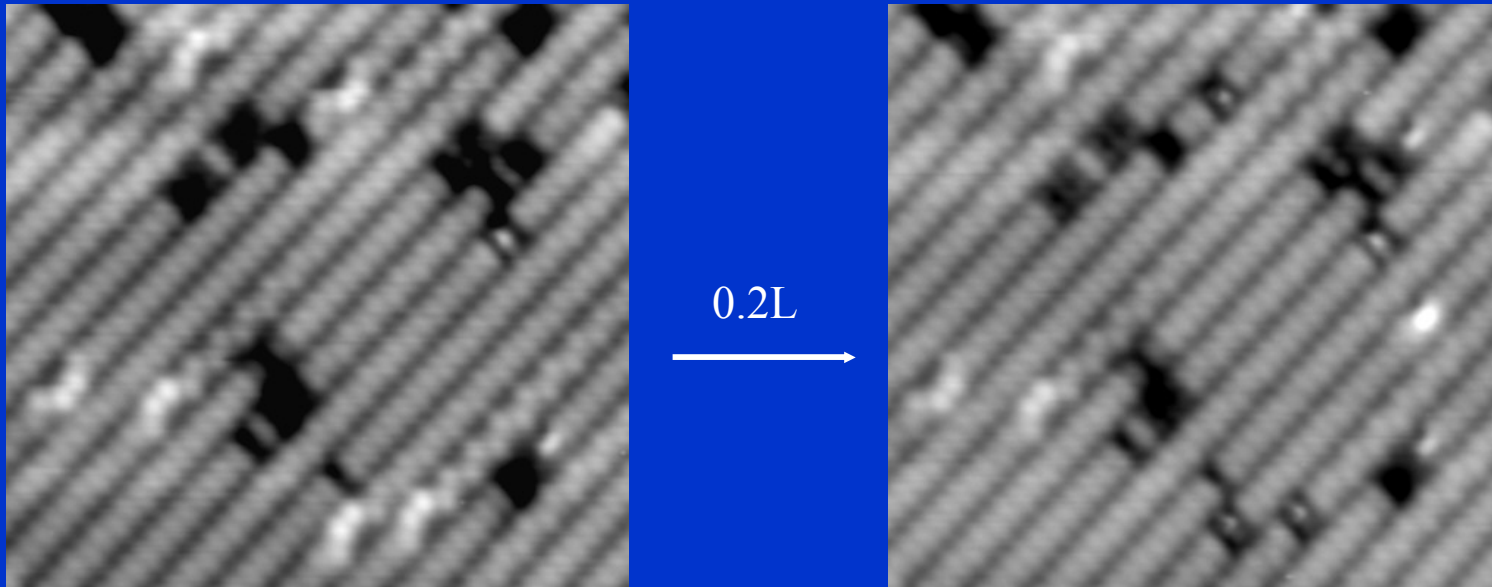


FIG. 4. STM images and line scans due to a LDOS contour of  $5 \times 10^{-7}$  states/eV. The simulation along *A-A'* shows the highest corrugation (1.6 Å), it is due to the tight-bridge configuration. The scan on a (1,4) configuration, along *B-B'* is lower, in the simulation, by about 0.2 Å. Experimental line scans (grey curves) are taken from a 50 pA constant current image.

# Benzene/Si(100) Bonding State Conversion @300K

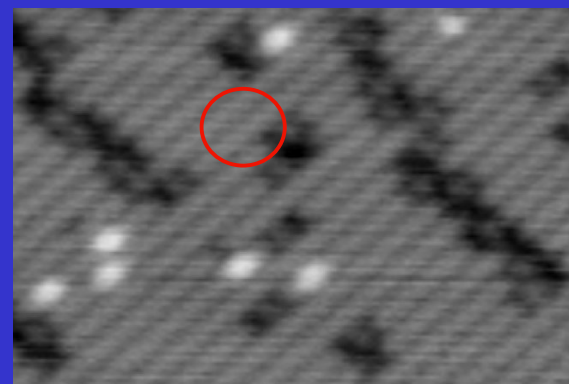
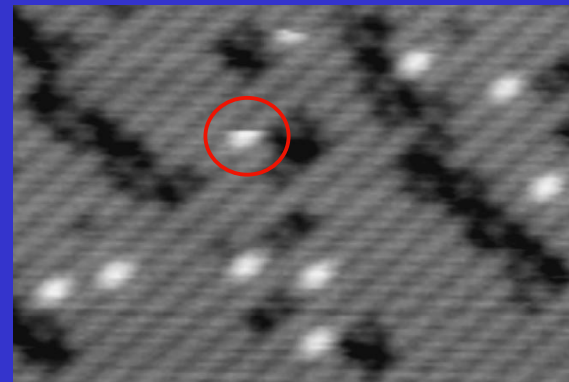
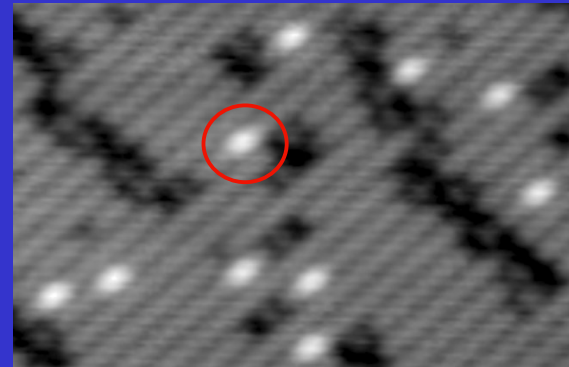


## Benzene Adsorption at type C defects



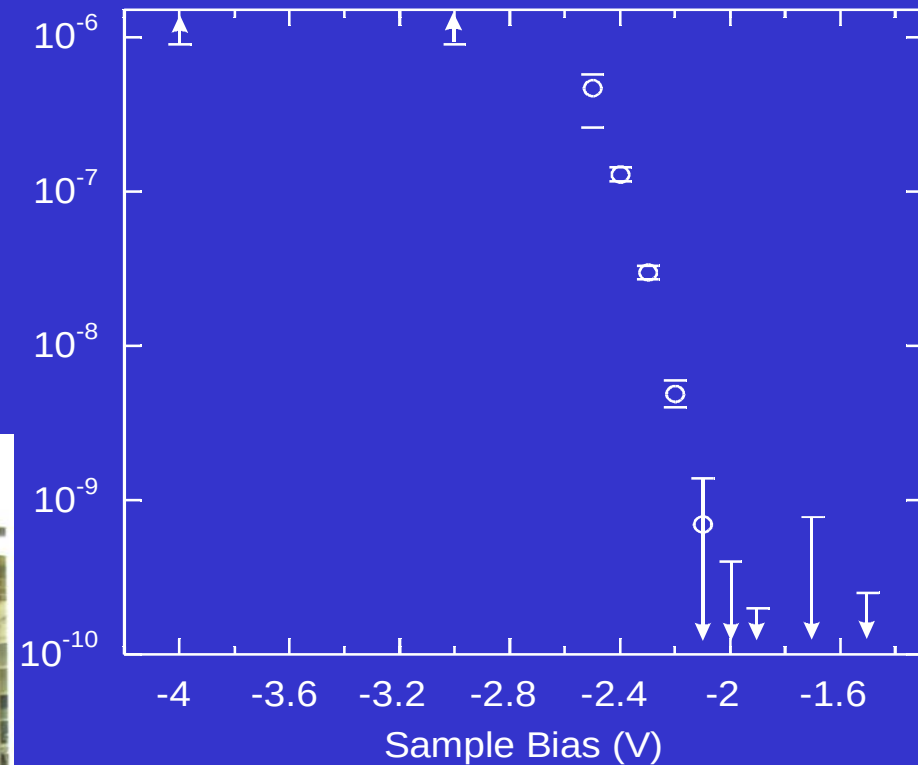
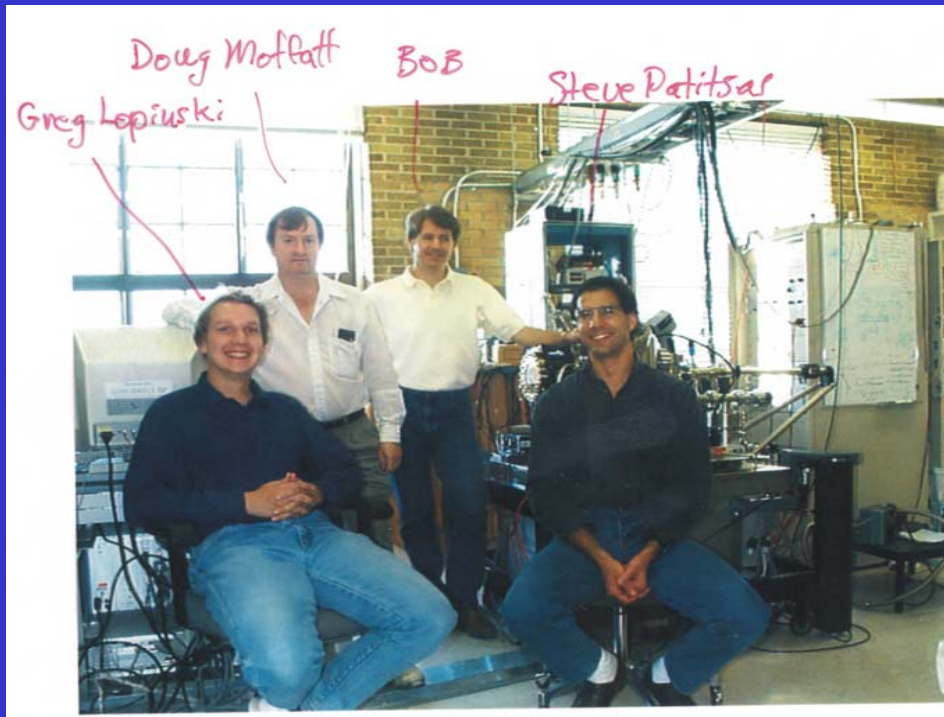
1. 5 additional adsorption events in this area, 3 at type C defects
2. preferential adsorption at type C defects
3. Taking relative populations (regular and defect) into account indicates 40:1 preference for defect
4. Requires substantial mobility before chemical adsorption locks molecule in place

Single molecule-silicon bond  
breaking



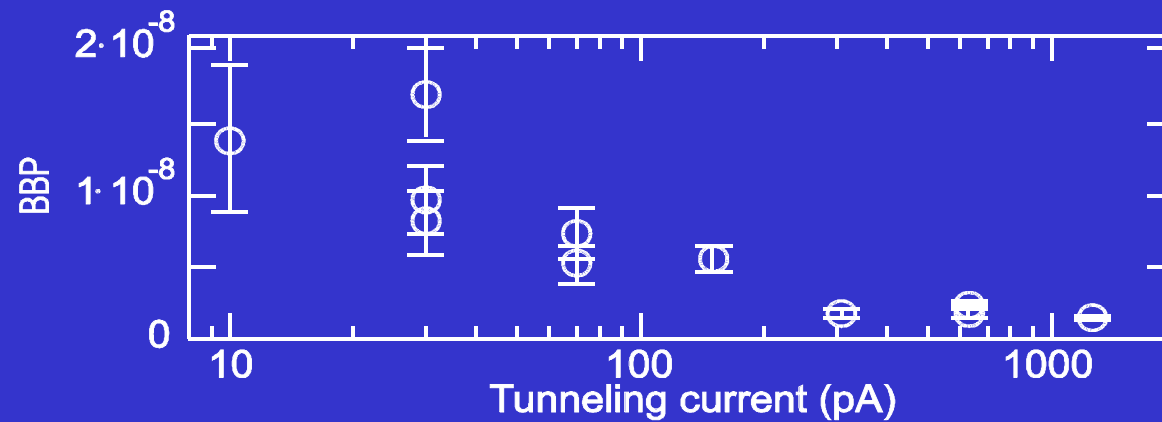
## bond breaking probability as a function of voltage

- bond breaking is not observable at lower voltages
- very sharp rise (note logarithmic graph)

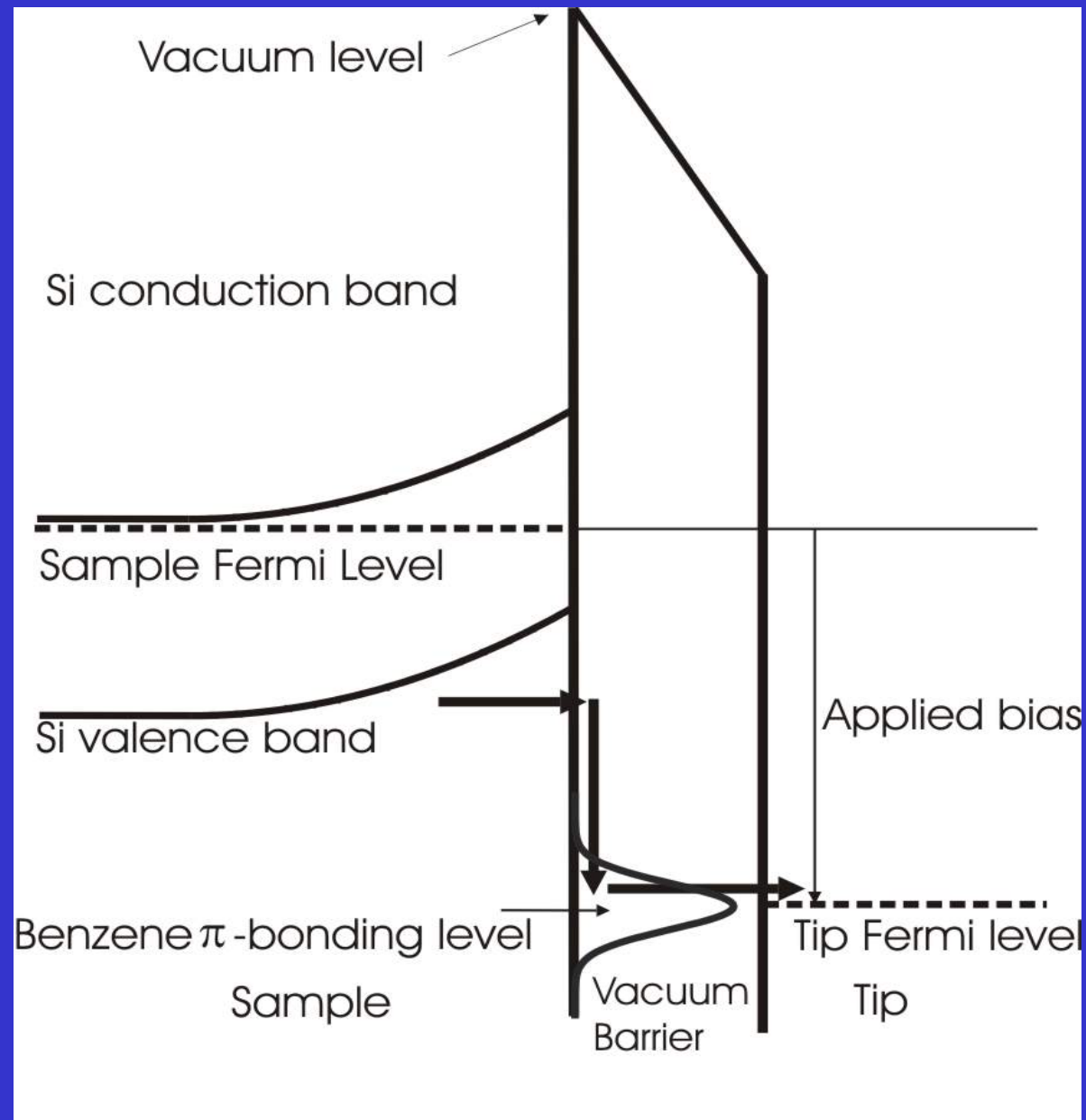


# Single electron process

- examine current dependence of bond breaking probability
- approximately linear
- single electron breaks the molecule-silicon bond (2 S-C bonds)

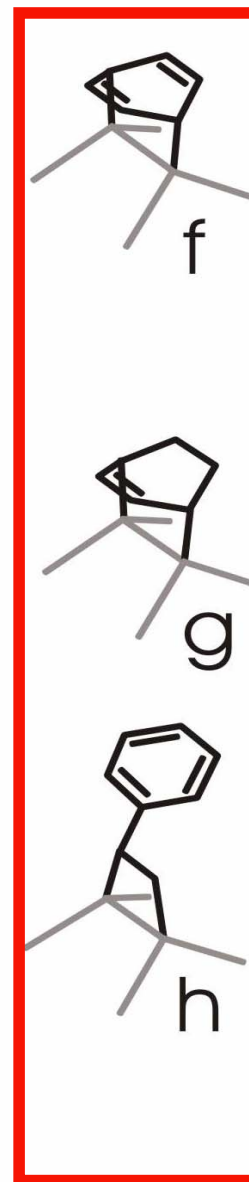
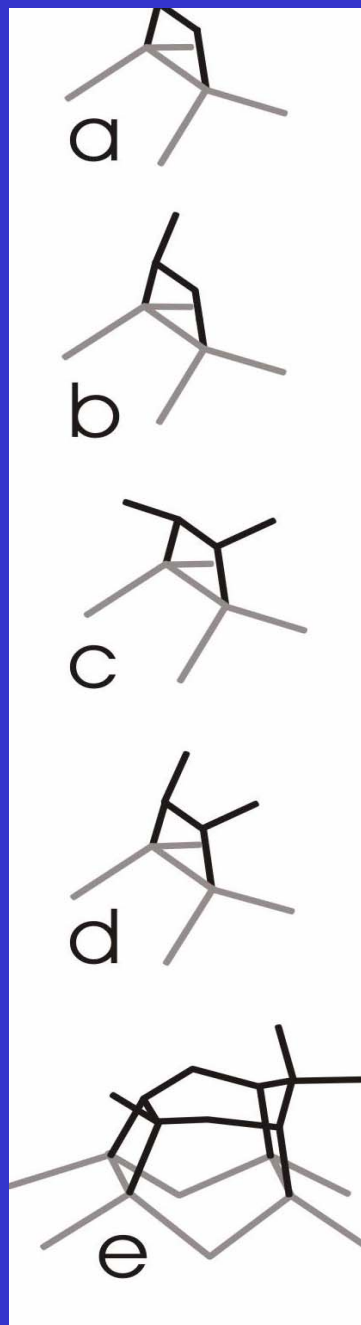






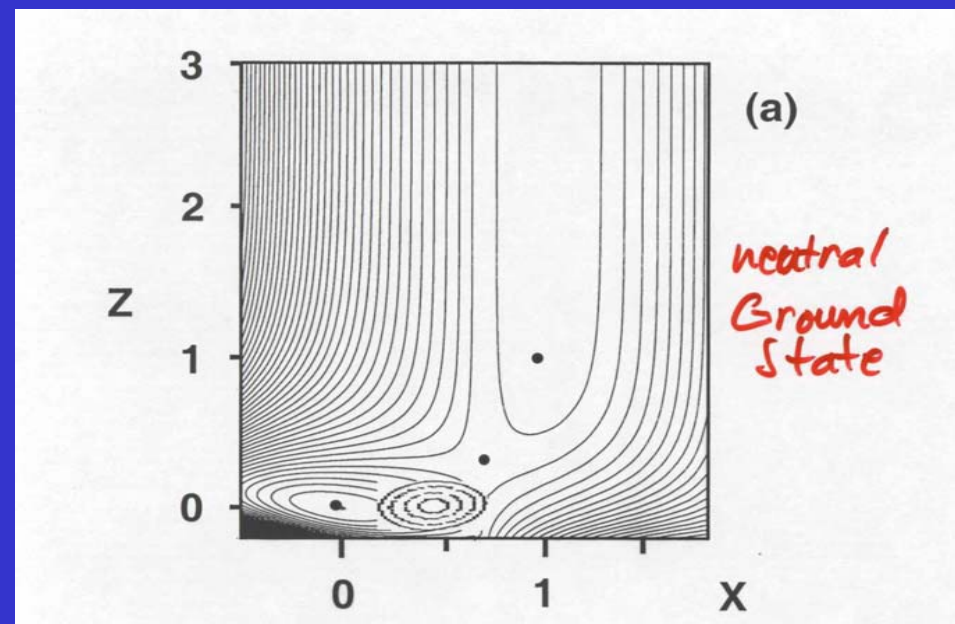
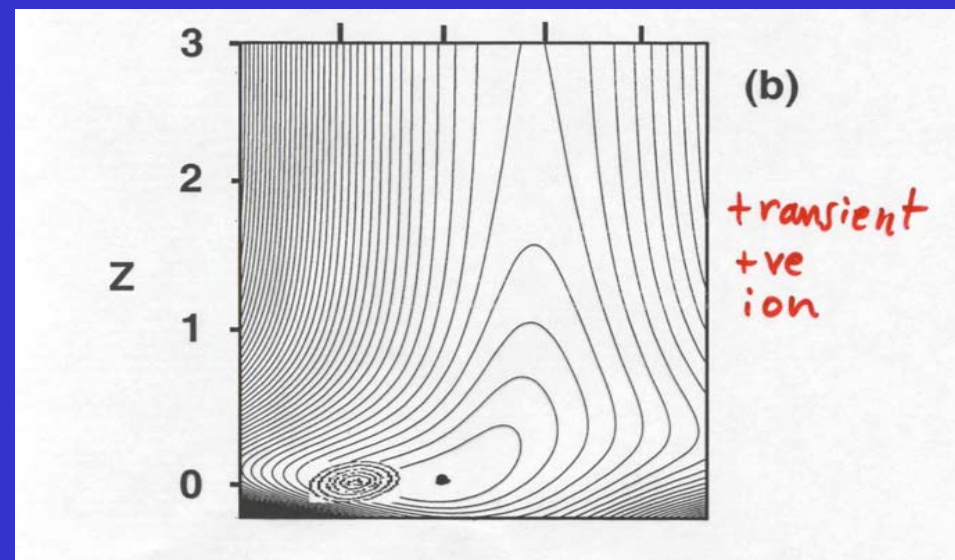
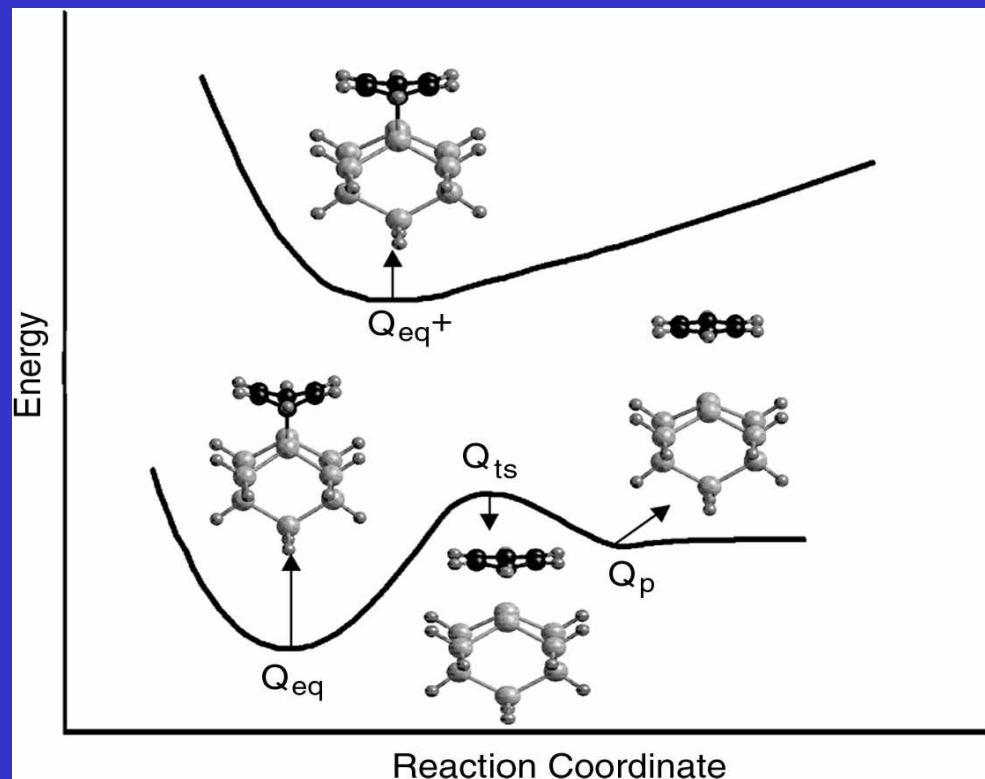
## Alkane-like adsorbates

Current-Induced Organic-Silicon  
Bond Breaking: Consequences for  
Molecular Devices  
S.N. Patitsas, G.P. Lopinski, O.  
Hul'ko, D.J. Moffatt and R.A.  
Wolkow, Sur. Sci., **457**, L425-L43,  
2000.



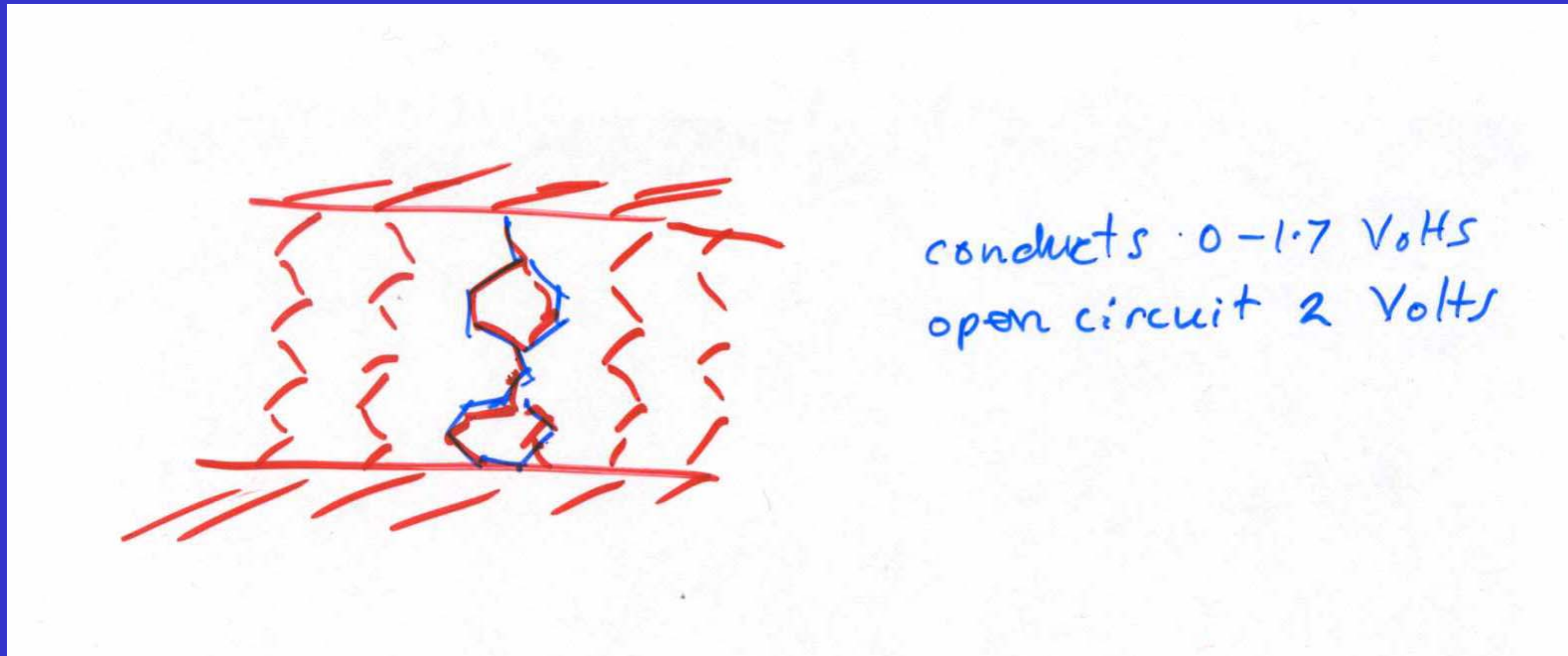
$\pi$ -bond  
containing  
adsorbates

These can be  
dislodged



Inducing Desorption of Organic Molecules with a scanning Tunneling Microscope: Theory and Experiments, Saman Alavi, Roger Rousseau, S.N Patitsas, Gregory P. Lopinski, Robert Wolkow and Tamar Seideman, Phys. Rev. Lett., **85**, 5372 (2000).

Can we use our knowledge to build and  
characterize new structures?



Negative differential resistance?

## “Gentle lithography” with benzene on Si(100)

Peter Kruse and Robert A. Wolkow<sup>a)</sup>

*Steacie Institute for Molecular Sciences, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario K1A 0R6, Canada*

- Si(100) surface passivated by a monolayer of benzene
- The arrows mark a line from which benzene has been removed – creating a very small reactive region

