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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
# Building a Foundation for Hybrid Silicon-organic Molecular Devices
## Part: I - II - III

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

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Bob Wolkow

Department of Physics, University of Alberta

*and*

National Institute for Nanotechnology
National Research Council of Canada
Edmonton, Alberta, Canada

# Building a foundation for hybrid silicon-organic molecular devices

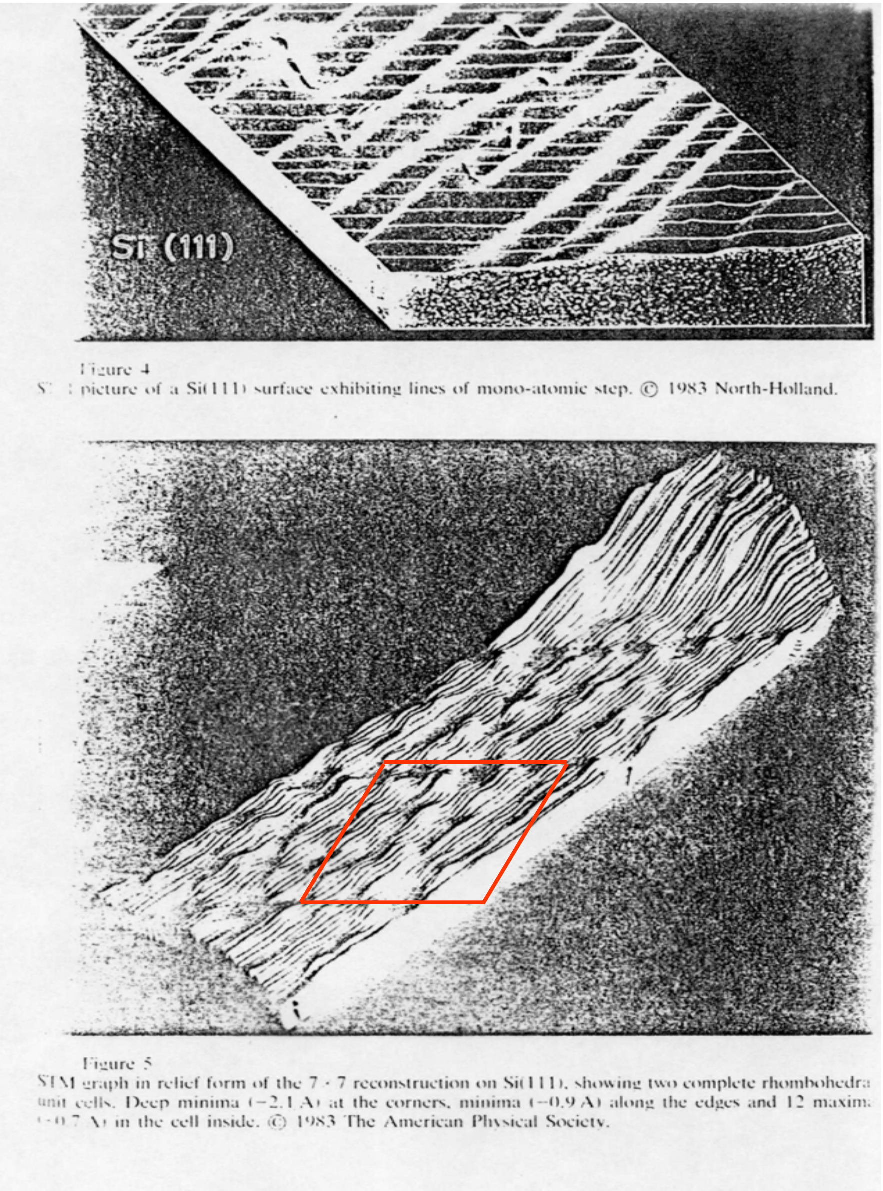
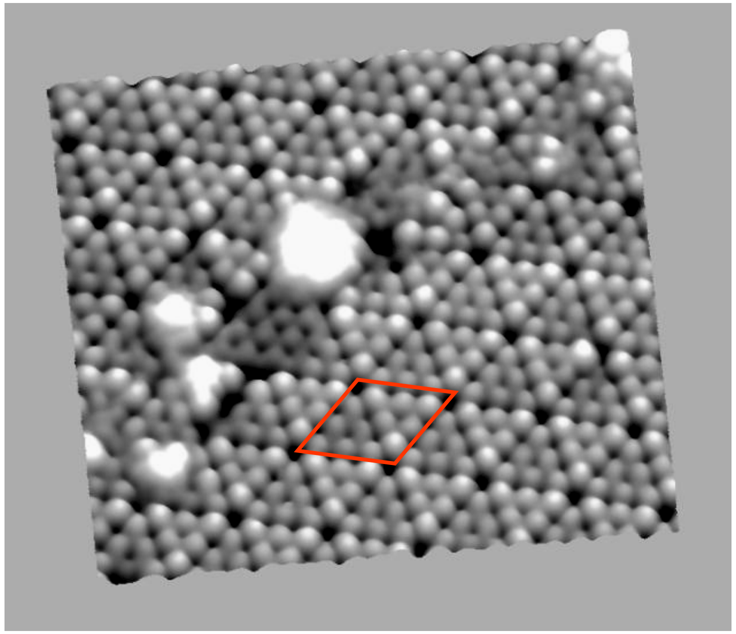
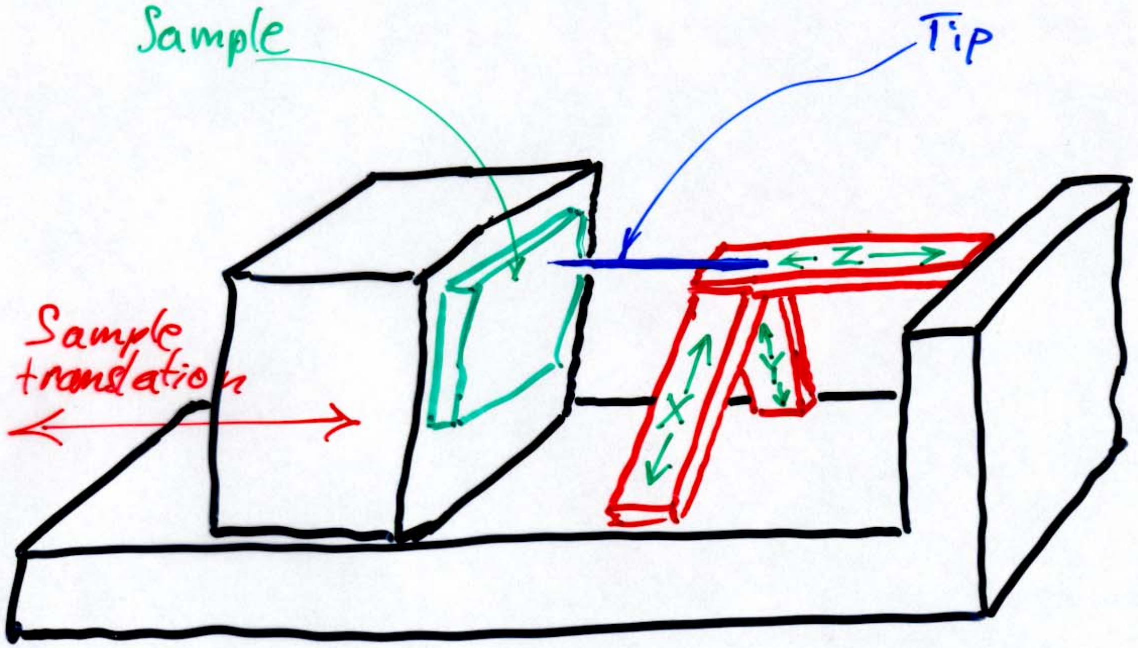


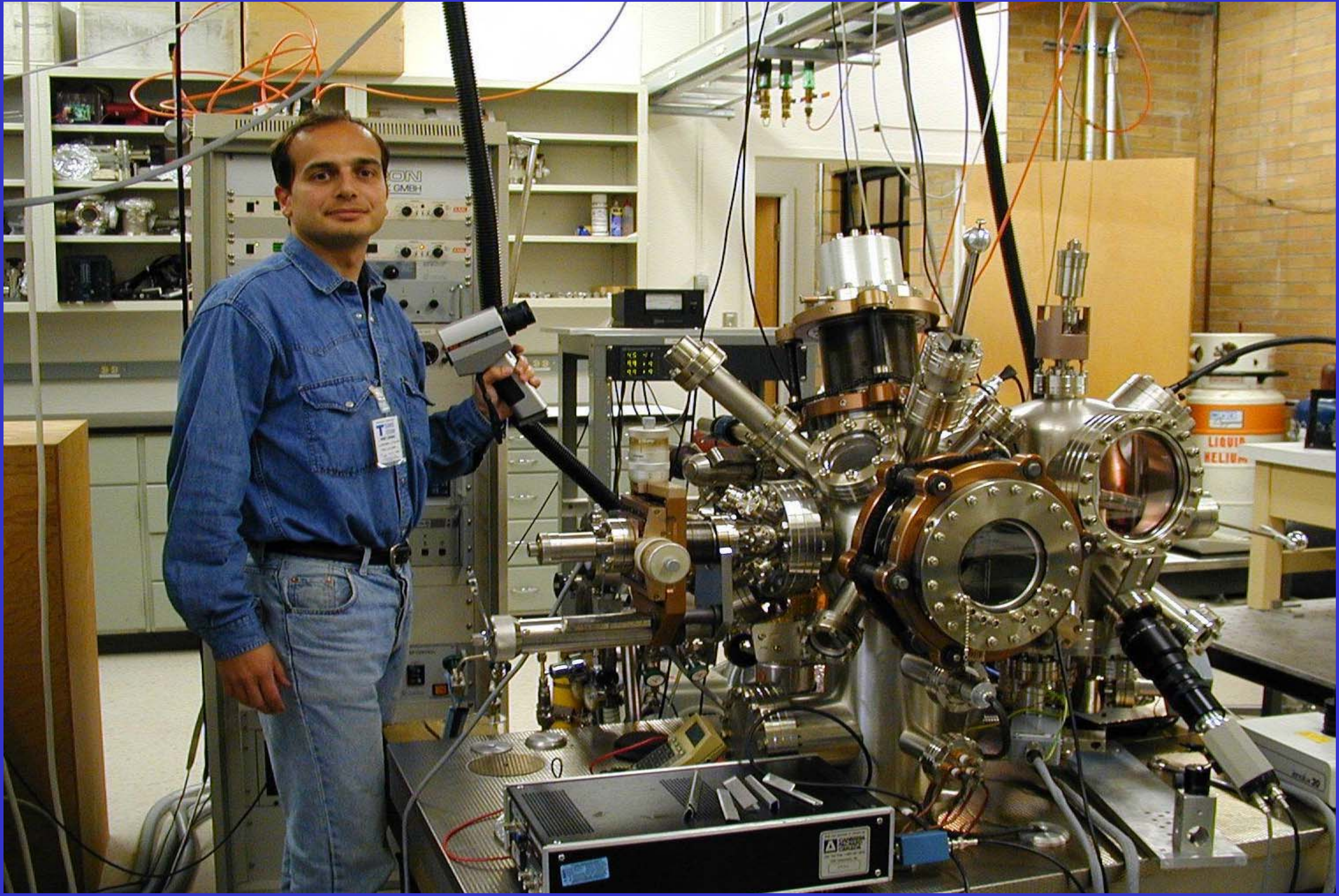
Figure 4
STM picture of a Si(111) surface exhibiting lines of mono-atomic step. © 1983 North-Holland.

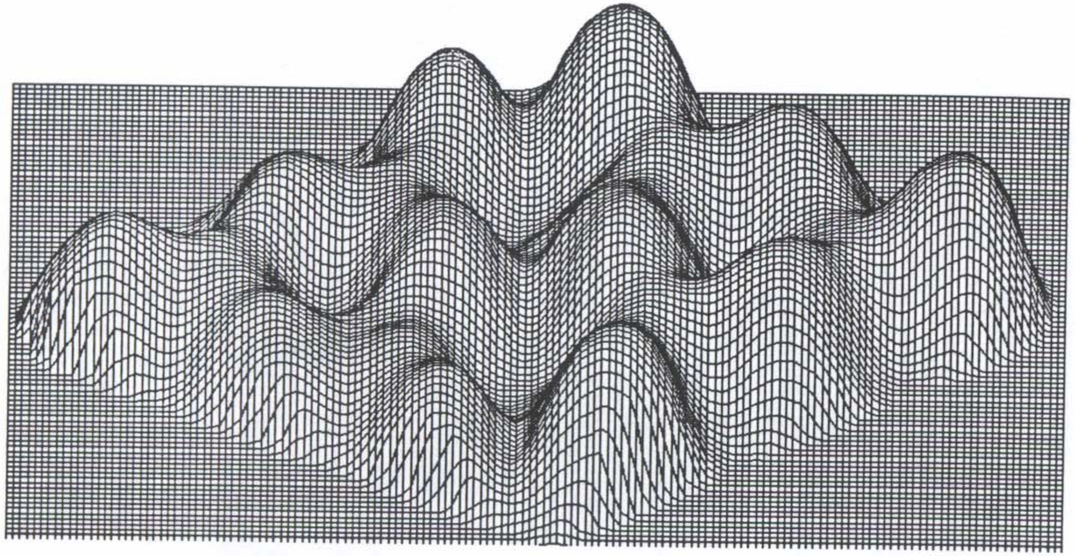
Figure 5
STM graph in relief form of the 7 × 7 reconstruction on Si(111), showing two complete rhombohedra unit cells. Deep minima (−2.1 Å) at the corners, minima (−0.9 Å) along the edges and 12 maxim (+0.7 Å) in the cell inside. © 1983 The American Physical Society.



STM (Binnig G., Rohrer H.,et al., Phys. Rev. Lett., 1982, 49, 57


Sample
Tip
Sample translation
Z
X
Y


LIQUID
HELIUM



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Submit an Invention Disclosure of anything possibly new and inventive.

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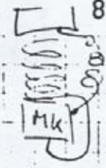
22.12.78 Zum Erden der Probe:



3.1.79 Längenfluktuationen

Stab: Länge $l$, Fläche: $F$
Kraft: $K$ Elastizitätsmodul $k^\circ$

$$\frac{\Delta x}{l} = \frac{K}{k^\circ \cdot F} \Rightarrow K = \frac{k^\circ \cdot F \cdot \Delta x}{l}$$

Energie $E = \frac{1}{2}\frac{k^\circ F}{l}(\Delta x)^2$

$k^\circ \approx 10^{12}$ dyn $= 10^7$ N

für $\left.\begin{array}{l}\Delta x = 0{,}1\,\text{Å} = 10^{-9}\,\text{cm} \\ l = 1\,\text{cm} \\ F = 0{,}001\,\text{cm}^2\end{array}\right\} \Rightarrow E = \frac{1}{2}\frac{10^7\,\text{N cm}^{-2} \cdot 10^{-3}\,\text{cm}^2 \cdot 10^{-18}\,\text{cm}^2}{1\,\text{cm}} = 10^{-14}\,\text{N cm} = 10$

$\triangleq 60\,\text{eV} \triangleq 6 \cdot 10^5$

oder $10^{-3}$

⇒ Längenfluktuationen vernachlässigbar!

3.1.79 Wie lang Stab von 10 Å ⌀, damit 6°K ≙ (Δx = 0,01 Å)

Antwort $l \cong 0{,}1$ Å!

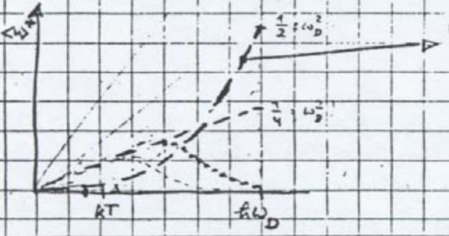
⇒ dünne kurze Fäden Problem.

oder $l = 10$
$F = 10$
→ $E = 60$

3.1.79 Nullpkts. energie: $U_0 = \sum_{k\lambda} \frac{\hbar\omega_\lambda(\vec{k})}{2}$

3.1.79 $\langle n\rangle^*$ = effektive Besetzung = Zustandsdichte mal $\langle n\rangle$

Phononen:

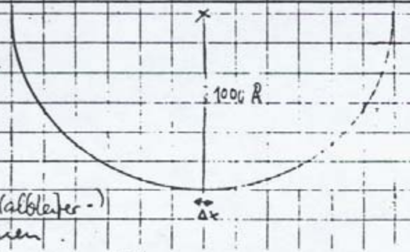


langwellige Phononen sind nur thermisch besetzt und versch linear mit abnehmender Temp

5.1.7

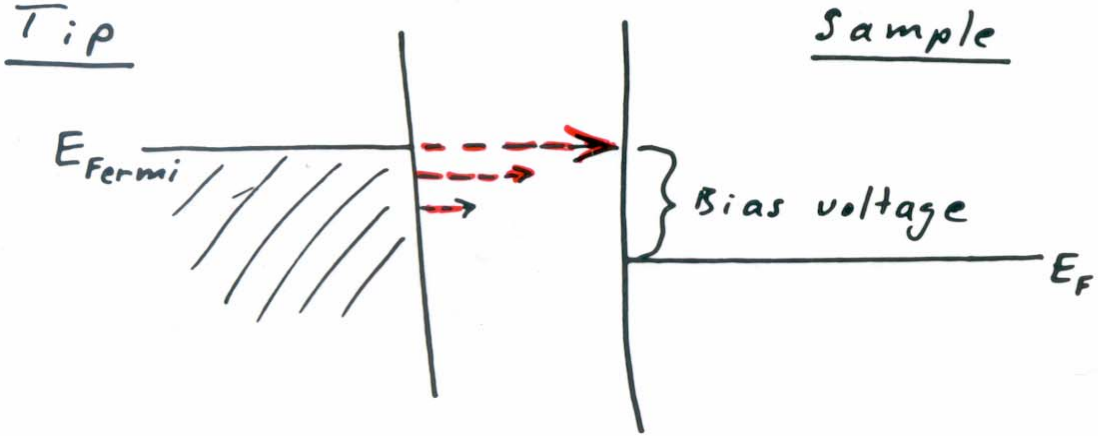
Mit einer Tunnelstromabklinglänge von 1 Å und einem Krümmungsradius der Nadel von 1000 Å

⇒ **Ortsauflösung Δx = 45 Å**



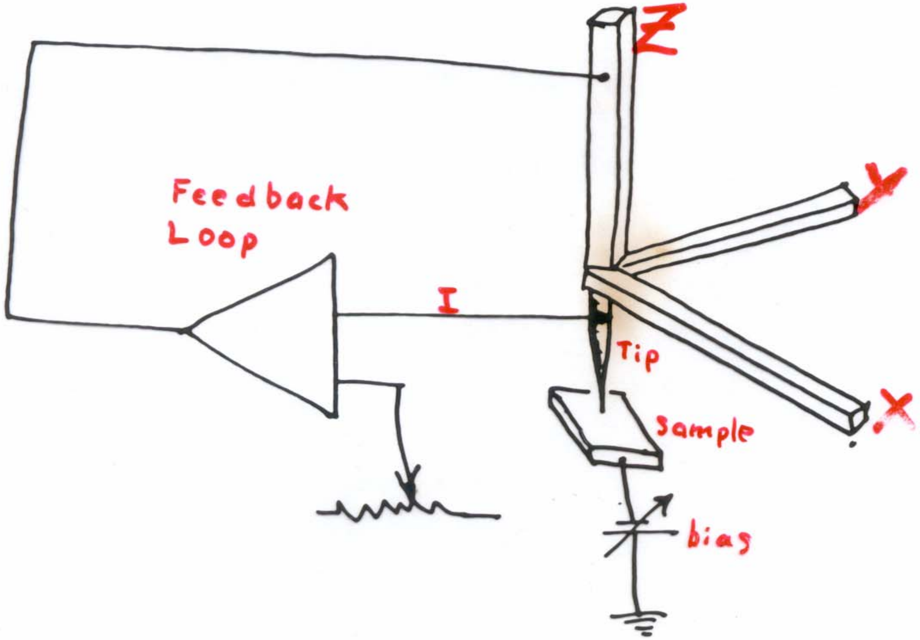
⇒ Mikroskop für Metall (Halbleiter-) Oberflächen.

The above understood and witnessed by ______ Date ______ and by ______ Date



$\boxed{I \propto \exp(-2\kappa d)}$ ; $d$ is distance

$\kappa \propto \sqrt{\phi}$

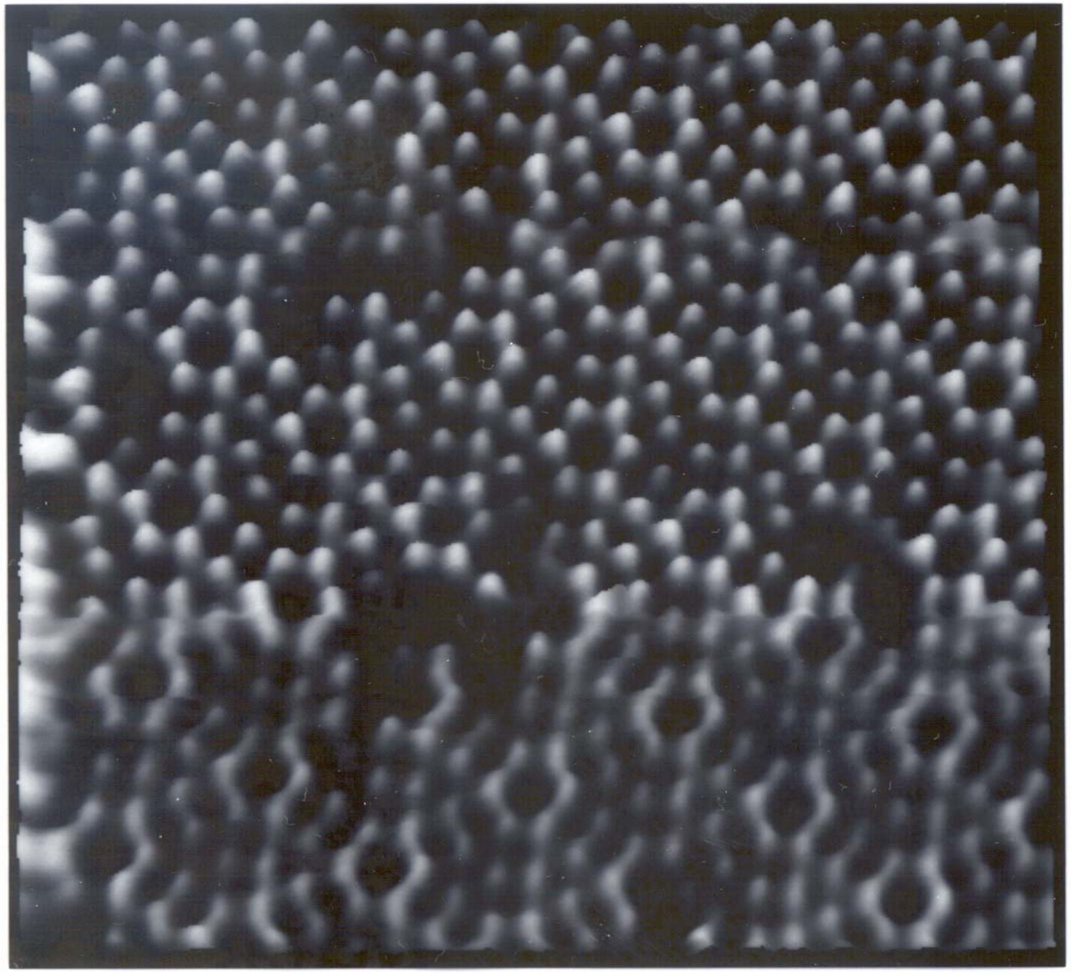

Z
Feedback Loop
Y
I
Tip
X
sample
bias

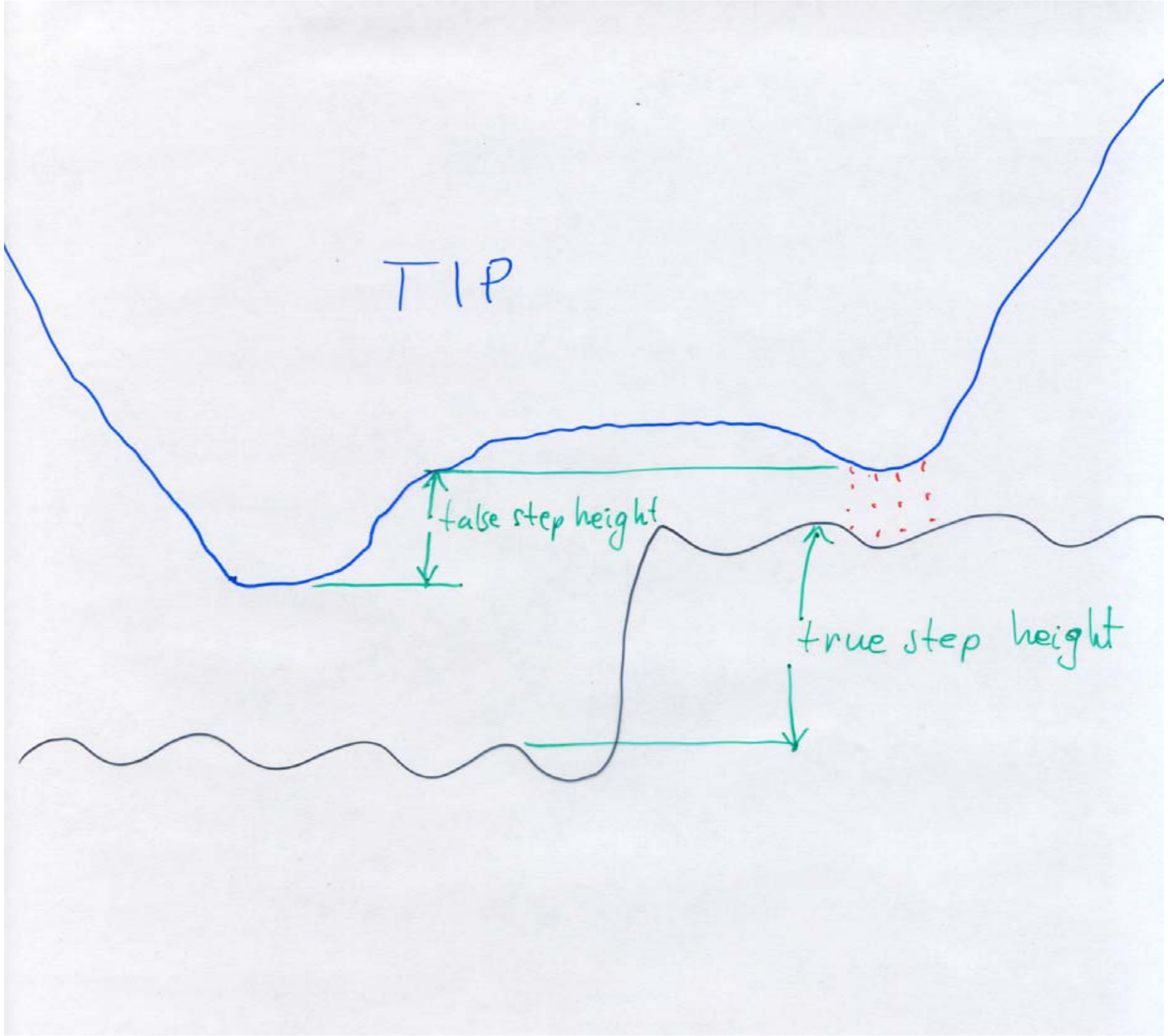
# ALMOST INVENTED ?

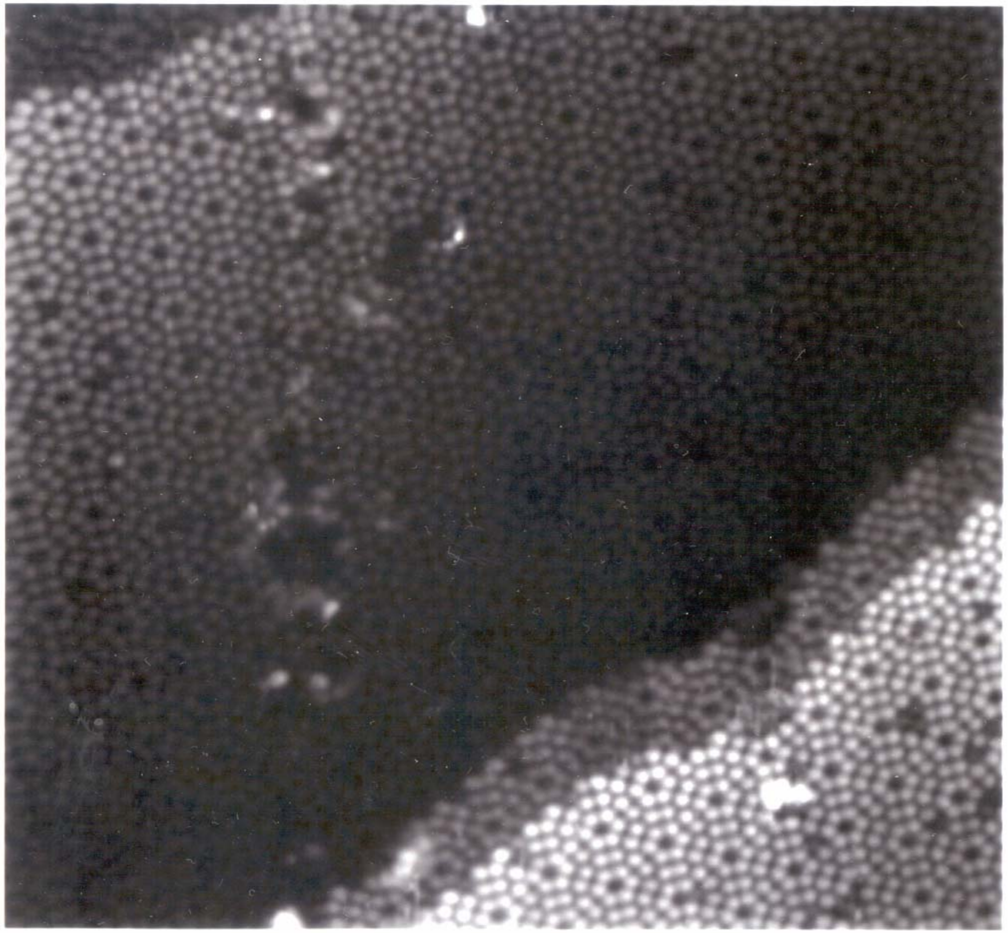
-record player

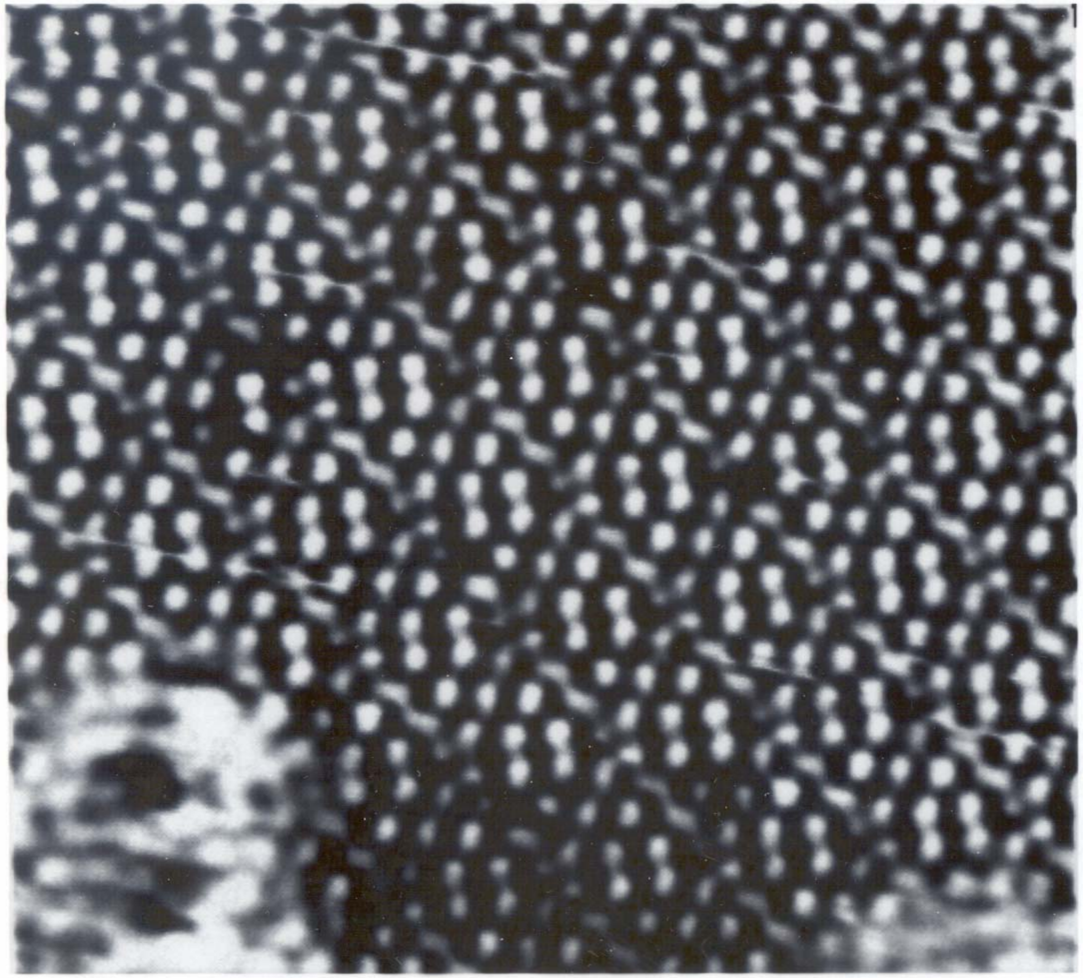
-“stylus profilimeter” commonly used in machine shops and metallurgical labs

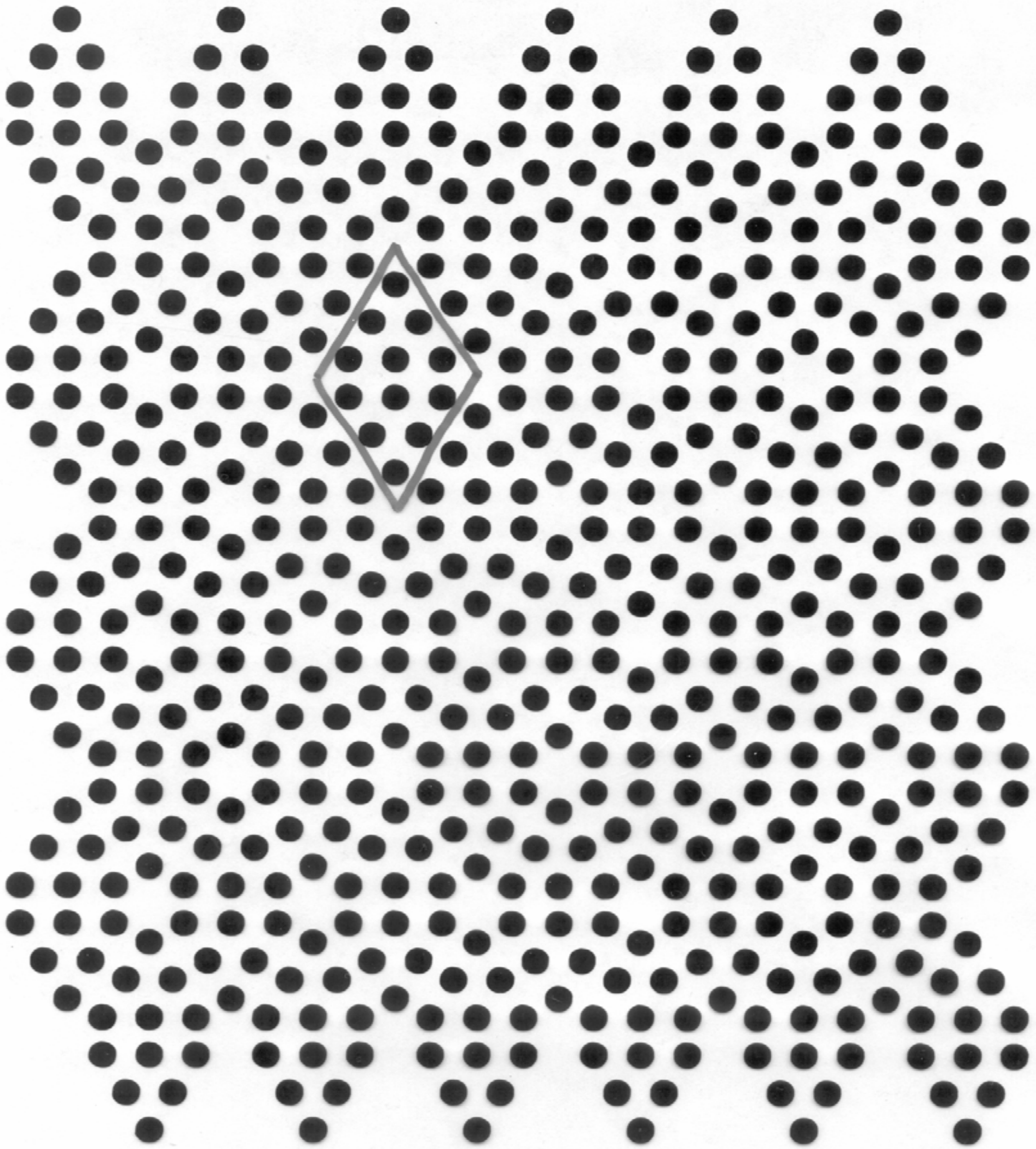
-R.Young, J.Ward, F.Scire, “The topographiner: An Instrument for Measuring Surface Microtopography”, Rev. Sci. Instrum. **43**, 999 (1972) - at NBS

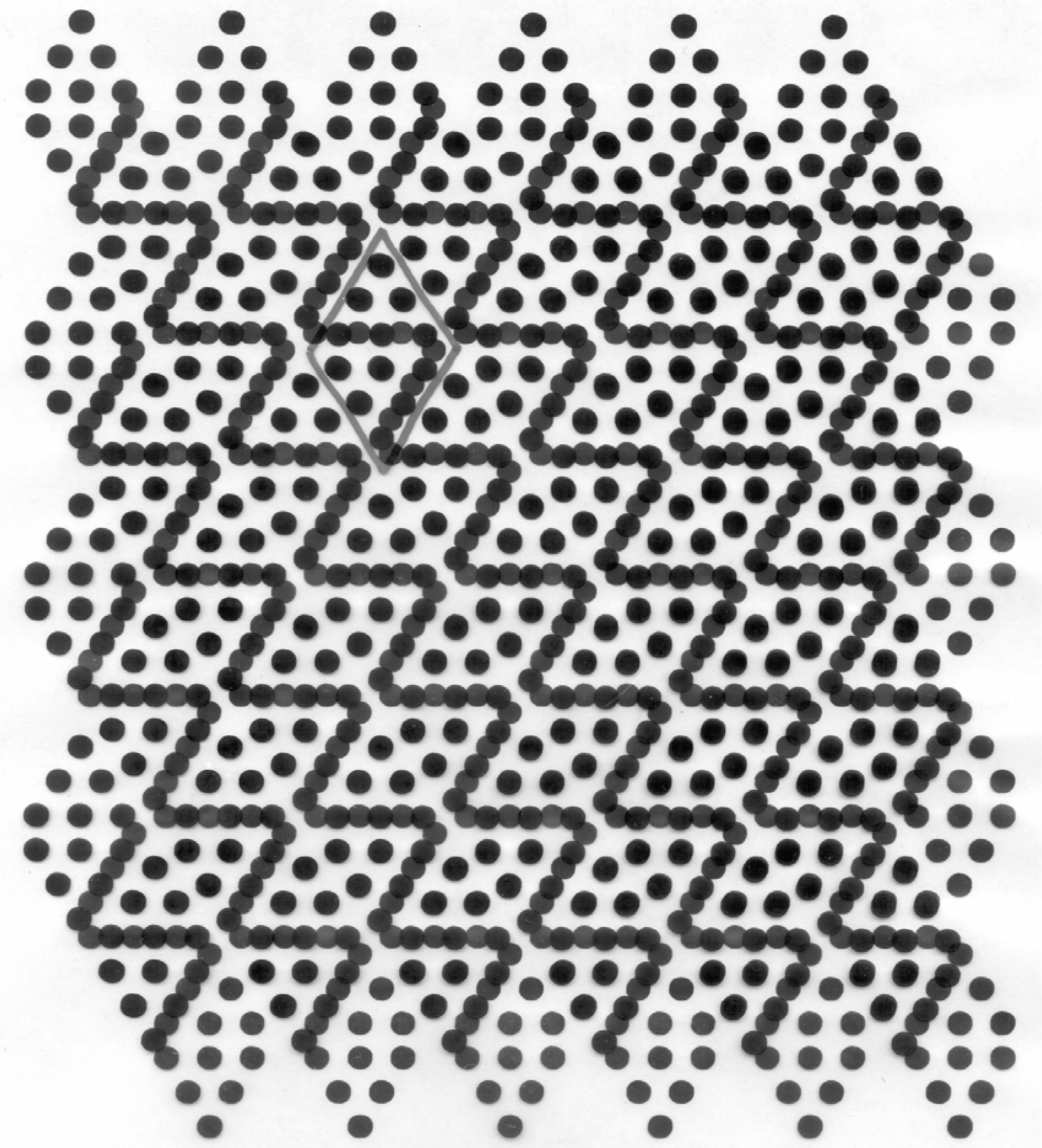


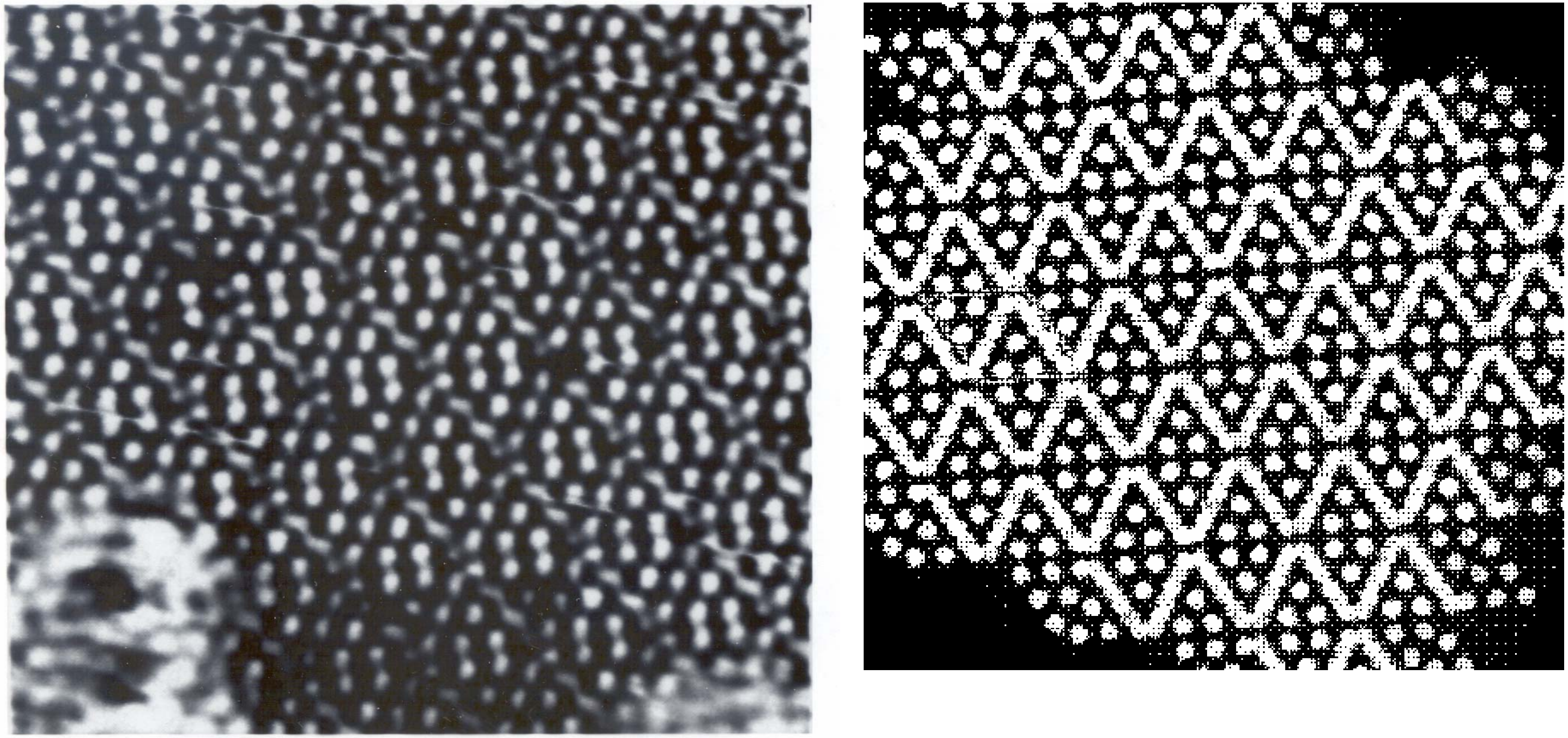

TIP
false step height
true step height



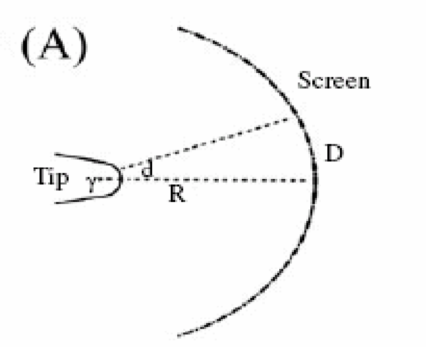


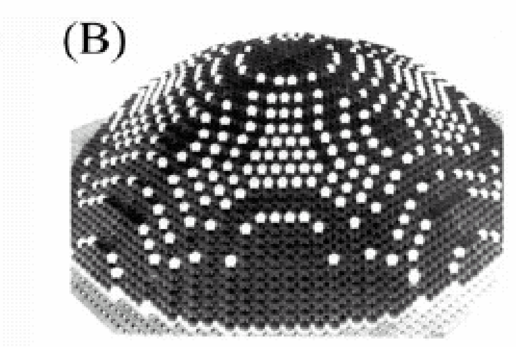


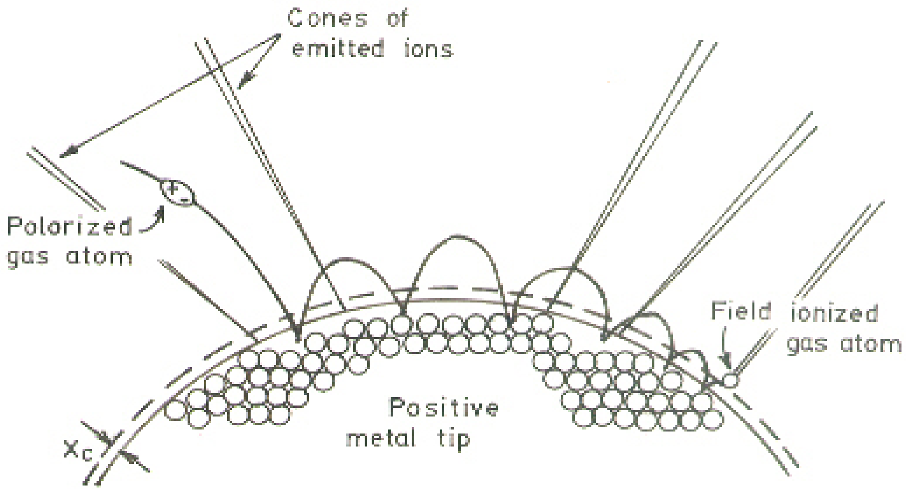




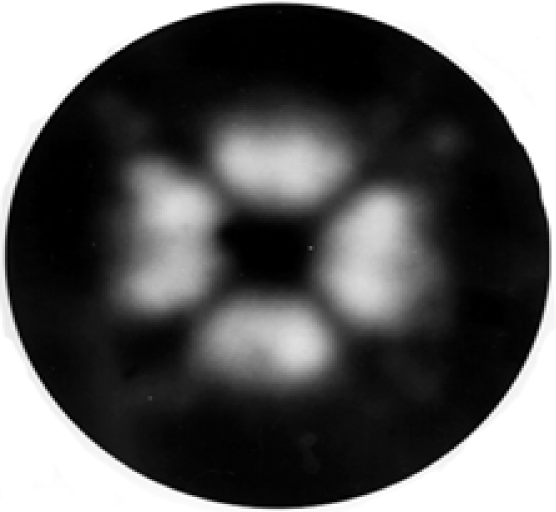
# Field Ion Microscope (see E.W. Mueller, Zeit. f. Phys. 131 (1951)136-142)



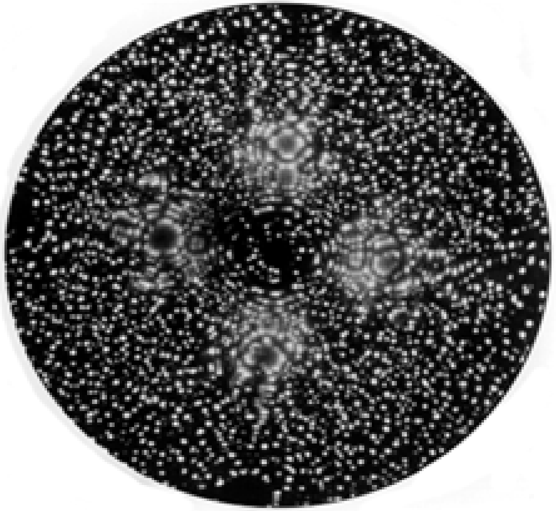


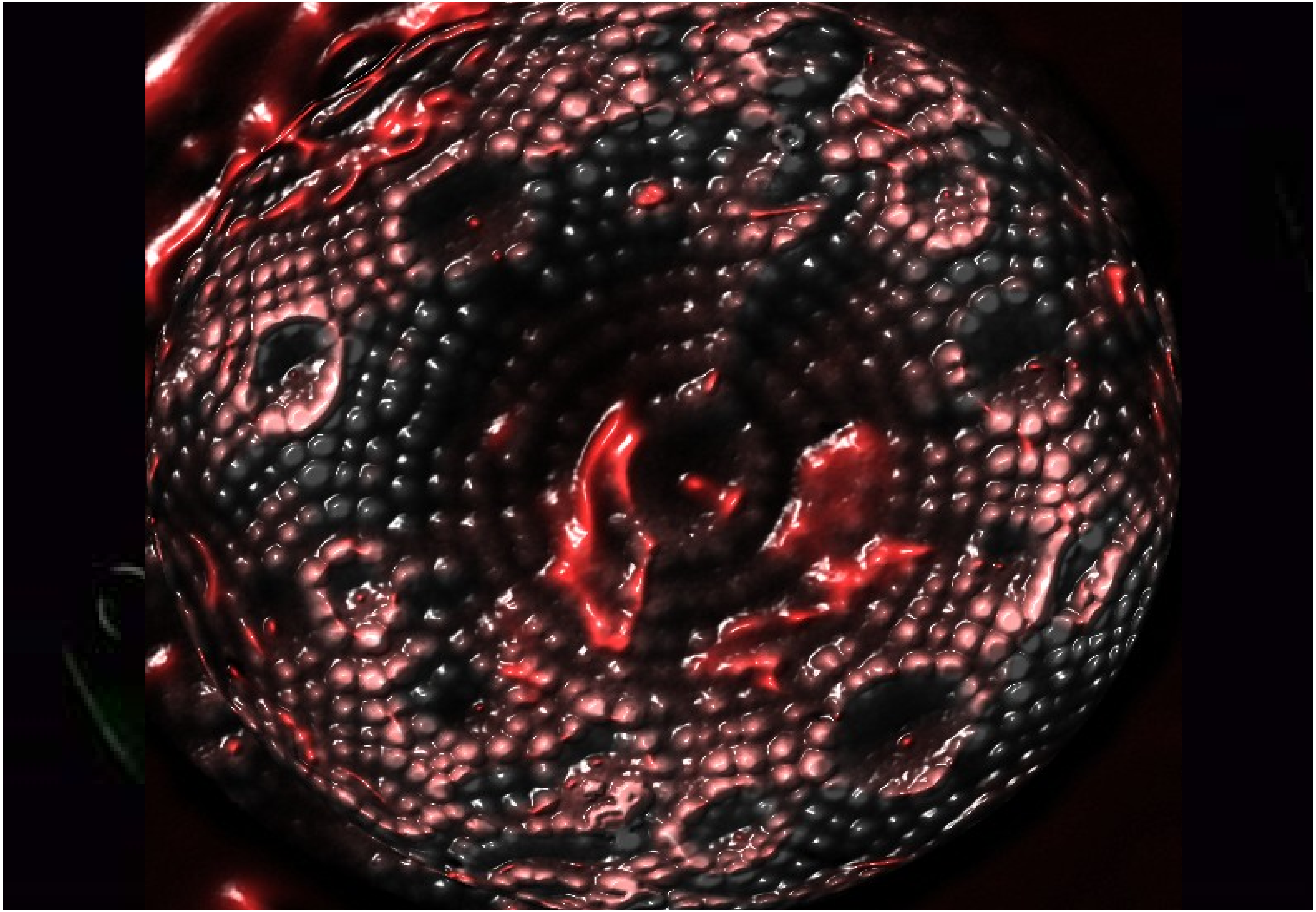


FEM (electrons)



FIM(ions)

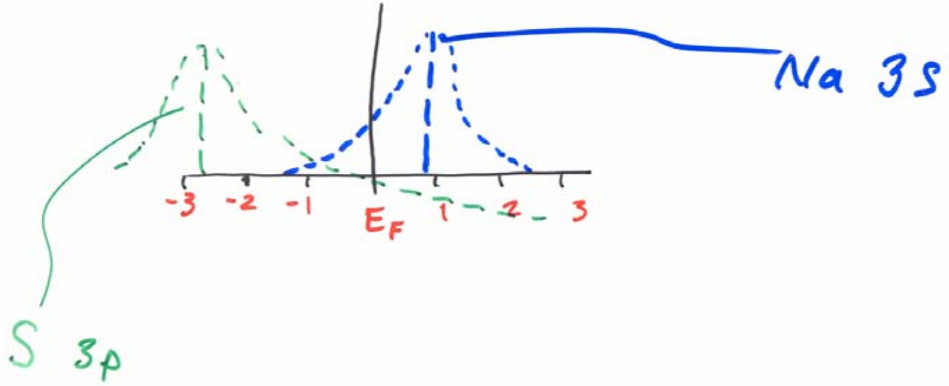




# Implications for AFM

-thought to never give atomic resolution
-Surprise – Franz Giessibl, Science **267**, 69 ~1995
-Our ultra sharp tips?

# Atomic adsorbates on metals



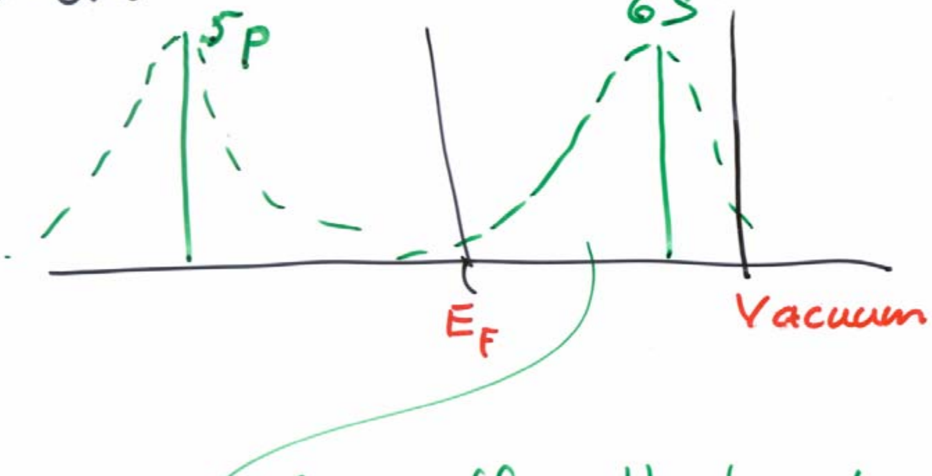
## Sulfur

- filled 3p level
- "bump" in occupied image
- invisible or dip unoccupied

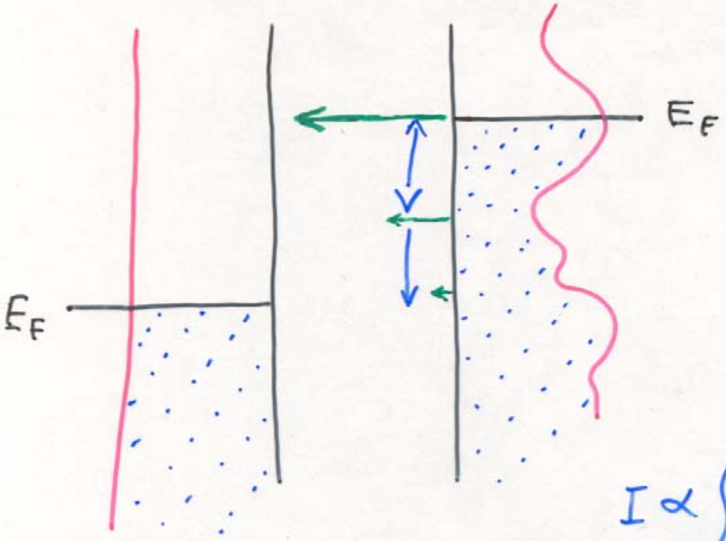
## Na

- visible at both polarities
- 3s mostly empty
- more prominent in unoccupied state image.
- see for example Norton Lang calc's.

Xenon



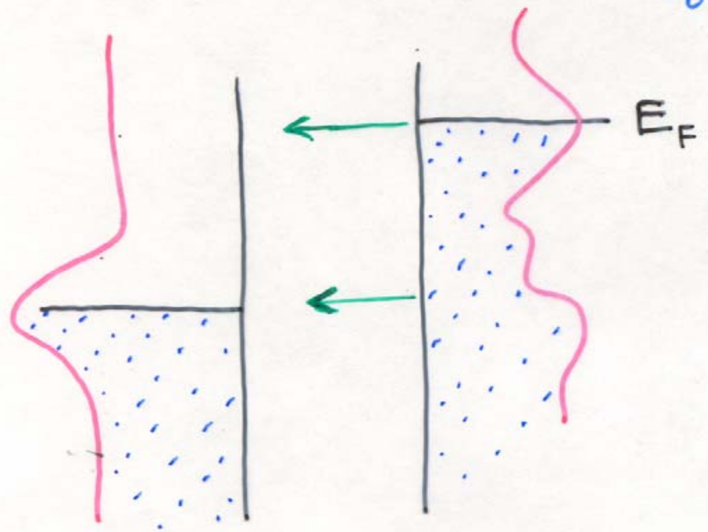
6s sufficiently broadens to give finite LDOS at $E_F$.



$$I \propto \int_0^{eV} \rho_{Tip}(E)\,\rho_{sample}(E)\,T(E,V)\,dE$$

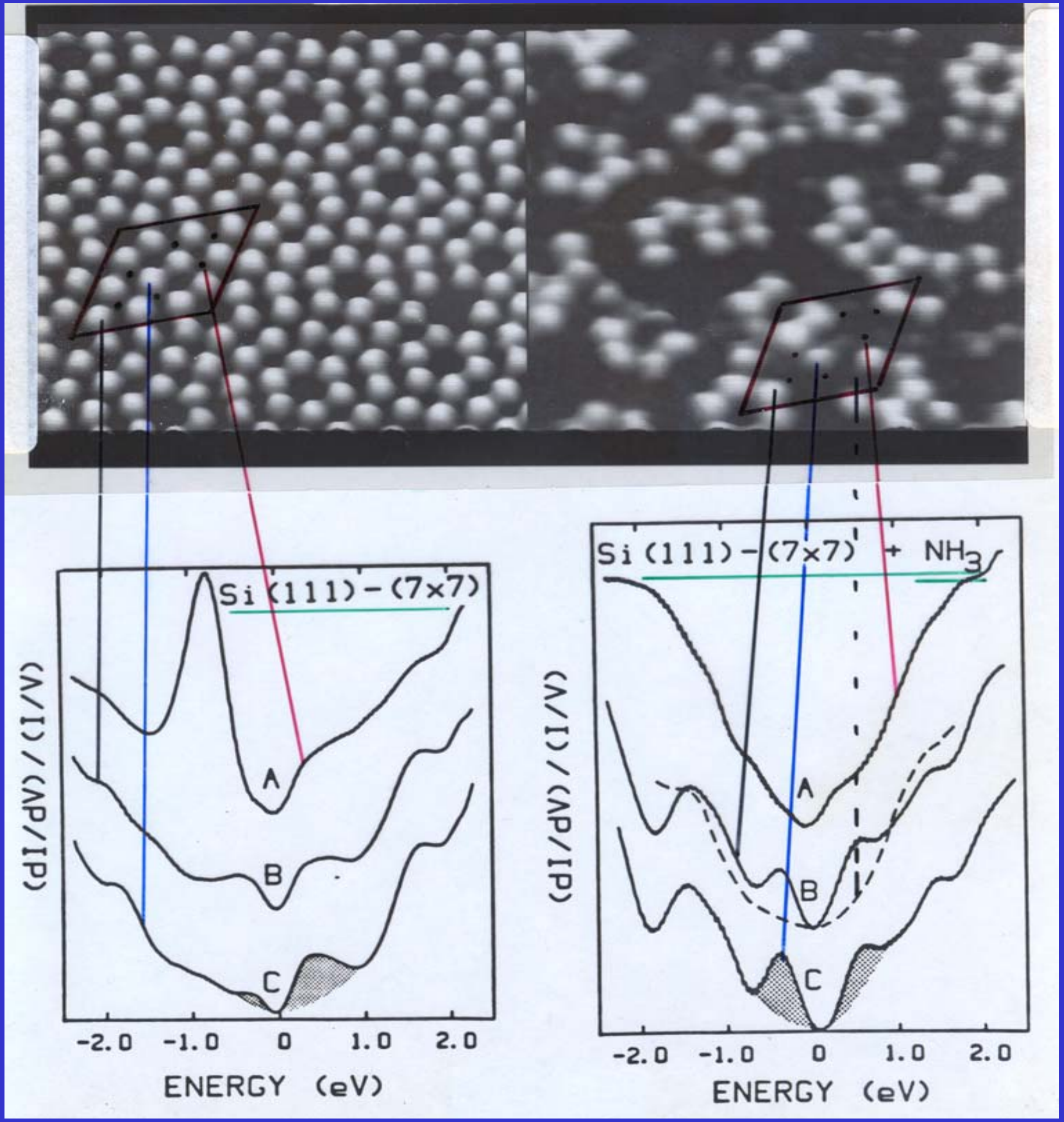
favours states at $E_F$

Altered by adsorbates/contaminants

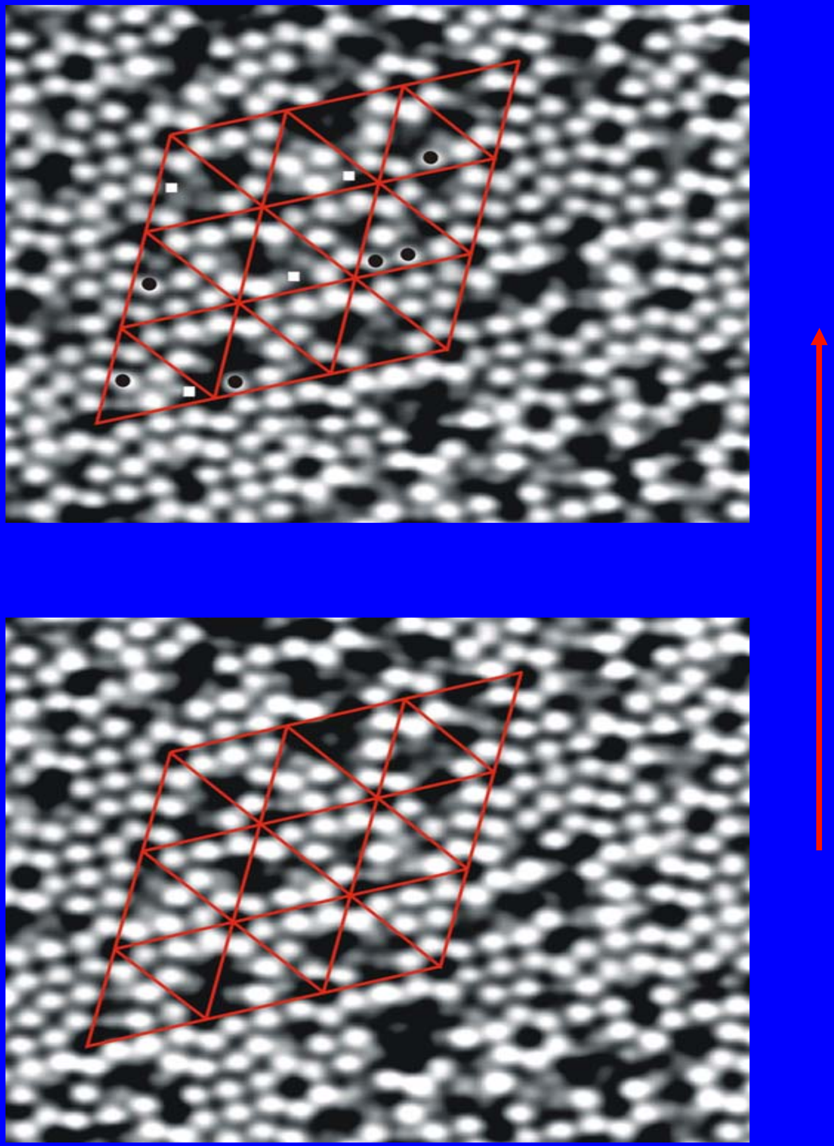


# Atom-resolved surface chemistry using STM

- Wolkow R.A. and Avouris Ph., Phys. Rev. Lett., **60**, 1049-52 (1988)
- Avouris Ph. And Wolkow R.A., Phys. Rev. B, **39**, 5091-9 (1989)



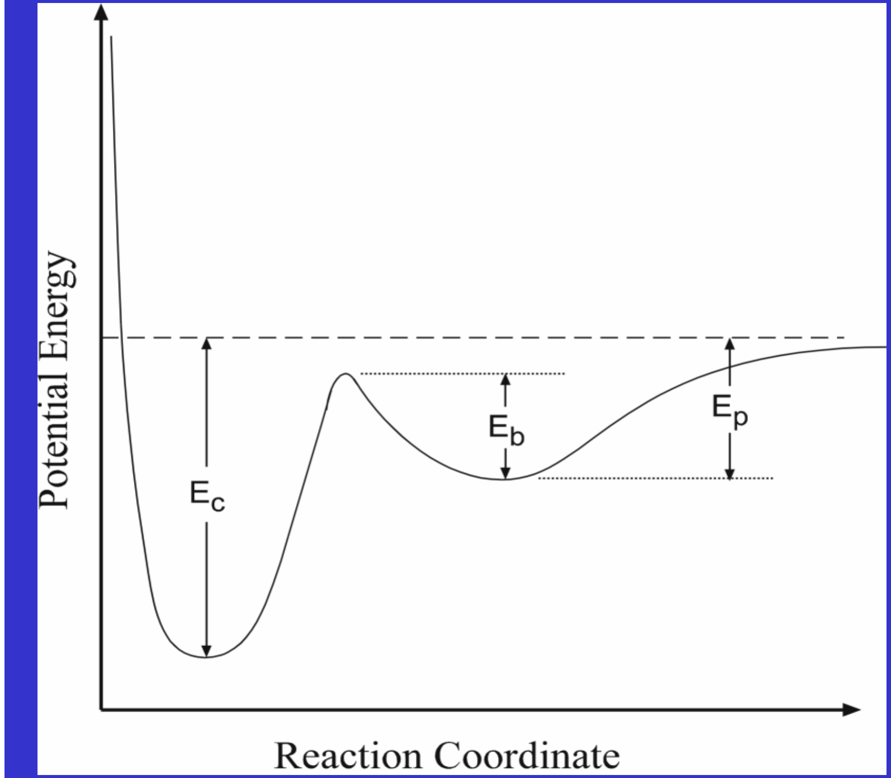
# Frustrated motion of adsorbates on silicon

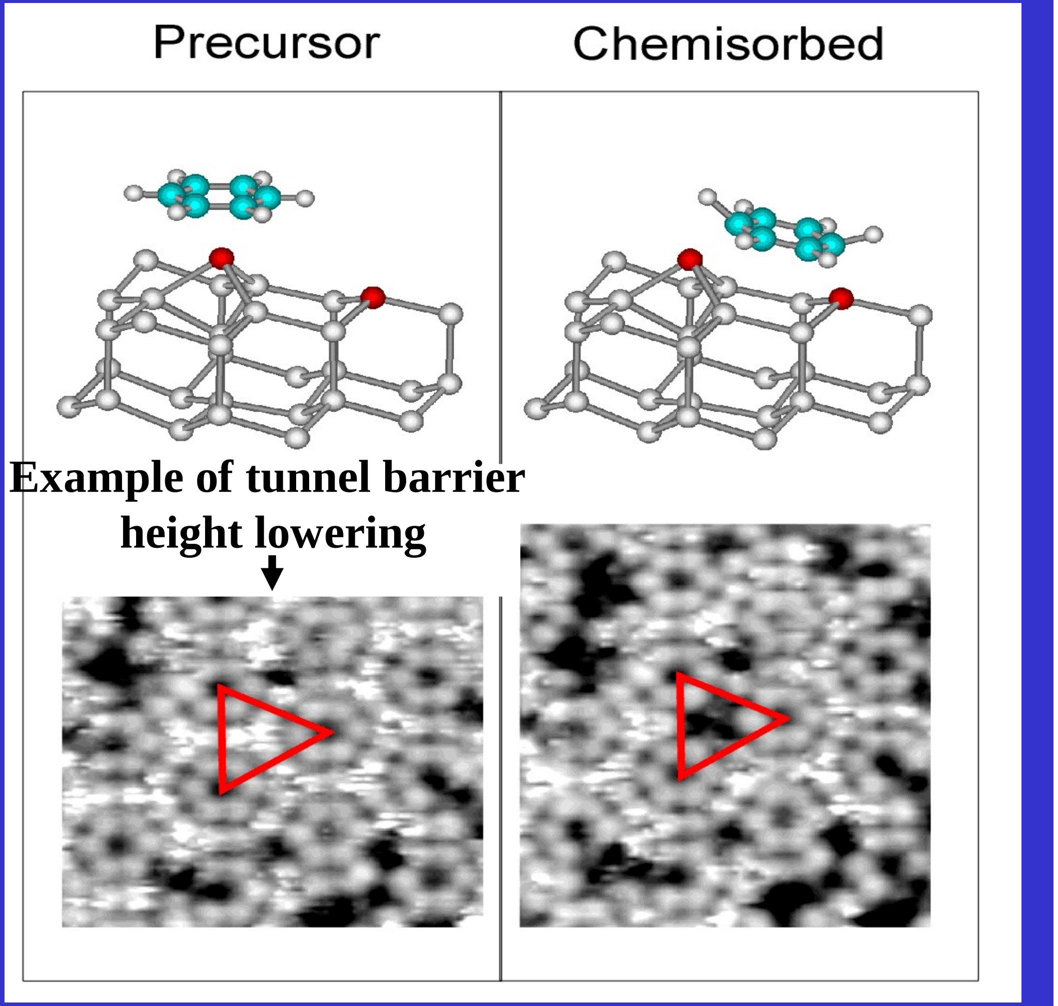


Several minutes later

The frustrated motion of benzene on the surface of Si(111), R.A. Wolkow and D.J. Moffatt, J. Chem. Phys., 103, 10696 (1995)

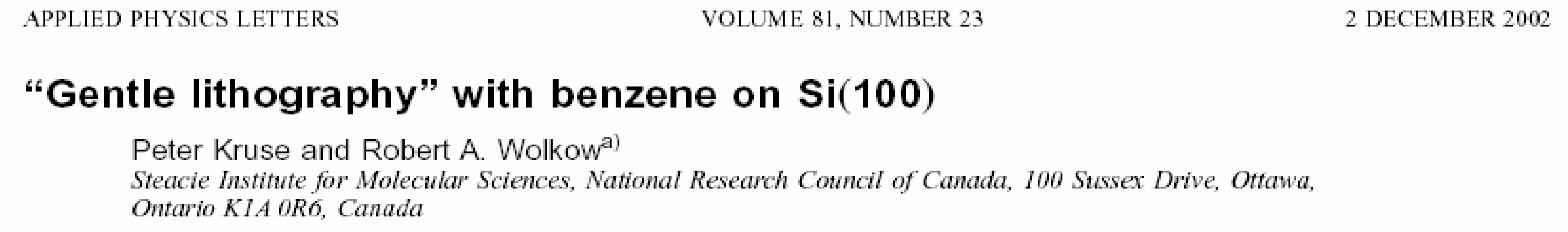
# Capturing normally transient precursors to adsorption





**Example of tunnel barrier height lowering**

D.E. Brown, D.J. Moffatt and R.A. Wolkow, *Science*, **279**, 542 (1998)



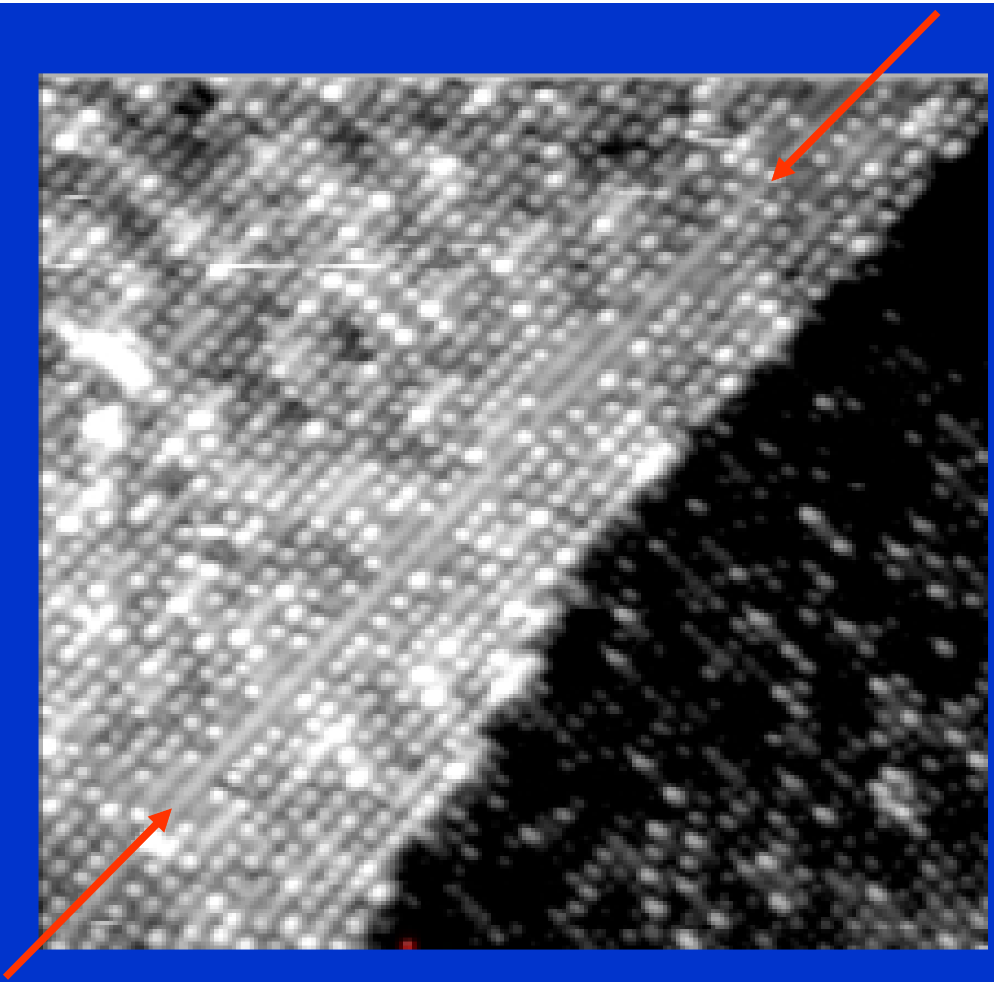
APPLIED PHYSICS LETTERS VOLUME 81, NUMBER 23 2 DECEMBER 2002

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

Peter Kruse and Robert A. Wolkow[a)]
*Steacie Institute for Molecular Sciences, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario K1A 0R6, Canada*

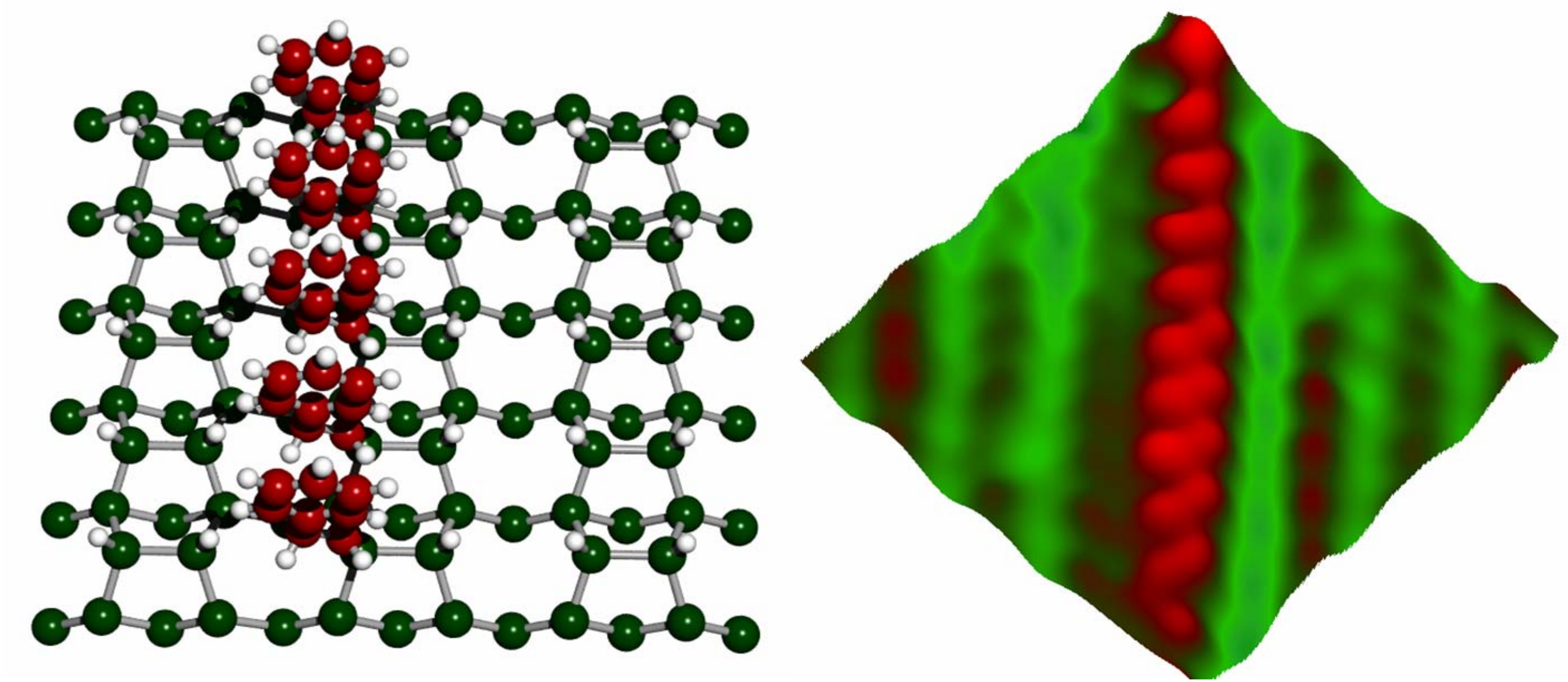
- Si(100) surface passivated by a monolayer of benzene

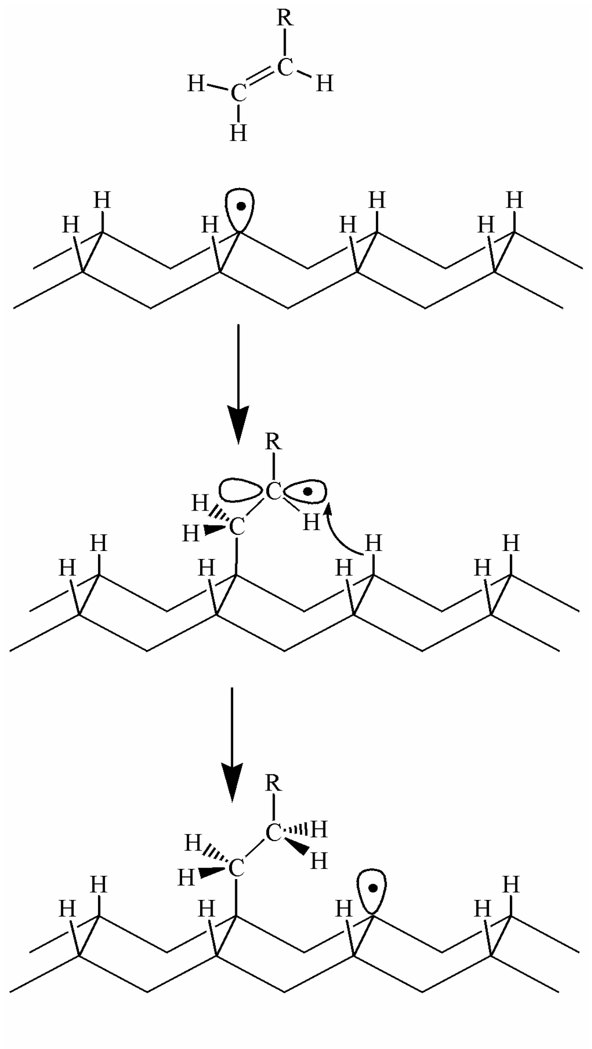
- The arrows mark a line from which benzene has been removed – creating a very small reactive region



End of day 2

# A new approach to making nanostructures



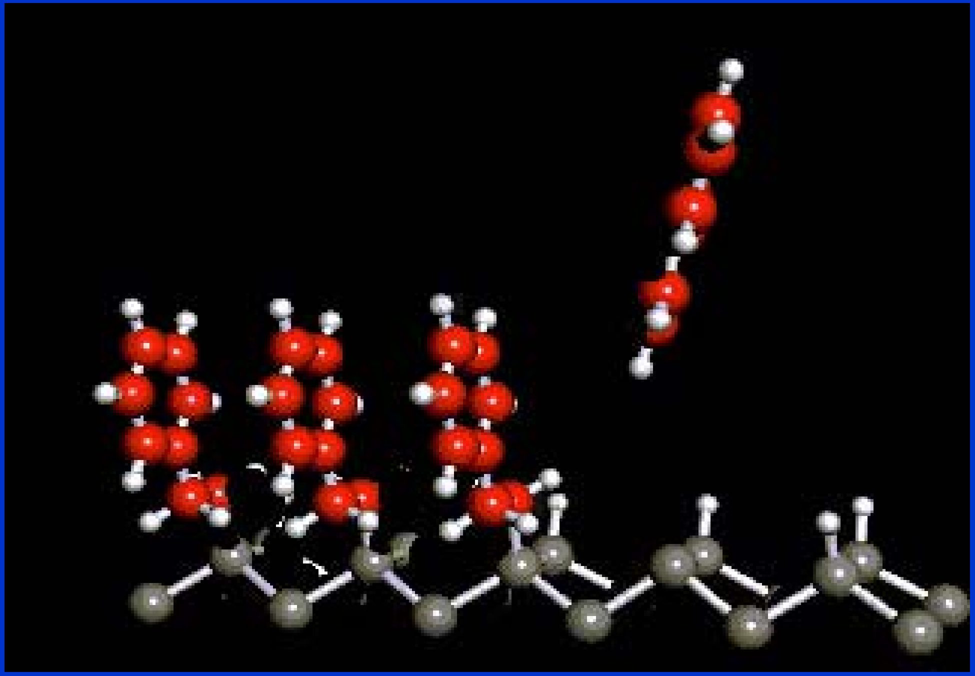


H-terminated Si(100) with single dangling bond exposed to alkene (we don’t allow alkene to form 2 bonds)

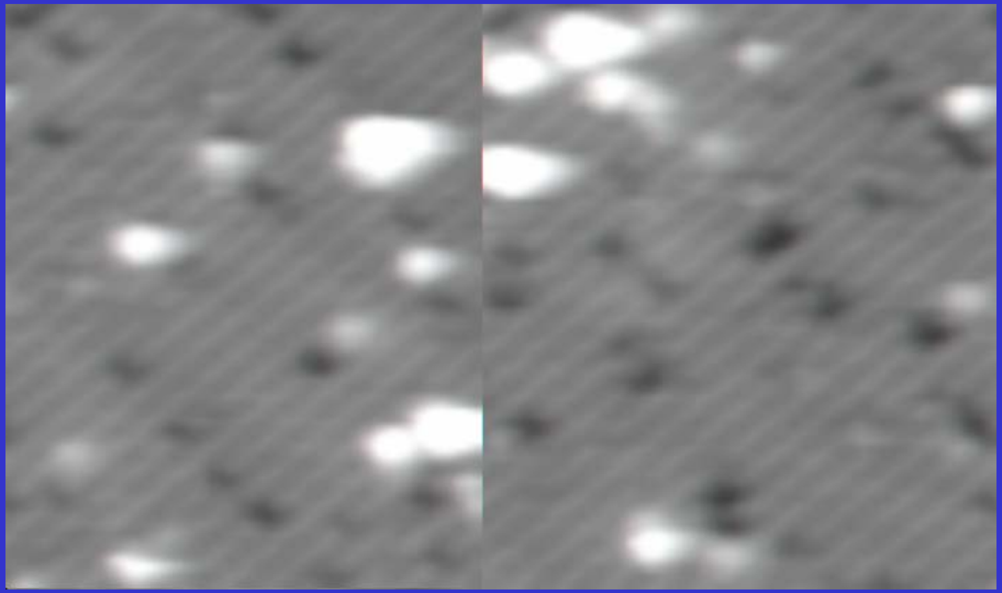
Alkene cannot form 2 bonds directly (simple alkene bound ~0.4 eV, styrene ~0.8)

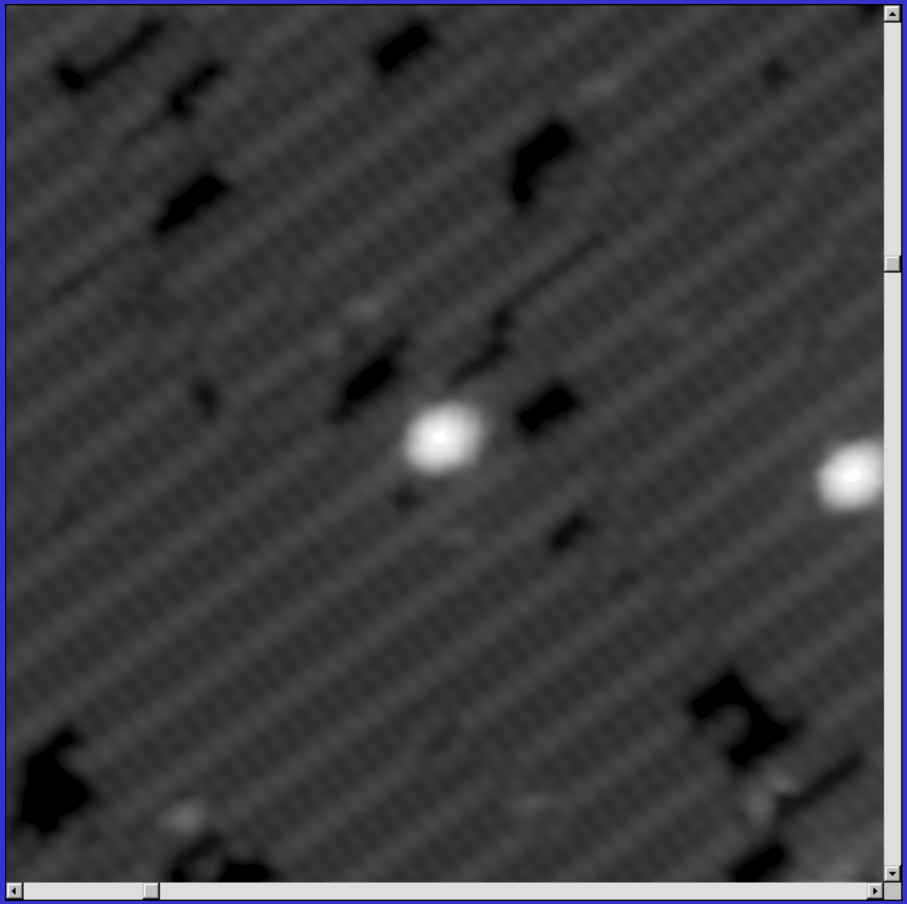
Abstraction of H from adjacent surface site satisfies molecule, creates opportunity for chain reaction (further stabilized, simple alkene by ~0.5 eV, styrene by 0.15 eV)

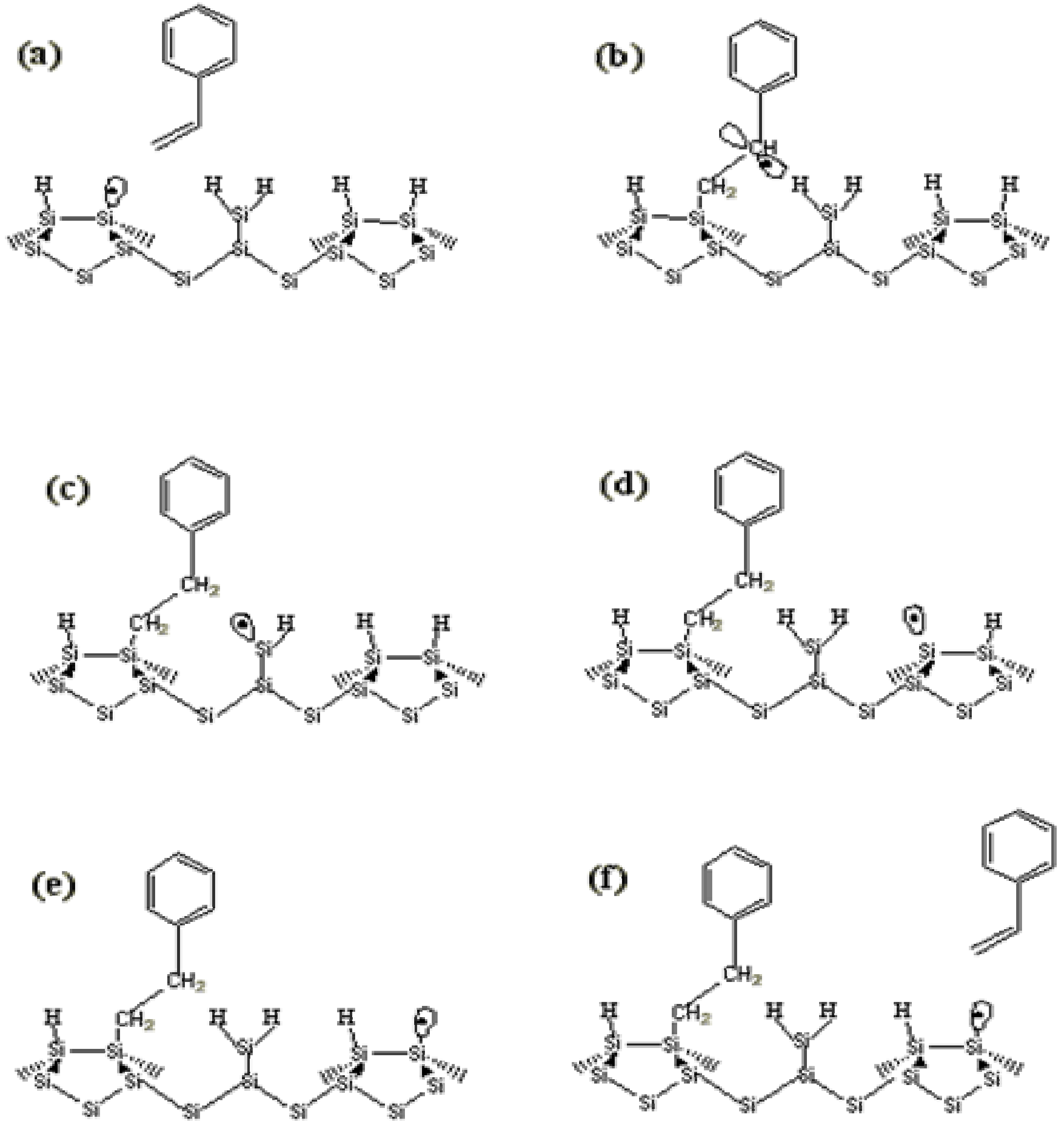
# Assembly of Molecular Lines

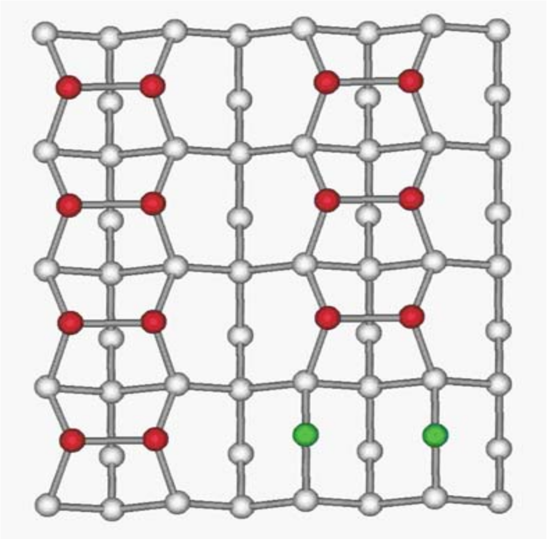


AM-1 Molecular Dynamics Calculation of the addition/abstraction process which underpins the self-directed growth of styrene lines on H-Si(100). Artificial forces were imposed to force the process along.

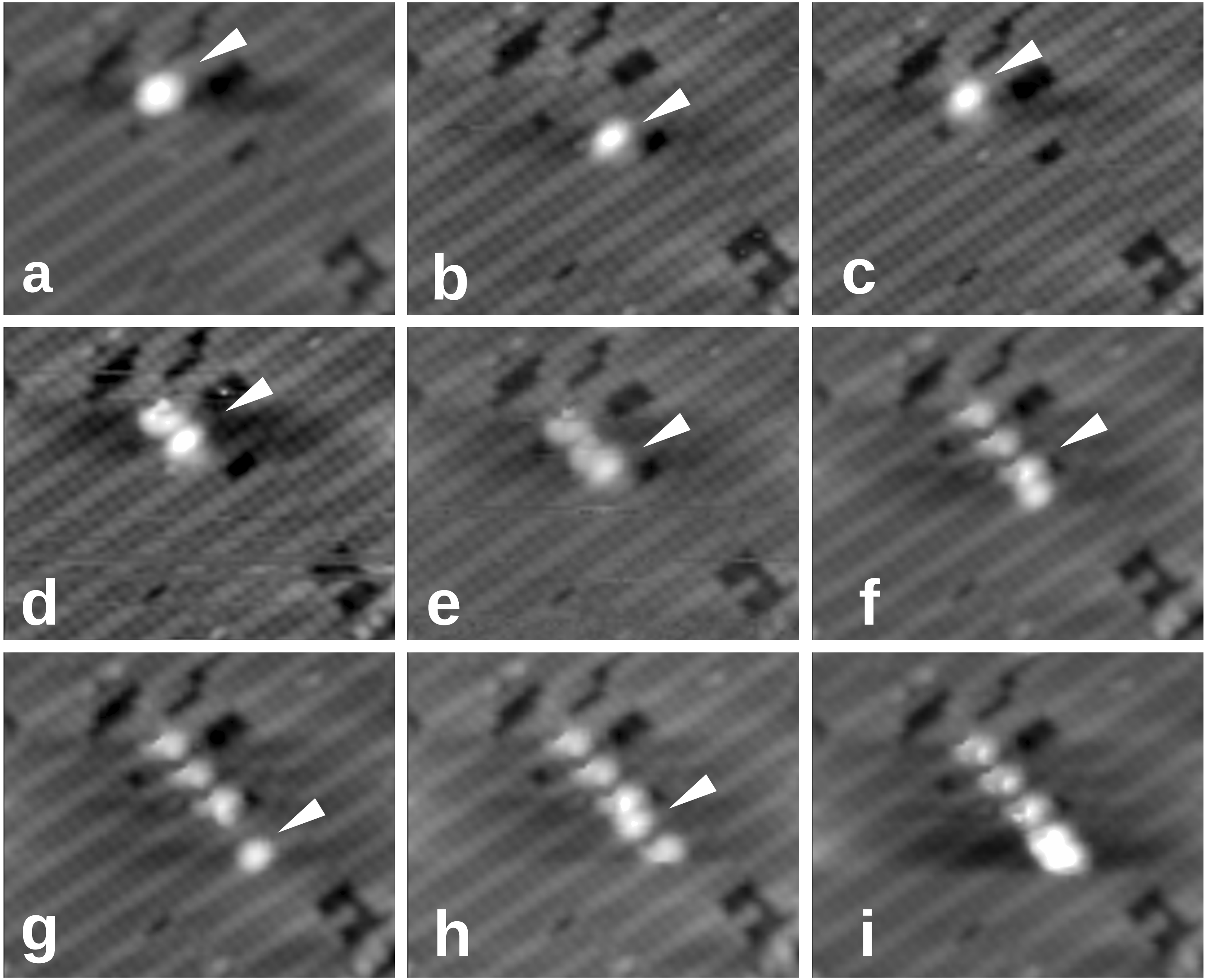




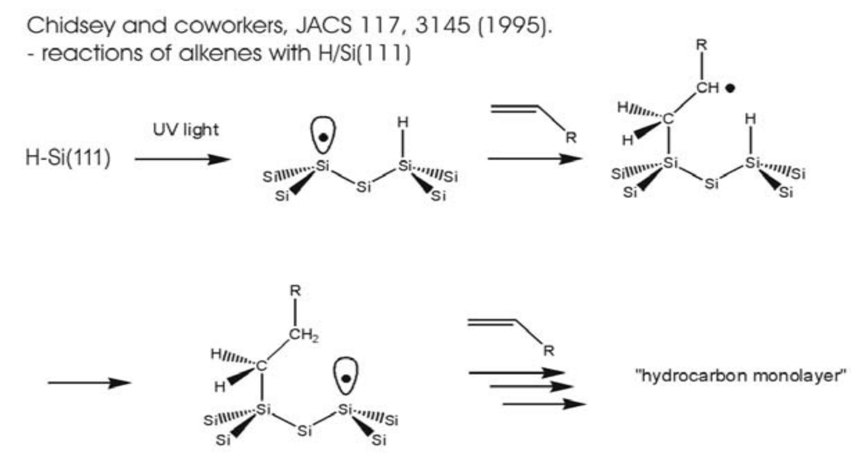




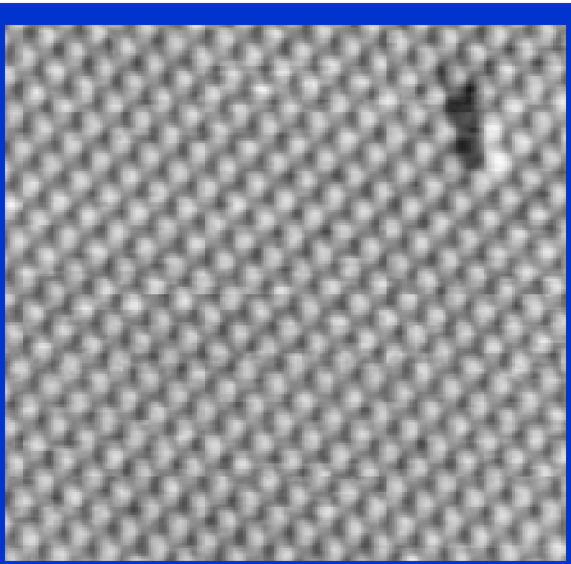
"A Self-Directed Growth Process for Creating Covalently Bonded Molecular Assemblies on the H-Si(100)-3×1 Surface." X. Tong, G. A. DiLabio and R. A. Wolkow, Nano Letters, 2004, 4,979-983.

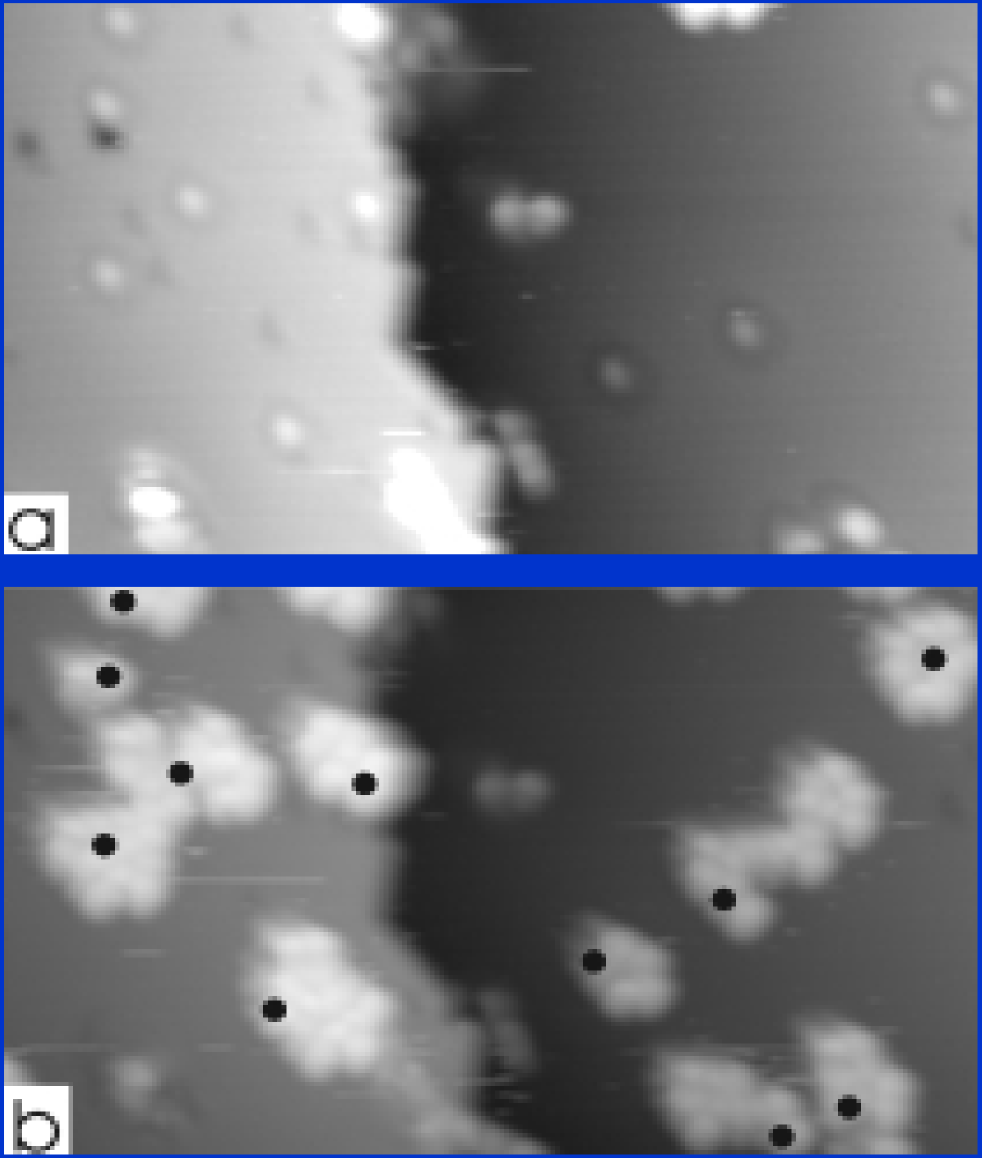

a
b
c
d
e
f
g
h
i

# Alkene reaction at single dangling bonds on H-Si(111)

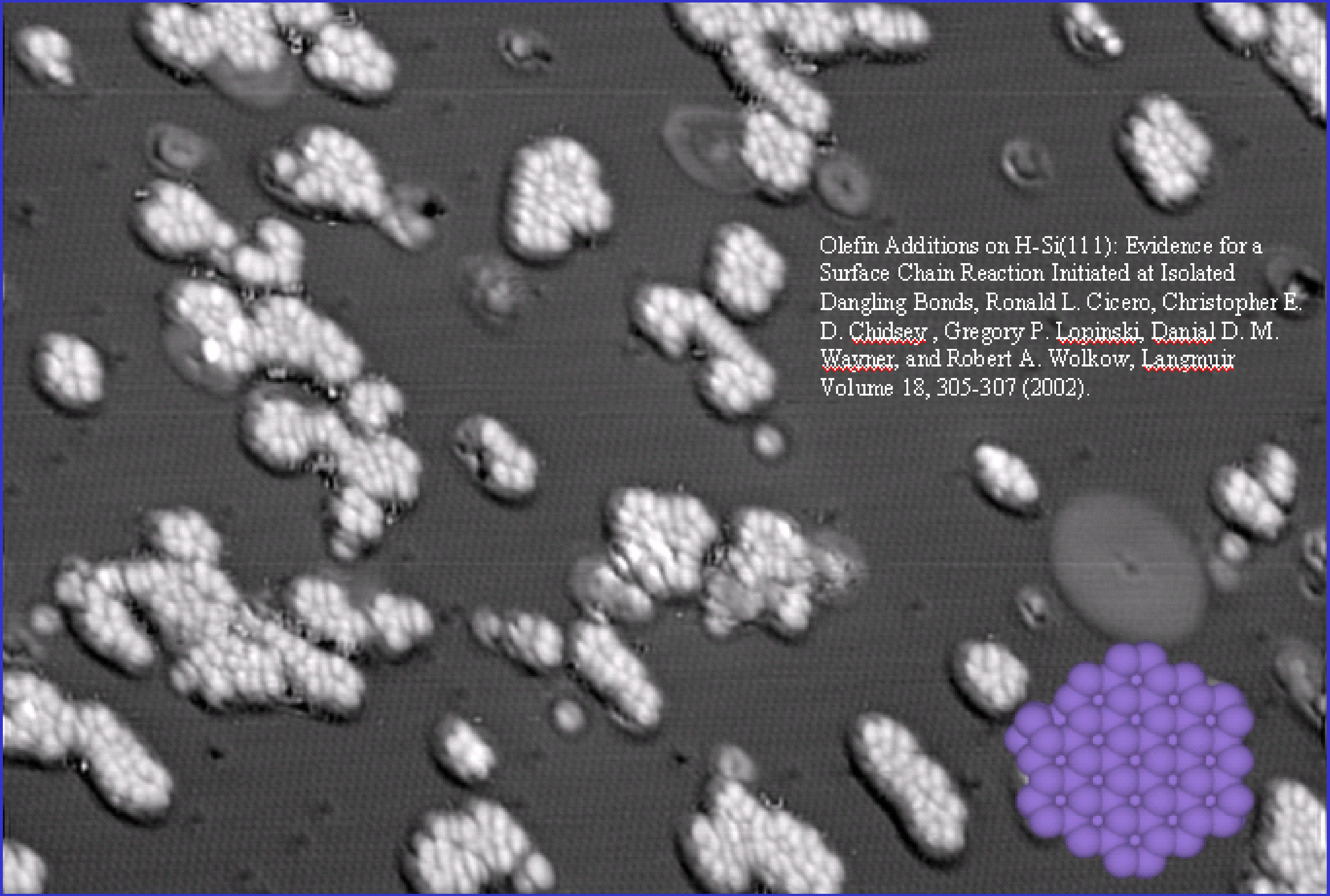


Chidsey and coworkers, JACS 117, 3145 (1995).
- reactions of alkenes with H/Si(111)





R.L. Cicero, C.E.D.Chidsey, G.P. Lopinski, D.D.M. Wayner and R.A. Wolkow, Langmuir, **18**,305-7 (2002)



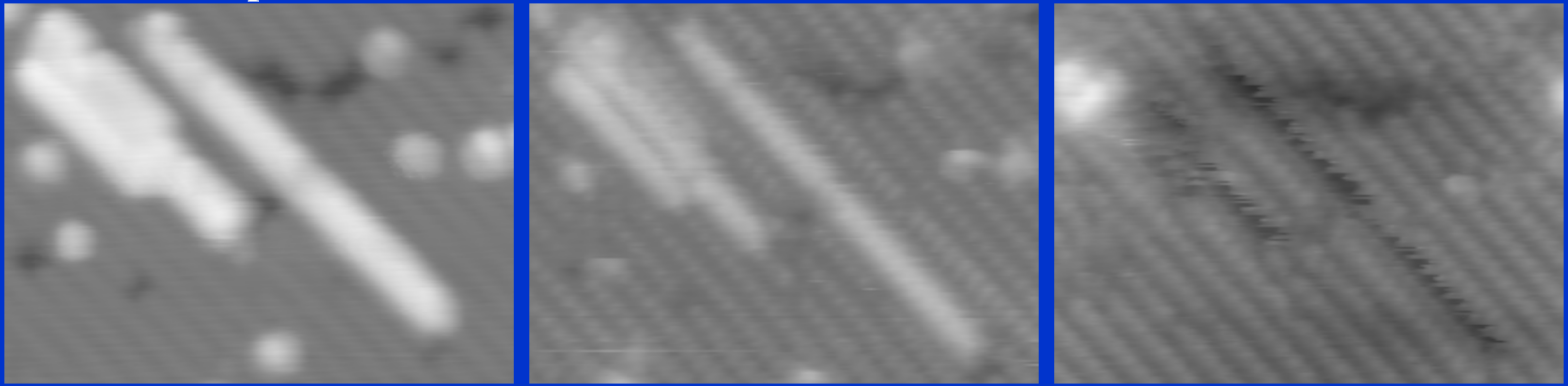
Olefin Additions on H-Si(111): Evidence for a Surface Chain Reaction Initiated at Isolated Dangling Bonds, Ronald L. Cicero, Christopher E. D. Chidsey , Gregory P. Lopinski, Danial D. M. Wayner, and Robert A. Wolkow, Langmuir Volume 18, 305-307 (2002).

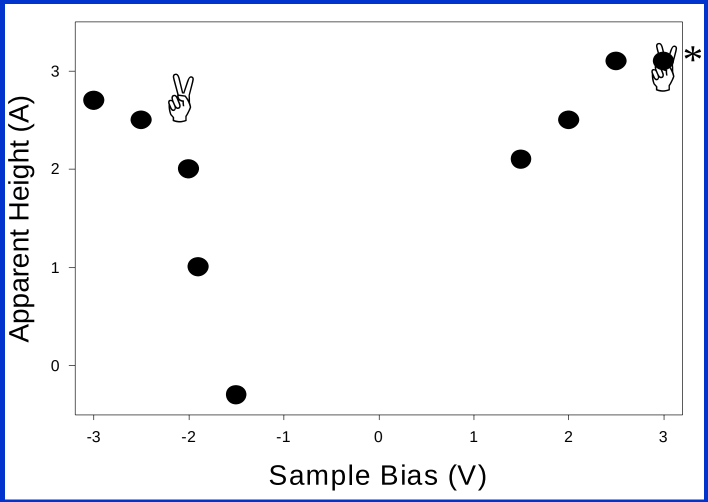
# Imaging Electronic States of Styrene Lines on H-Si(100)

-3V sample bias

-2V

-1.5V





Apparent height of styrene molecules is strongly bias dependent, reflecting HOMO-LUMO gap

# Electronic structure and STM images of self-assembled styrene lines on a Si(100) surface.

W. A. Hofer* and A. J. Fisher
*Department of Physics and Astronomy, University College, Gower Street, London WC1E 6BT, UK*

G. P. Lopinski and R. A. Wolkow
*Steacie Institute for Molecular Sciences, National Research Council, 100 Sussex Drive, Ottawa, K1A 0R6 Canada*

First principles electronic structure calculations are applied to styrene lines on a Si(100) surface grown via a recently reported "self-directed" growth process. Molecule-derived delocalized $\pi$ states are situated about 3eV above the Fermi level of the system. The change in the apparent height of the molecule due to a variation of the bias voltage is a direct indication of the bandgap of semiconductor and molecular states. While tunneling spectroscopies can only measure the bandgap of the compound system, it is demonstrated here that topographic images in conjunction with first principles simulations allow a clear discrimination between the molecular bandgap and the bandgap of the substrate surface.

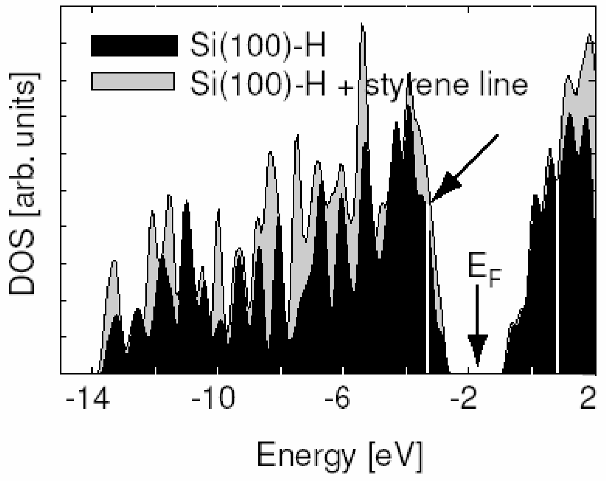


FIG. 4: Density of states (DOS) of the H-terminated Si(100)-(2×4) surface (black) and a styrene line adsorbed on the same surface (grey). The occupied states of styrene are located below -1.5eV relative to the Fermi level of the system (see arrows). The bandgap in the electronic structure of the molecules is about 4eV wide (see white lines).

FIG. 3: Charge density contour plots of single empty states (0.005 Å$^{-3}$). These states along the direction of the molecule are the only orbitals suitable for charge transport within the molecular structure. Due to the energy values of these states of 2.8 to 3.0 eV above the Fermi level of the system, it seems unlikely that they will be of any practical relevance.

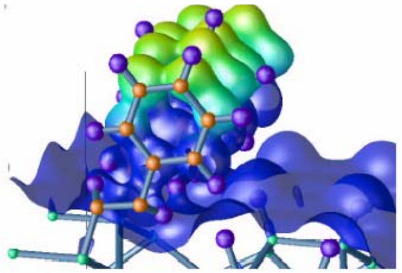


FIG. 2: Charge density contour plot of all empty states of the organic-semiconductor interface. The contour plot describes a constant contour of 0.01 Å$^{-3}$. The charge density distribution along the direction of the molecular line suggests that the self-assembled structure is suitable as a molecular wire.

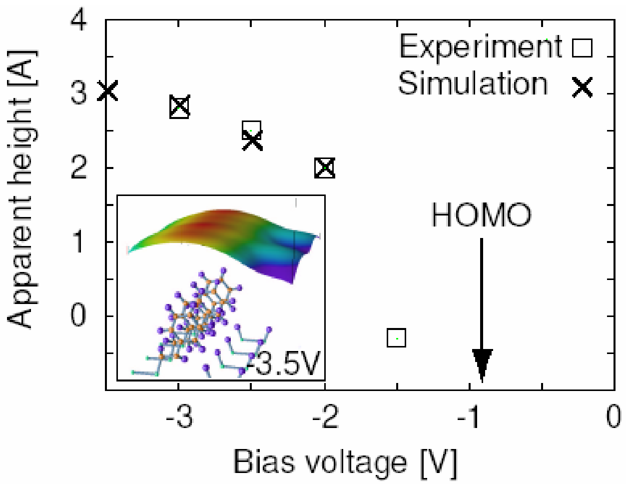
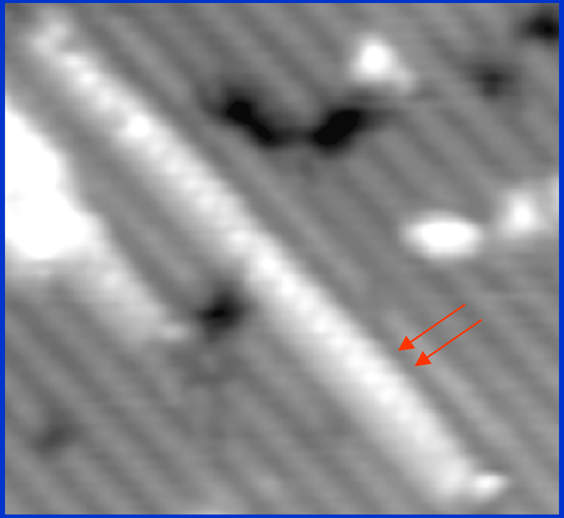


FIG. 6: Simulated STM image of the styrene line at -3.5V (inset) and voltage dependent apparent height. Experimental and theoretical results are in excellent agreement, the vanishing apparent height of the styrene molecule above -1.5eV is a consequence of the fact that no occupied states of the molecule exist in this energy range (see Fig. 4).

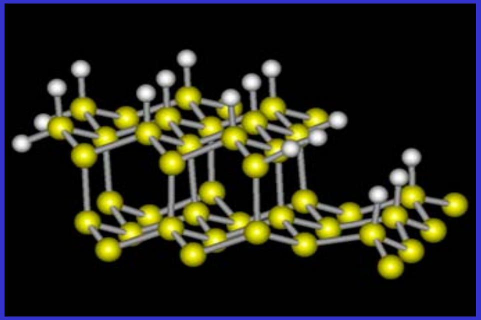


Molecule spacing is related to Si lattice

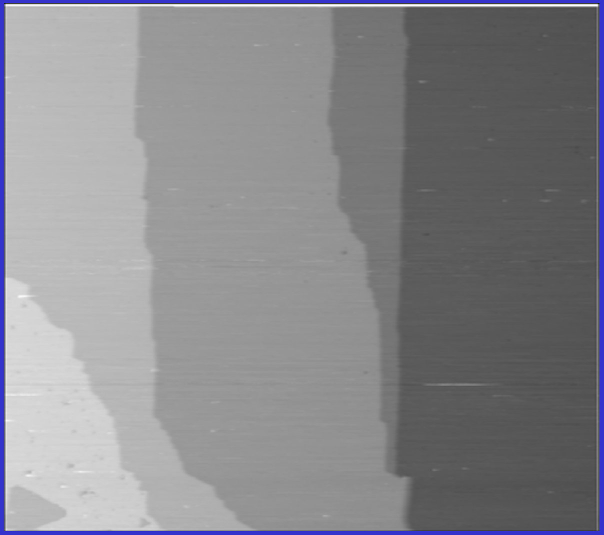
Surface lattice spacing is 3.84 Angstrom

That is close to the spacing found in condensed benzene

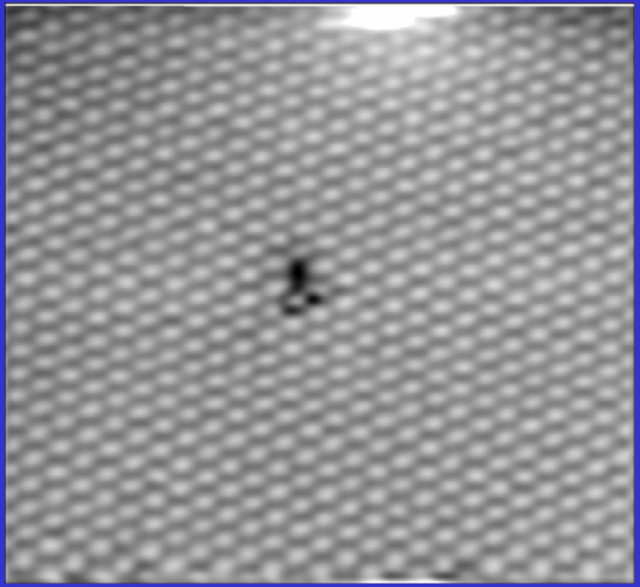
# STM of Si(111)-H



5000 Å: -2.3V,55pA

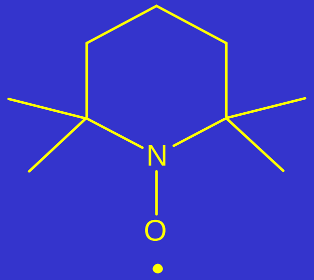


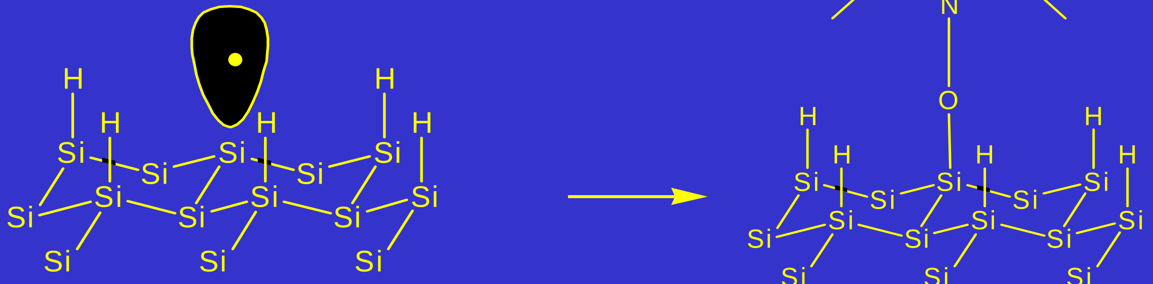
100 Å: -1.5V,300pA



Prepared through wet chemical etch with 40% $NH_4F$

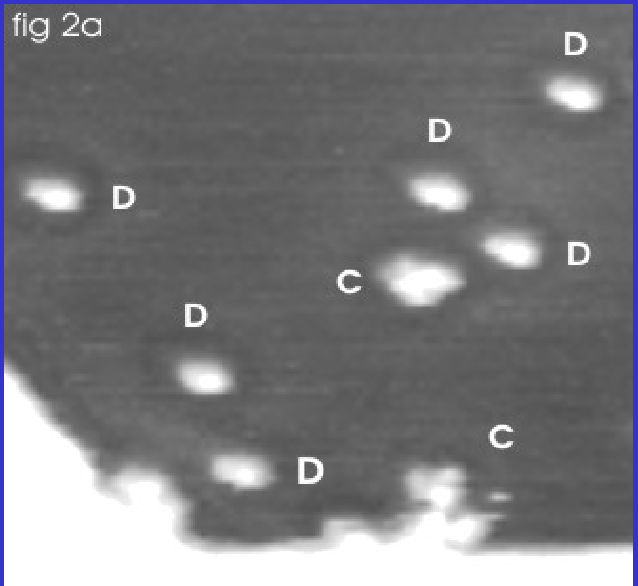
# TEMPO

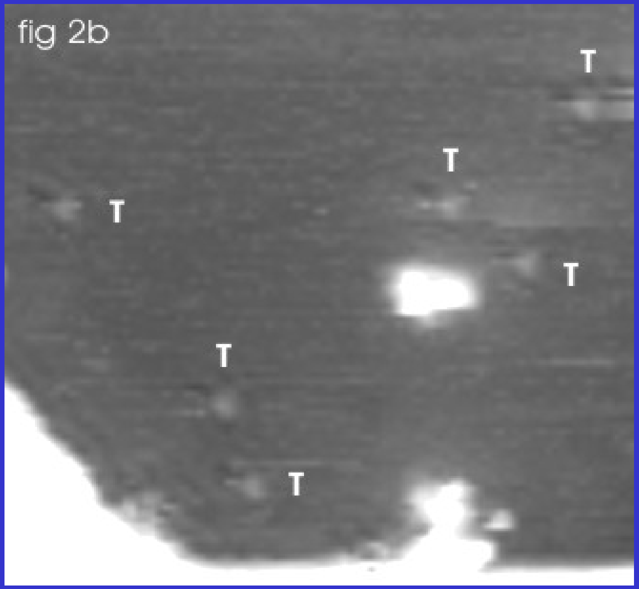




Reversible Passivation of Silicon Dangling Bonds with the Stable Radical TEMPO, Pitters, J. L.; Piva, P. G.; Tong, X.; Wolkow, R. A. Nano Lett.;3, 1431-1435 (2003).

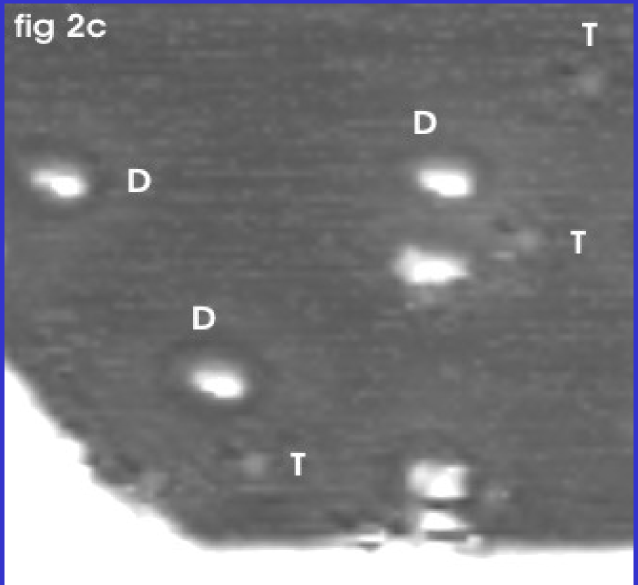
180 Å:
-2.25V
100pA

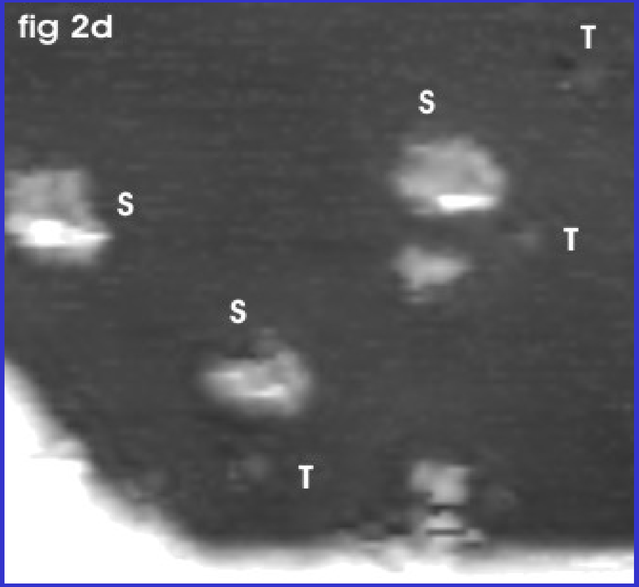




180 Å:
-2.25V
100pA

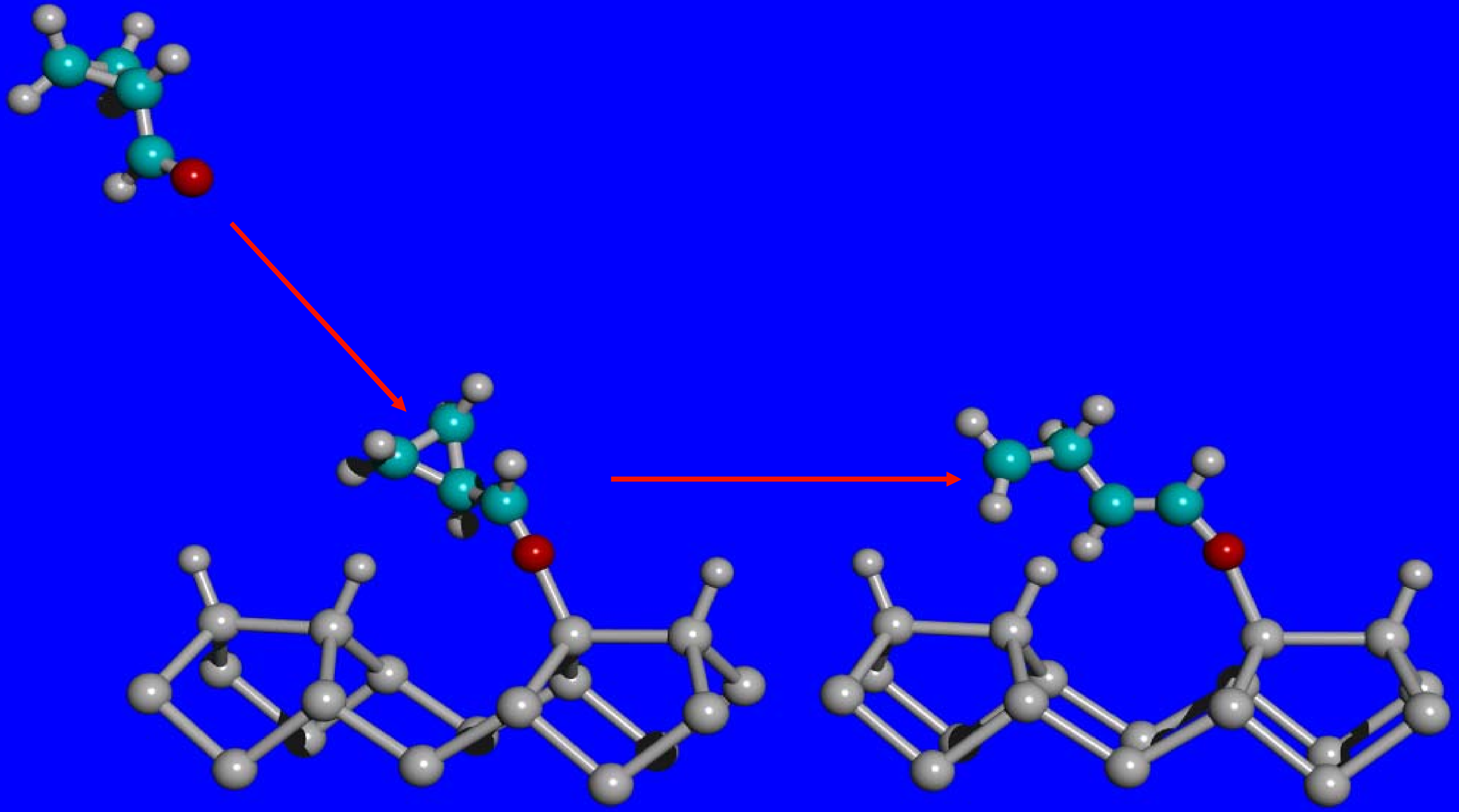
180 Å:
-2.00V
100pA

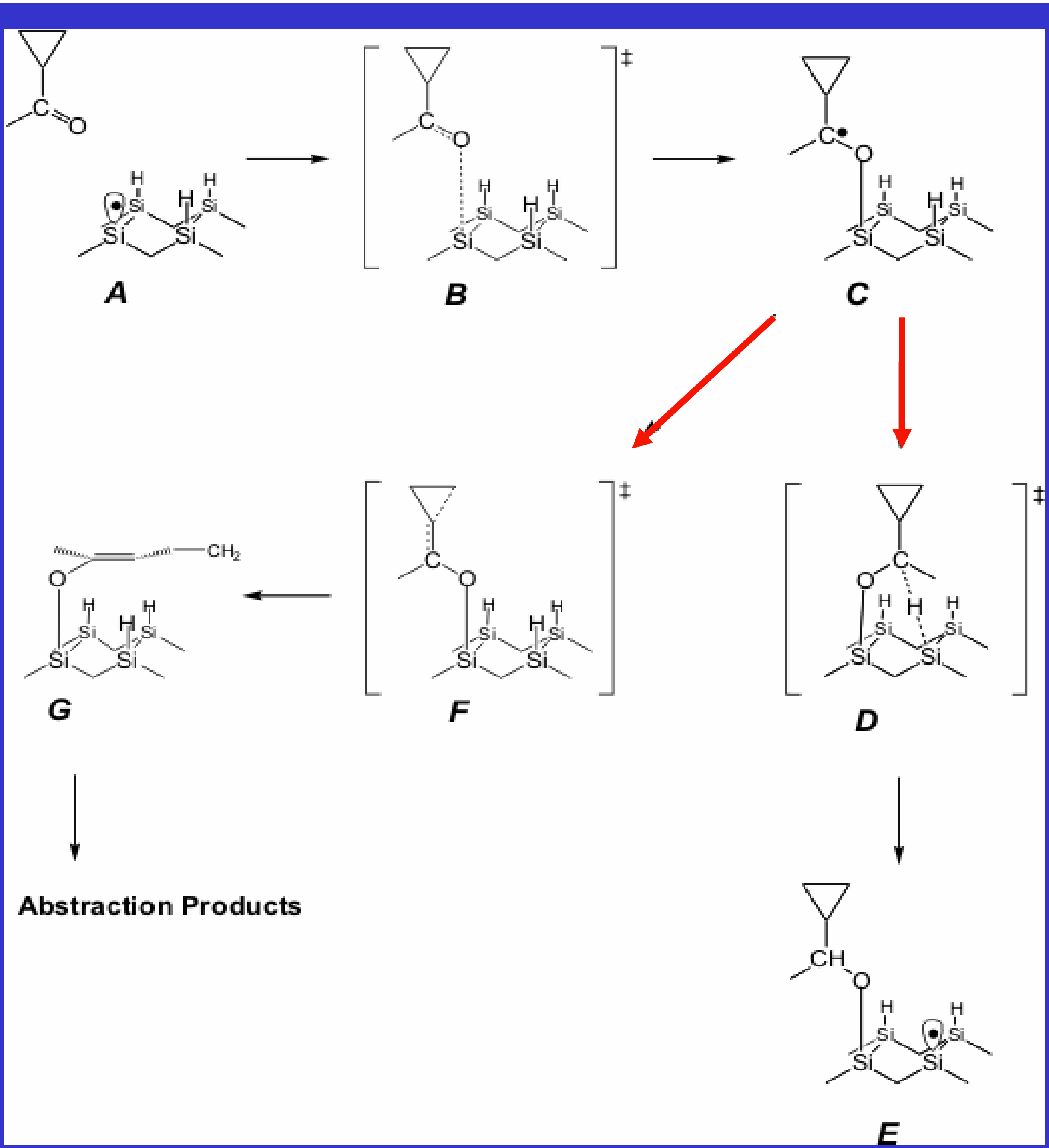




180 Å:
-2.00V
100pA

# Different growth mechanism




A
B
‡
C
D
‡
E
F
‡
G
Abstraction Products

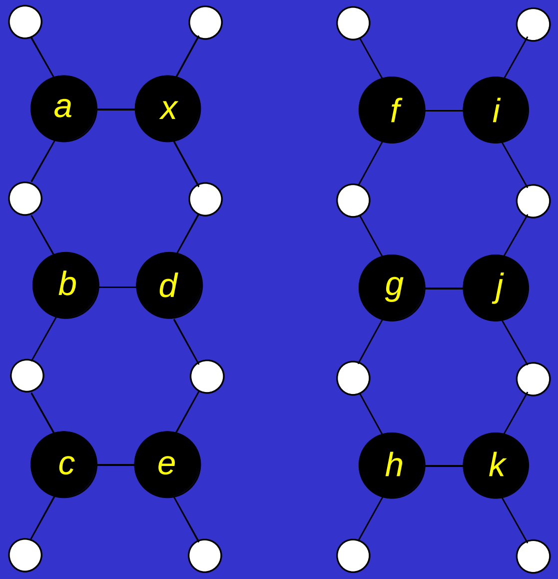
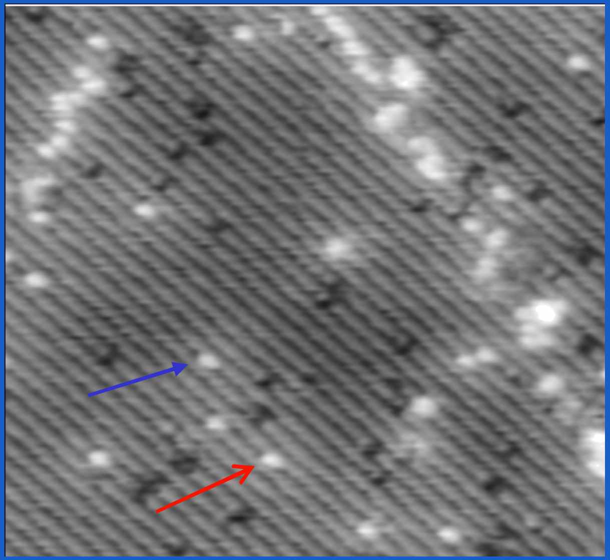
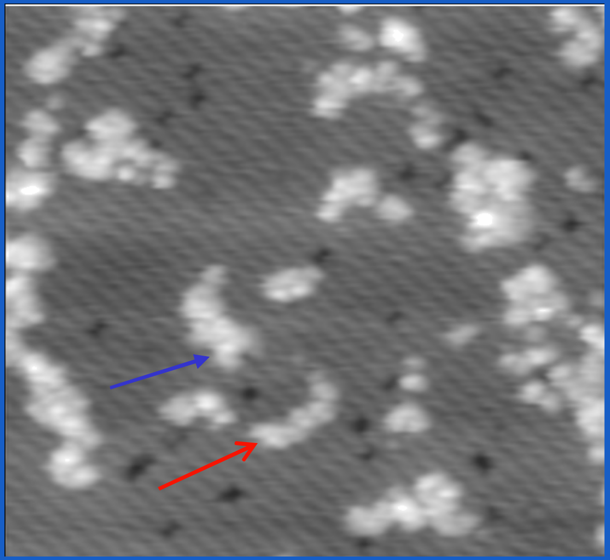


**Figure 2**. Schematic of the top view of a 2×1 H-Si(100) surface. Filled and open circles represent the first and second layer of silicon atoms, respectively. Calculated classical barrier heights associated with hydrogen atom abstraction by the butenyl-type radical (chemisorbed to site x) from surface sites (in eV) are: a = 0.3, b = 0.4, c = 2.2, d = 0.1, e = 1.7, f = 0.2, g = 0.3, h = 2.4. Barrier heights associated with other sites are much higher that 2.4 eV.

# cyclopropylmethylketone growth



Various initiation points



Growth from each point – growth is ***not*** restricted to Si row direction

1)"Ring-Opening Radical Clock Reactions for Hybrid Organic-Silicon Surface Nanostructures: A New Self-Directed Growth Mechanism and Kinetic Insights." X. Tong, G. A. DiLabio, O. J. Clarkin and R. A. Wolkow, Nano Letters, 2004, 4, 357-360.

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# Patterning of Vinylferrocene on H−Si(100) via Self-Directed Growth of Molecular Lines and STM-Induced Decomposition

**Peter Kruse, Erin R. Johnson, Gino A. DiLabio, and Robert A. Wolkow***

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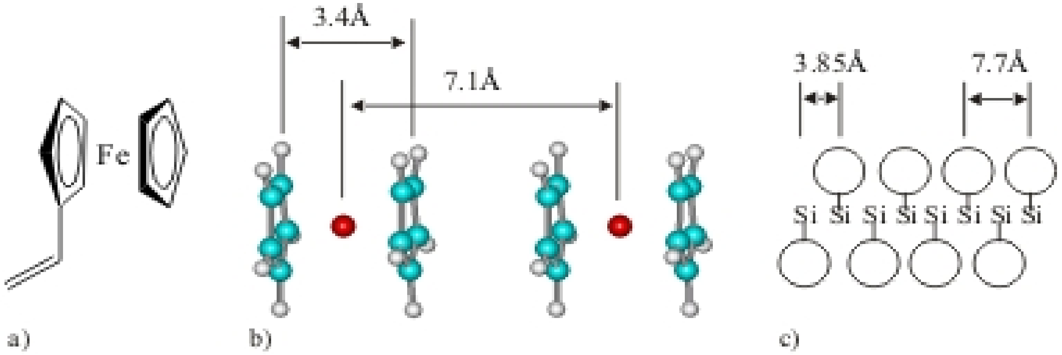
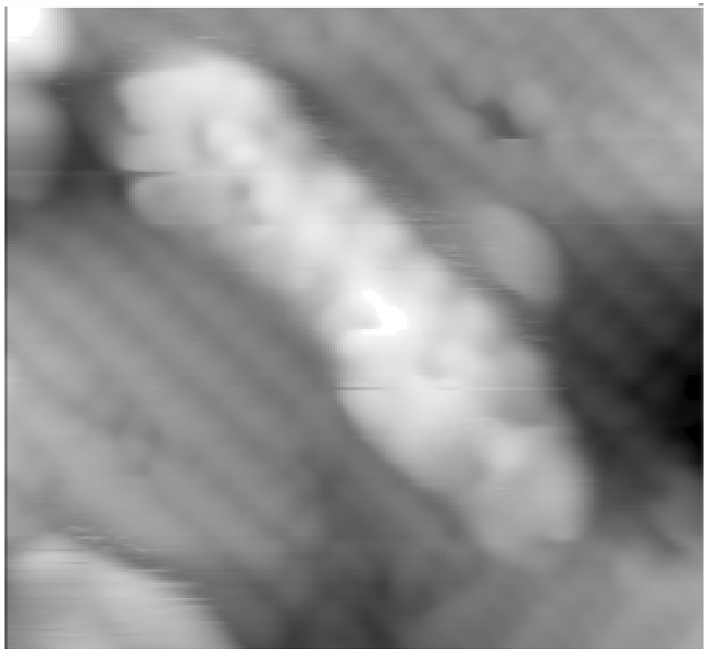
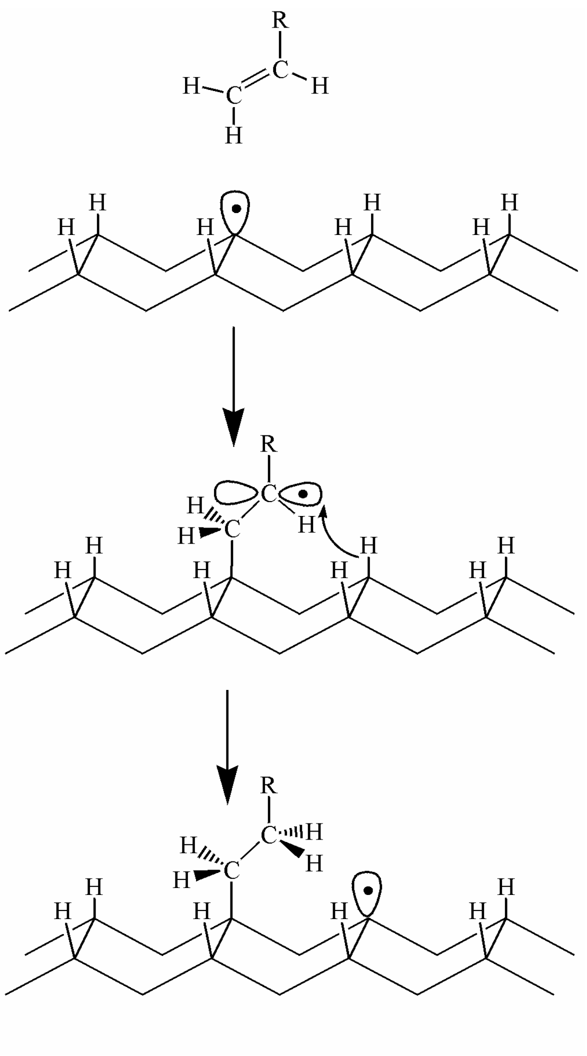
*100 Sussex Drive, Ottawa, Ontario K1A 0R6, Canada*

*Received May 31, 2002; Revised Manuscript Received June 27, 2002*







H-terminated Si(100) with single dangling bond exposed to alkene (we don’t allow alkene to form 2 bonds)

Alkene cannot form 2 bonds directly (simple alkene bound ~0.4 eV, styrene ~0.8)

Abstraction of H from adjacent surface site satisfies molecule, creates opportunity for chain reaction (further stabilized, simple alkene by ~0.5 eV, styrene by 0.15 eV)

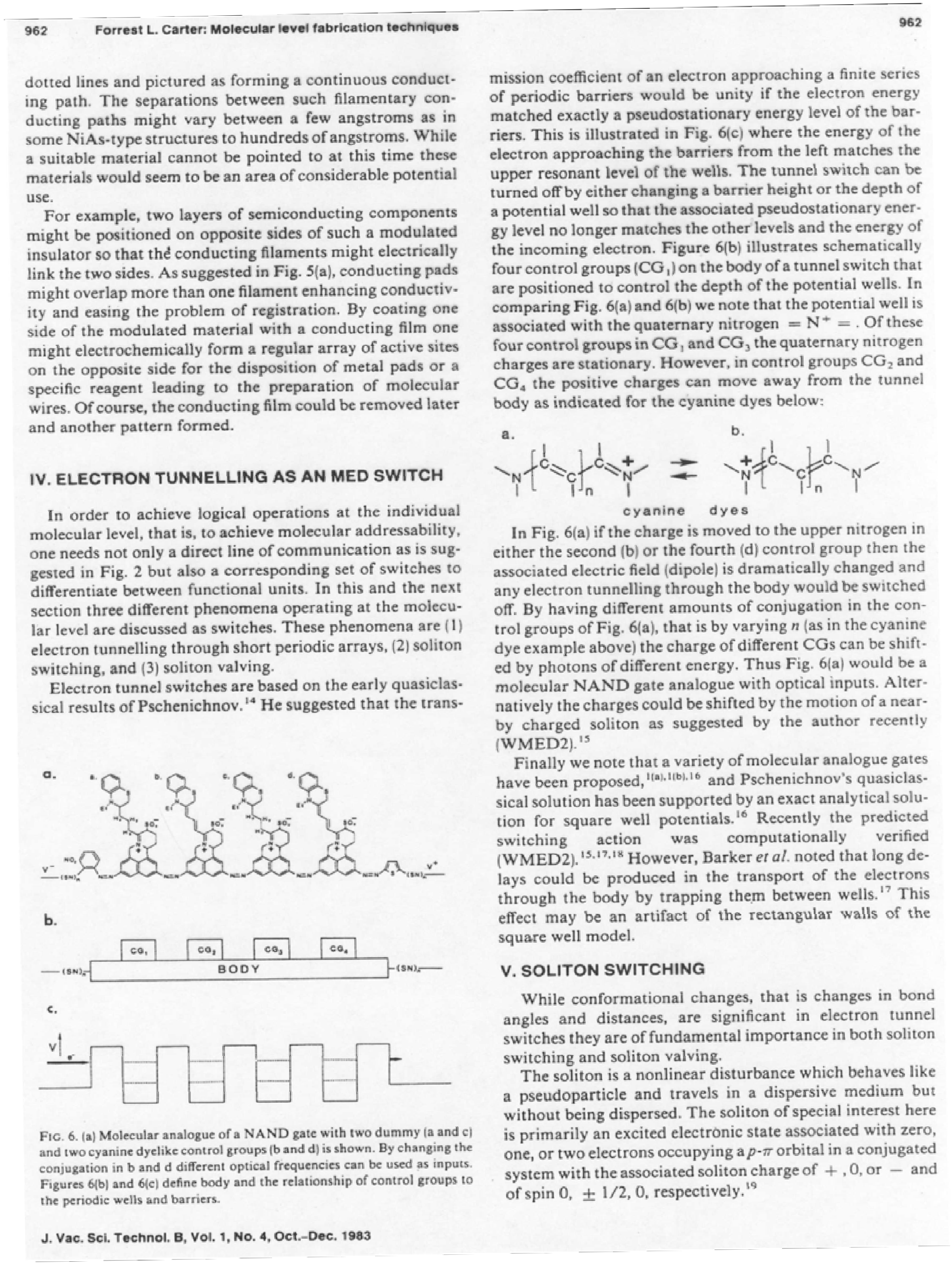
1) Parallel (simultaneous) fabrication

2) General direction control

3) Defect tolerance

4) "wires", other

5) lithography



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.[14] He suggested that the transmission 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 ($CG_i$) 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 $=N^+=$. Of these four control groups in $CG_1$ and $CG_3$ the quaternary nitrogen charges are stationary. However, in control groups $CG_2$ and $CG_4$ the positive charges can move away from the tunnel body as indicated for the cyanine dyes below:

cyanine dyes

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.

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).[15]

Finally we note that a variety of molecular analogue gates have been proposed,[1(a),1(b),16] and Pschenichnov's quasiclassical solution has been supported by an exact analytical solution for square well potentials.[16] Recently the predicted switching action was computationally verified (WMED2).[15,17,18] 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.[17] 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, ± 1/2, 0, respectively.[19]

Forest Carter

Thanks to group members:

Dr. Jason Pitters, experimental staff scientist
Dr. Gino DiLabio, theorist staff scientist

Doug Moffatt, former technician
Martin Cloutier, new technician
Dr. Judy Xu, group administrator

Dr. Paul Piva, postdoc
Dr. Adam Dickie, postdoc
Dr. Mohamed Rezeq, postdoc
Dr. Lin Wu, postdoc

Mark Salomons, instrument design engineer
Tony Tadic,undergraduate student
Erin Johnson undergrad with Gino DiLabio
Owen Clarkin, MSc with Gino DiLabio
Andrea Evans, summer student

Visiting Professor Qiao Sun, engineer,Calgary
Visiting Professor Joachim Burghartz, Scientific Director DIMES
Delft University of Technology

Some of our collaborators
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Alain Rochefort, Montreal
George Kirczenow, Simon Fraser
AndrewFisher, UCL

*former postdocs/RAs*
David McComb
Charlie MacPherson
David Brown
Peter Kruse
XiaoTong
Steve Patitsas

- 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.

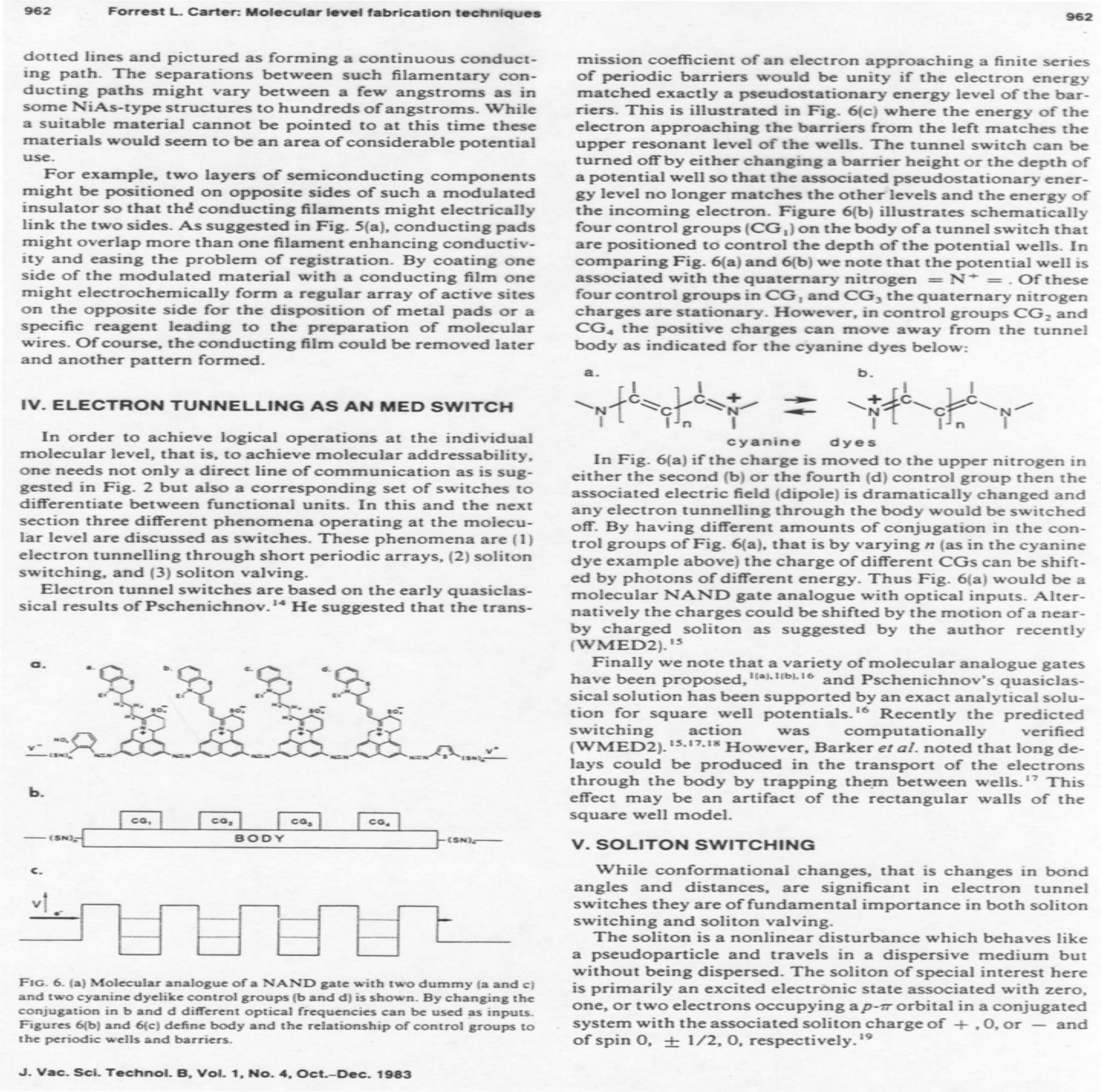
- Then, prepared to explore more complex structures, relevant for computation.

- 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.

Forest Carter



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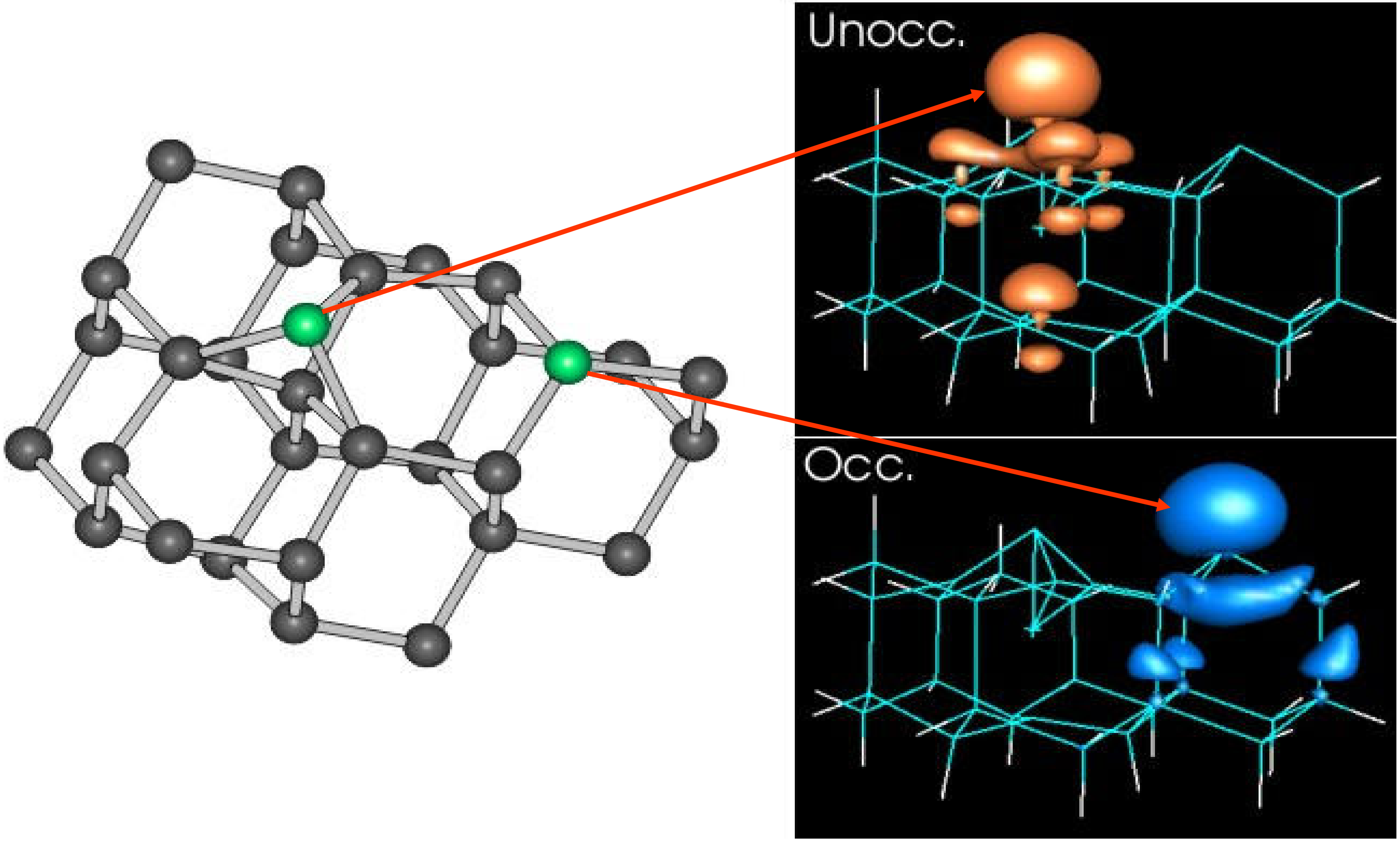
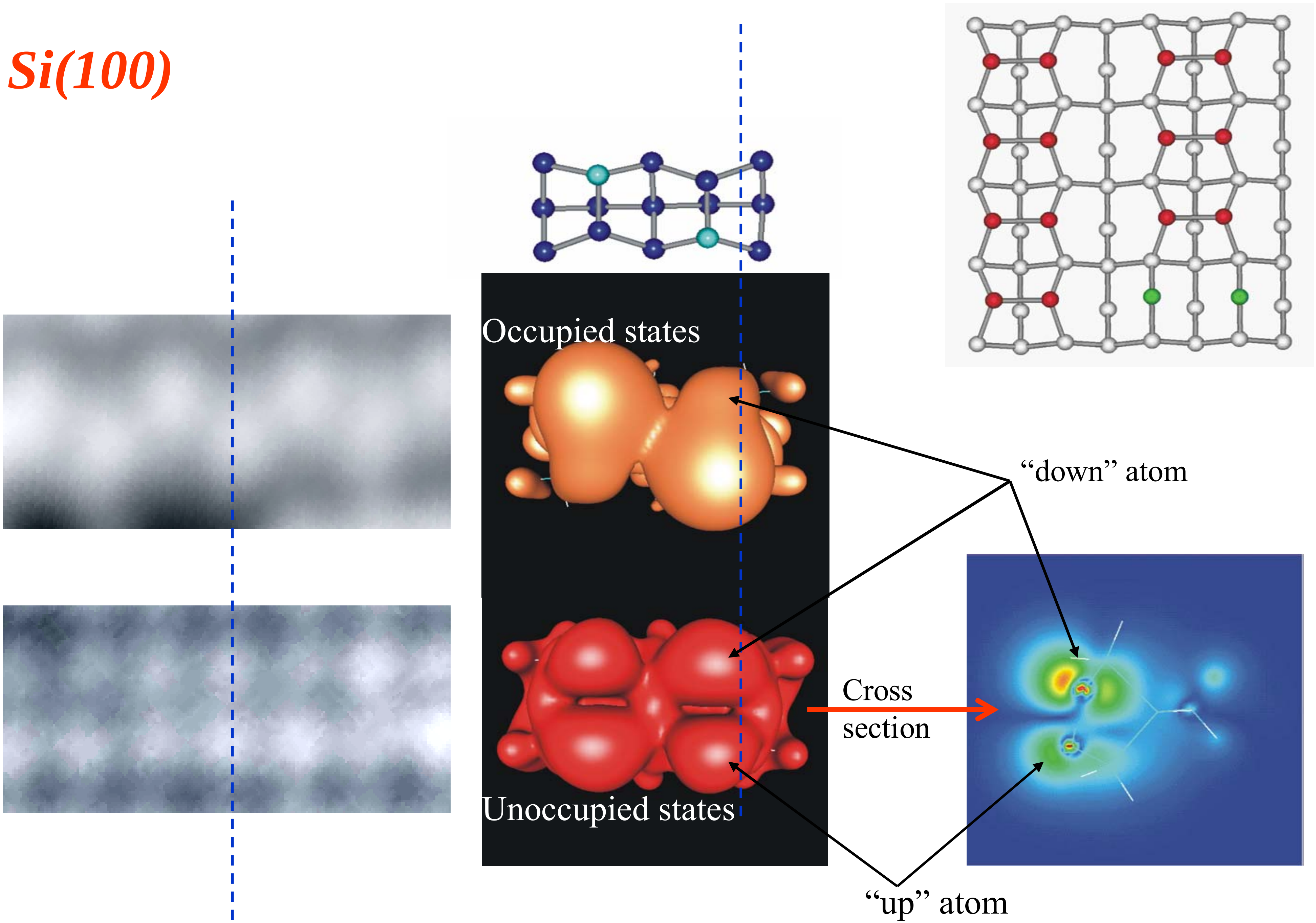
Now, figuring out the fussy details

- 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)*



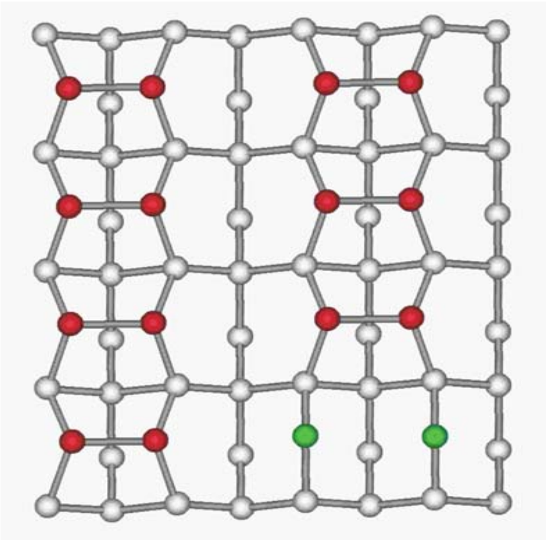
Occupied states

Unoccupied states

“down” atom

“up” atom

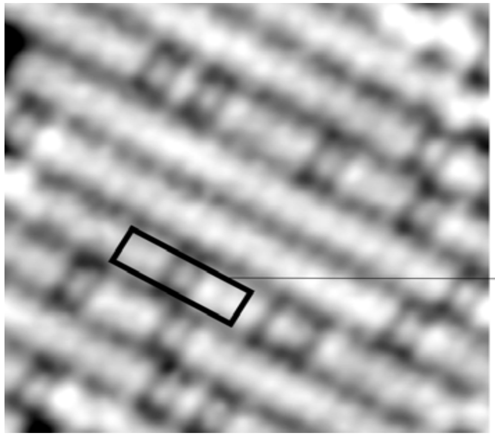
Cross section



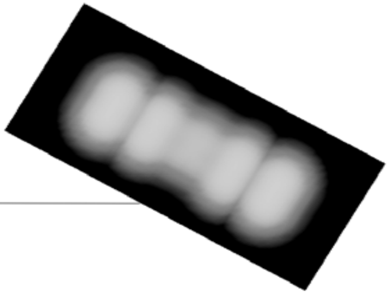
Si(100)

# Ethylene ($C_2H_4$) on Si(100)

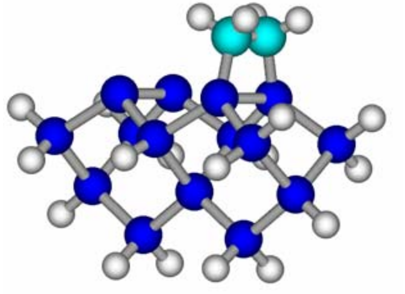
Occupied states -2V



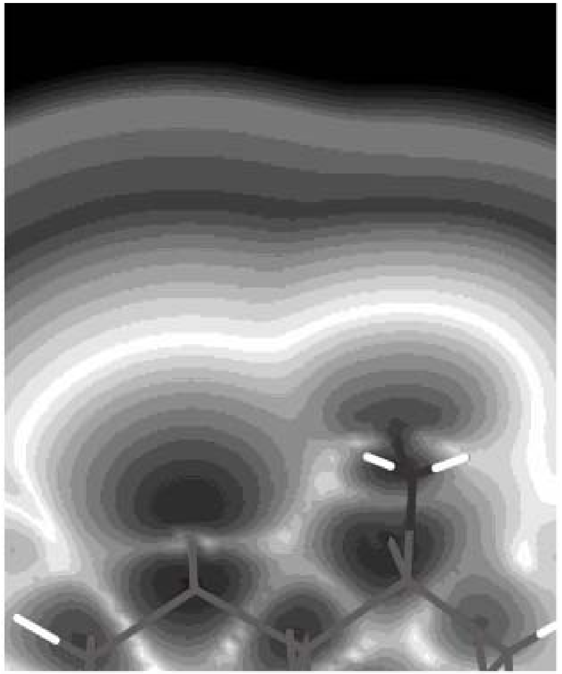
Simulation
5 dimers + ethylene

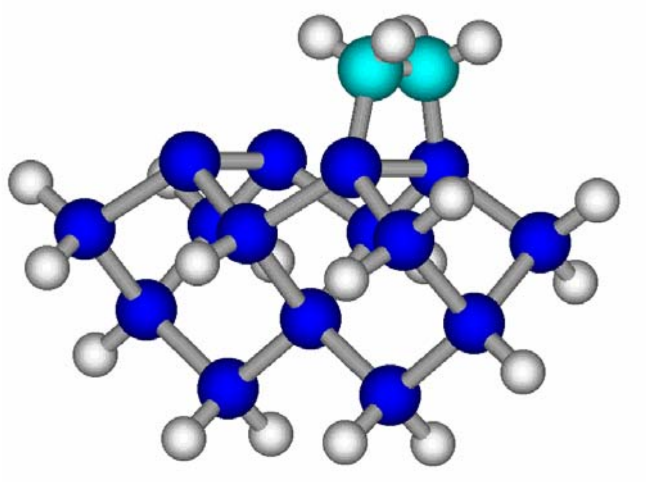


2 dimers + ethylene

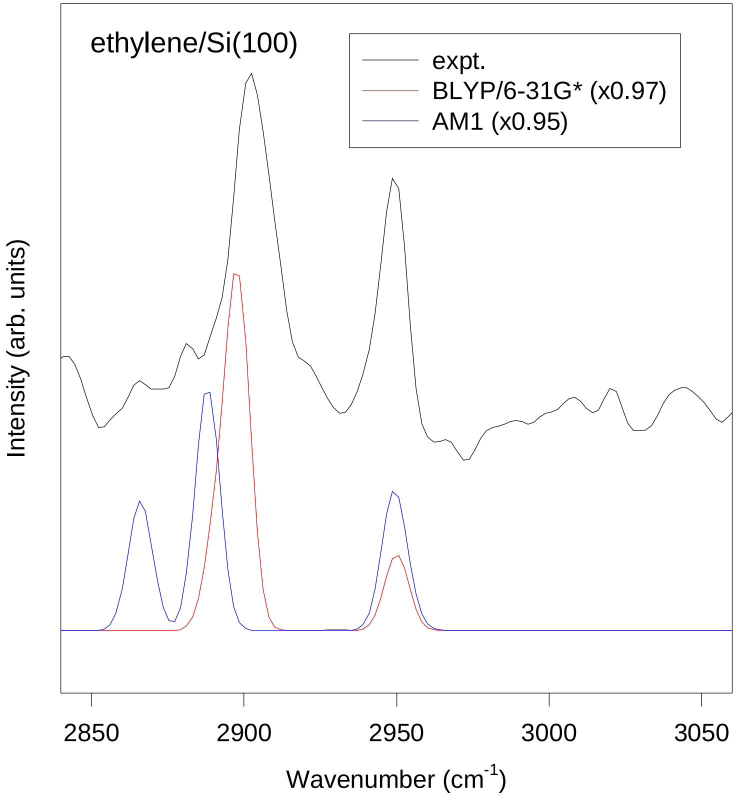


near-Fermi level iso-charge density
surfaces simulate STM contours





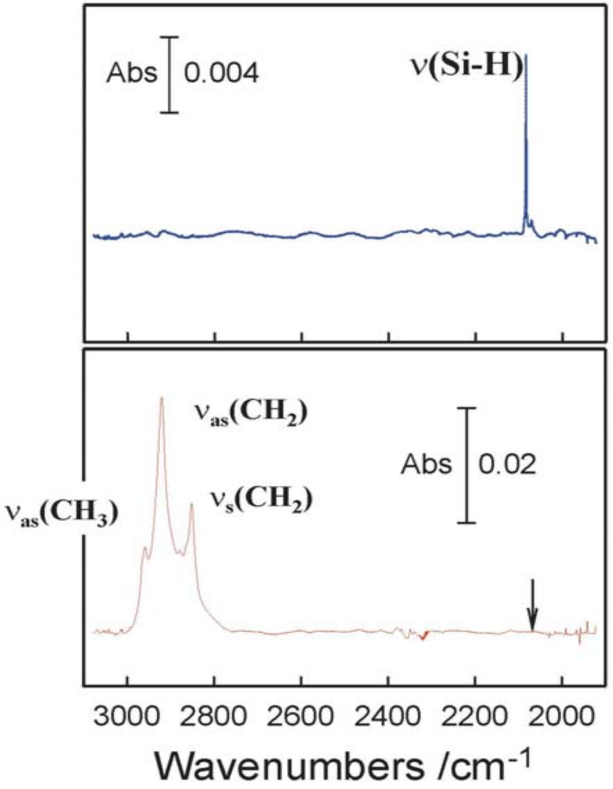
# Vibrational Spectrum of ethylene/Si(100)

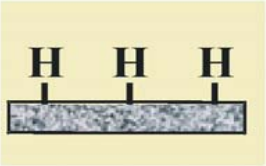


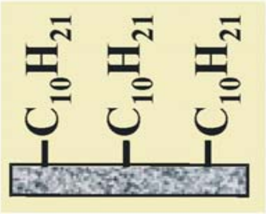
- C-H stretch frequencies shifted below 3000cm-1, indicating sp3 hybridization.
- AM-1 level calculations give fair agreement with experiment, BLYP/6-31G* in excellent agreement.

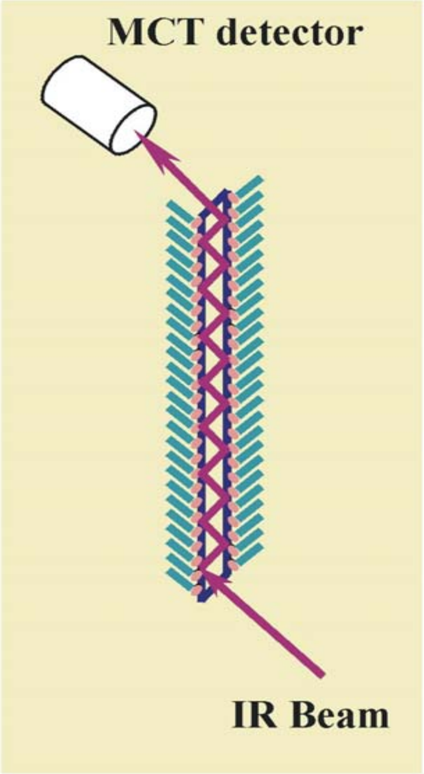
A Step Toward Making and Wiring-up Molecular-Scale Devices, R.A. Wolkow, Japanese Journal of Applied Physics, 2001.

# ATR-FTIR Spectra of Modified Si(111)







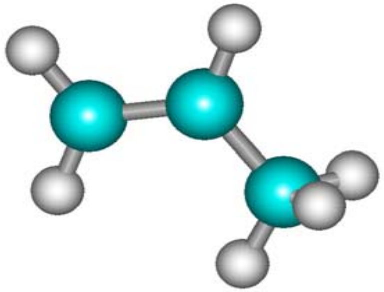


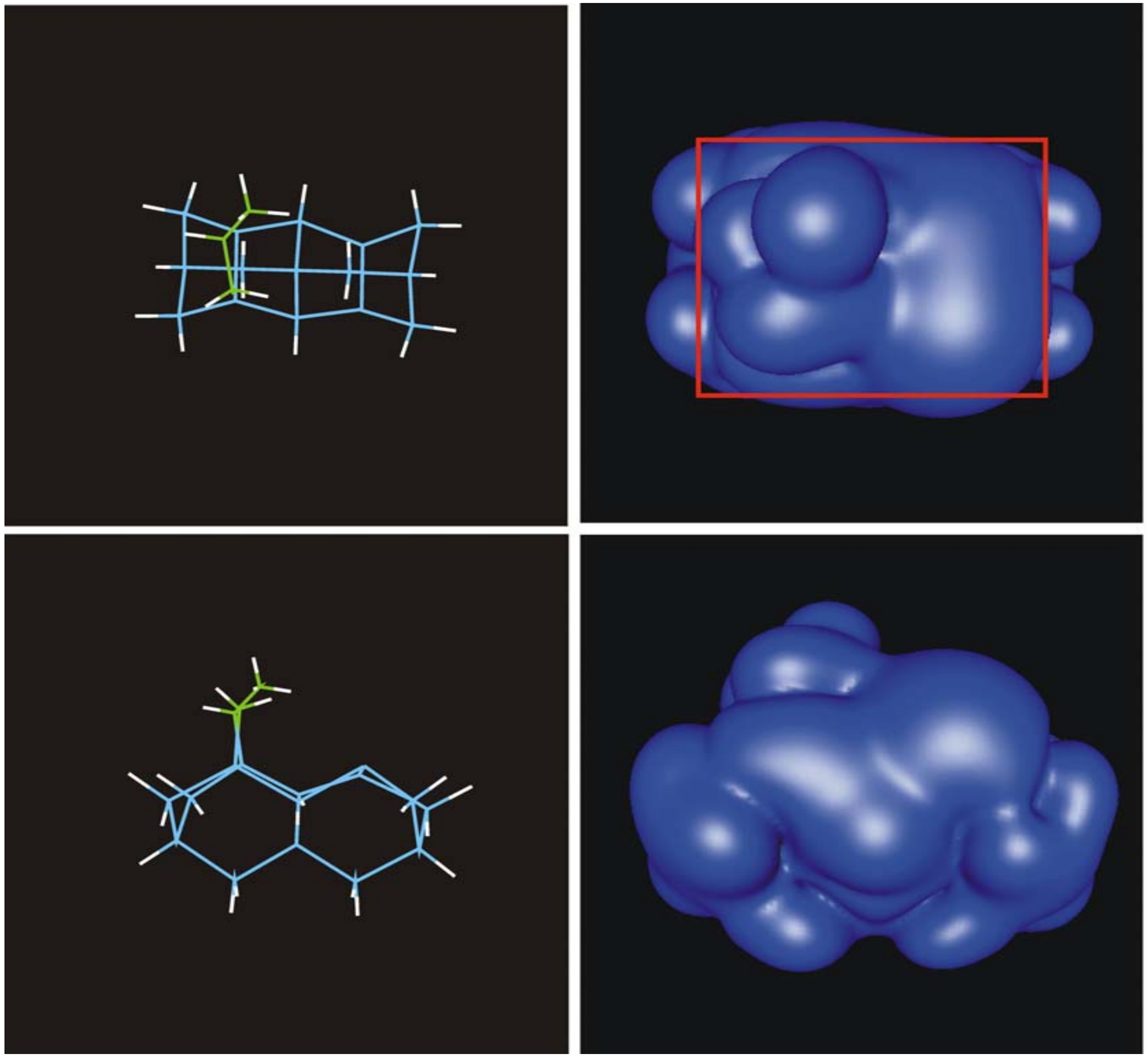
Organic modification of hydrogen terminated silicon surfaces, Danial D. M. Wayner and Robert A. Wolkow, J. Chem. Soc., Perkin Trans. **2**, 23-34 (2002).

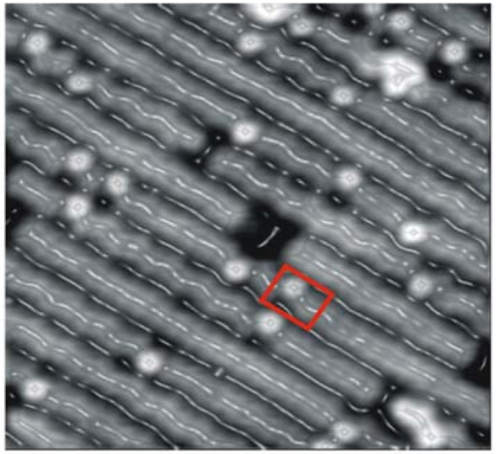
Soon, high resolution electron energy loss spectroscopy combined with STM

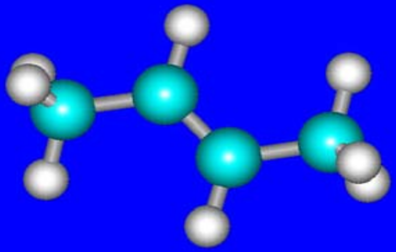
- ~100x more sensitive
- Can do (must do) in vacuum
- combined with STM will allow “white bumps” to be identified

# Propylene on Si(100)

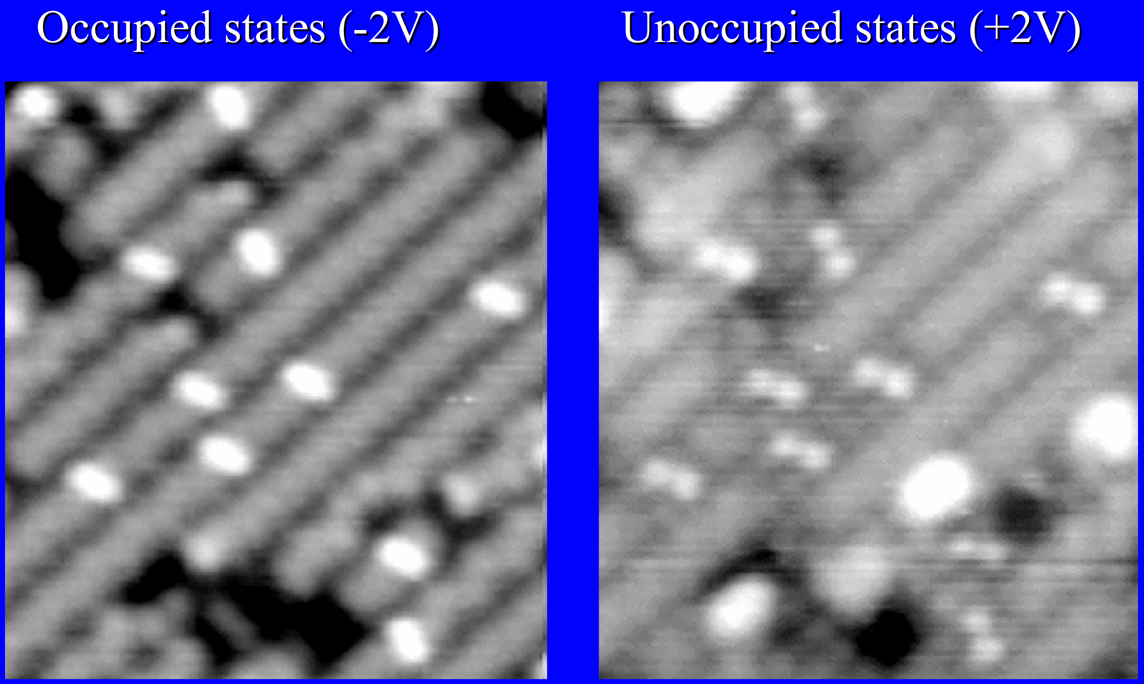








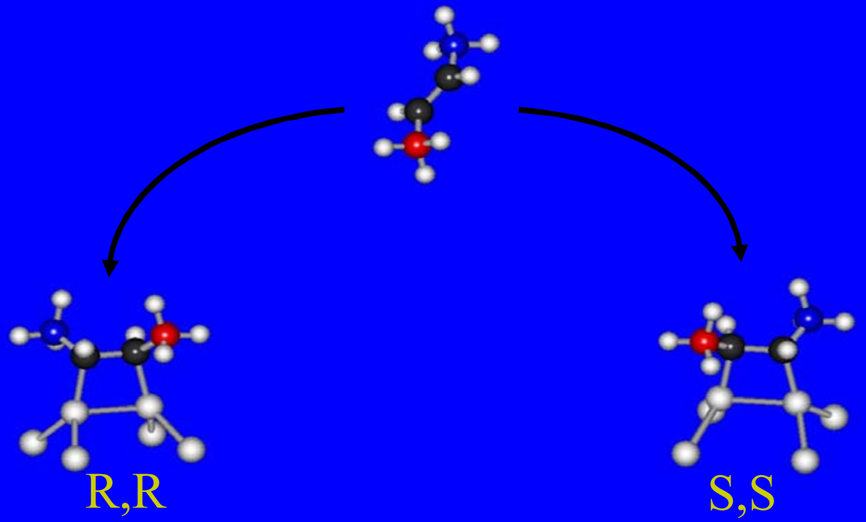
# *trans*-2-butene on Si(100)

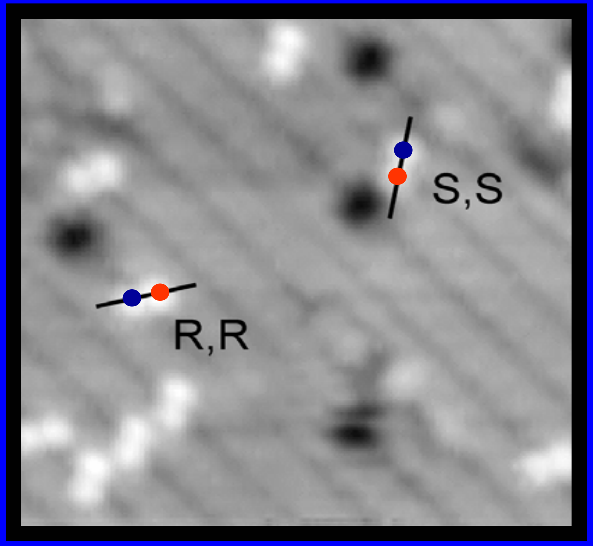


unoccupied

occupied

# Determination of absolute chirality



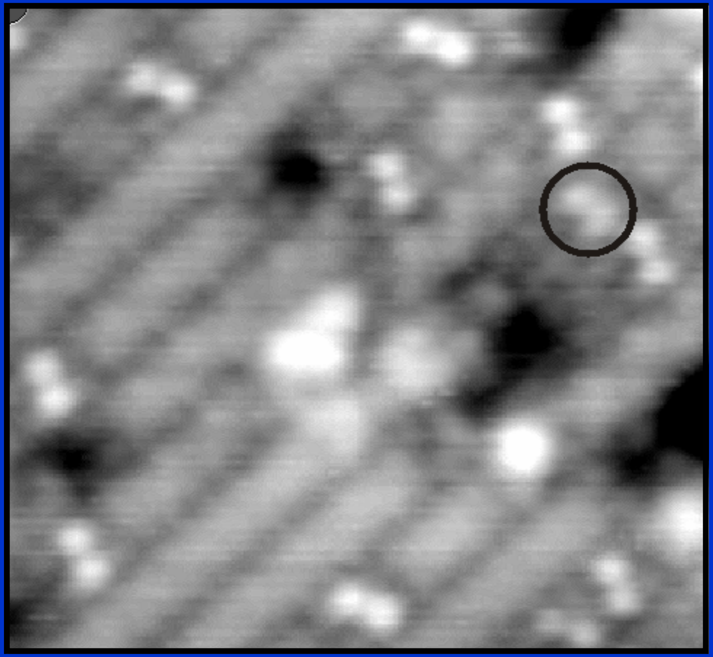


1. the molecule *trans*-2-butene has 2 “faces”
2. reaction at these results in products with different chirality.
3. the two enantiomers formed, though spectroscopically indistinguishable are clearly identified in the STM image.
4. Since reaction at the 2 faces is equally likely, equal numbers of the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

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

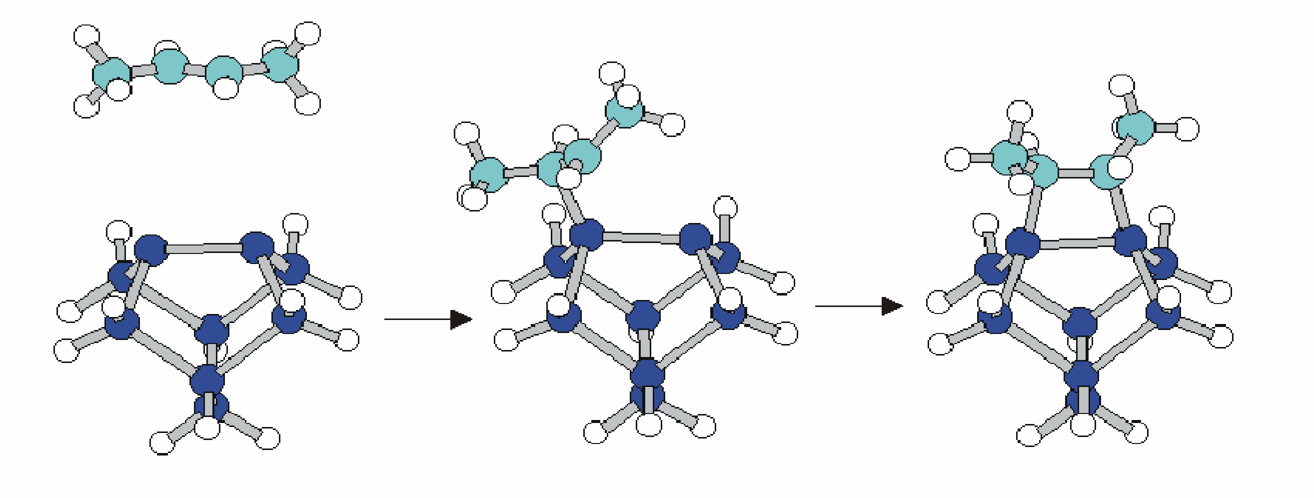
# Observation of isomerization in 2-butene addition

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



- Small fraction of molecules undergo isomerization upon addition to the surface at 295K.
  - 2.1+/-0.7% *cis* in *trans*
  - 2.6+/-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+/-0.5% *trans* in *cis*

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



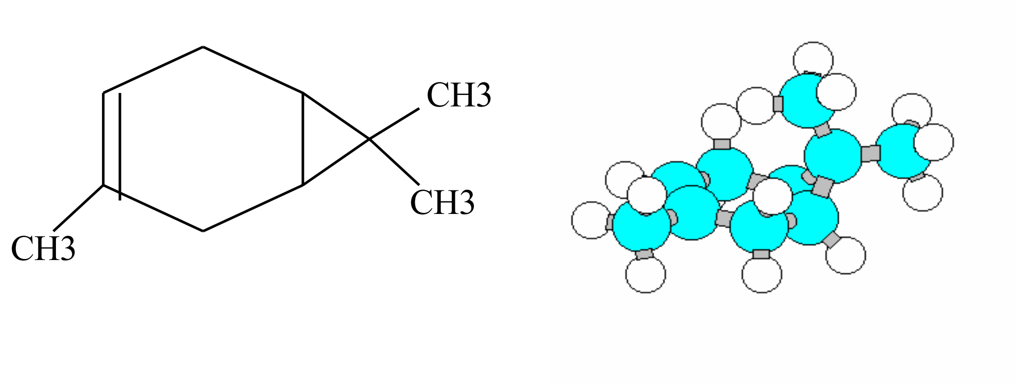
1) Some isomerization is observed, indicating sequential, but rapid formation of second Si-C bond.
2) Only a small probability of rotation about the C-C single bond. *For rotational barrier of 4 kcal this timescale is 2 ps.*
3) Weak temperature dependence suggests three scenarios;
   - *small barrier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

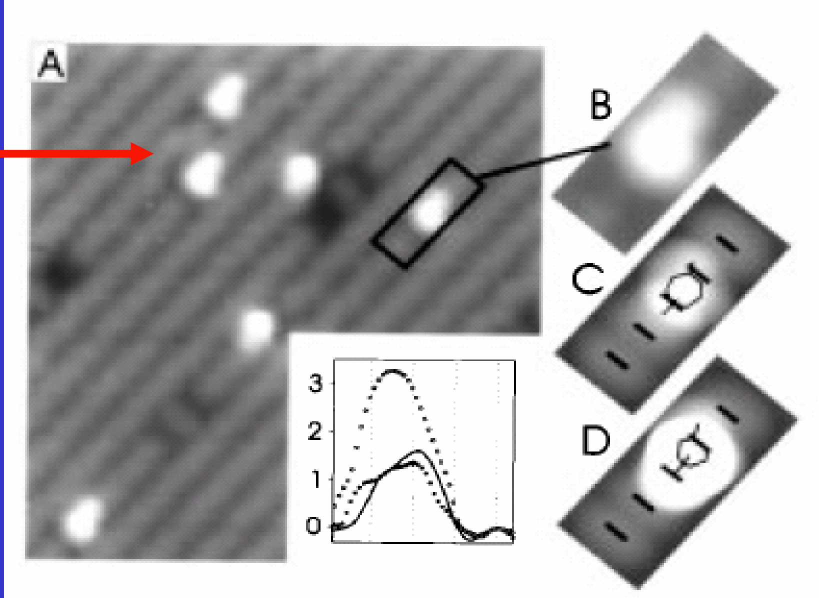
Carene, reaction at one face is blocked

An enatiospecific reaction ("asymmetric induction") results

Formation of a macroscopically chiral surface.

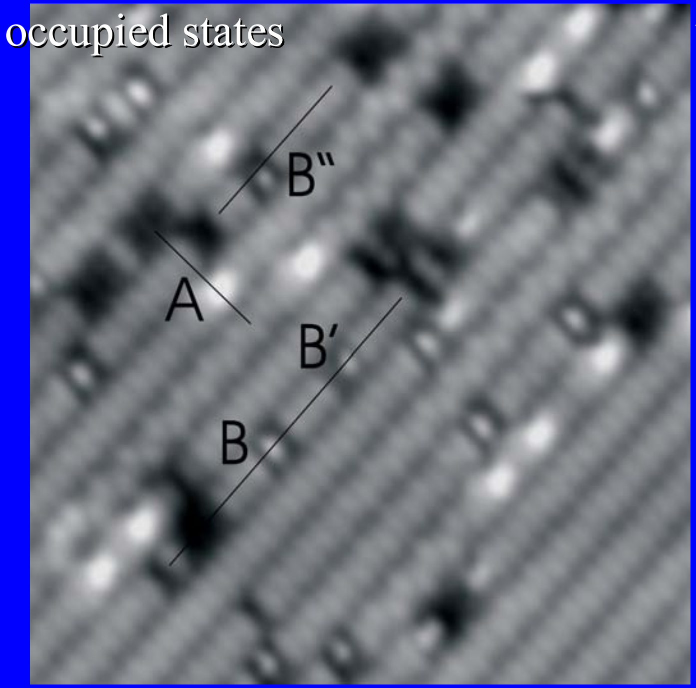


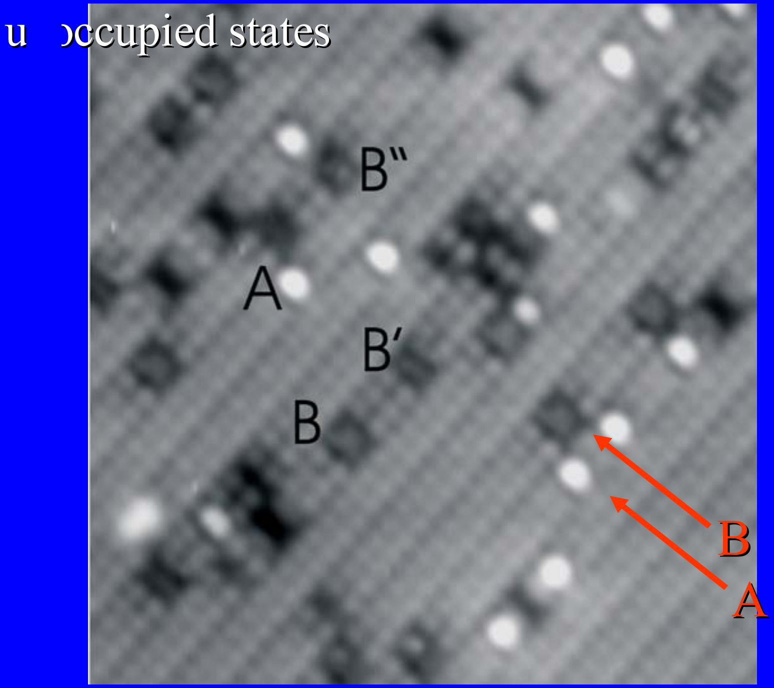
Wrong Enantiomer ?



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)

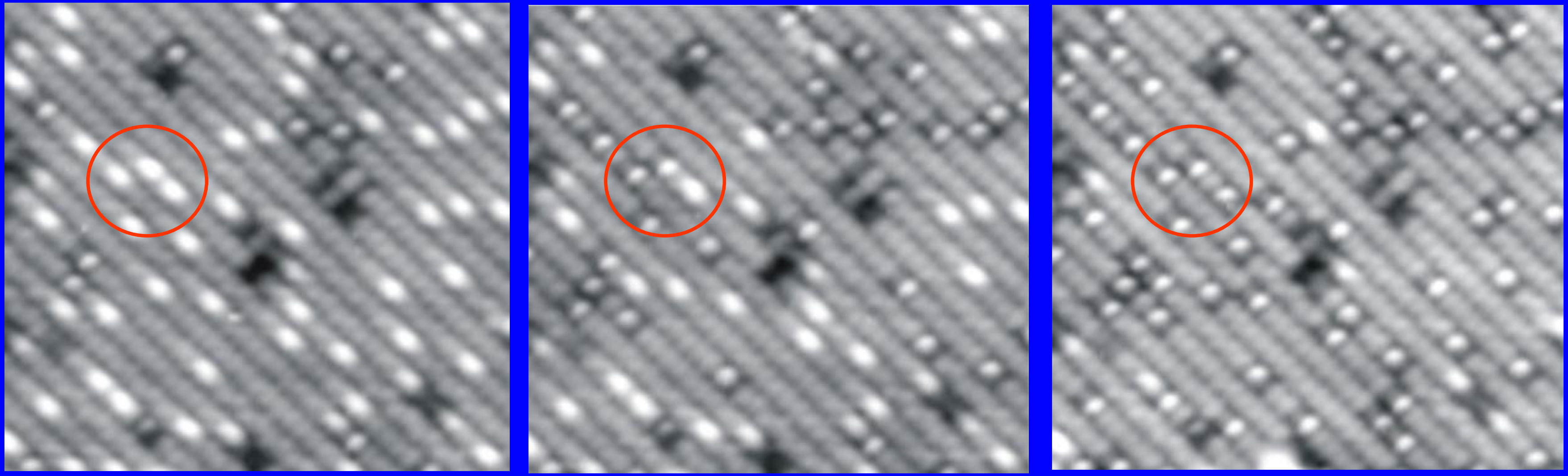




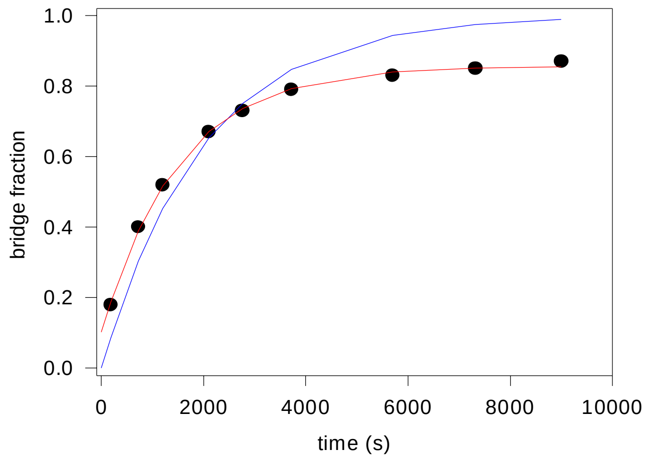
- don’t see C or H atoms - only blobs
- more than one configuration evident – very diff. appearances

- can’t solve this structure

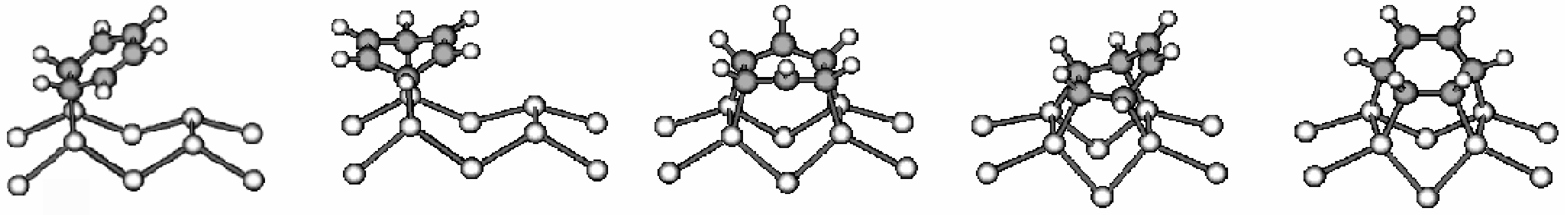
# Adsorbed benzene shows changes with time



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

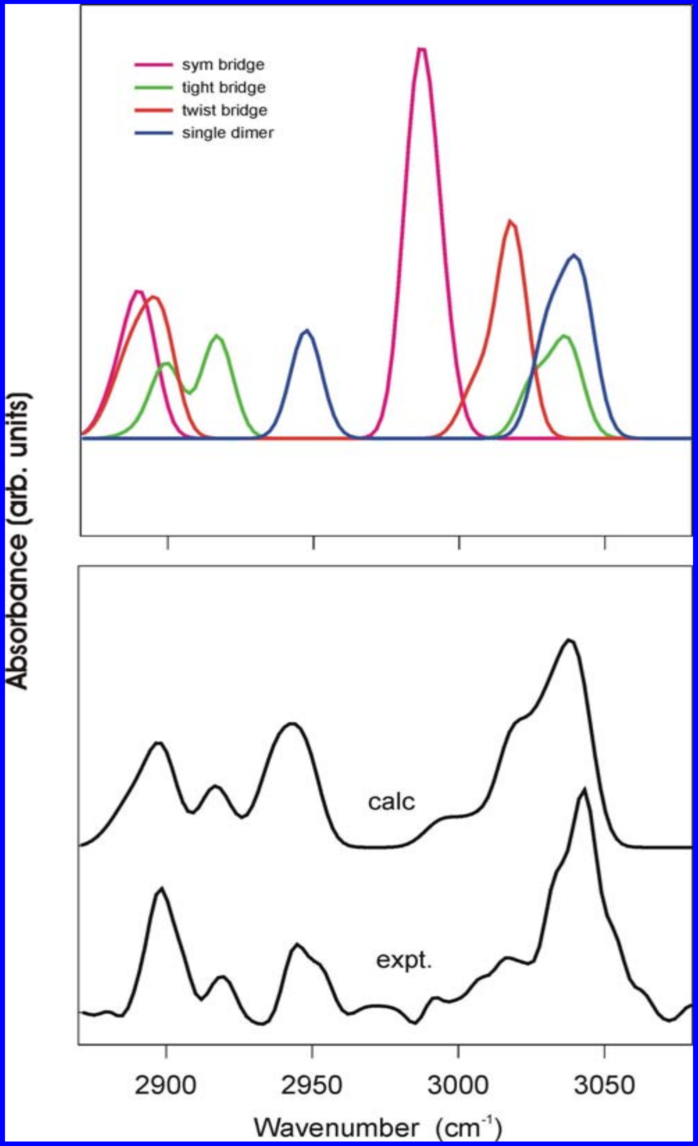


# Benzene/Si(100) Calculated Bonding Geometries

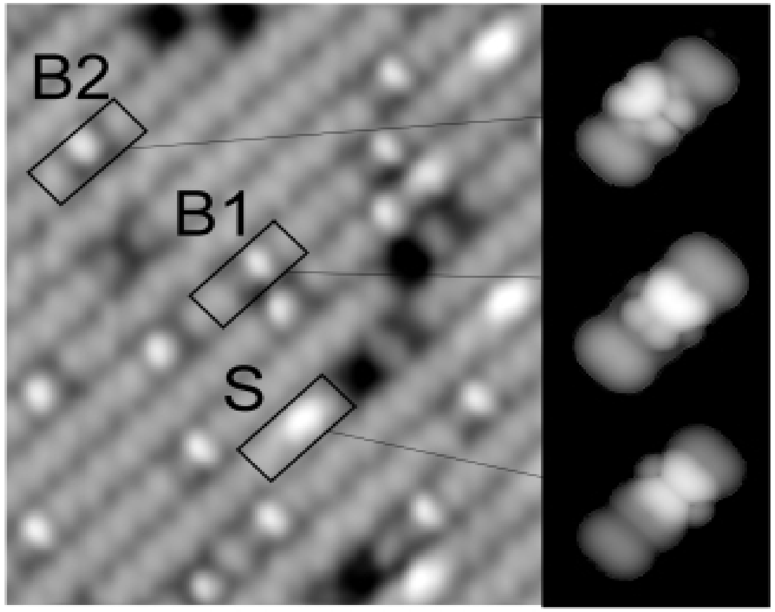


| | Single dimer | | bridge | | |
|---|---|---|---|---|---|
| | 1,2 | 1,4 | symmetric | tight | twist |
| AM1 | 1.07eV | 1.02eV | 1.58eV | 1.64eV | 1.74eV |
| DFT<br>(B3LYP/6-31G*) | 0.17eV | 0.88eV | x | 1.49eV | 0.91eV |

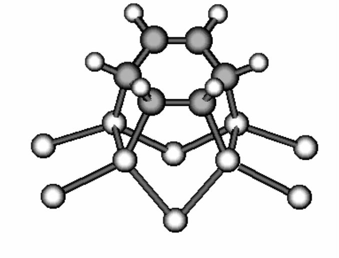
# Benzene/Si(100): Calculated Vibrational Spectrum



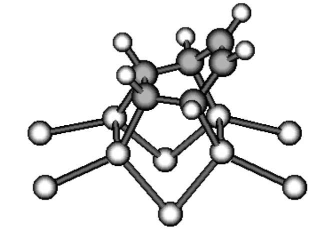
- Can assign all the observed modes to either single dimer, tight or twist bridge bonding geometries.
- Symmetric bridge can be ruled out, consistent with calculated adsorption energy



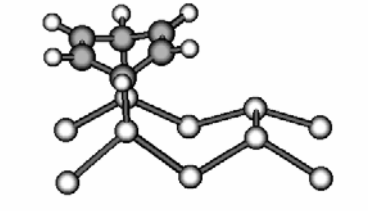
Twist bridge



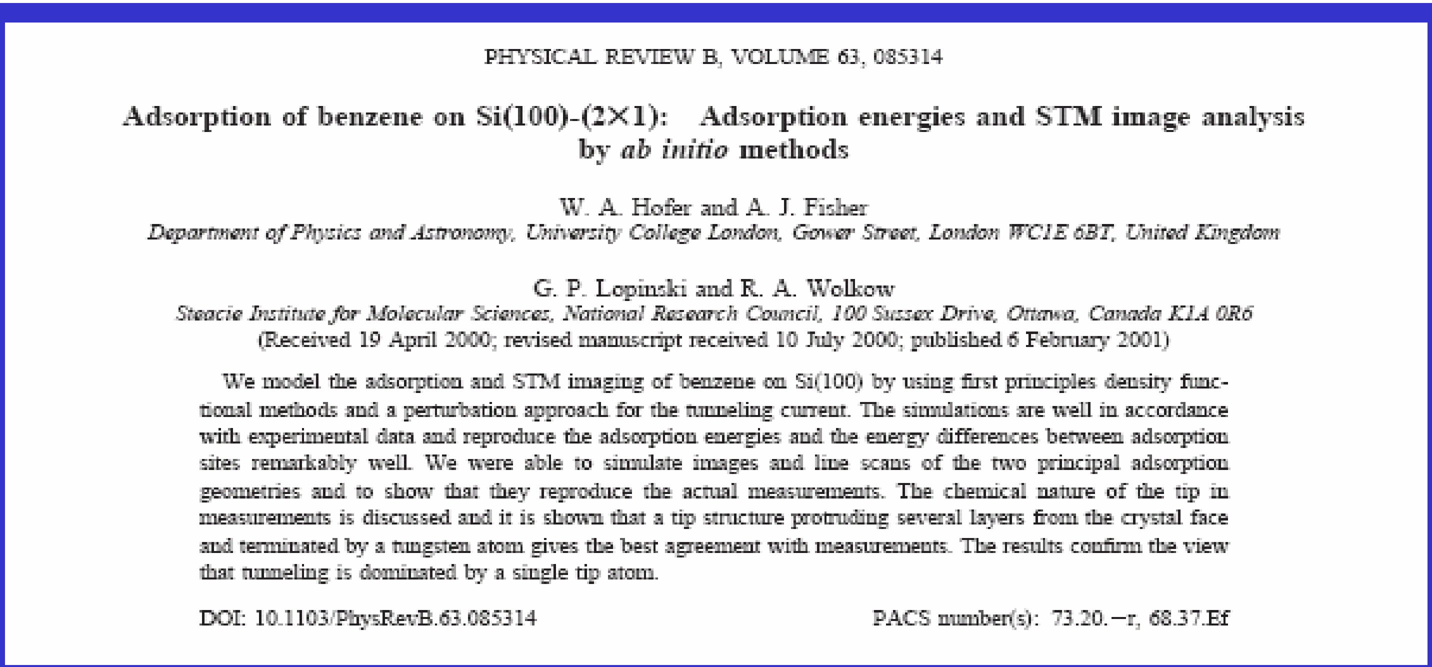
Tight bridge



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).



PHYSICAL REVIEW B, VOLUME 63, 085314

# 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

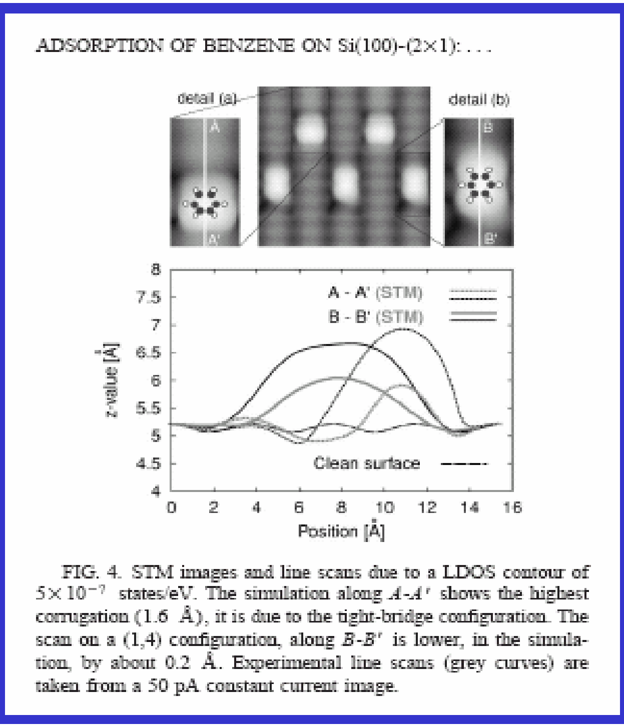
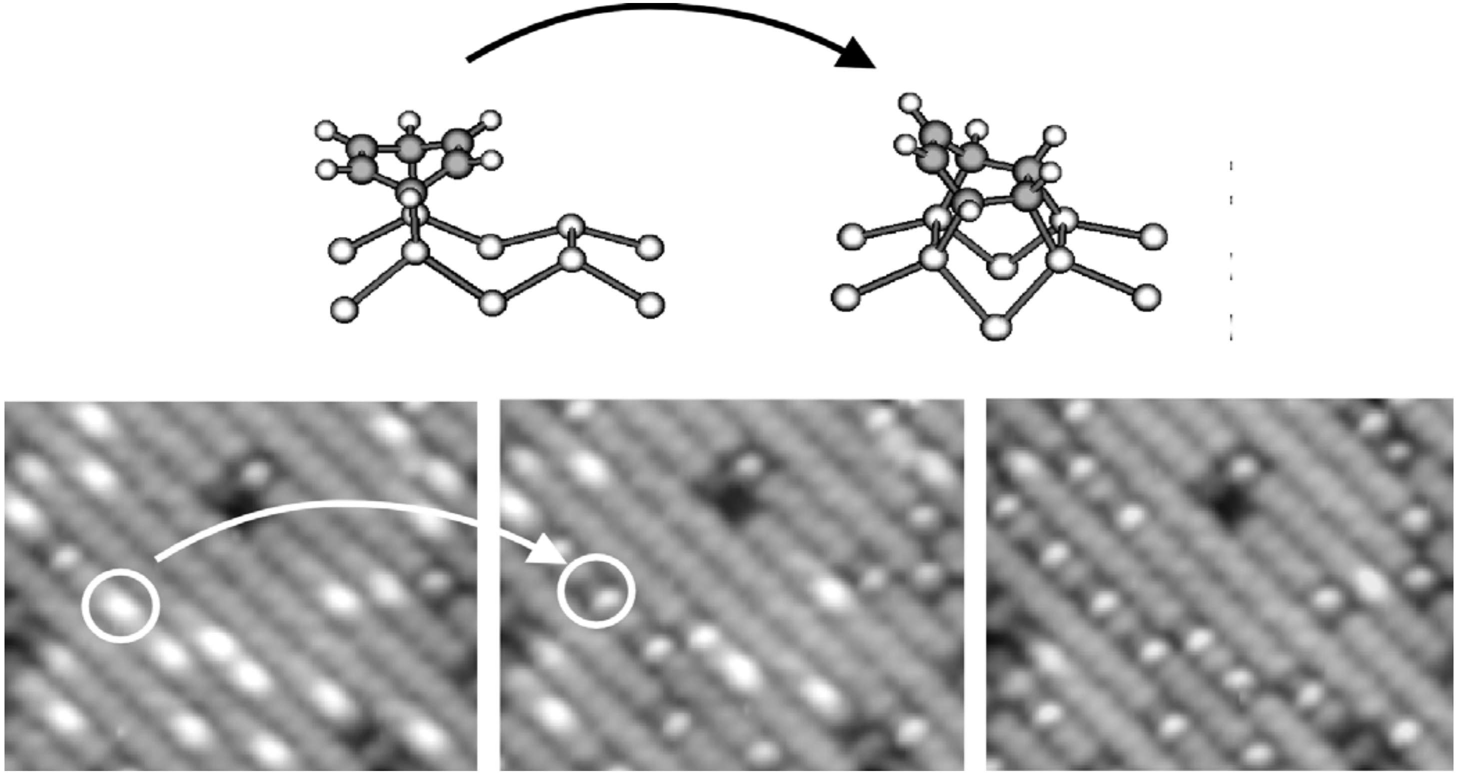
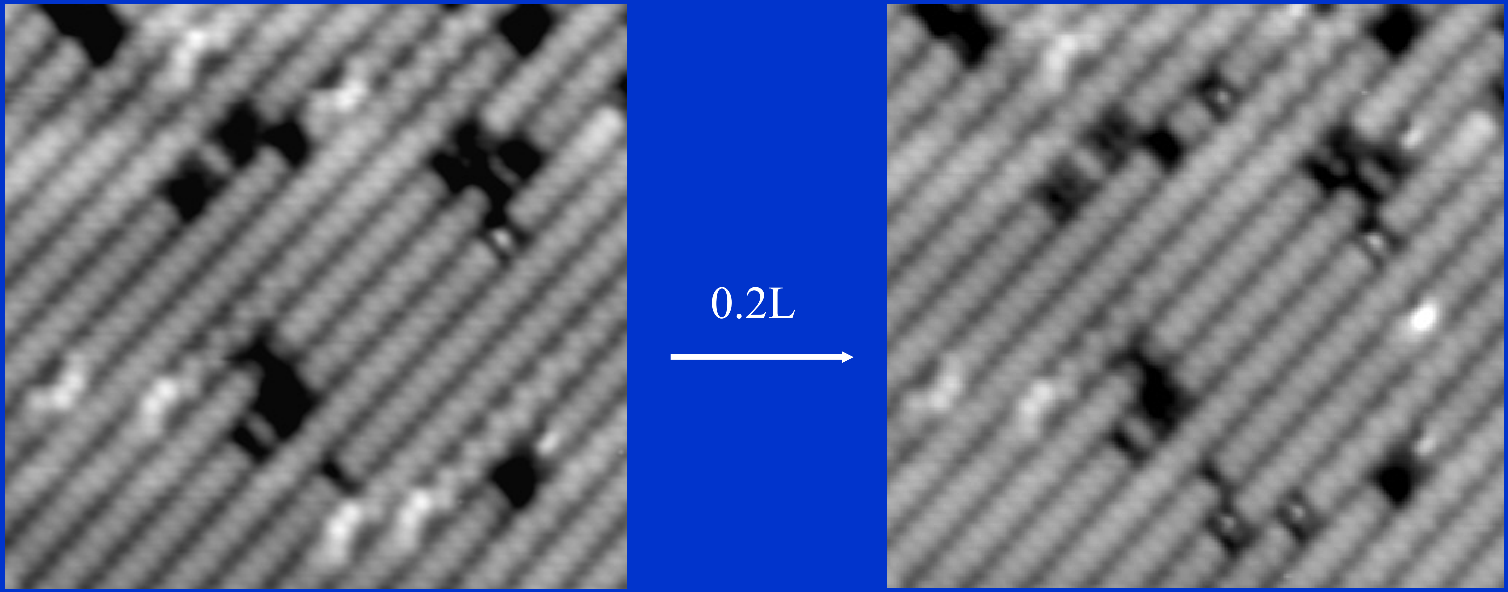


FIG. 4. STM images and line scans due to a LDOS contour of $5\times10^{-7}$ states/eV. The simulation along $A$-$A'$ shows the highest corrugation (1.6 Å), it is due to the tight-bridge configuration. The scan on a (1,4) configuration, along $B$-$B'$ is lower, in the simulation, by about 0.2 Å. Experimental line scans (grey curves) are taken from a 50 pA constant current image.

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

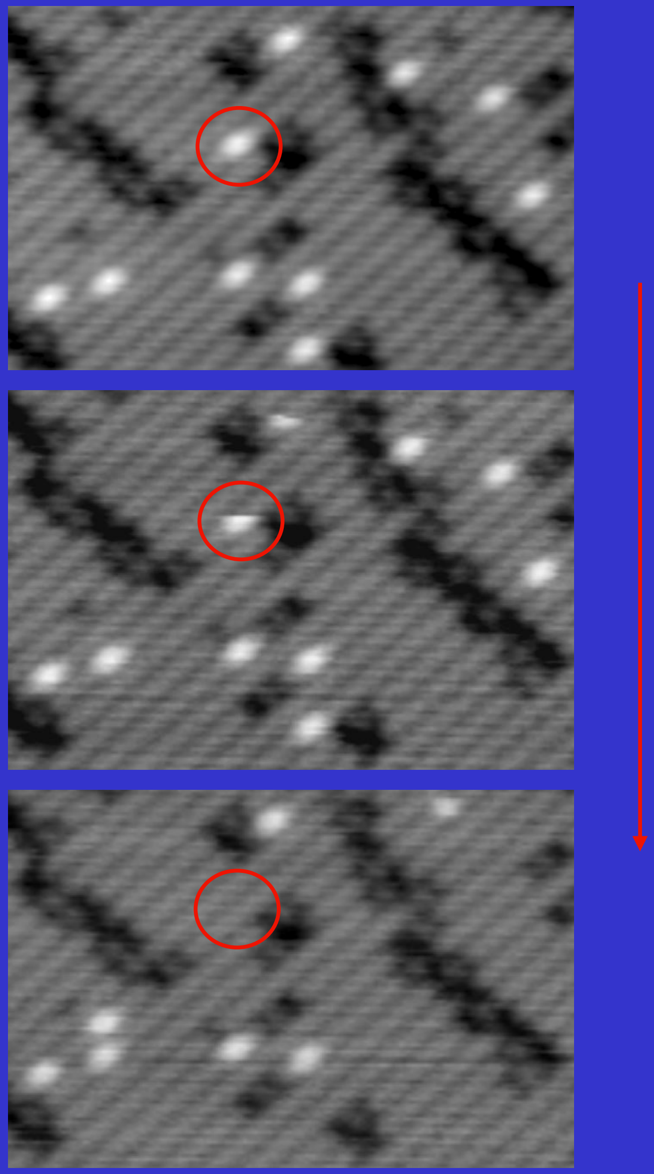


# Benzene Adsorption at type C defects



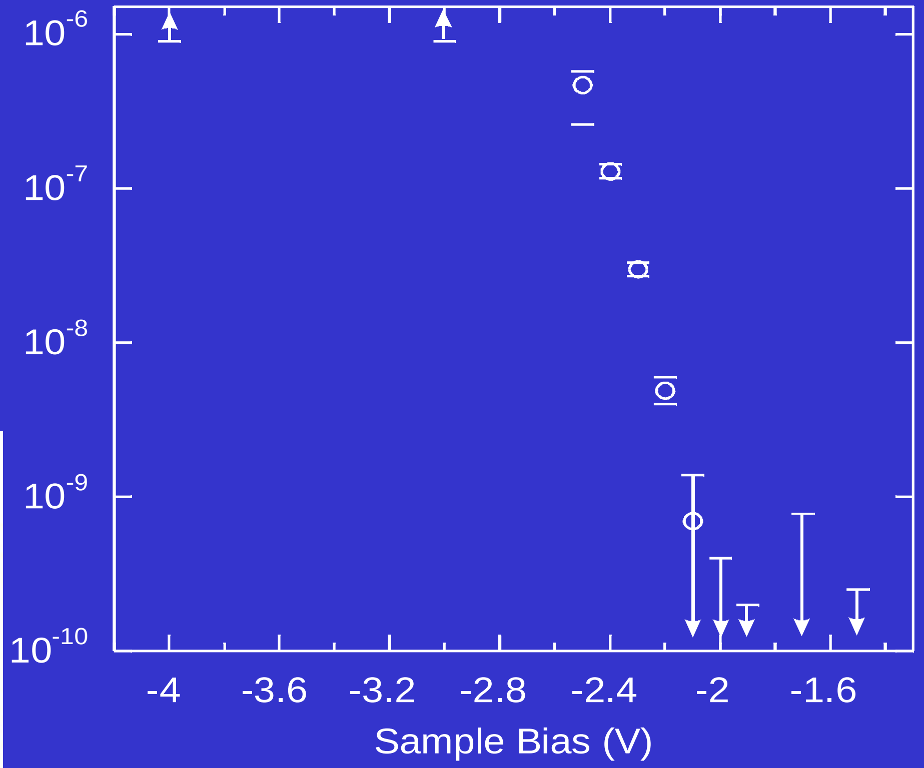
1. 5 additional adsorption events in this area, 3 at type C defects
2. preferential adsorption at type C defects
3. Taking relative populations (regular and defect) into account indicates 40:1 preference for defect
4. Requires substantial mobility before chemical adsorption locks molecule in place

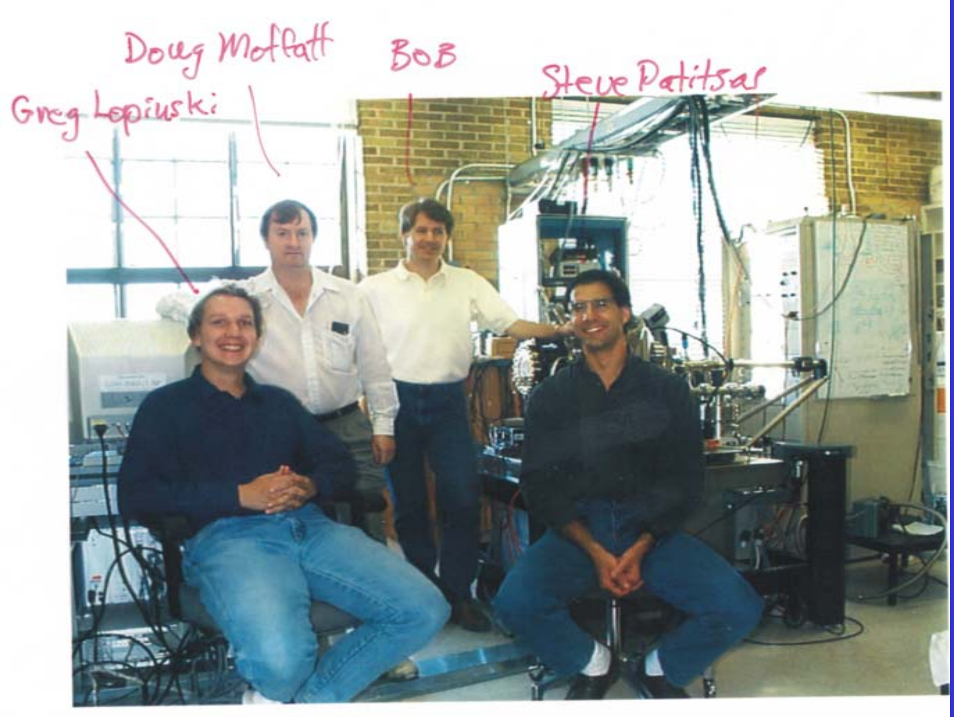
# Single molecule-silicon bond breaking



# bond breaking probability as a function of voltage

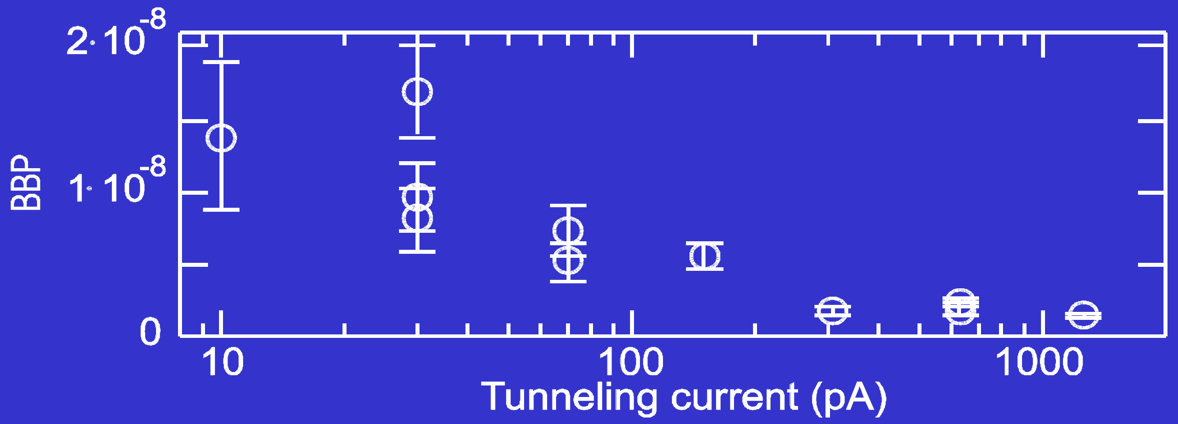
- bond breaking is not observable at lower voltages
- very sharp rise (note logarithmic graph)

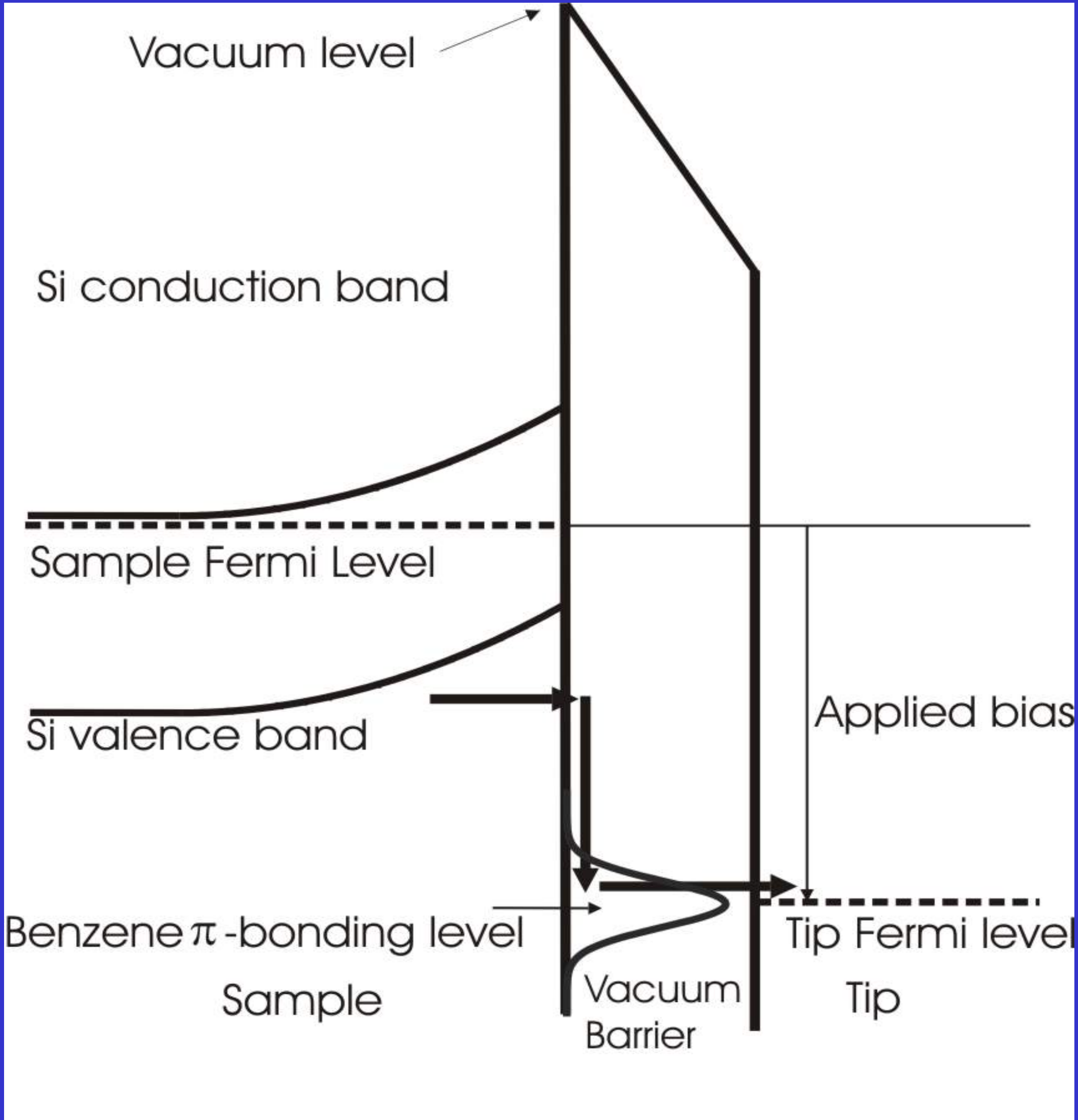




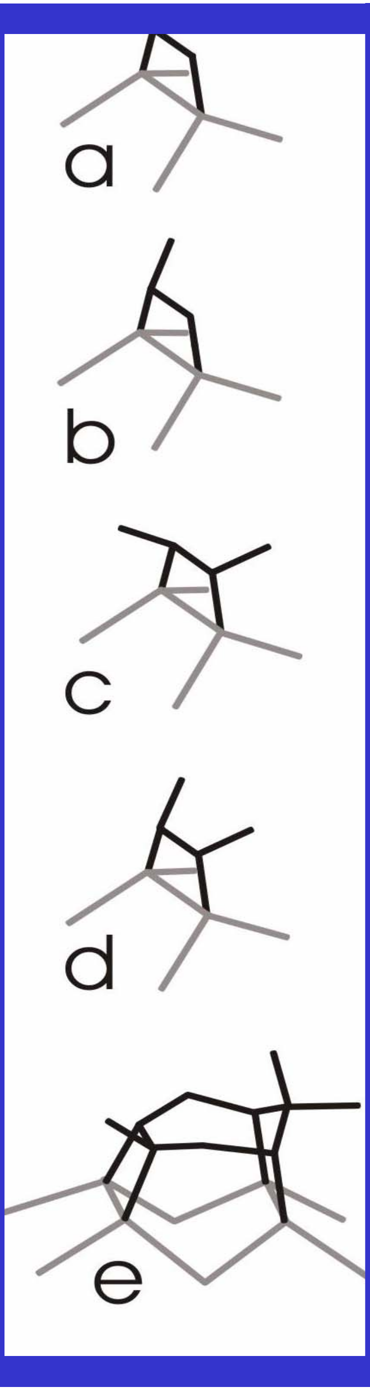
# Single electron process

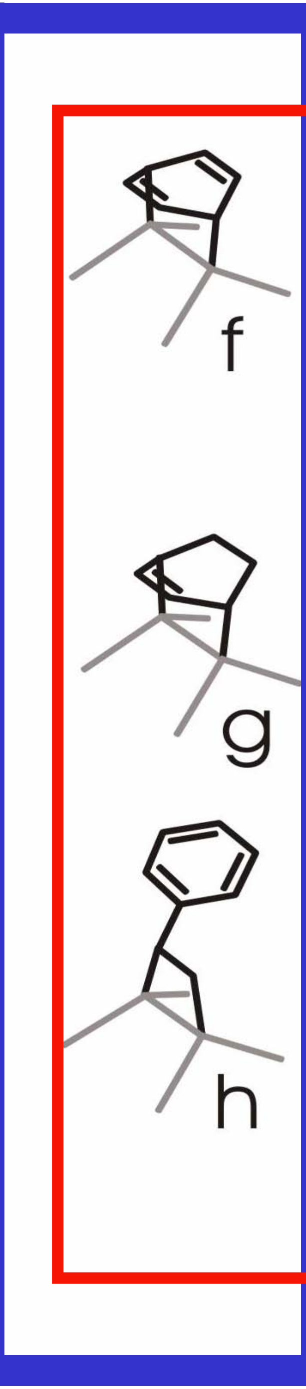
- examine current dependence of bond breaking probability
- approximately linear
- single electron breaks the molecule-silicon bond (2 S-C bonds)




Vacuum level
Si conduction band
Sample Fermi Level
Si valence band
Applied bias
Benzene π -bonding level
Tip Fermi level
Sample
Vacuum
Barrier
Tip

Alkane-like
adsorbates

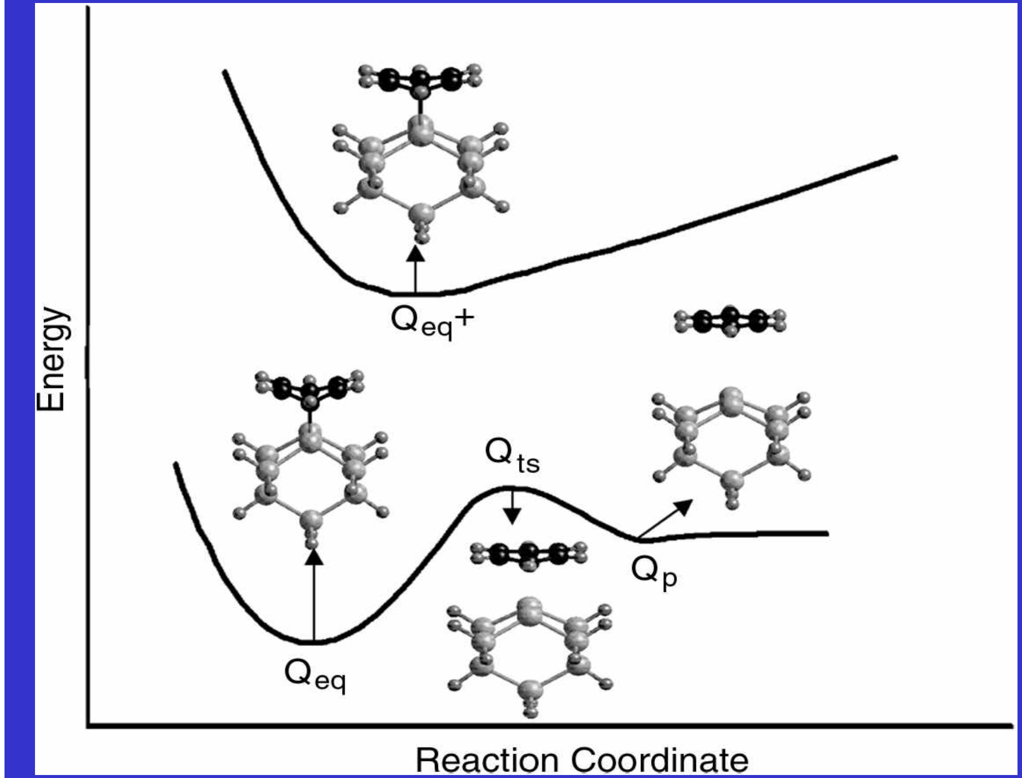


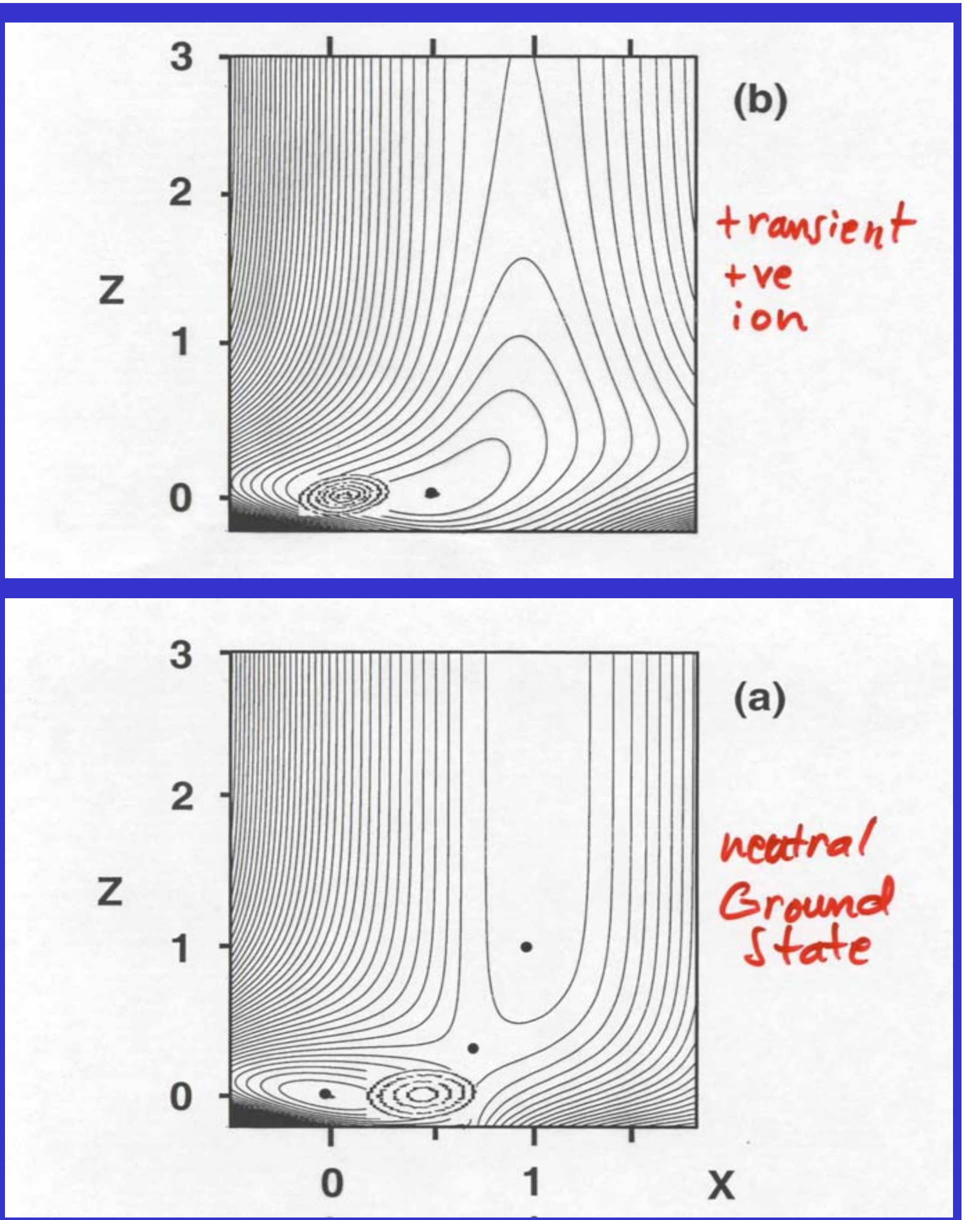


Π-bond
containing
adsorbates

These can be
dislodged

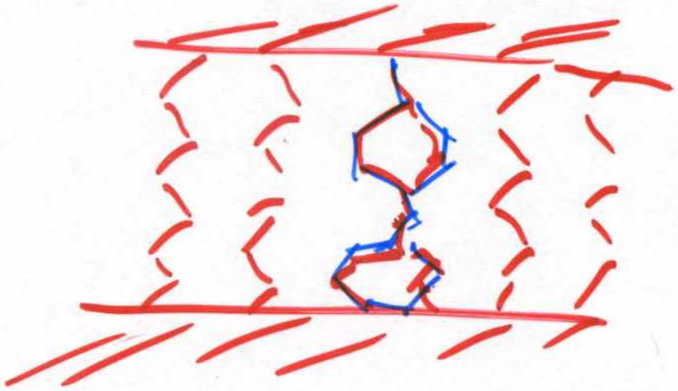
Current-Induced Organic-Silicon Bond Breaking: Consequences for Molecular Devices
S.N. Patitsas, G.P. Lopinski, O. Hul’ko, D.J. Moffatt and R.A. Wolkow, Sur. Sci., **457**, L425-L43, 2000.





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?



conducts 0–1·7 Volts
open circuit 2 Volts

Negative differential resistance?

APPLIED PHYSICS LETTERS VOLUME 81, NUMBER 23 2 DECEMBER 2002

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

Peter Kruse and Robert A. Wolkow[a)]
*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