Fundamental Issues in Building A Molecular Electronics Technology

Rationale for A Molecular Electronics Technology

I-V Behavior of Molecules

Potential Applications and Device Types

Selected Issues in Single Molecule Devices

Manufacturability Issues

Planar Devices: Molecular Level Design & Testing Issues

Conclusions and Perspectives

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National Science Foundation
Molecular Electronics Corp.

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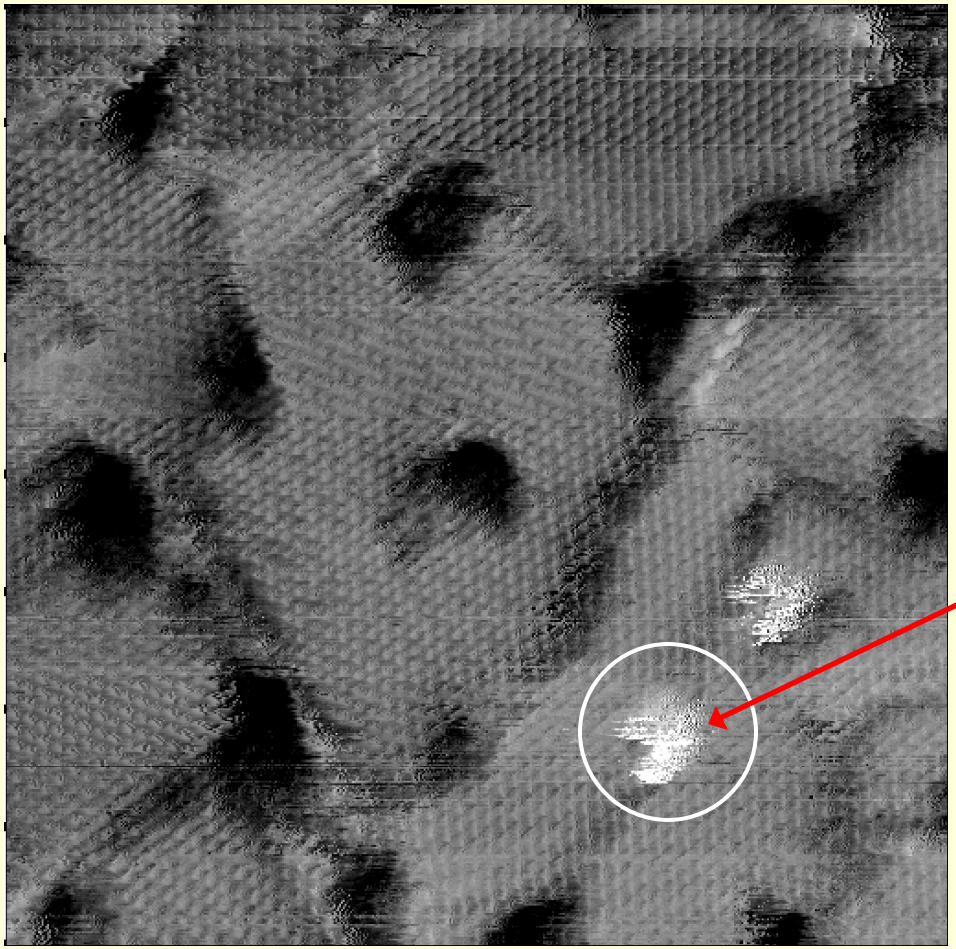
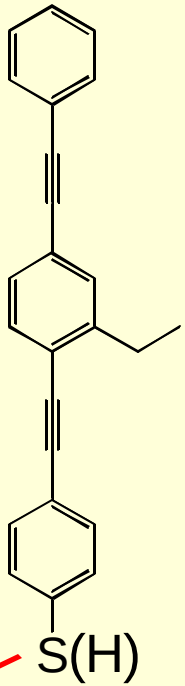
Conductance of a Single Molecule via STM

$C_{12}H_{25}S$- Host lattice on Au{111}



40 x 40 nm



Guest molecule

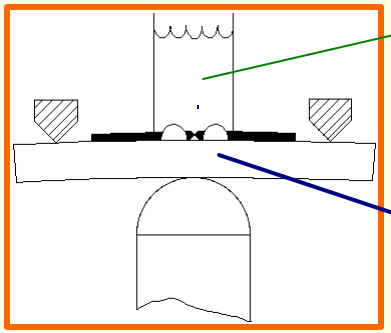
STM:

* Guest ~0.7 nm above host lattice at constant current
* *Enhanced conductivity*

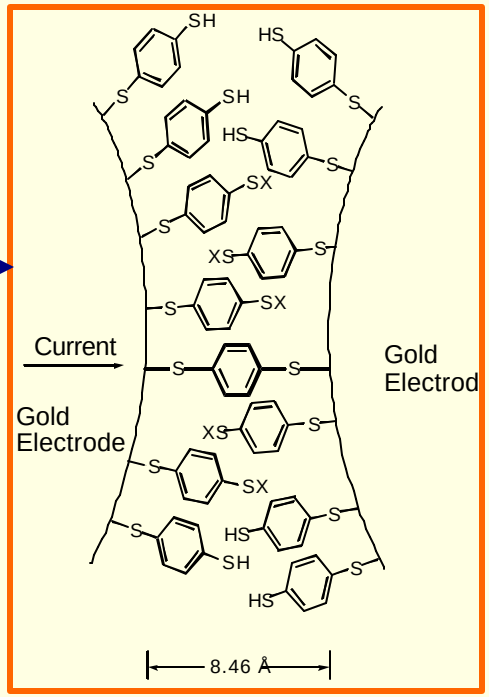
Bumm, Arnold, Cygan, Dunbar, Burgin, Jones, Allara, Tour, Weiss, *Science*, 271 1705(1996)

Cygan, Dunbar, Arnold, Bumm, Shedlock, Burgin, Jones, Allara, Tour, Weiss *JACS* 120, 2721(1998)

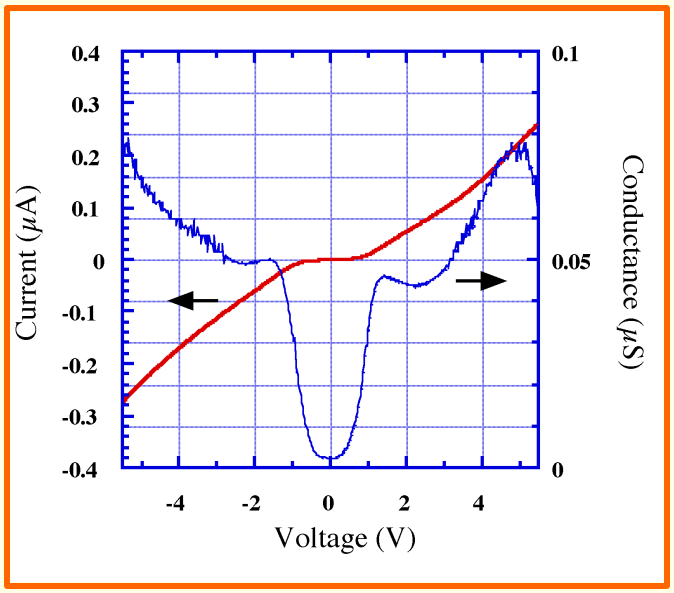
Conductance of a Single Molecule via A Break Junction



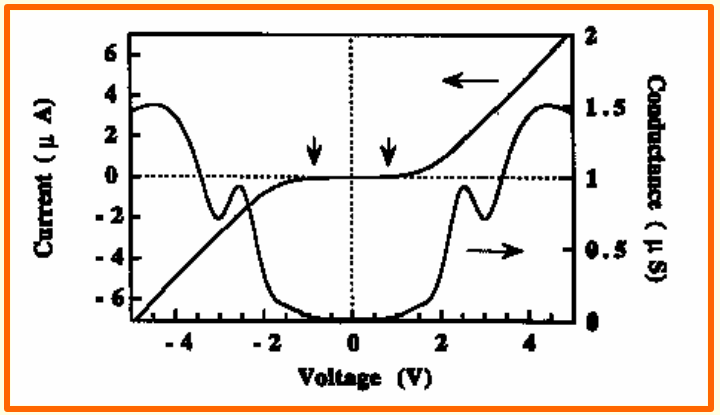
Break Junction allows
measurement of single molecule



~10^8 – 10^9 Amps/cm^2 !!

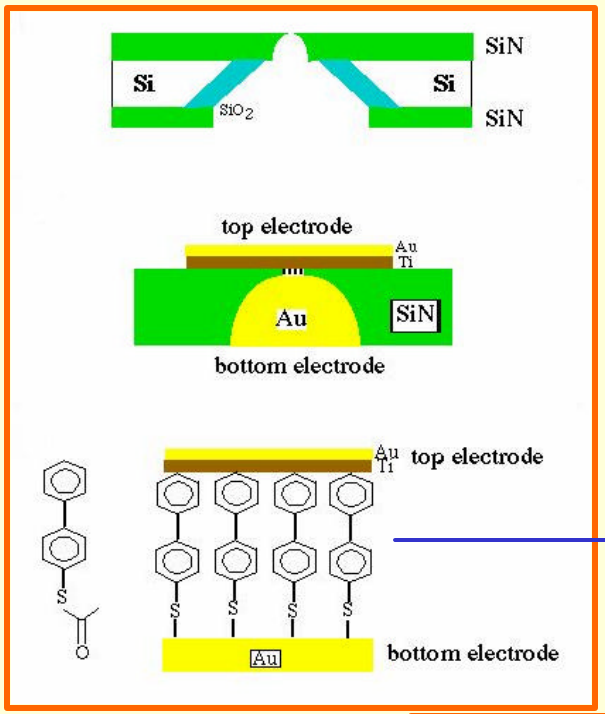


M.A. Reed *et. al*, *Science* 278, 252 (1997)



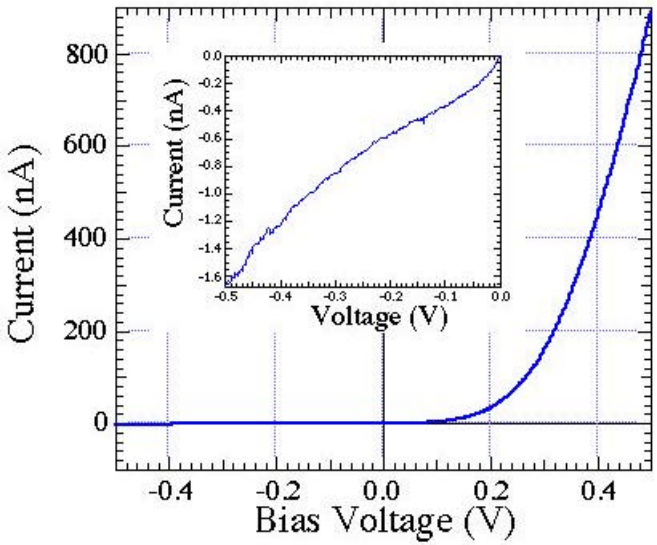
Theory: Di Ventra, Pantelides, and Lang
D (E_F-E_{HOMO}) ~ 0.7 eV

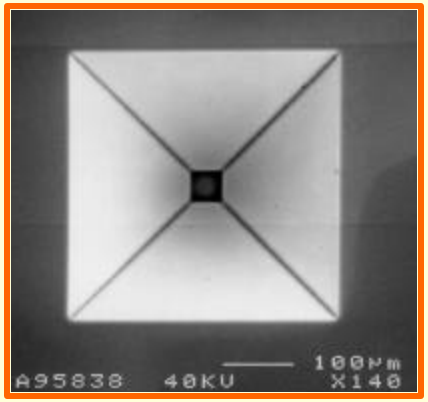
Small Molecular Ensembles in A Nanopore Show Device Functions



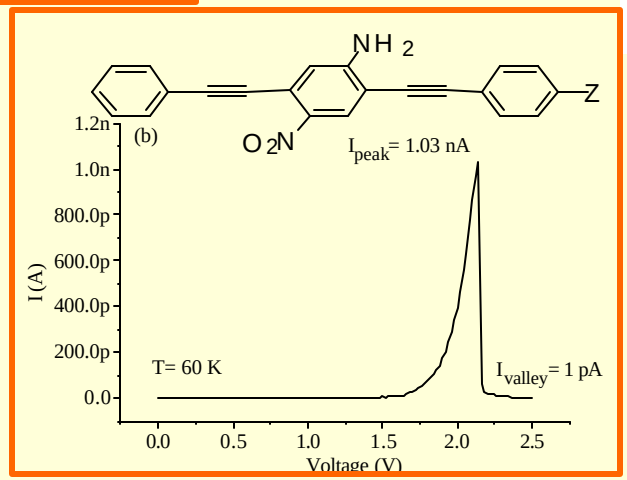
Pores contain
~10^3 molecules

Diode Behavior

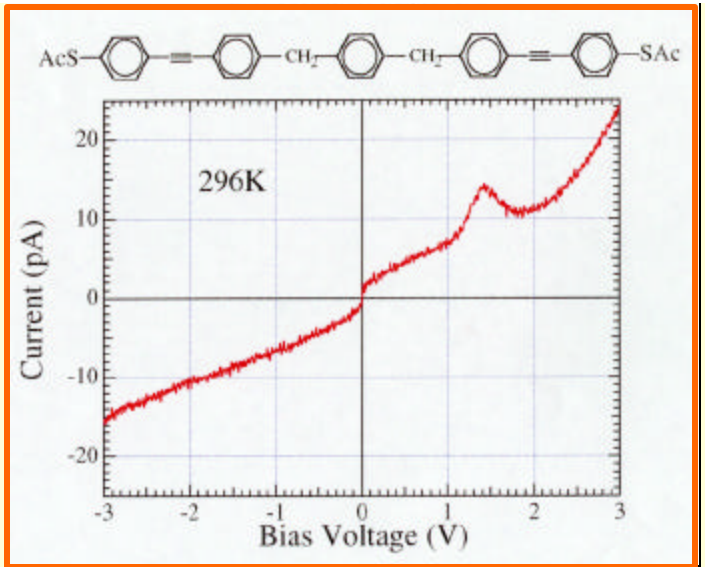




100 nm



Resonant Tunneling Diodes (RTD)



C. Zhou *et. al*, *Appl. Phys. Lett*. 71, 611 (1997);
Chen, Reed, Rawlett, Tour, *Science* 286 1551 (1999)

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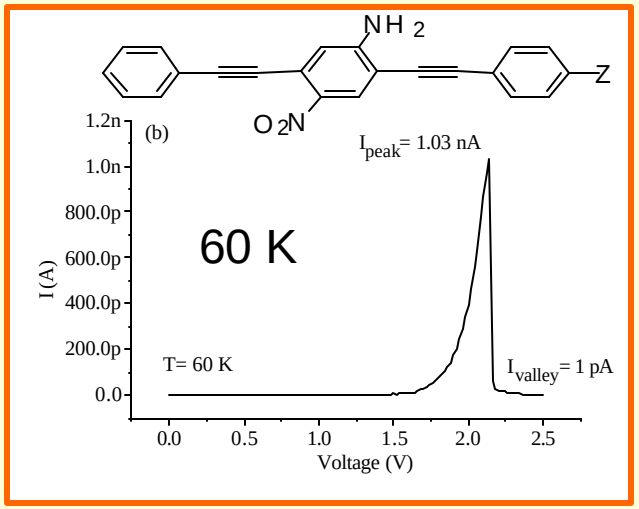

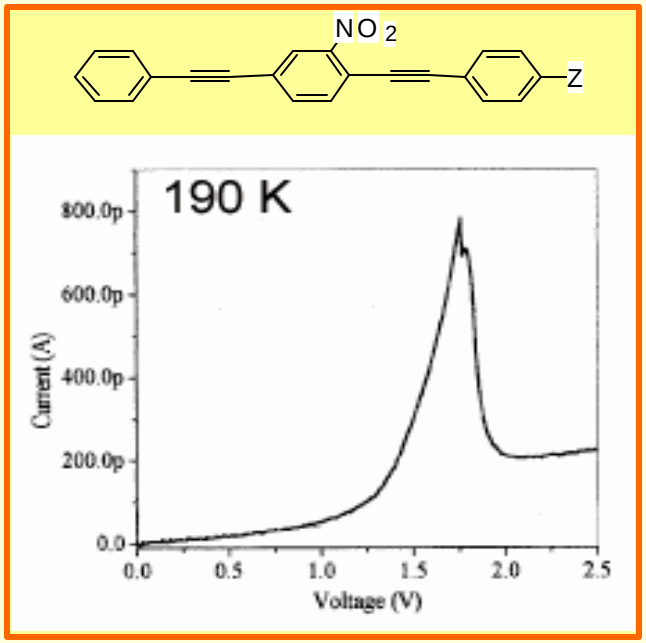

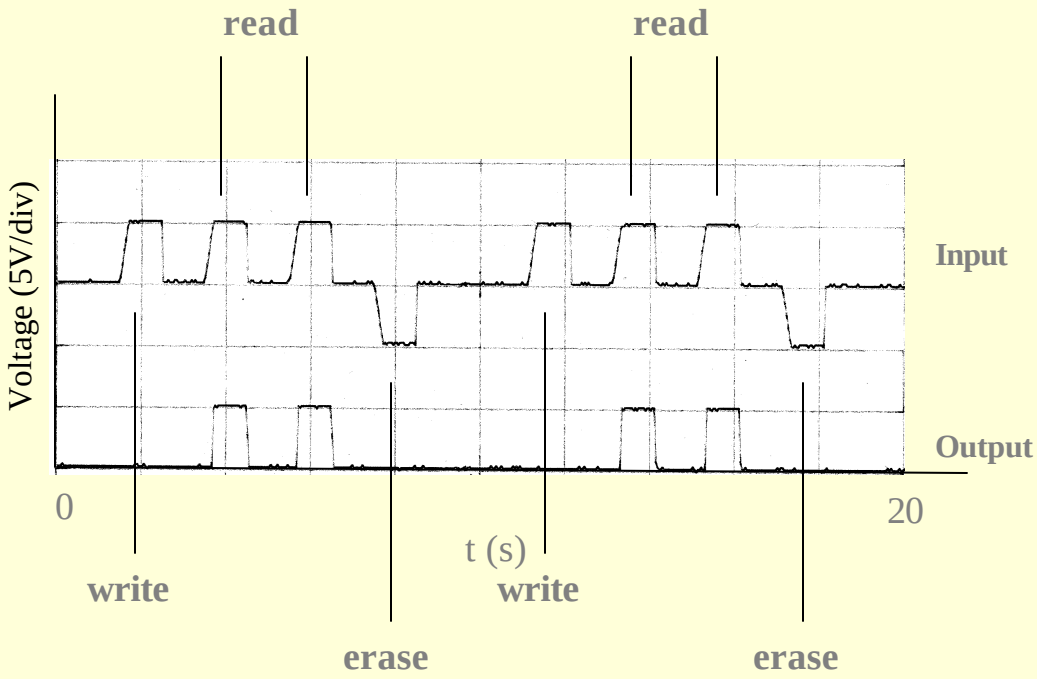

Memory function can be created from these types of device structures

Reed, Chen, Rawlett, Price, Tour, *Appl.Phys.Lett.*, 78, 3735(2001)

Chen, Reed, Rawlett, Tour, *Appl.Phys.Lett* 77 1224 (2000)

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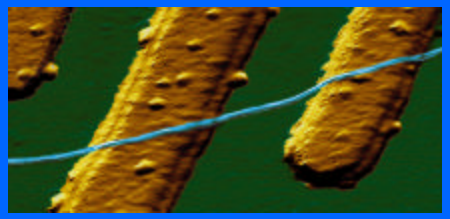
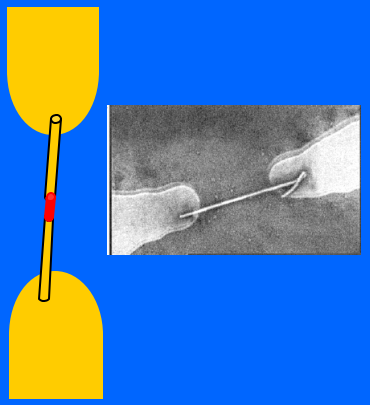


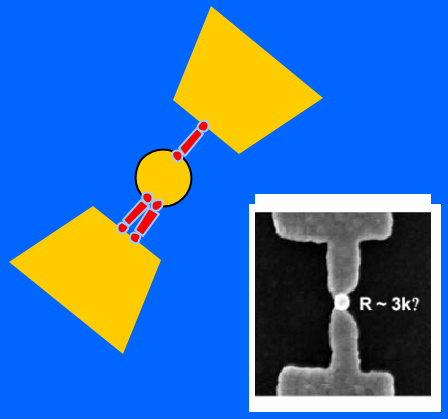
n-Rod-Molecule-n-Rod junctions



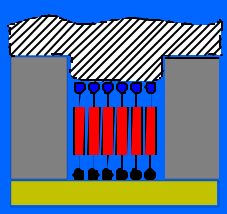
Single "*Molecule*" Logic Devices-I
- **nanotubes**

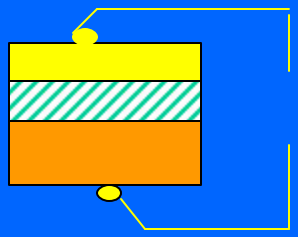
Molecular Electronics

n-Particle-Molecule Bridges



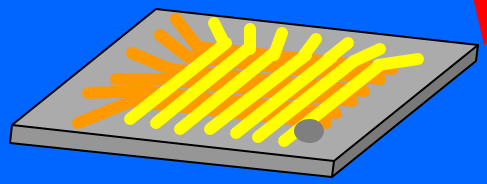
Metal/Molecule/Metal (M3-planar) Switching & Memory

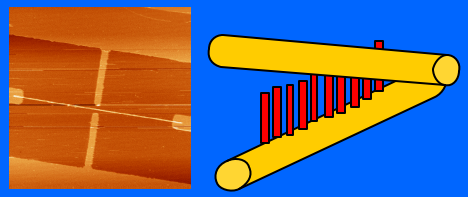




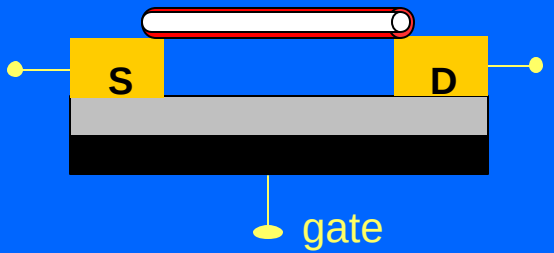
Molecular Electronics

Crossbar Devices
- **M3 - nanowires**
- ***nano*-mechanical (nanotubes)**

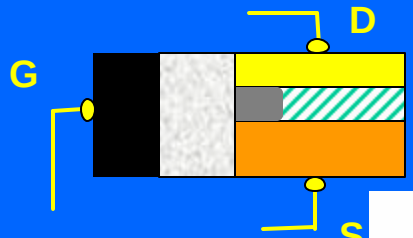


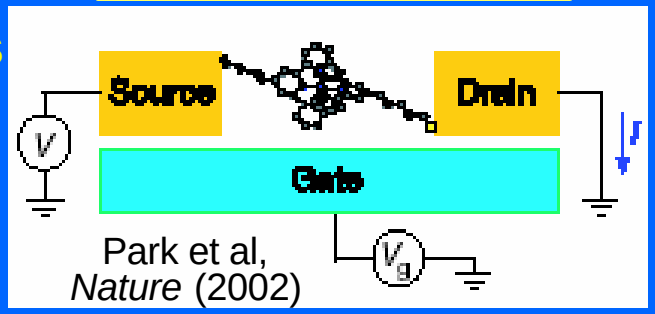


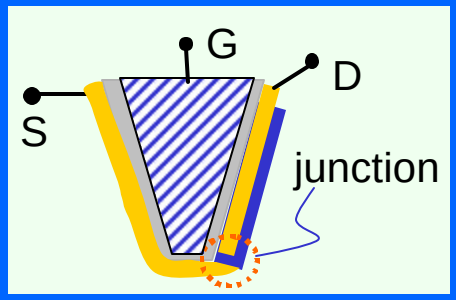
3-Terminal Memory: Molecule-Coated Semiconductor n-Rod



Junctions with Field Gates

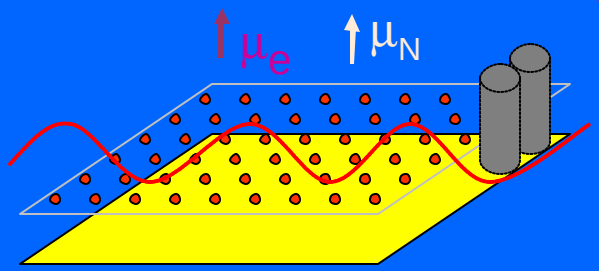




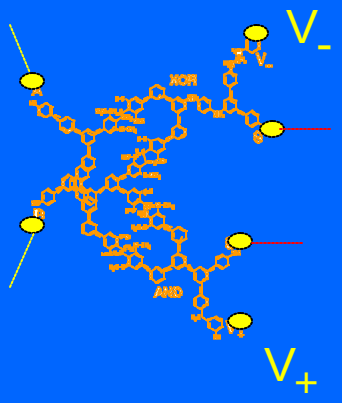


Molecular Electronics

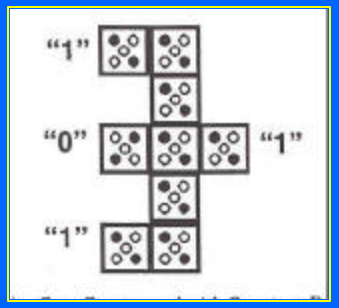
Molecular Q-Dot Quantum Computers

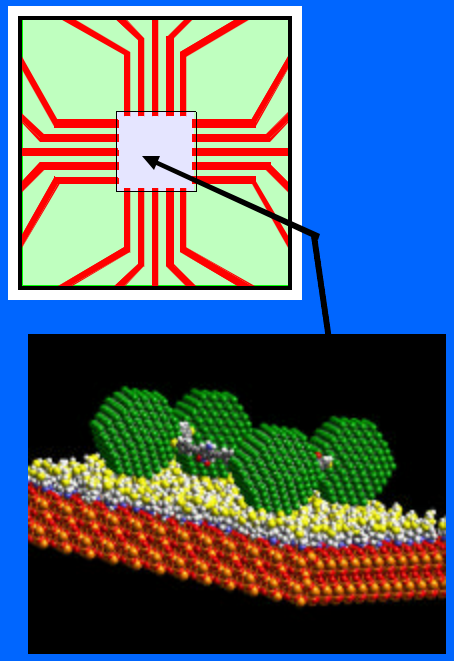


Single Molecule Logic Devices-II
• large molecules



Molecular Q-Dot Cellular Automata Computers





Molecule-*n*-Particle Logic Blocks

Chemical Attachment / Surface Chemistry is Common to All Devices

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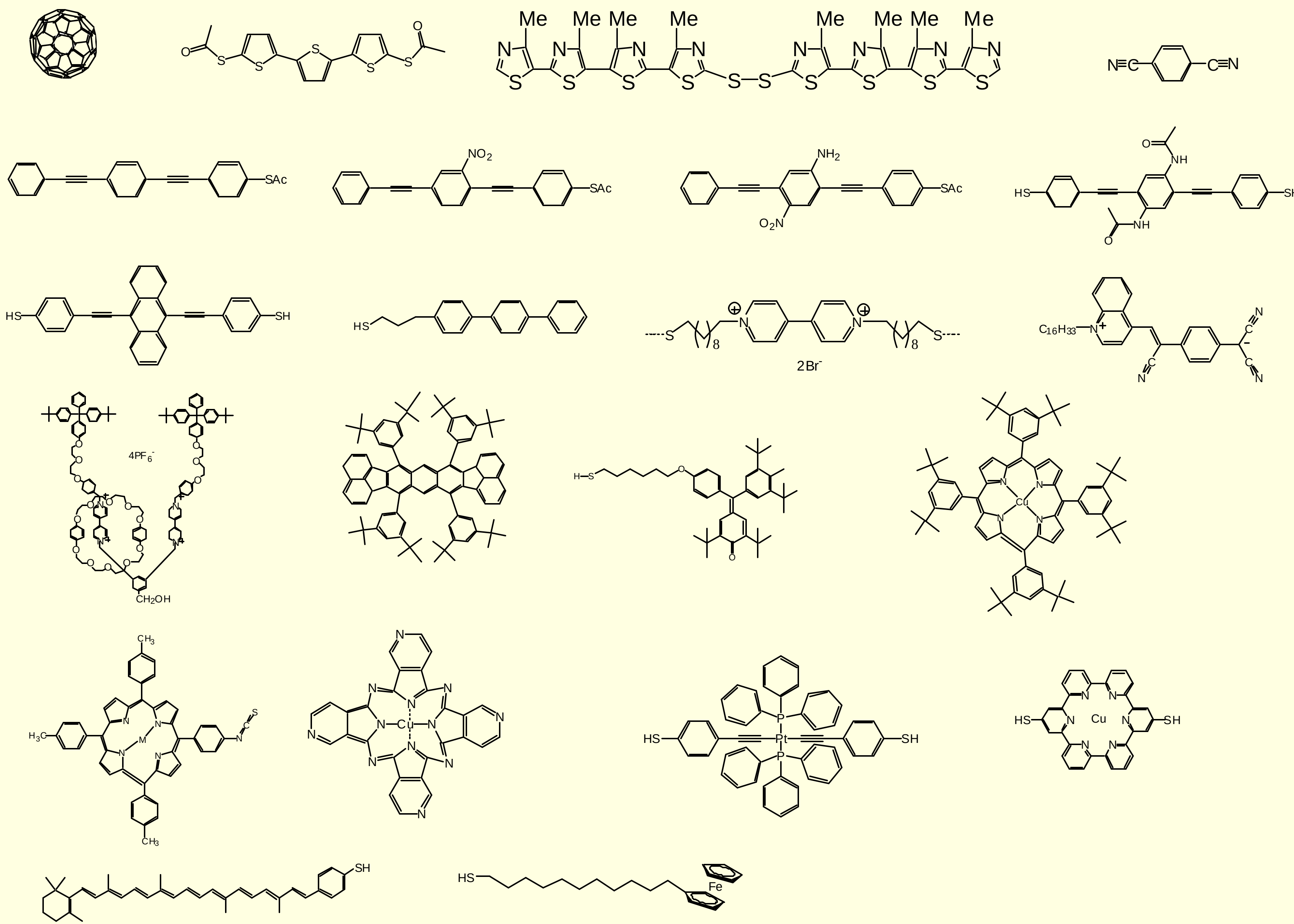
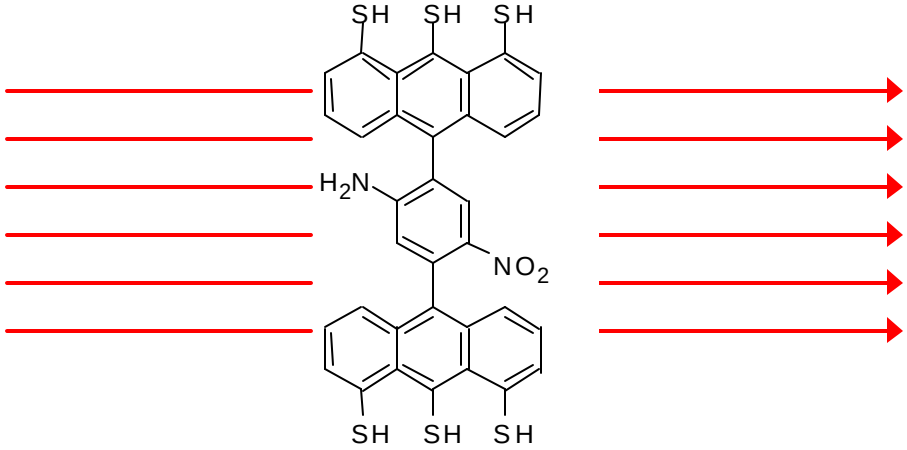
Selected Issues in Single Molecule Devices

- **Molecules**
  - 2-terminal
  - multi-terminal, complex functions
- **Molecule-Electrode Attachment**
  - chemical bonding
  - molecule-electrode geometry
- **Molecule Alignment and Distribution**
  - guest-host placement
  - multi-terminal registry

Selected Examples (Zoo) of Molecules with Reported I-V Characteristics

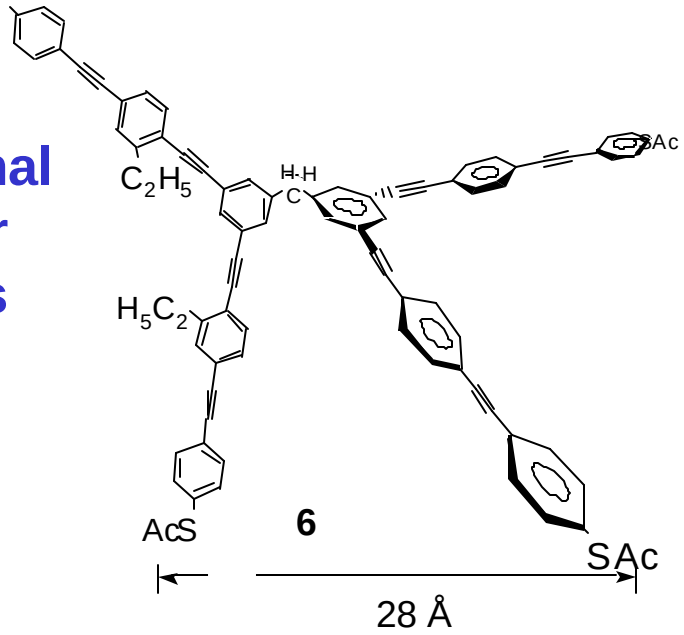


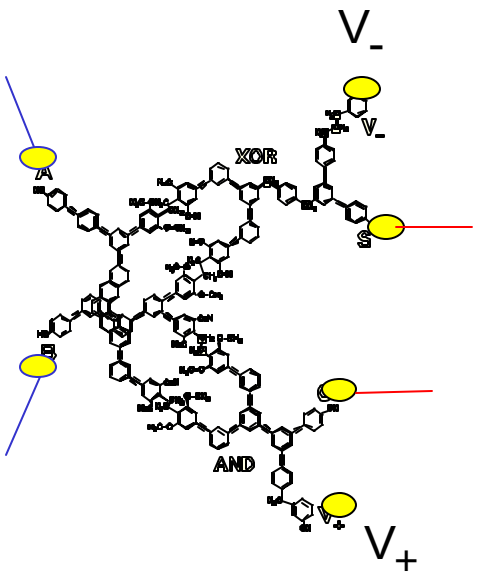
Examples of Proposed Specialized Function Molecules



Controllers modulated by external fields

Multi-terminal transistor molecules





Logic Operation Molecules

J. Ellenbogen (Mitre Corp)

[www.mitre.org/]

- current theory ineffective in predicting actual device behavior
- device measurement feedback: slow - almost non-existent

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Useful Established Attachment Combinations

Attachment (selected)	Base Electrode Metal					
	Au	Pt	Pd	Cu, etc	GaAs	Si
RSH	✓	✓	✓	✓	✓	
RSAc	✓	✓	✓	✓	✓	
RNC	✓	✓	✓			
RSe, -Te	✓				✓	
RC-			✓		✓?	✓

Au-SR: Simplest starting combination

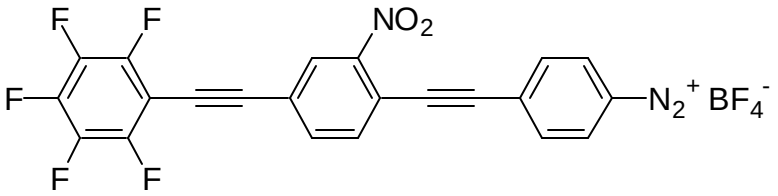
+ well-established chemistry
– -SAc needed for stability
but then
Au-S coupling problematic
– high junction barriers?

Pt(Pd)-CNR:

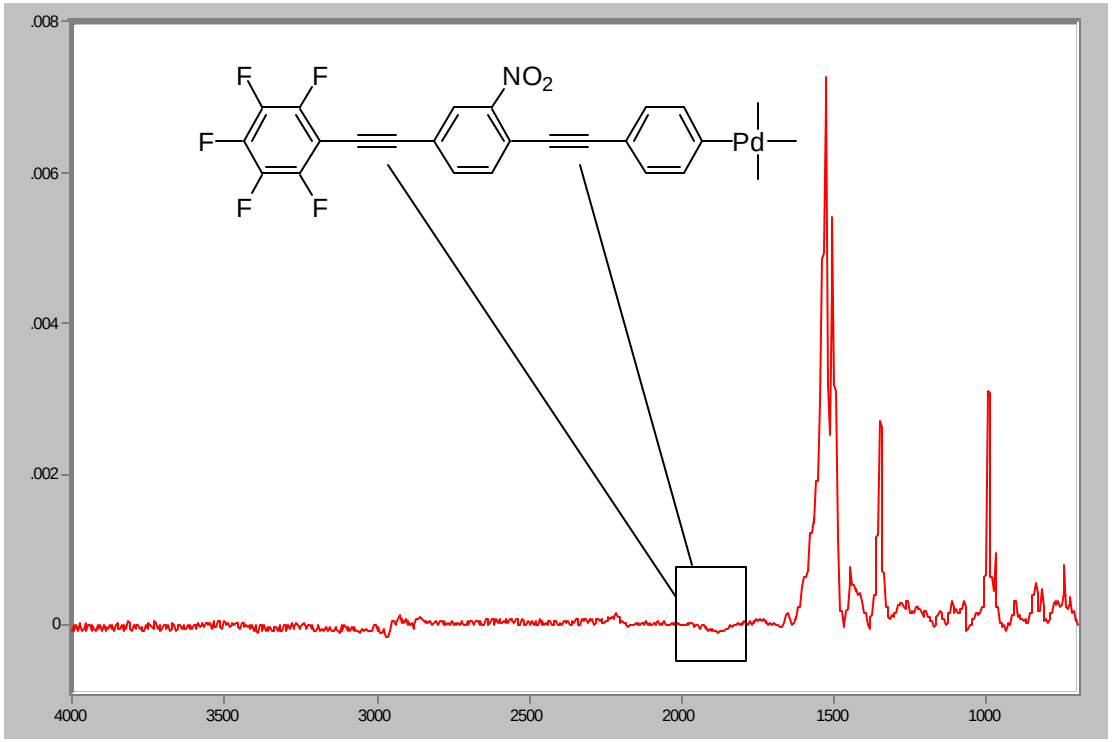
+ low junction barriers (~0.2 eV)
– preps more difficult
– less well known chemistry

- need more effort on molecule attachment group – electrode combinations
  - low junction impedance
  - chemical stability
  - device operation stability
  - Ni, W, Ti, Al?

Diazonium Coupling Chemistry for Direct Aromatic Ring-Electrode Attachment



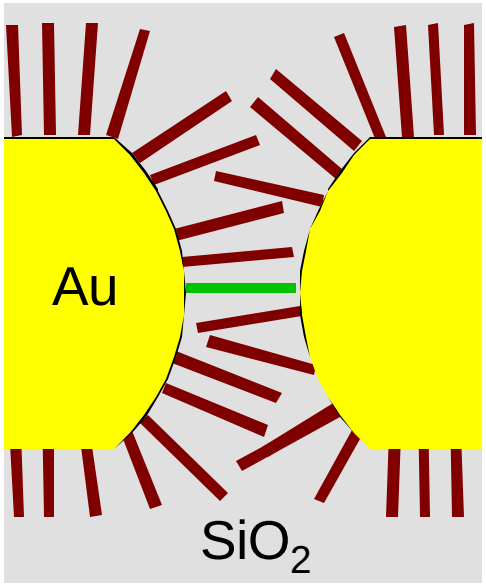
+ Pd (planar)



- **direct molecule-electrode bonding via C- bonds --- improved conduction??**
- **strong bonding precludes self-organization (kinetic vs thermodynamic control)**
- **extensions to Si, GaAs, C, Pt, etc.**

Stewart, Kosynkin, Dirk, Allara, Tour, submitted

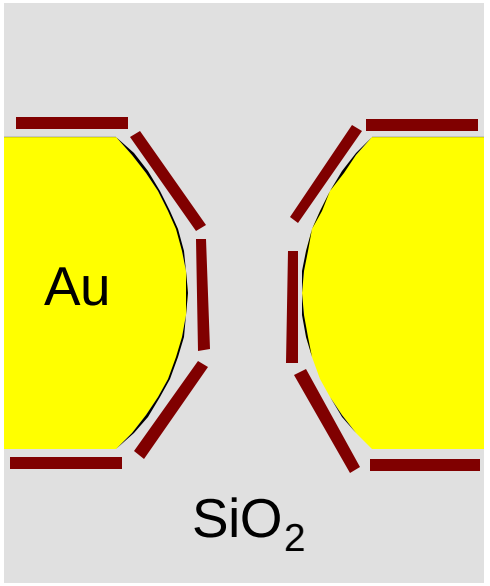
Oligomer Alignment and Distribution



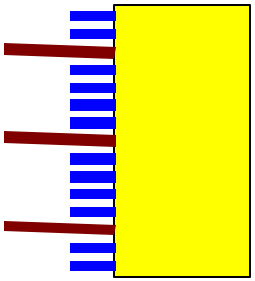
Will adsobate-surface bond force ♌ orientation?

OR

Will π-stacking force ❹ orientation?



Can insertion be used to control guest molecule orientation?



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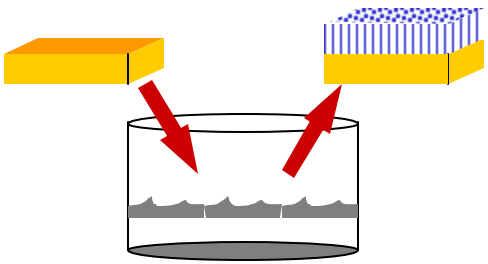
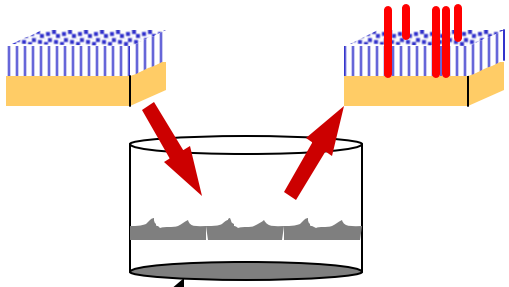
Using Self-Assembled Monolayers (SAMs) as Model Molecule Layers ----- Matrix Isolation of Electronically Active Molecules

Pre-assemble alkanethiolate SAM

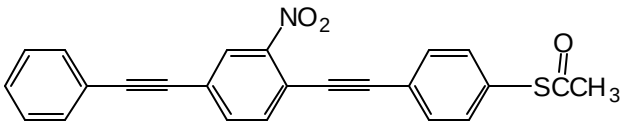


Solution of $HS(CH_2)_nCH_3$
n = 7 - 13

Immerse at controlled T and concs. of "molewires"



Solution of



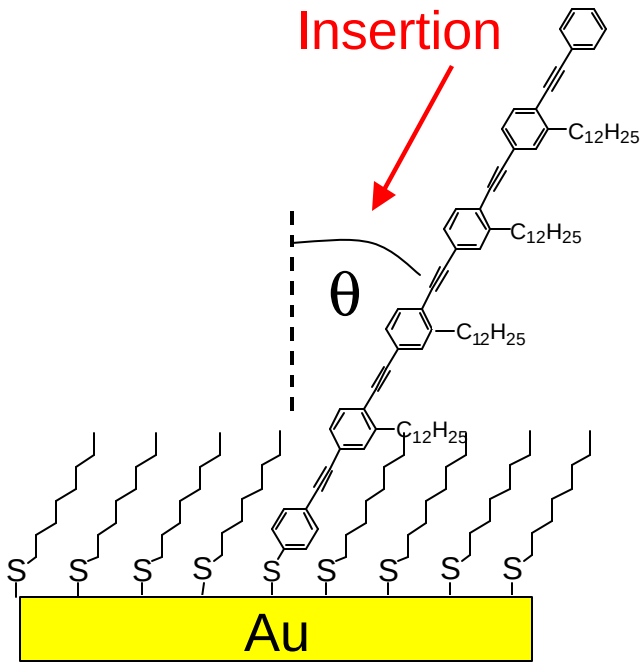
+ deprotection acid;
etc.

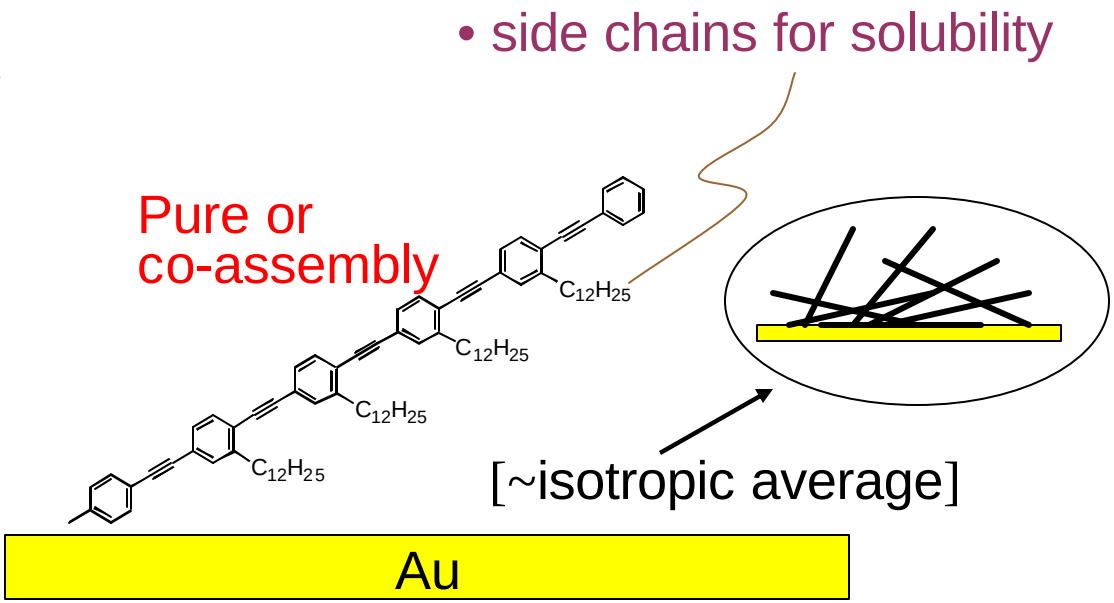
- remove at time t
- rinse

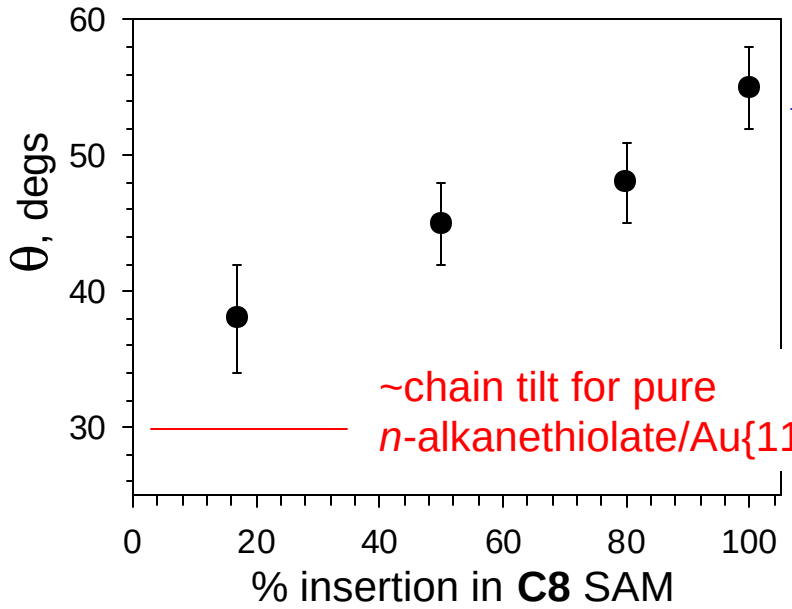
analysis of SAM composition
- **IR**
- **XPS**

STM

Large Molecules Resist Self-Organization --- Can Align via Insertion







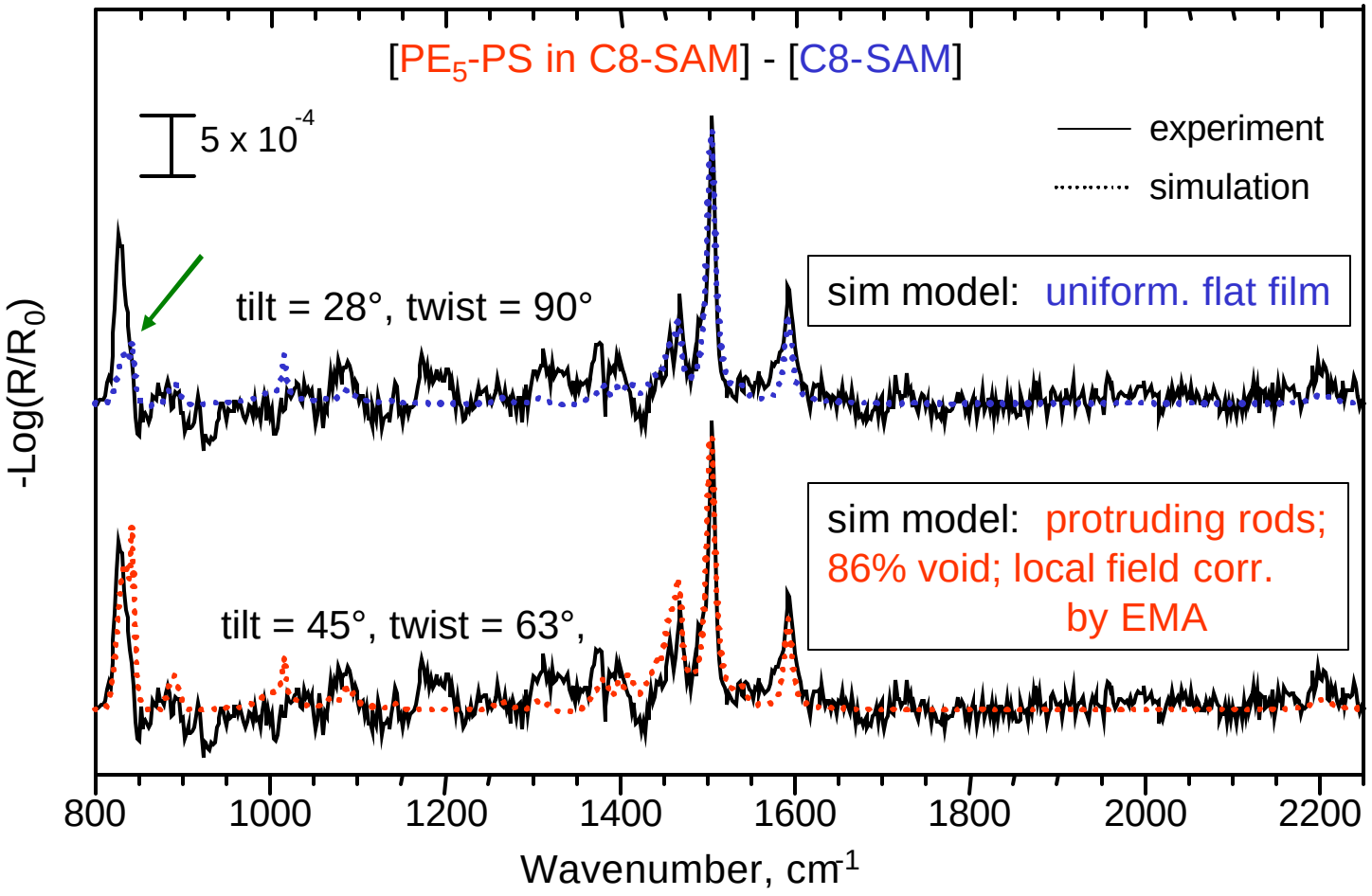
IRS data

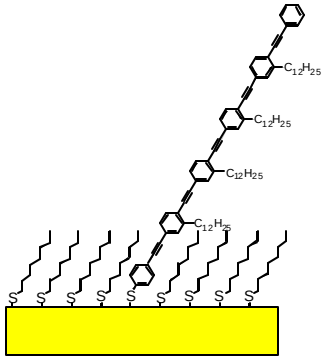
- orientation tensor analysis--5 modes
- effective medium approximation for heterogeneous character (local E-field corrections)

J.Phys.Chem, *B*., 104, 4880(2000)

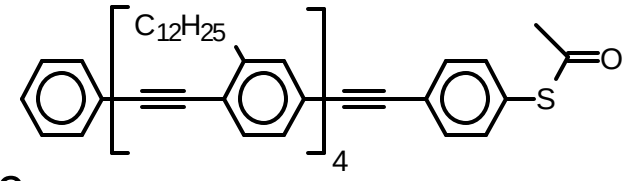
Interpretation of IR Spectra Requires Rigorous Consideration of Medium Effects

Inserted PE5-PS(~12%) in Host C8 SAM



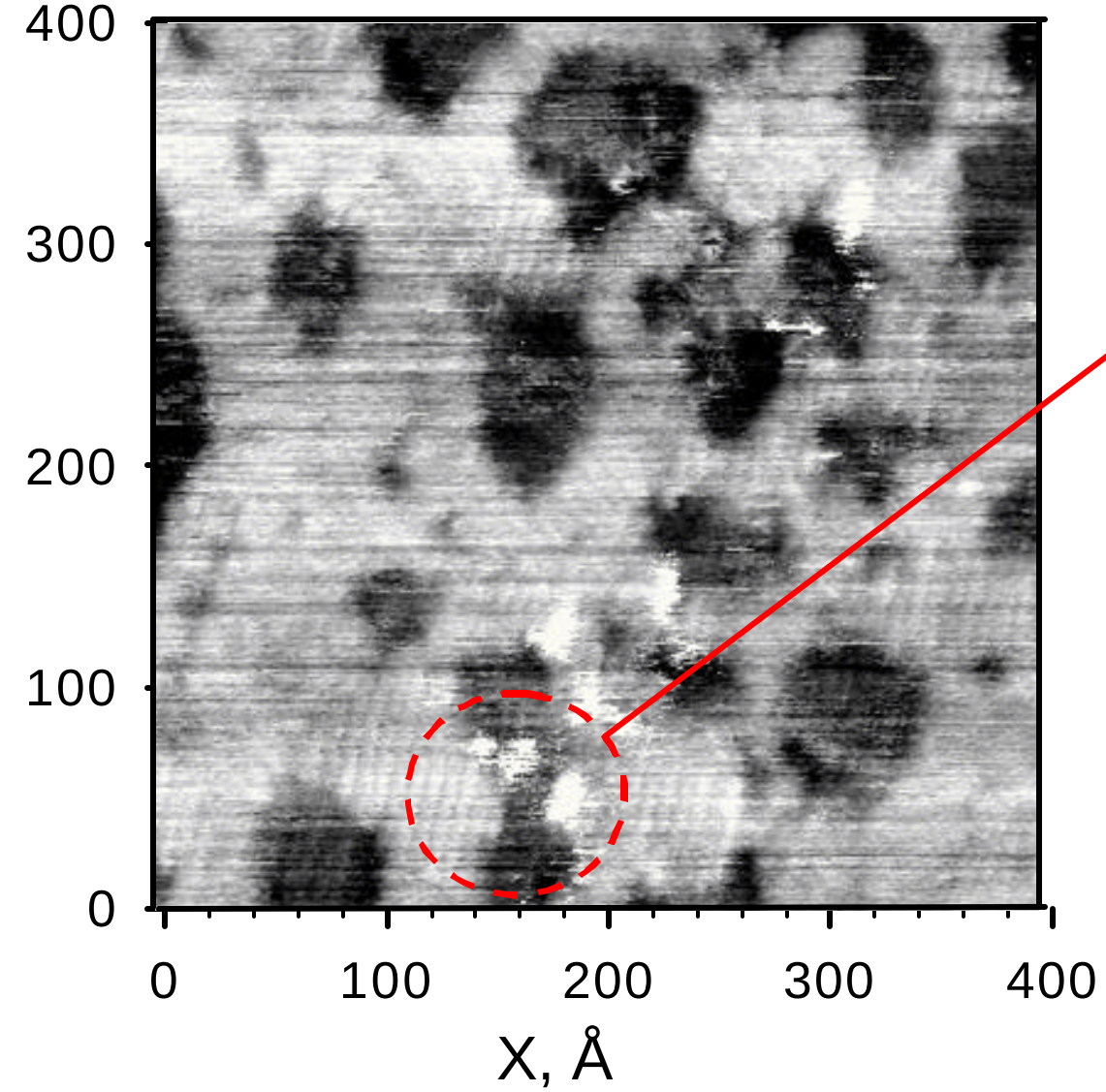


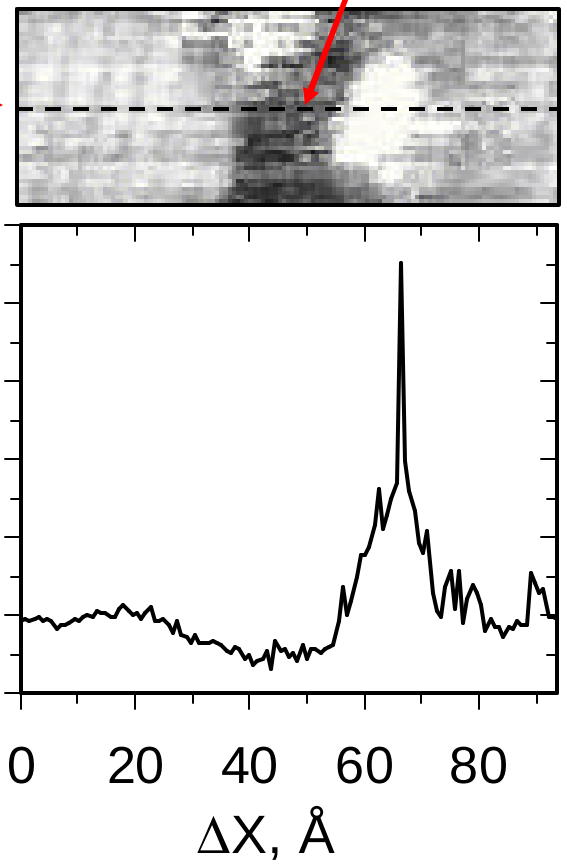
Oligomer Distribution in Host C8 SAM Matrix Defect Regions

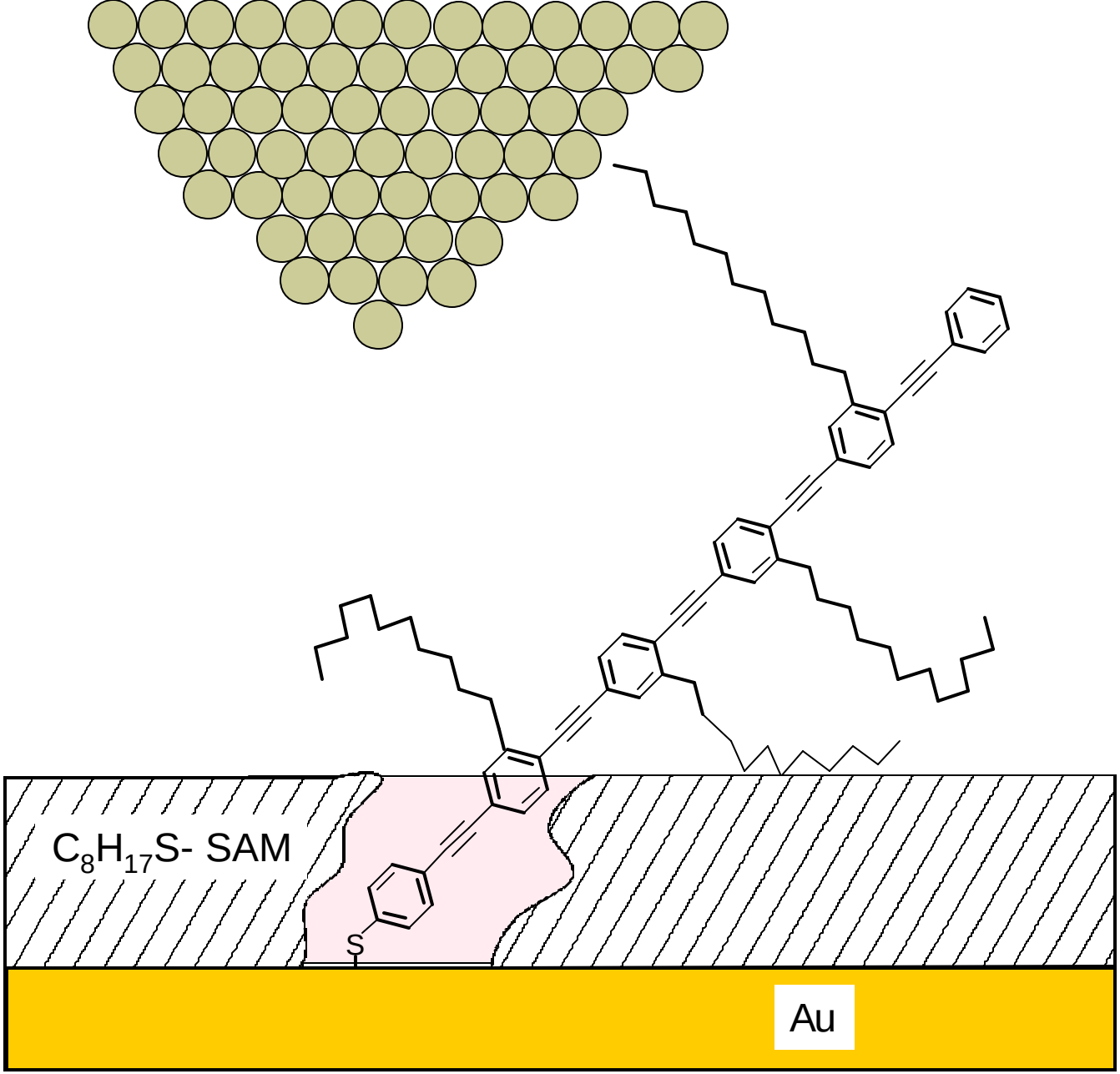


in C8 Host SAM

Au pit defect (black area)



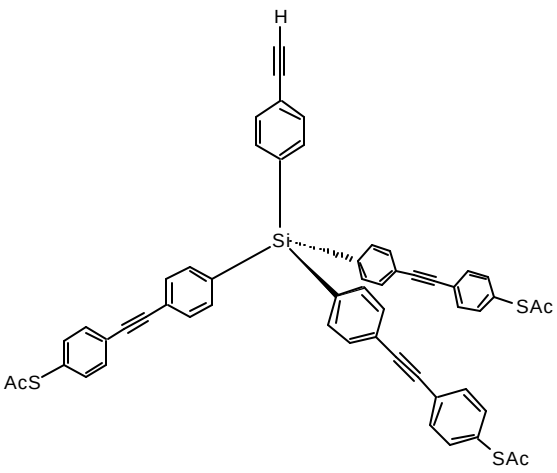


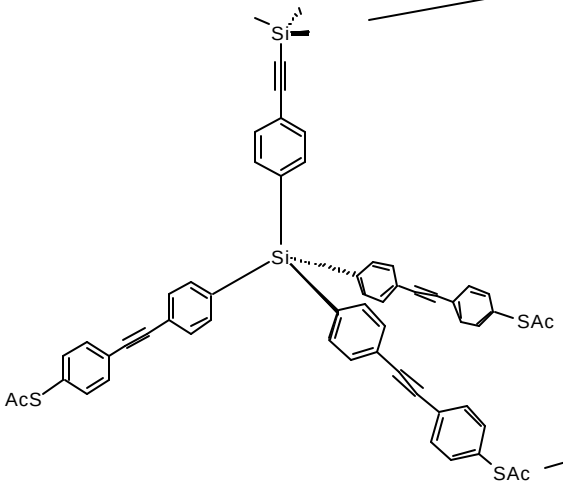

$C_8H_{17}S$- SAM
S
Au

Nano-Device Assembly at Planar Surfaces

* General: Find assembly protocols for orienting multi-functional molecules (e.g., for 3-terminal devices) at planar (Au) surfaces

* Testing the 3-legged approach for rigid, self-orienting molwire attachment





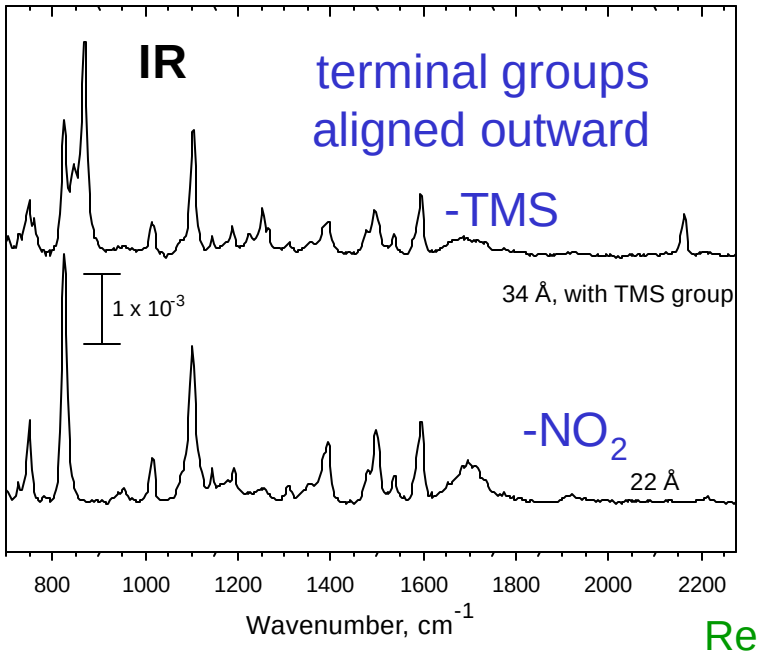
terminal groups:

- $-Si(CH_3)_3$
- $-H$
- $-NO_2$

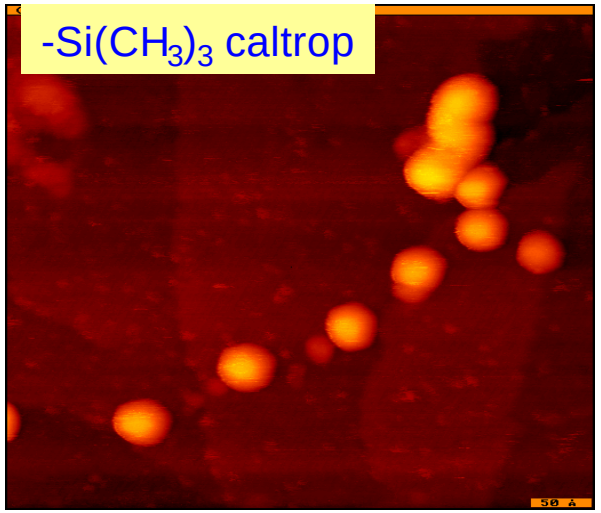
sticker groups (3): -SAc (for Au)

"caltrops" molecules

Self-Orienting Oligomers at Electrodes?



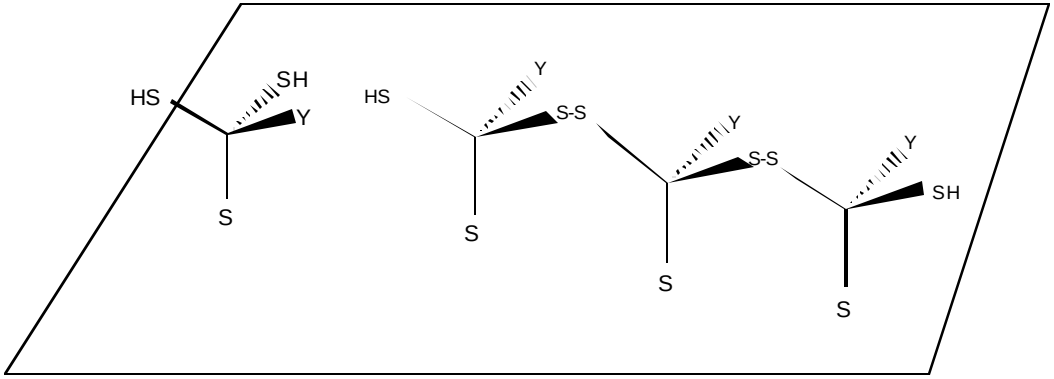
STM



50 x 50 nm (V=700 mV, i = 200 pA)

Reproducible features:
~40 Å dia.x ~30 Å height

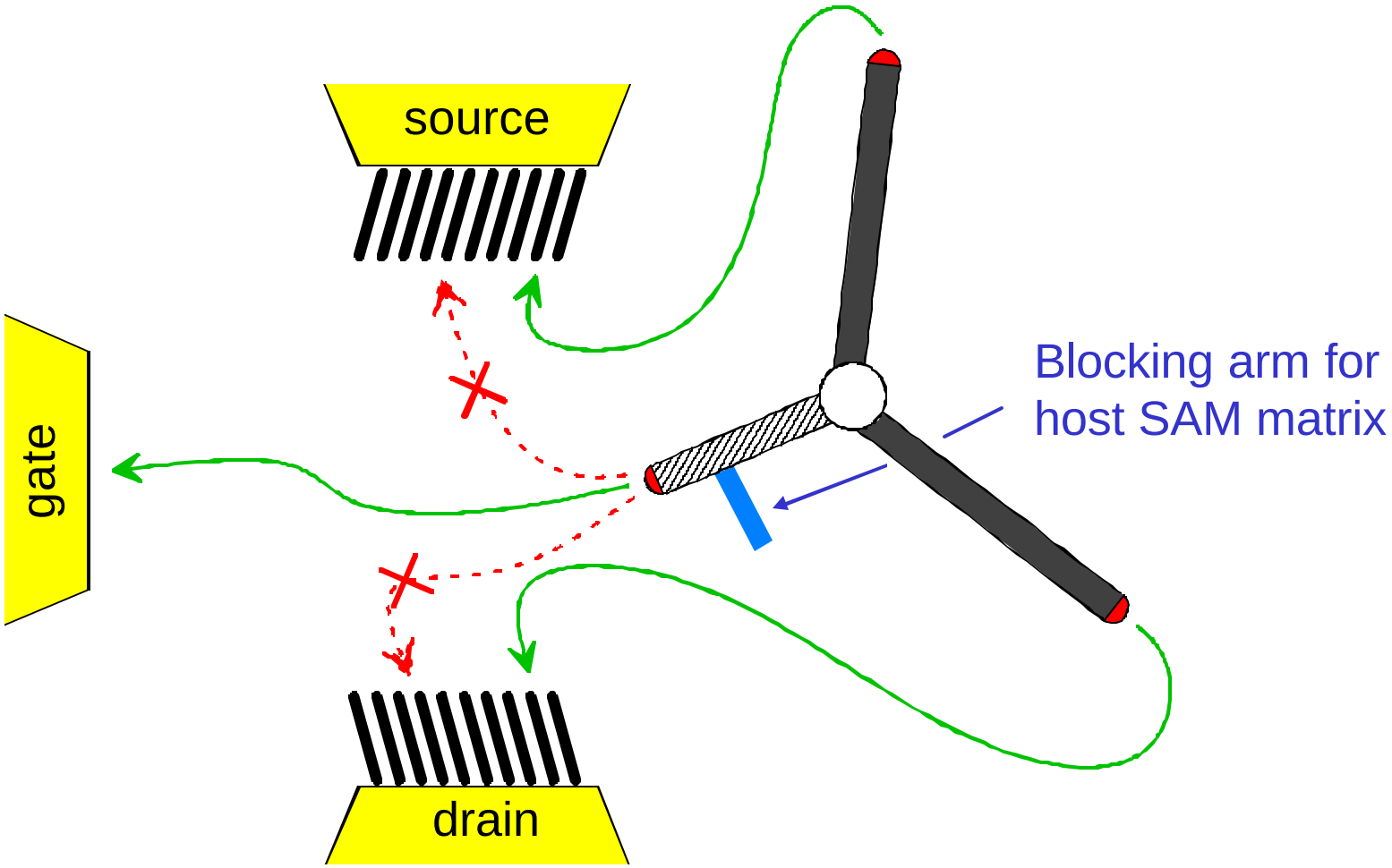
Data: McCarty, Hatzor, Fuchs, D'Onofrio and Weiss



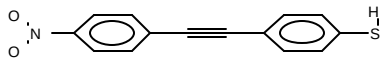
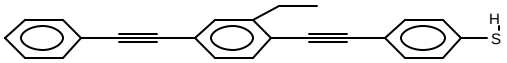
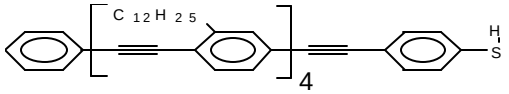
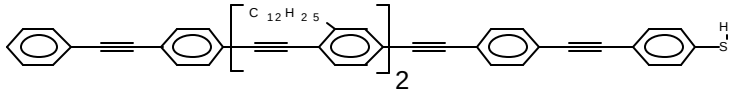
IR, STM, XPS, ellipsometry:
Mixture of surface configurations

Conclude:
need more "equilibrium" conditions for assembly?

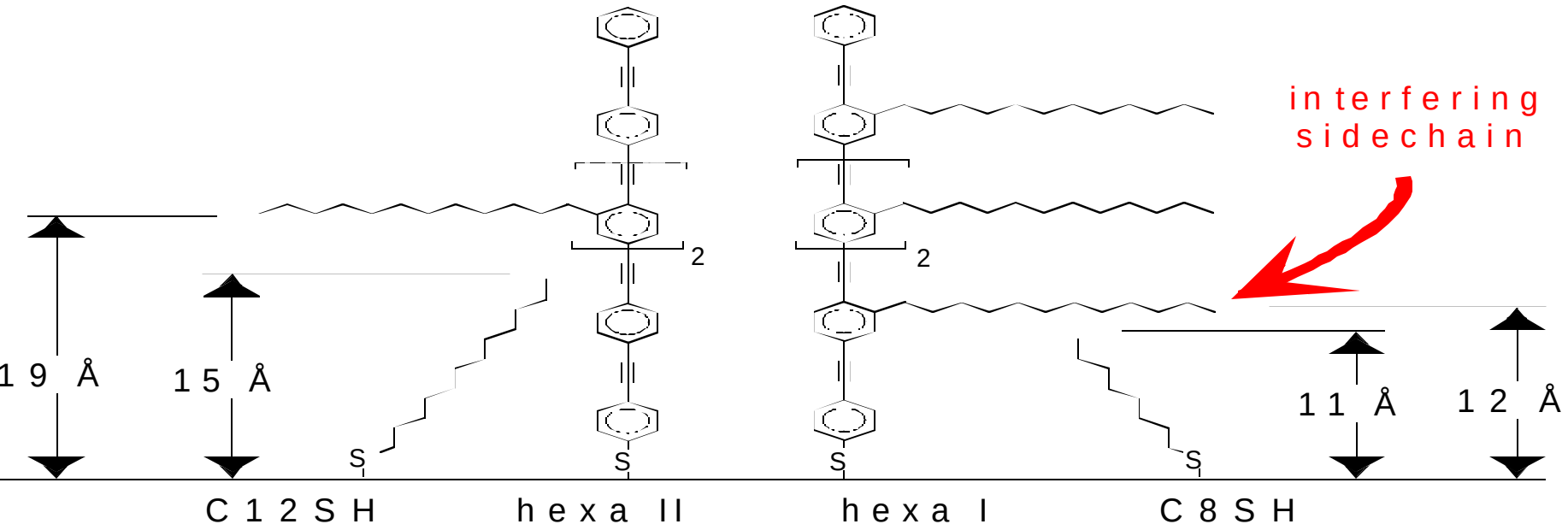
Selective Assembly of a 3-Terminal Device: Steric Effect Methods



Side-chain Steric Effect

molecule	% inserted in C12 ML in 1 hr.	10 hrs.
	4.1	8.8
	5.1	--
	0.0	0.0 *
	4.5	--

*no insertion until 50 hrs.



Selective Assembly of a 3-Terminal Device: Chemical and Electrochemical Control Methods

Release active thiolate or thiol by base/acid deprotection of thioacetate, etc.

Application of V at selected electrodes:

- induce selective chemisorption [thiosulfate derviatives, (G. Ferguson, Langmuir)]
- induce selective thiolate desorption (M. Porter)

Overall:
Intense development needed to allow high yields of selective assembly on large scale multi-terminal device chips

Rationale for A Molecular Electronics Technology

I-V Behavior of Molecules

Potential Applications and Device Types

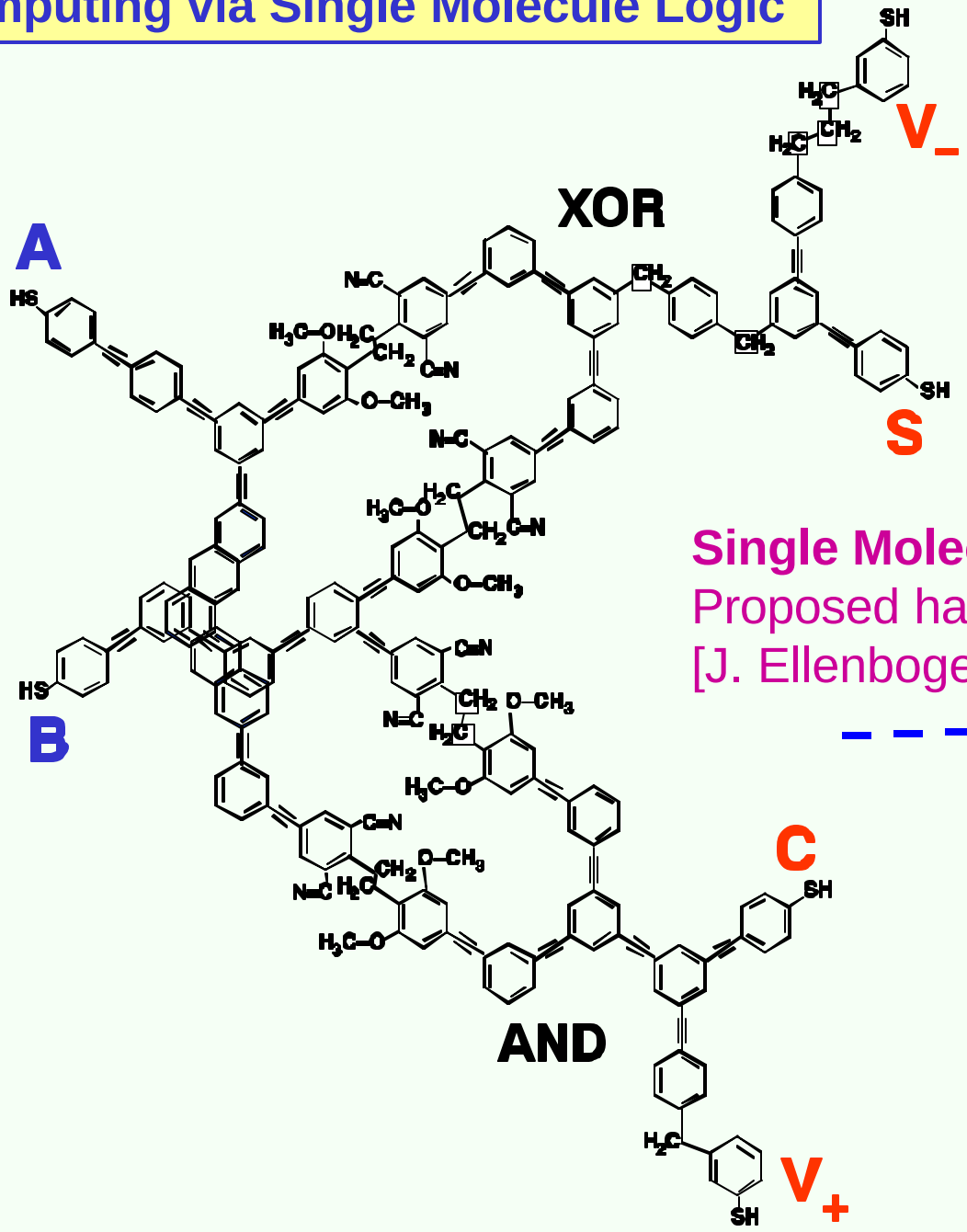
Selected Issues in Single Molecule Devices

Manufacturability Issues

Planar Devices: Molecular Level Design & Testing Issues

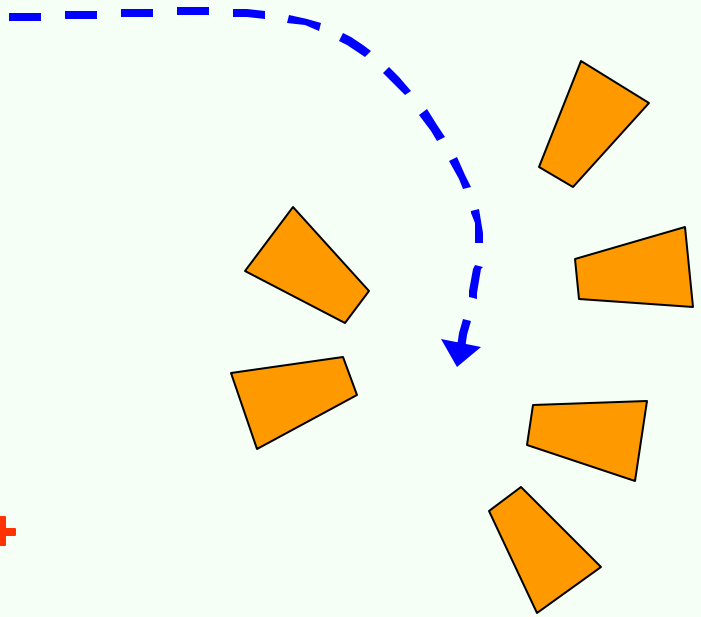
Conclusions and Perspectives

Computing via Single Molecule Logic



Exquisite control needed
impossible at present:
- **accurate electrode pad fab**
- **molecule "drop-in"**

Single Molecule Logic Devices:
Proposed half adder; ~10 nm x 10 nm
[J. Ellenbogen, Mitre Corp.]



Rationale for A Molecular Electronics Technology

I-V Behavior of Molecules

Potential Applications and Device Types

Manufacturability Issues

Selected Issues in Single Molecule Devices

Planar Devices: Molecular Level Design & Testing Issues

Conclusions and Perspectives

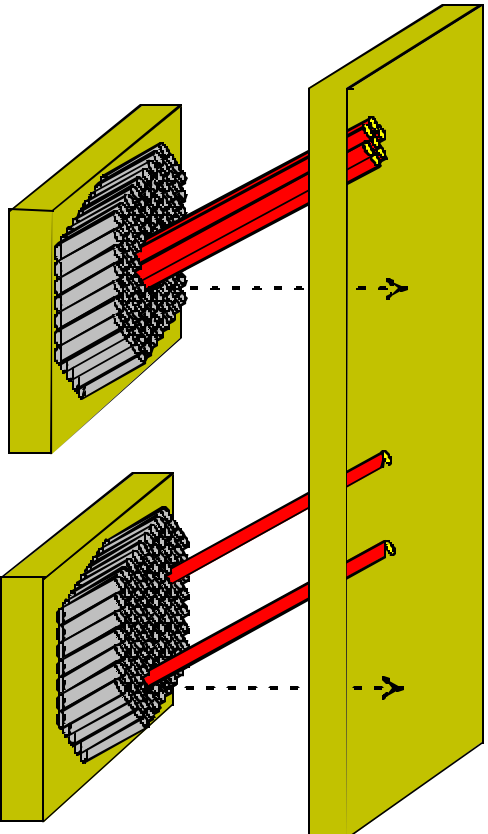
Planar Devices: Molecular Level Design & Testing Issues

- molecules
- bottom contacts
- self-assembly
  - molecular geometry
  - chemistry
- matrix effects in molecule switching
- electron injection states
- top contact metallization issues

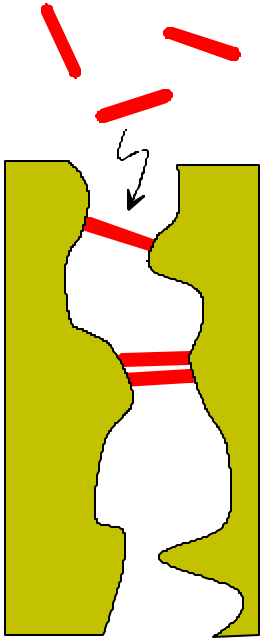
Issues in Rigid Molecule Contacts

Multicontact Self-Assembly (e.g., nanorod crossbar) vs Top Contact Metallization

- Molecular tilt changes required gap spacing
- Isolated vs bundles

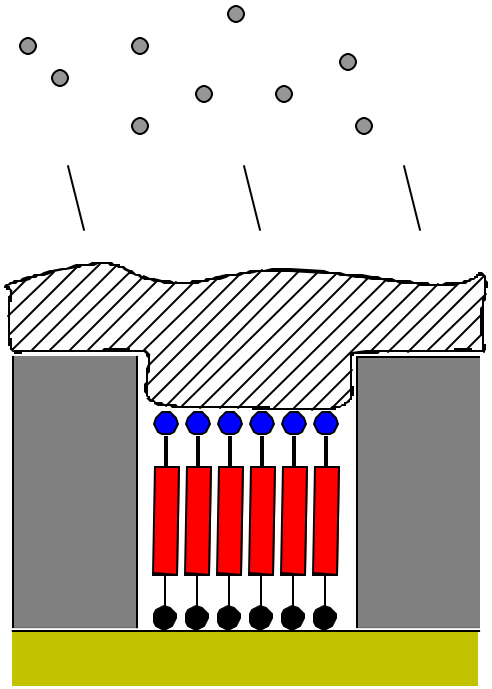


- Electrode topography
  unpredictable attachment density



Deposition should be Conformal but:

- Shorts
- Molecule damage
- Metal morphology



Rationale for A Molecular Electronics Technology

I-V Behavior of Molecules

Potential Applications and Device Types

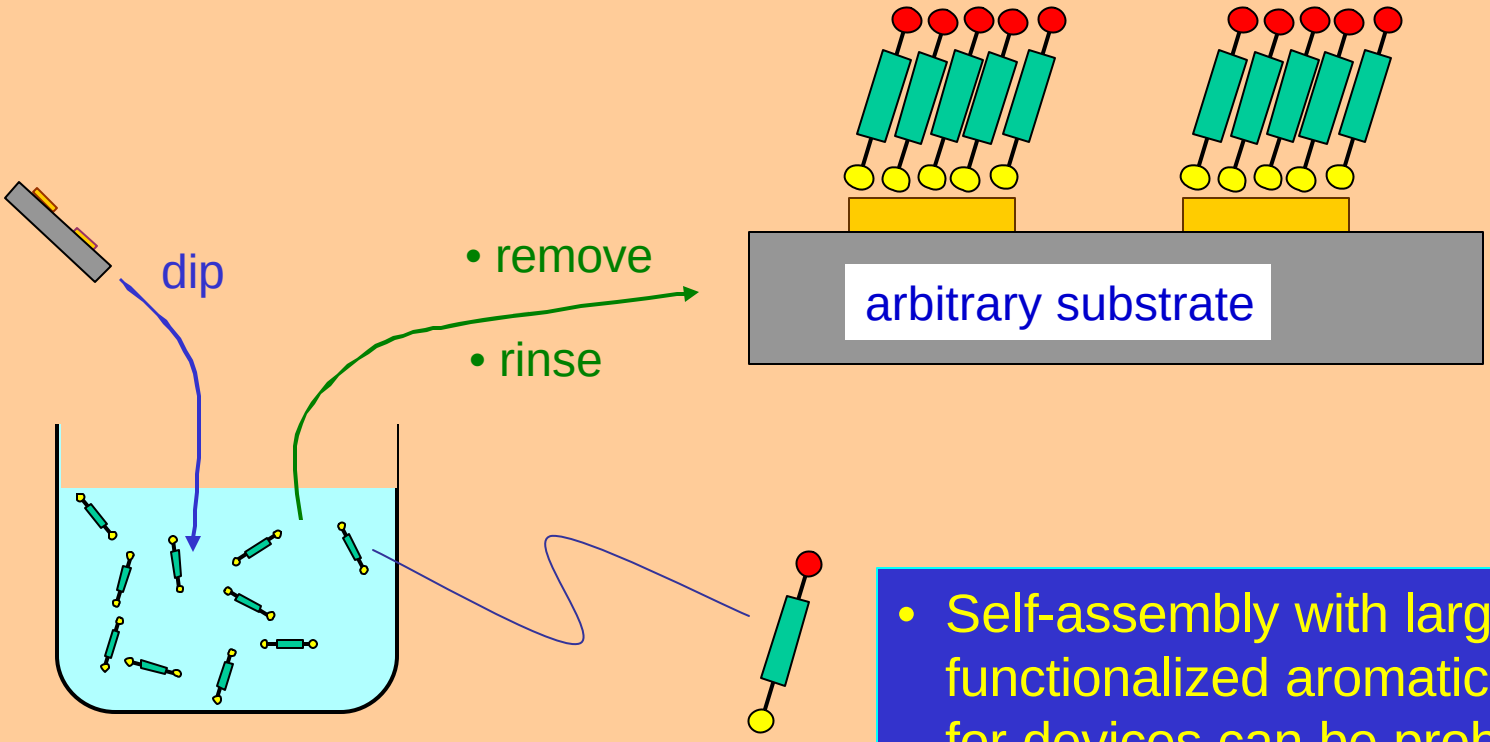
Manufacturability Issues

Planar Devices : Molecular Level Design & Testing Issues

- molecules
- bottom contacts
- **self-assembly**
  - molecular geometry
  - **chemistry**
- matrix effects in molecule switching
- electron injection states
- top contact metallization issues

Conclusions and Perspectives

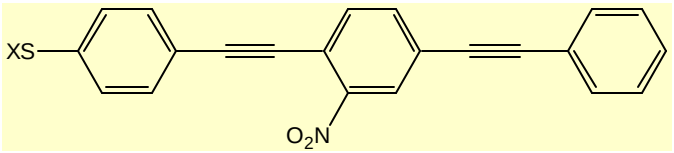
Molecular Assembly



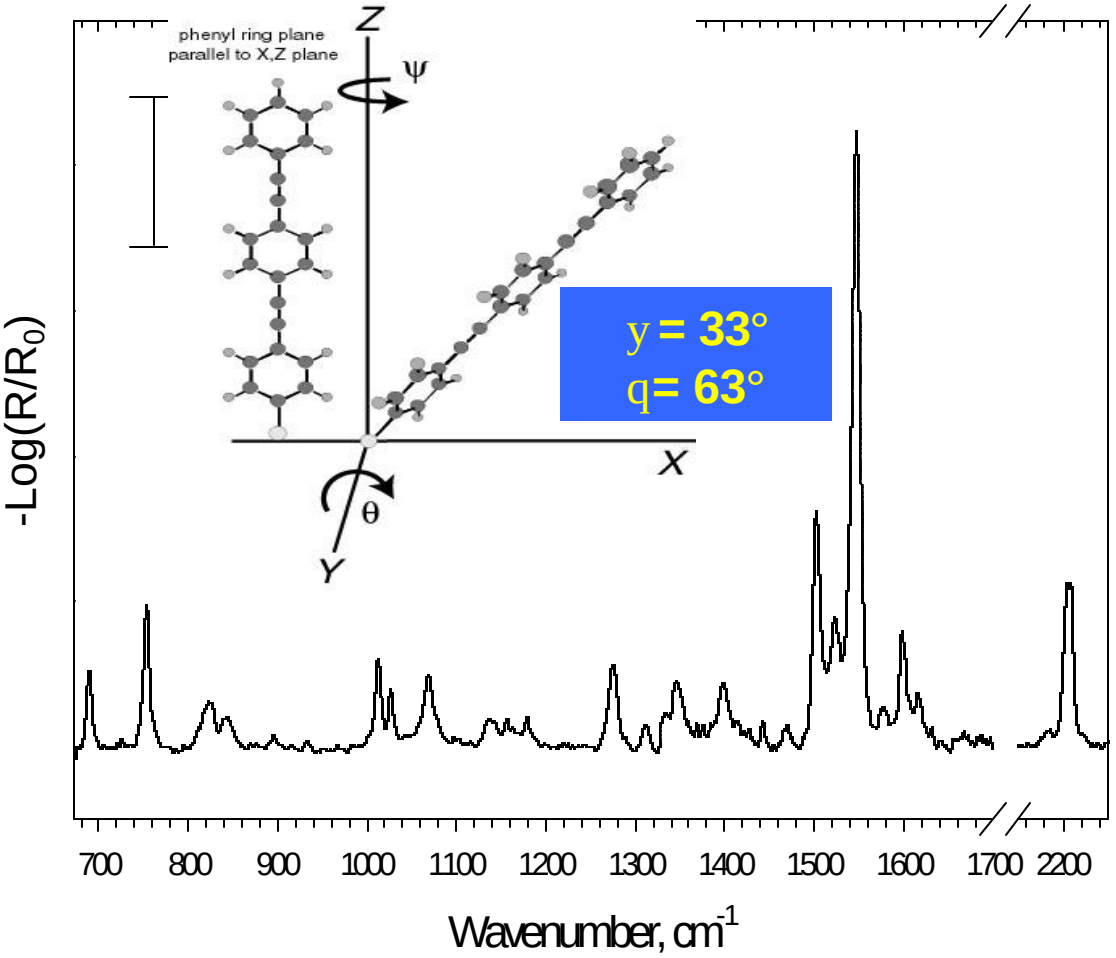
- Self-assembly with large, rigid, functionalized aromatic molecules for devices can be problematic
  - solubility
  - chemical stability

Molecular Packing: a major bottleneck in molecular electronics?

Careful Control of Assembly Procedures Can Produce Ordered Pure MoleSwitch SAMs

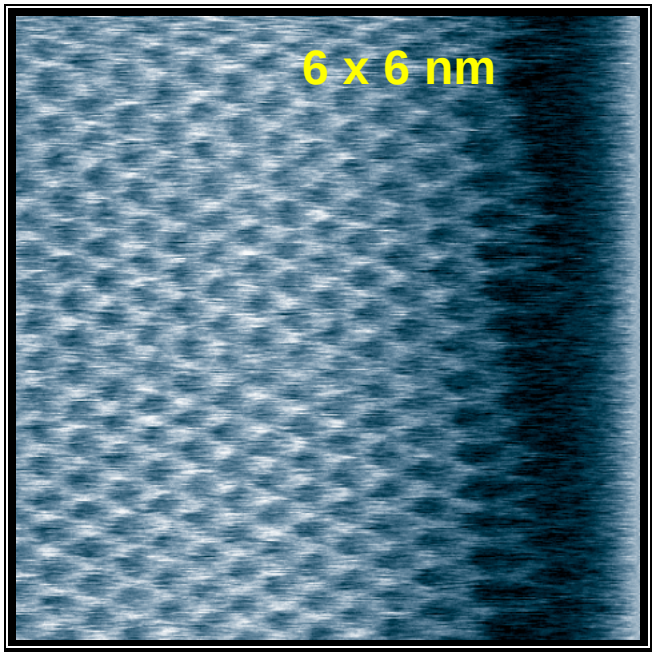


IRS



Full Monolayer of Mono Nitro Switch on Au(111)

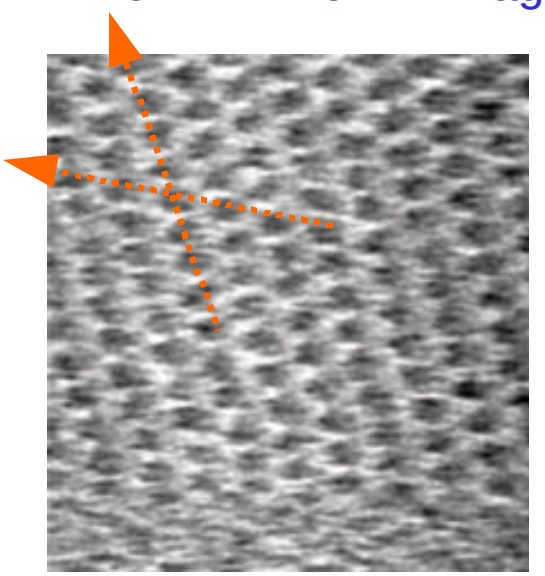
AFM

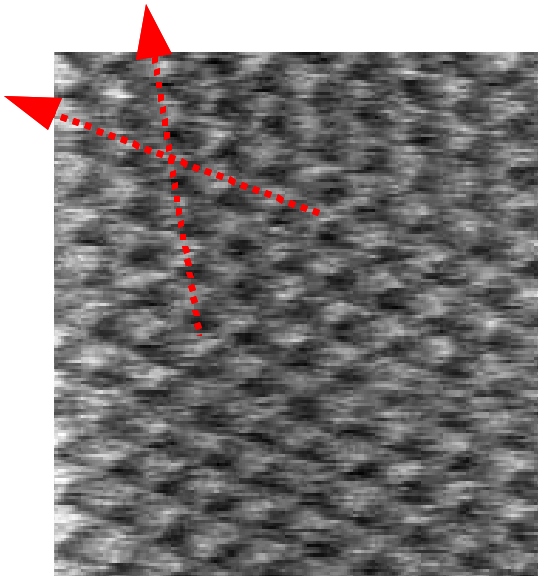


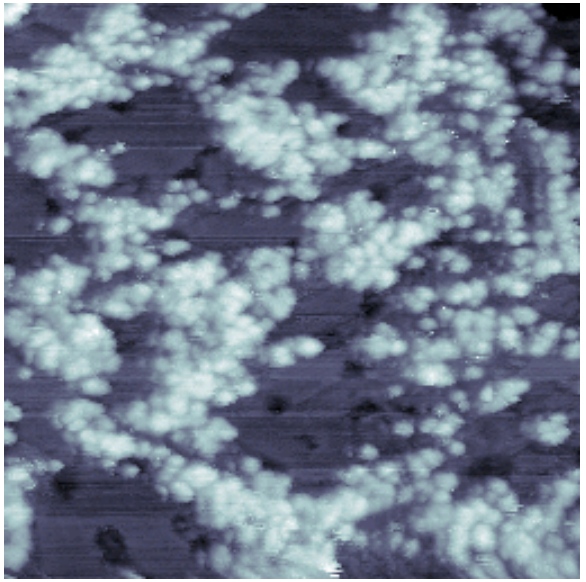
Stapleton, Daniel, Allara (submitted)

Contact Mode AFM Images of Molewire SAMs on Au(111)

4.0 nm x 4.0 nm images; lateral force, unfiltered

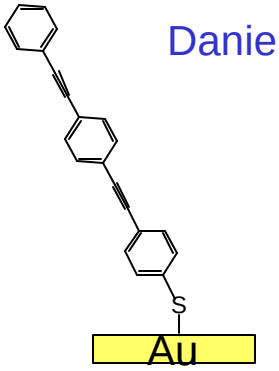


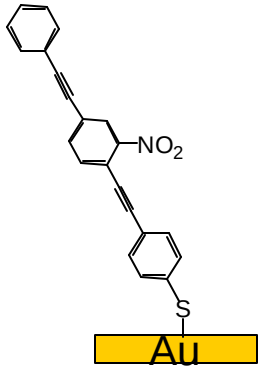




100x100 nm
STM image pre-surface clean

Daniel, Stapleton, Allara

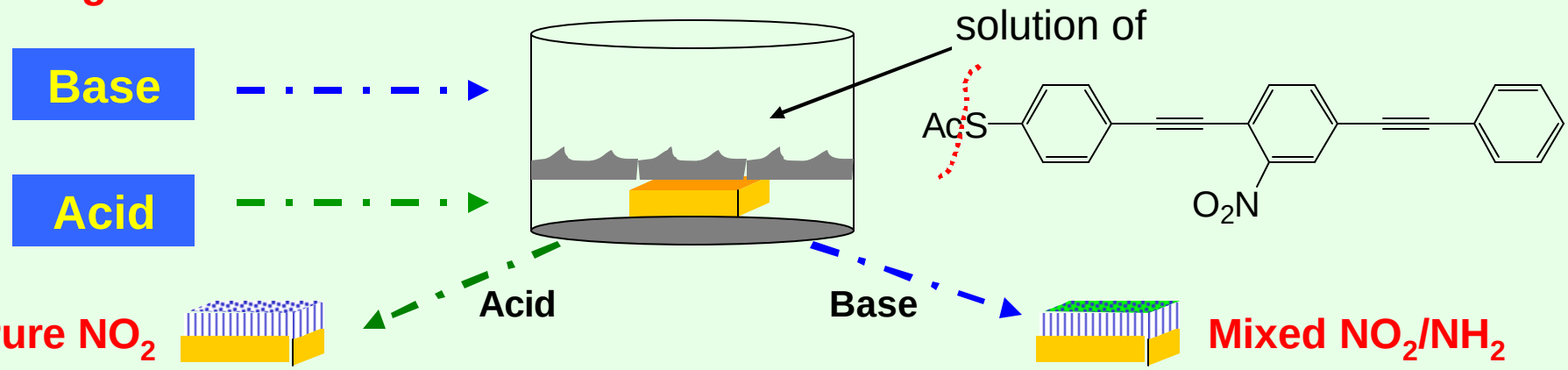


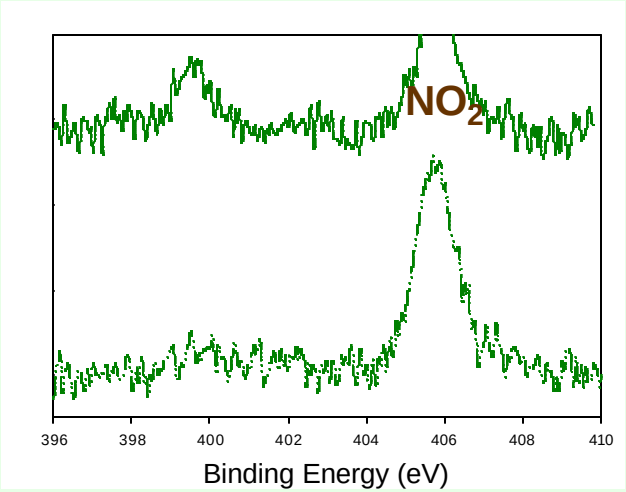


- **SAMs can order**
- **~ $(\sqrt{3}x\sqrt{3})$ Au(111) superlattice spacing**

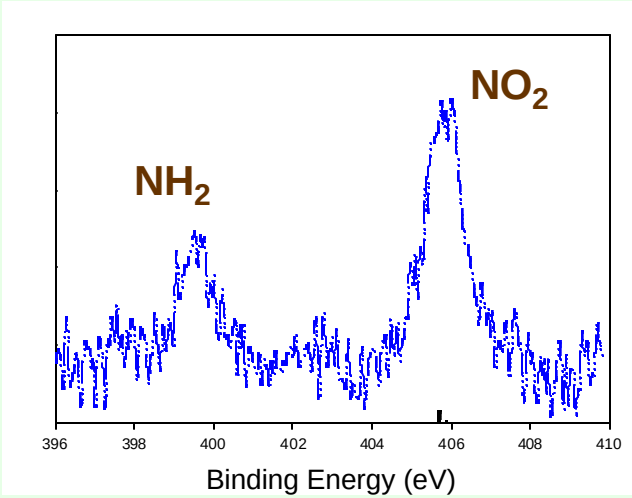
Side Reactions May Cause Mixed Composition SAMs

Cleavage method





XPS N(1s) Region



Typically ~30% -NH2 in SAM

Zinin Reduction: $RNO_2 + RS^- \rightarrow RNH_2$

Stapleton, Daniel, Yao, Tour, Allara, submitted

Planar Devices: Molecular Level Design & Testing Issues

- molecules
- bottom contacts
- self-assembly
  - molecular geometry
  - chemistry
- matrix effects in molecule switching
- electron injection states
- top contact metallization issues

Strategies for Probing Matrix Effects on Switching

Compare I-V behavior:

- Planar devices with dense-packed SAMs (Reed et al)
- STM of inserted moleswitches in alkanethiolate SAMs
- Conducting AFM/STM with nanoparticle contacts to inserted moleswitches in alkanethiolate SAMs
- Single molecule devices

Quasi-2-D Matrix Isolation of Individual Molecules and Bundles

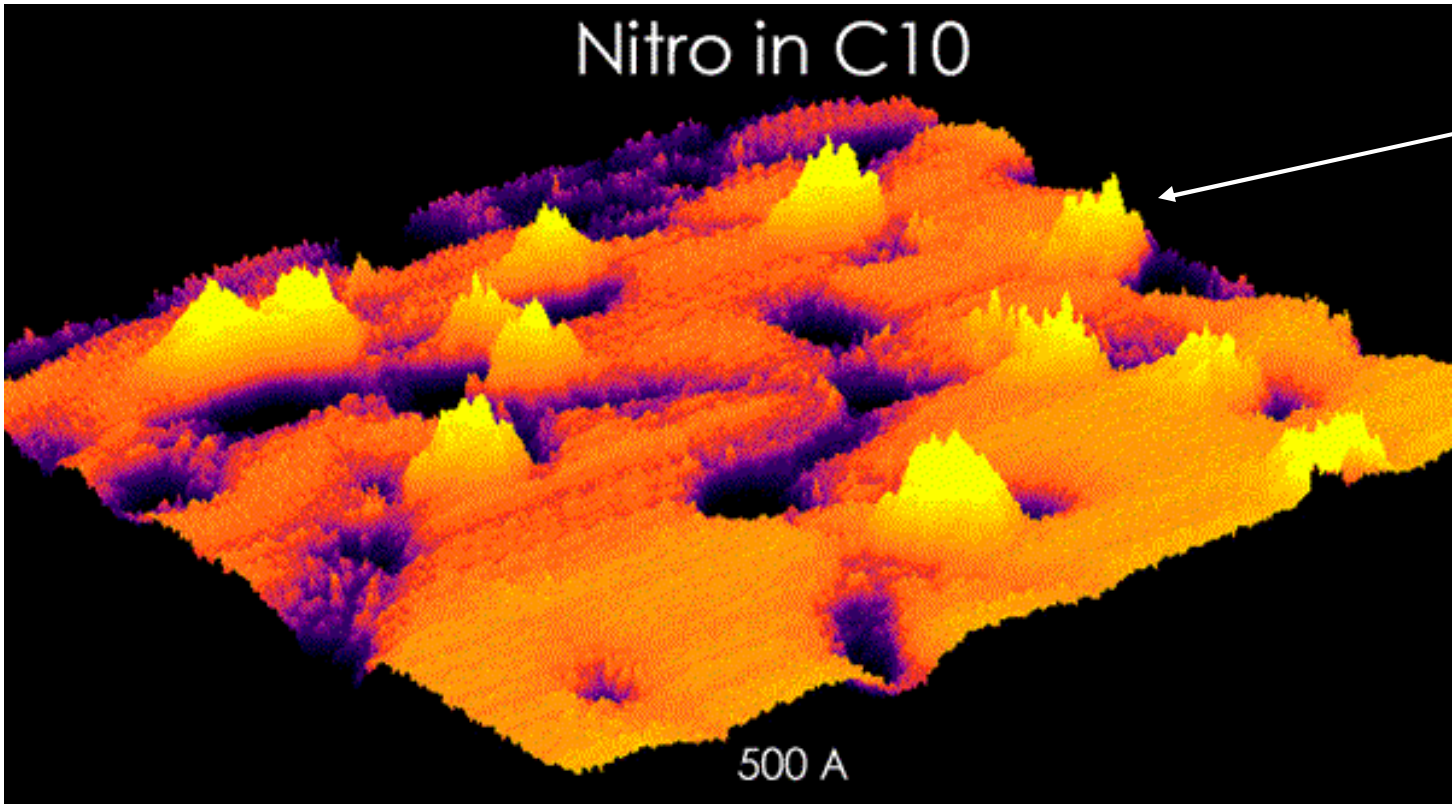
- Control molecular orientation at electrodes for devices
- Control local molecular environment
- Position molecules for precision **local probe** characterization of electrical properties as a function of:
  - molecule structure
  - metal-molecule junction
  - local molecular environment

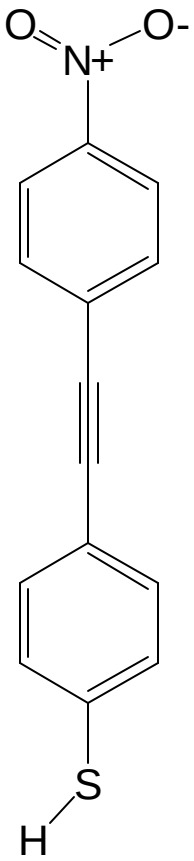
Quasi-2-D Matrix Isolation of Individual Molecules and Bundles

Insertion of 1.4 nm Nitro Molecule in a C10 SAM
- Valuable Test System

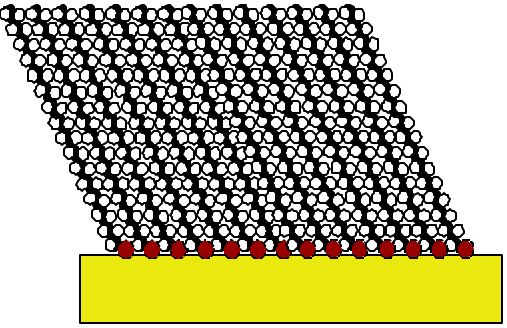
-NO_2 groups:

- important in switching and memory
- vibrational spectroscopy tag



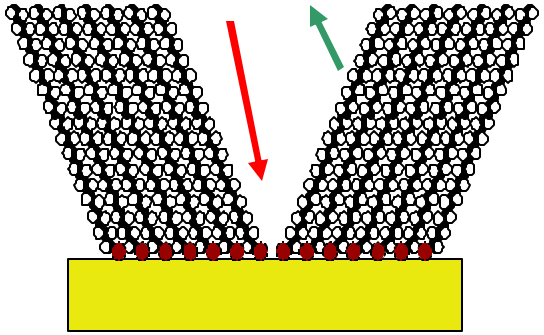


SAM Defect Sites for Insertion/Exchange in RS/Au{111}



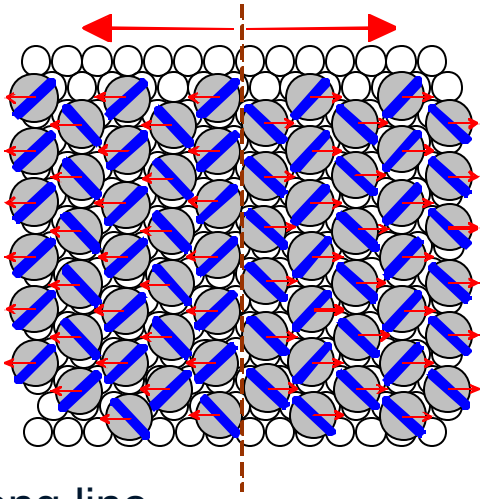
Tightly packed domain:

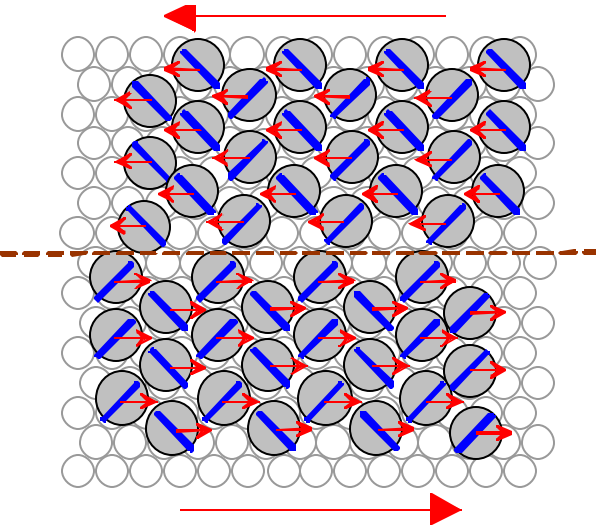
- 5.0 Å S-S distance; 30º tilt
- 4.6 molecules/·nm^2



Tilt Domain line defect - I

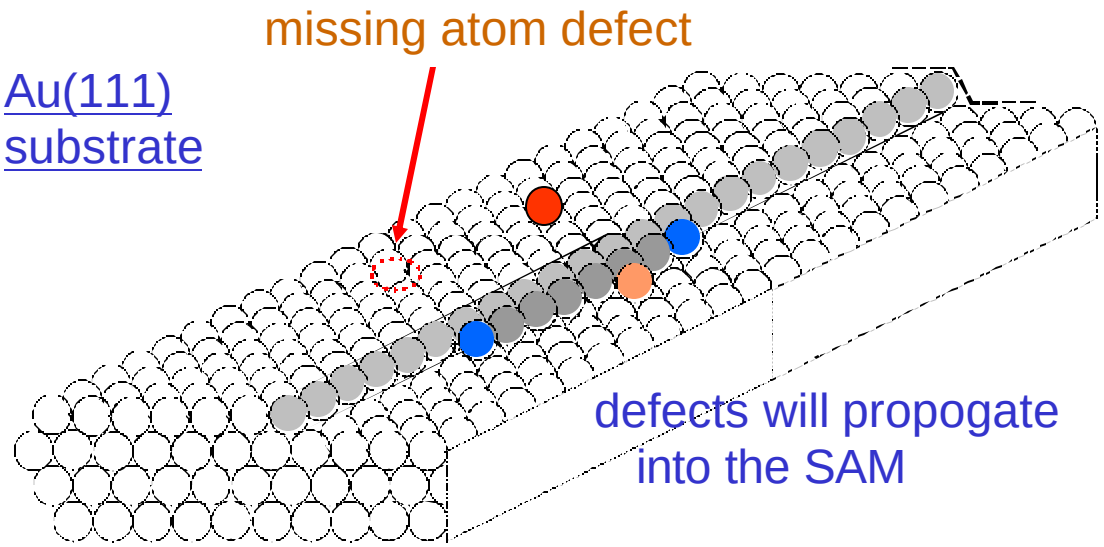
- conformational disorder along line





Tilt Domain line defect - II

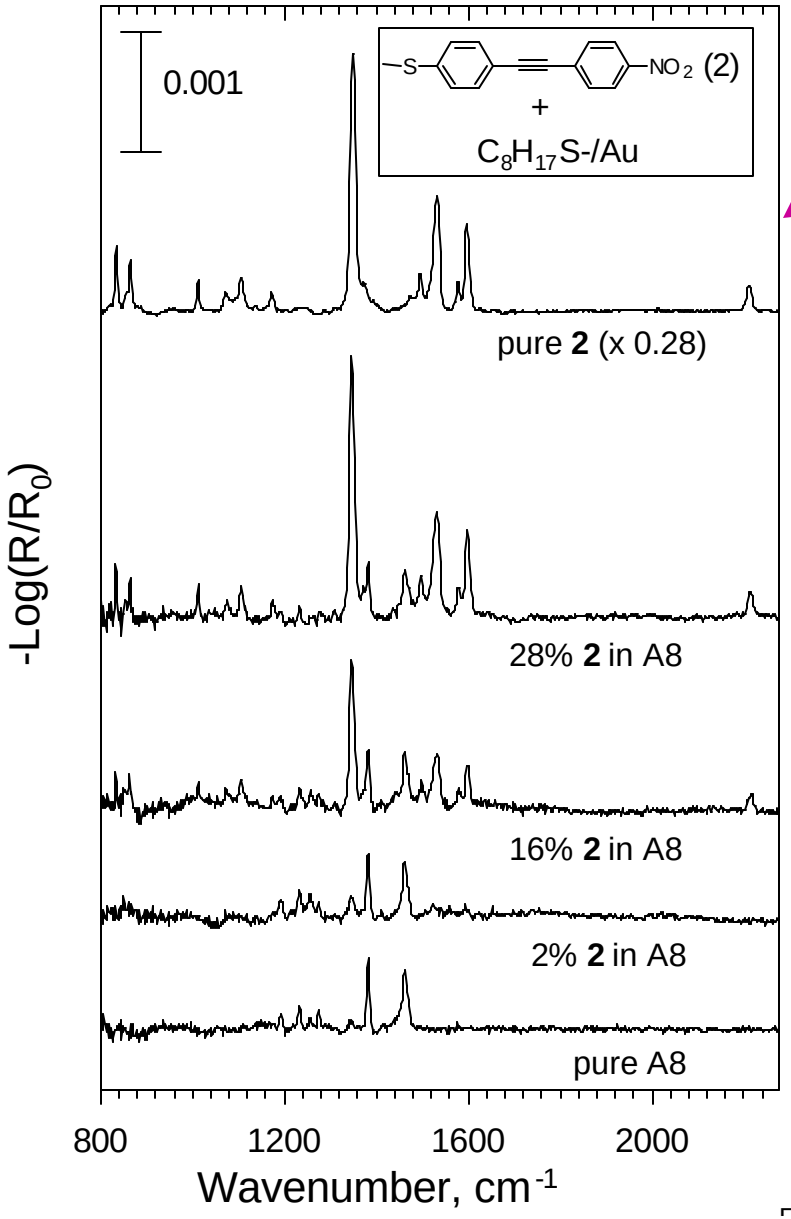
- conformational disorder along line
- exposed Au atoms along line



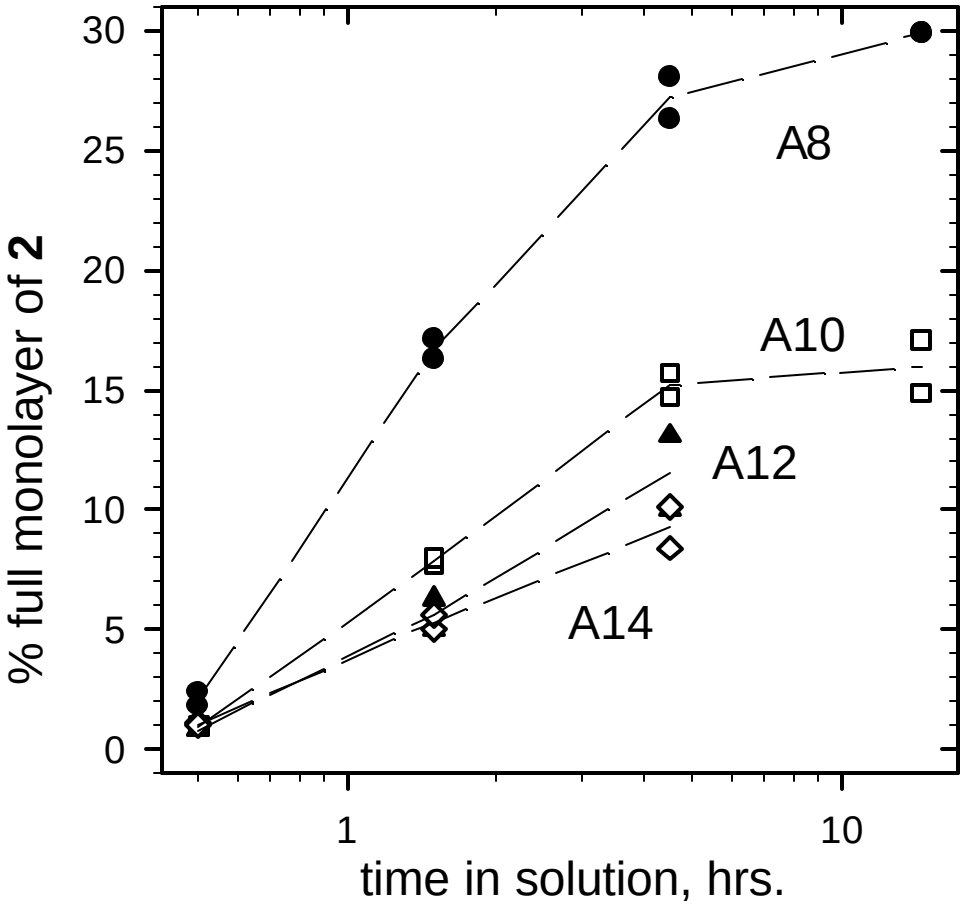
steps, kinks, missing atoms, etc.

- on imperfect terraces
- in crystallite grain boundaries

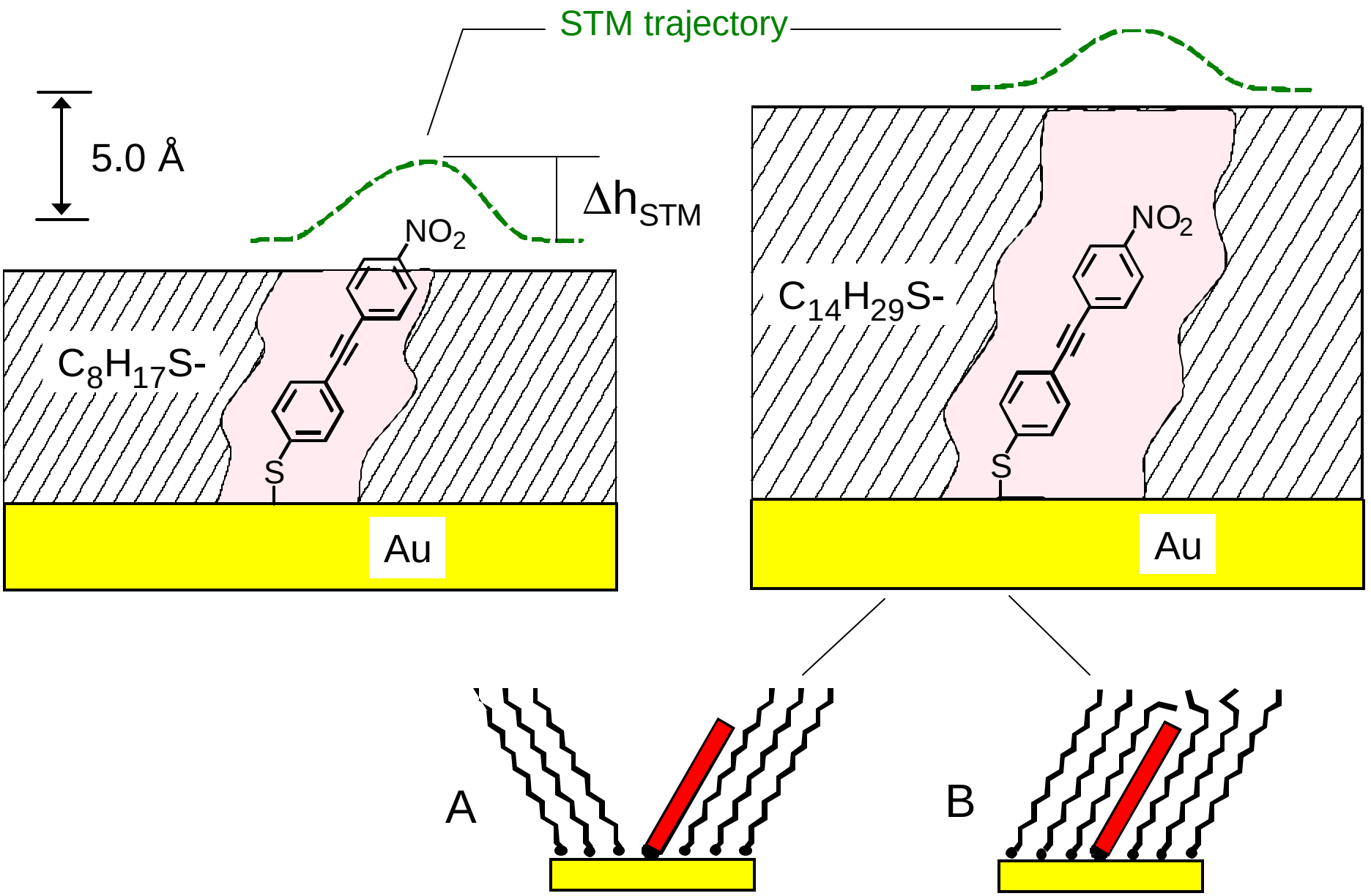
Insertion Rates of Nitro Molecule in Several Host SAMs

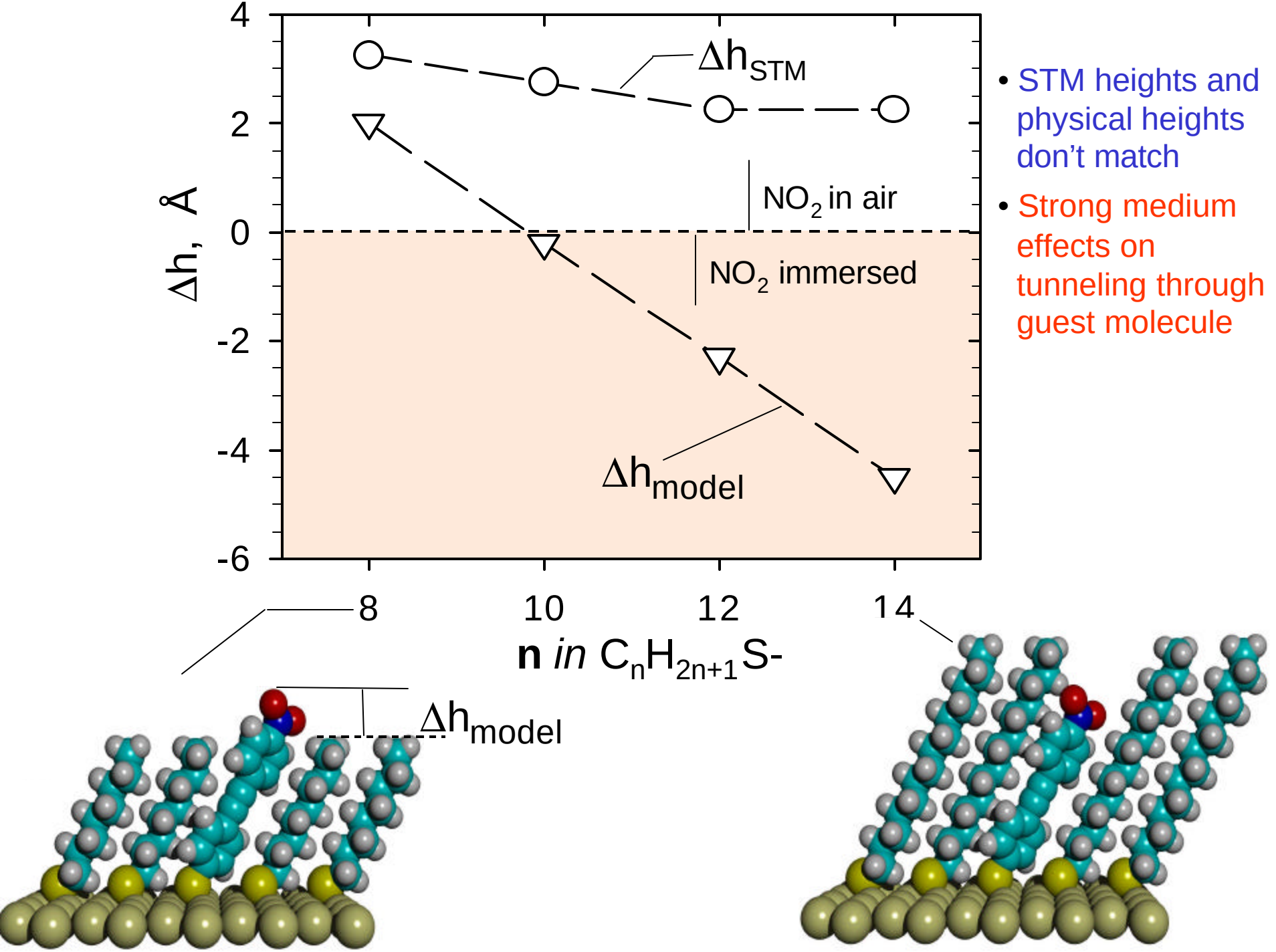


- Orientation invariant with % insertion
- ~1% insertion detection limit



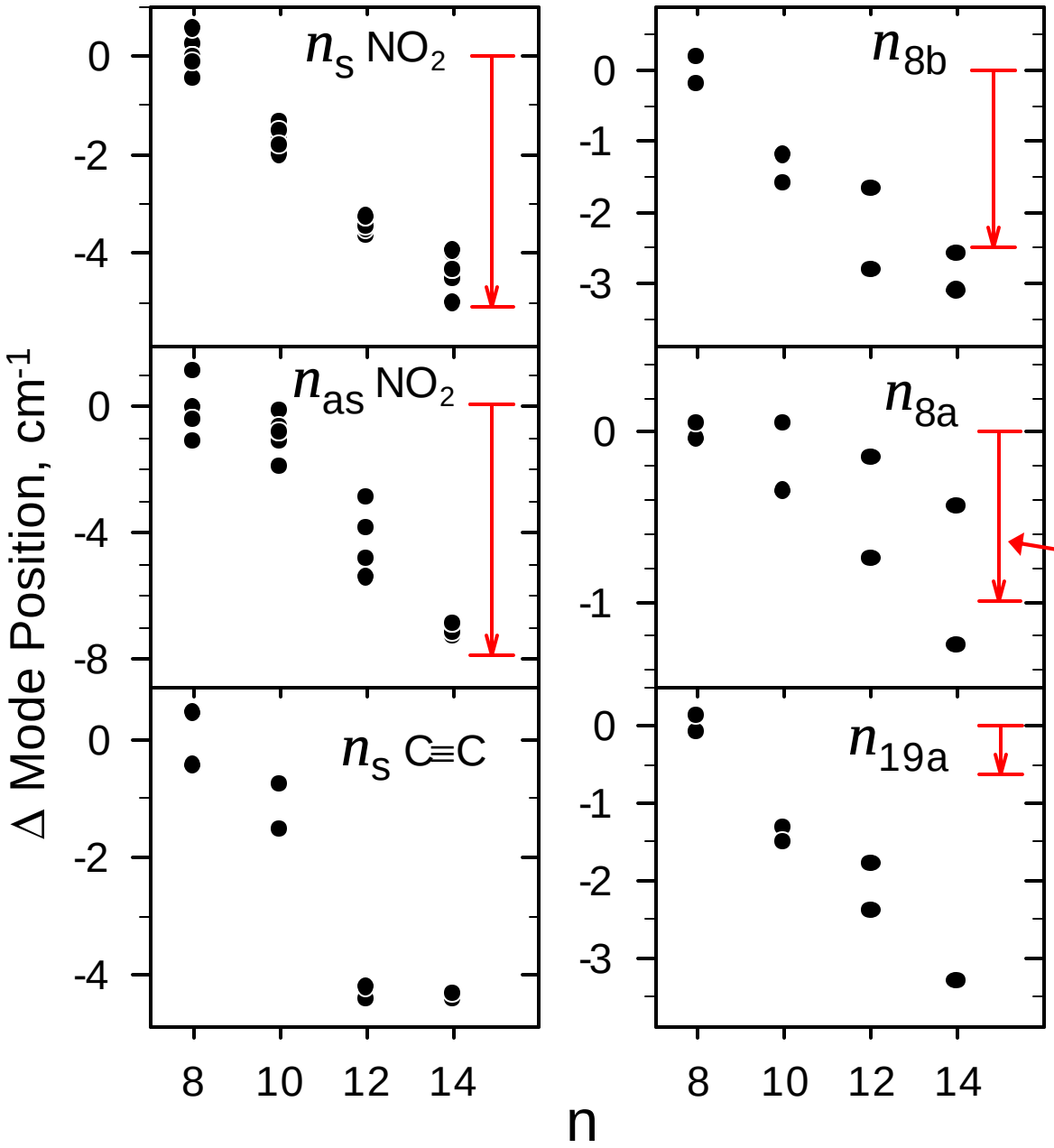
The Local Environment of Guest Molecules in Host Matrices: - Effects on Electrical Response





- STM heights and physical heights don't match
- Strong medium effects on tunneling through guest molecule

IR Frequency Shifts Show Host Matrix Packed Densely Around Guest Molecules

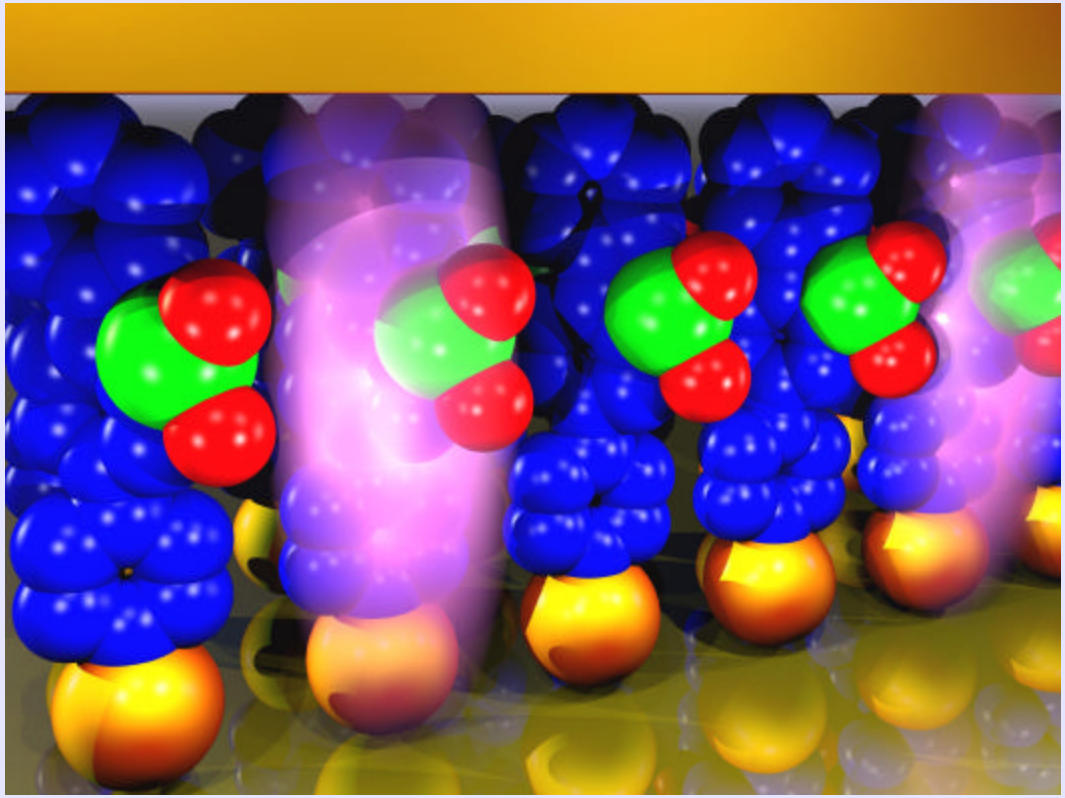


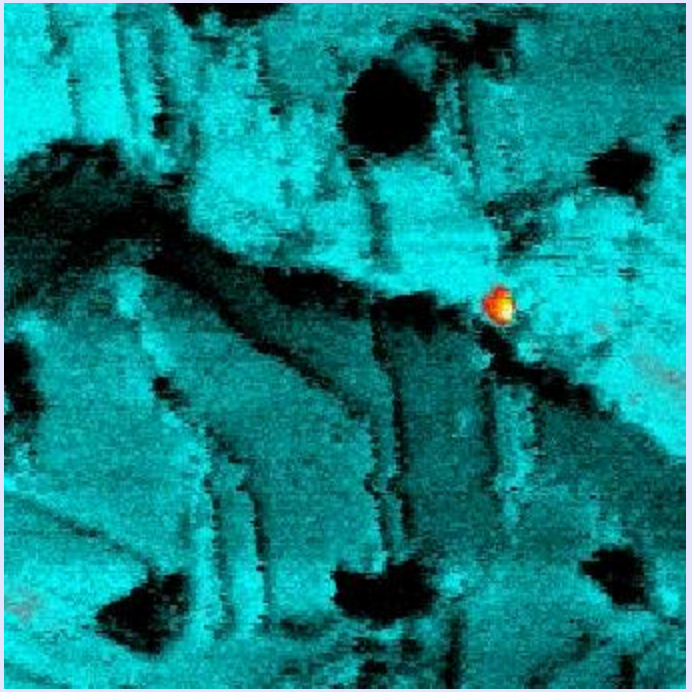
- IR modes shift to lower frequencies as length of surrounding host alkyl chains exceeds length of guest molecule
- Shifts correlate with DFT(B3LYP/6-31G*; Onsager dipole-sphere medium) calculations for shifts as a function of immersion in hydrocarbon media
- Correlation shows **short guest molecules insert into a fully hydrocarbon host environment**

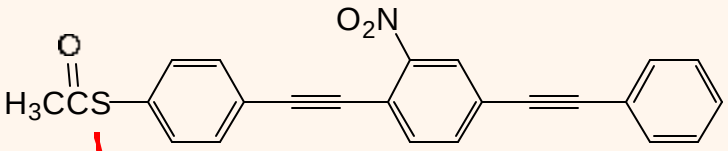
JPCB, 104, 4880(2000)

STM of inserted moleswitches in alkanethiolate SAMs

How Does Ensemble Switching (e.g., *n*-pore devices) Scale to The Molecular Level?



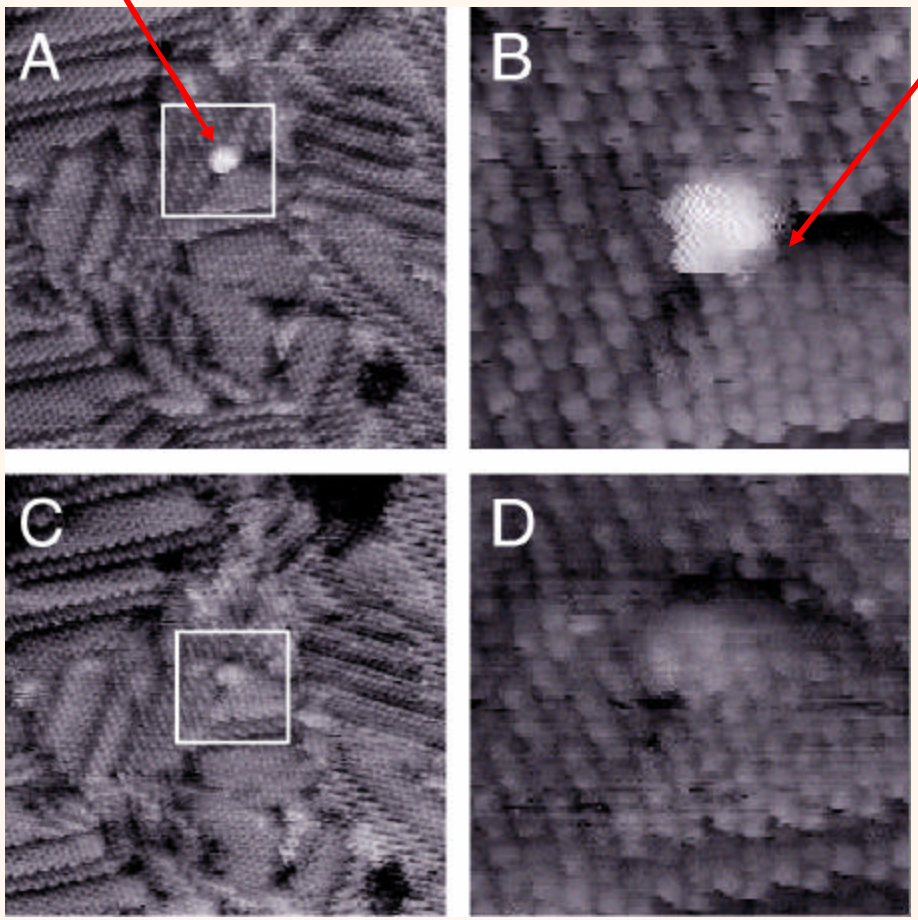




in C12S/Au SAM

MoleSwitch in C12 domain boundary region

200 Å × 200 Å 50 Å × 50 Å



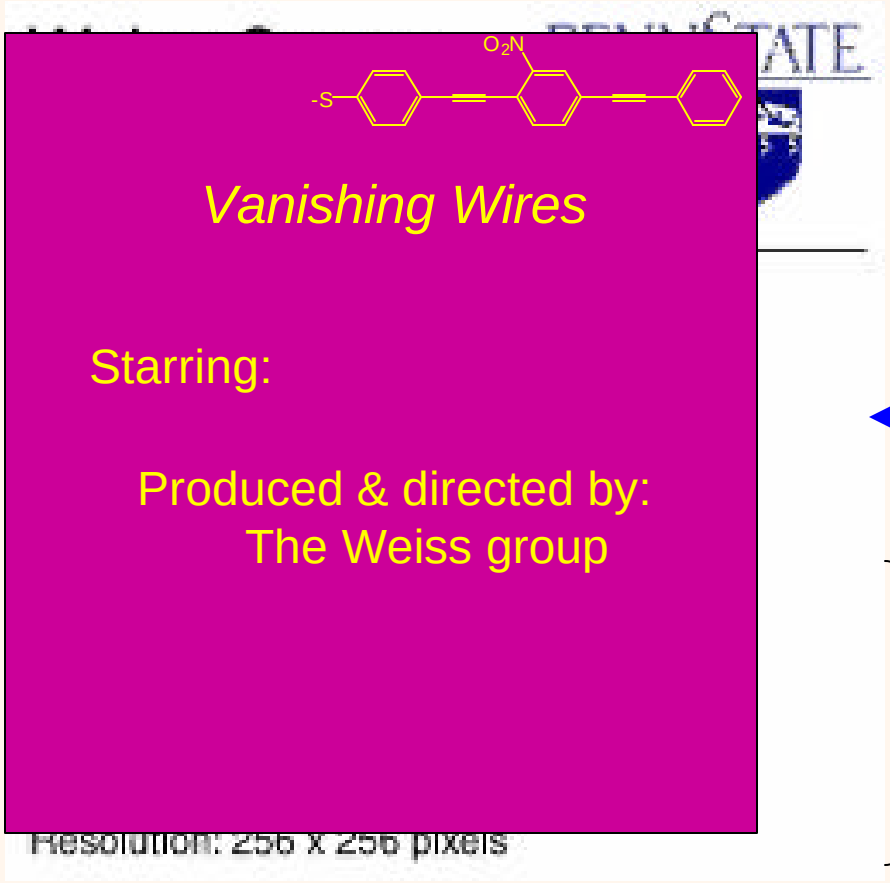
on state

off state

-1.0 V tip bias; 1.0 pA current

- single molecule switching
- STM height change ® **on**/**off** conductance ~10^3
- switches turn **on** occasionally as tip passes by
- decay to **off** is random **but** avg **on** time longer **in ordered regions**
- ramping to +4 V can switch to **off**

Donhauser, Mantooth, Kelly, Bumm, Monnell, Stapleton, Allara, Tour, Weiss; *Science , 292, 2303-2307(2001)*



disordered host lattice region

- single molecule switching
- STM height change ® **on**/**off** conductance ~10^3
- switches turn **on** occasionally as tip passes by
- decay to **off** is random **but** avg **on** time longer **in ordered regions**
- ramping to +4 V can switch to **off**

-1.0 V tip bias; 1.0 pA current

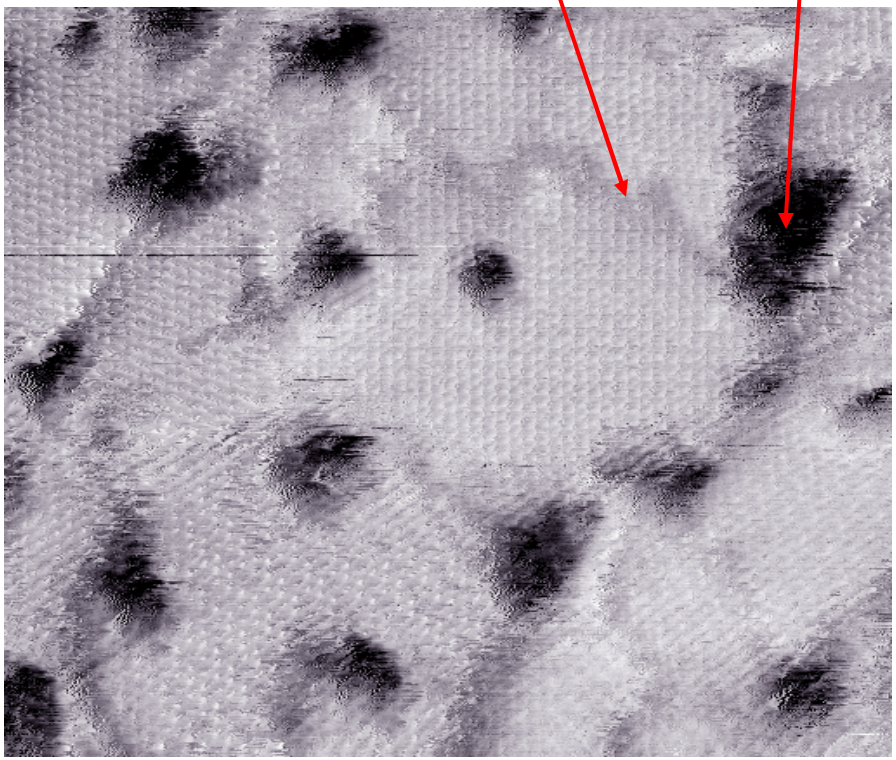
Donhauser, Mantooth, Kelly, Bumm, Monnell, Stapleton, Allara, Tour, Weiss; *Science , 292, 2303-2307(2001)*

Increase in Film Order by Annealing: 1 mM RSH / EtOH at 75 °C

Pre-Anneal

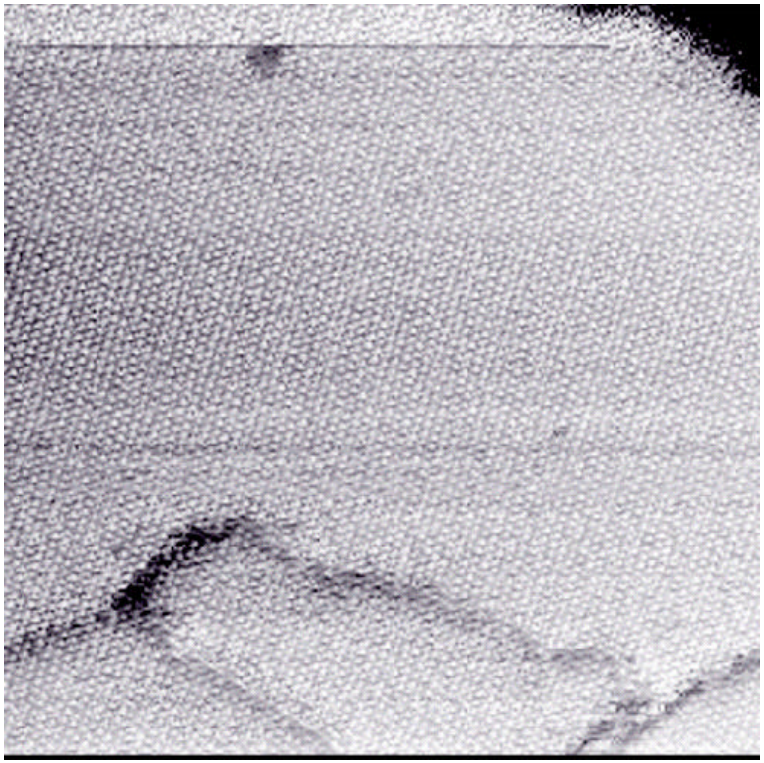
Molecular domain defects

Pit (typical) defects



40 nm x 40 nm;
V_{Tip}=$^{+}$1 V; I=1.0 pA

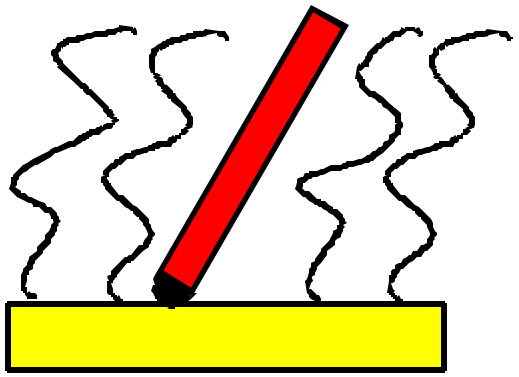
Post-anneal



40 nm x 40 nm
V_{Tip}=$^{+}$1 V; I=10 pA

J. Am. Chem. Soc. **1999,** *121,* 8017-8021

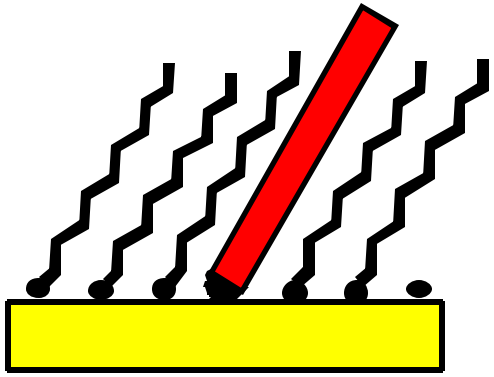
Switch ON Times Depend on Host Matrix Packing

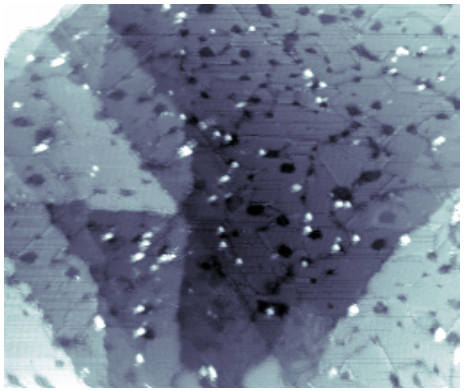


Low

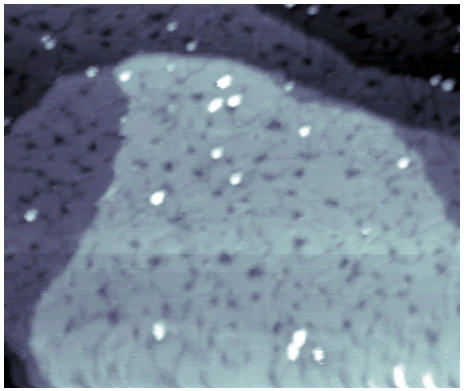
Switch ON/OFF Ratio

High

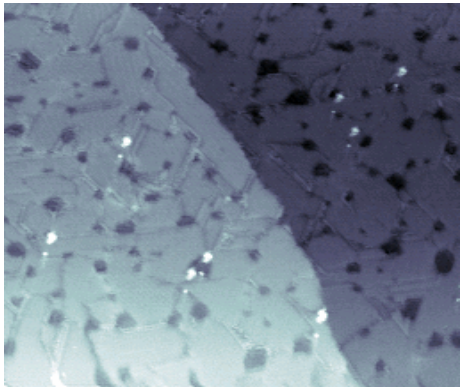




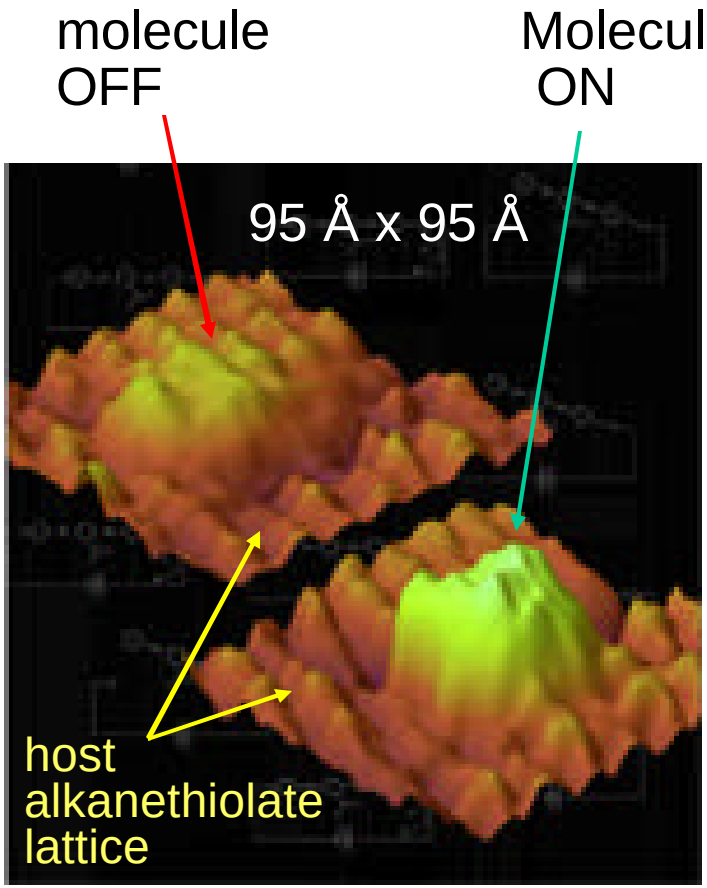
Defect populated SAM (5 min deposition)



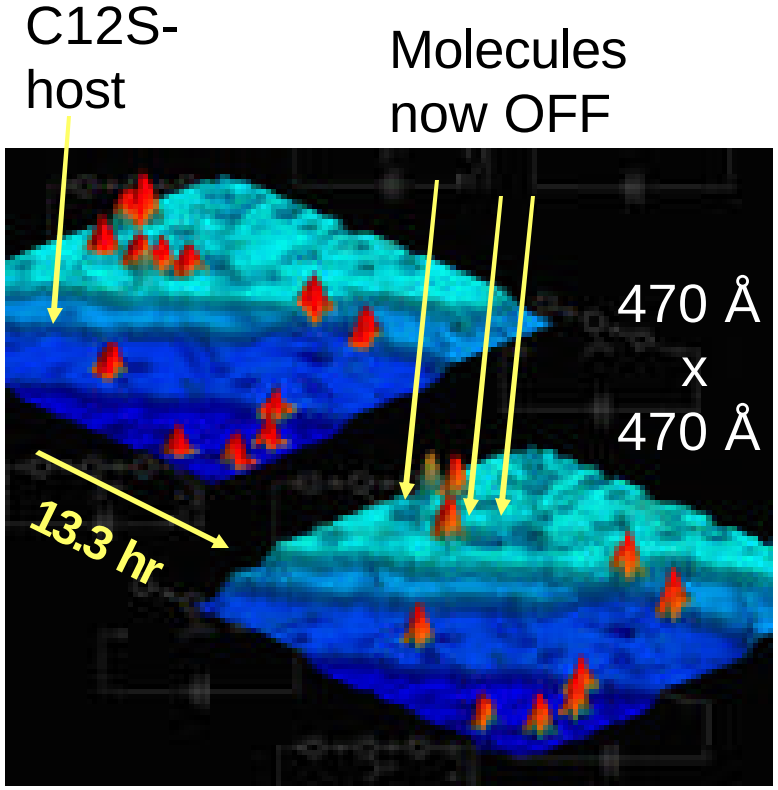
Std. SAM (24 hr deposition)



Vapor Annealed SAM (24 hr+)



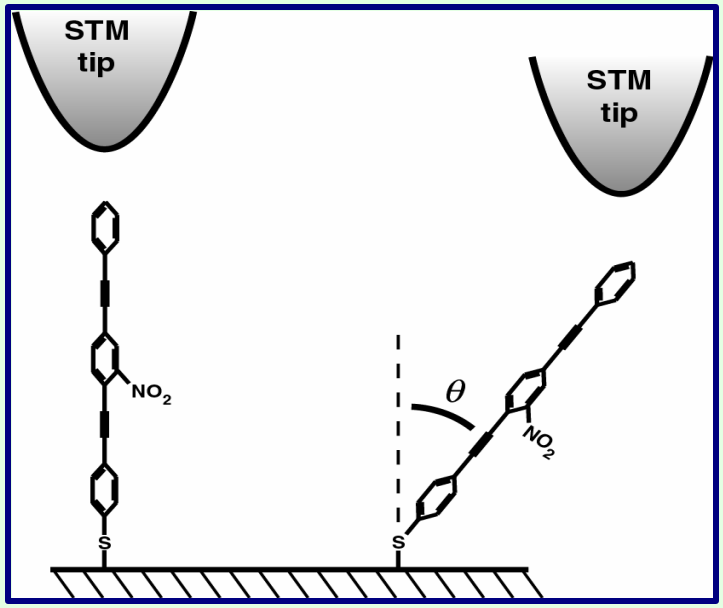
1.0 pA; V_{tip}=+1.0 V;
Frame interval: 30 min



1.0 pA; V_{tip}=-1.5 V

Switching for both isolated and grouped molecules

Switching Mechanism(s)??

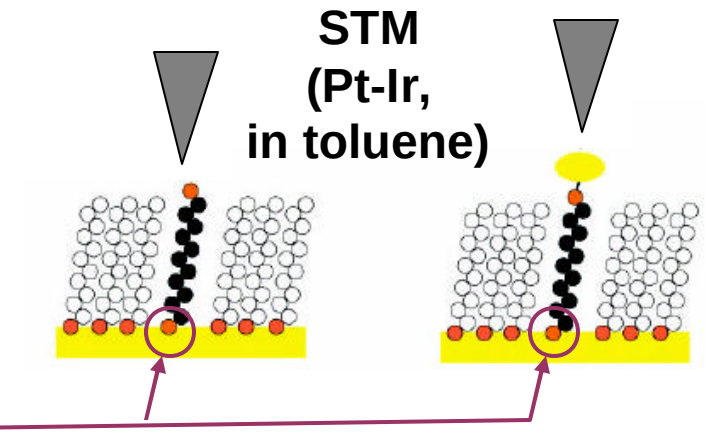


STM data suggest
Molecular Tilt Change??:

Donhauser, Mantooth, Pearl, Kelly,
Nanayakkara & Weiss, unpublished

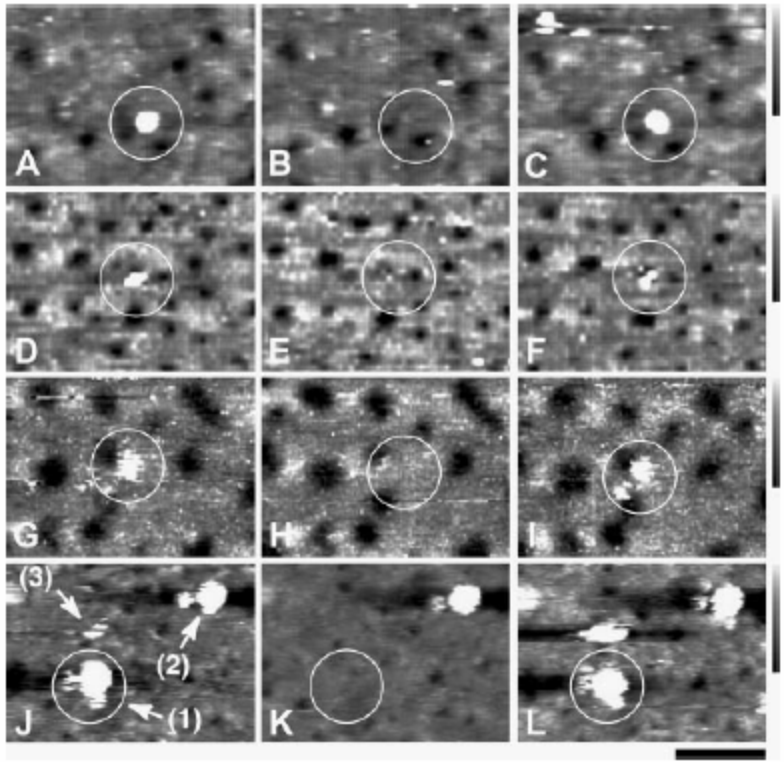
STM-Induced Molecule Switching
Recently Observed in Alkane Chain Molecules

[Lindsay et al, Science, 300, 1413 (2003)]



Switching via Au-S bond scission at bottom contact??

- **no electronic mechanism for -CH_2- structure**
- **switching with or without n-particle**
- **switching with n-particle precludes tilt mechanism?**
- **Au-S bottom contact scission common to both structures**



HS-C8-SH in C8-S SAM

HS-C10-SH in C10-S SAM

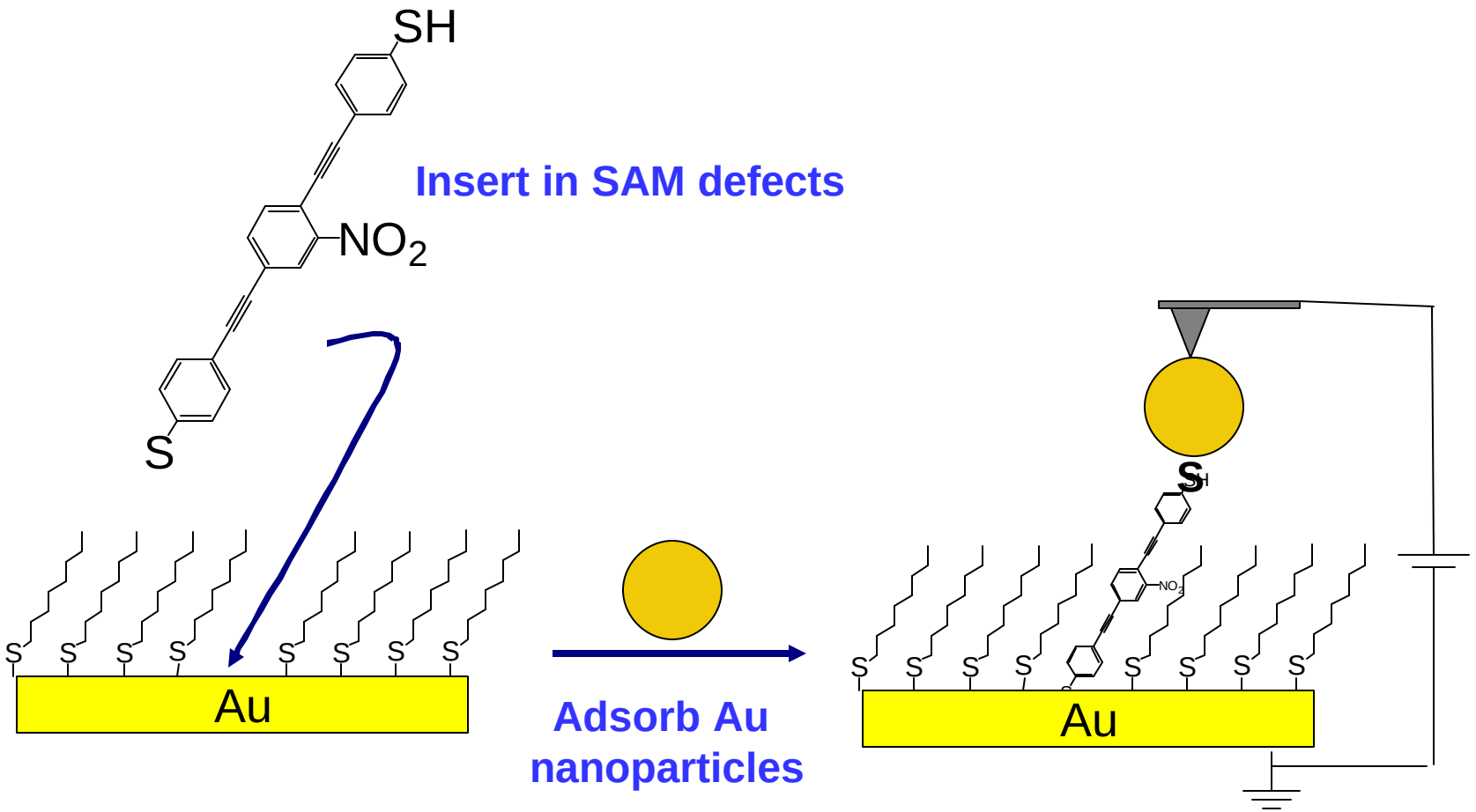
HS-C12-SH in C12-S SAM

HS-C12-SH in C12-S SAM + 1.5 nm Au n-particle

effect of toluene medium???

Conducting AFM with nanoparticle contacts to inserted moleswitches in alkanethiolate SAMs

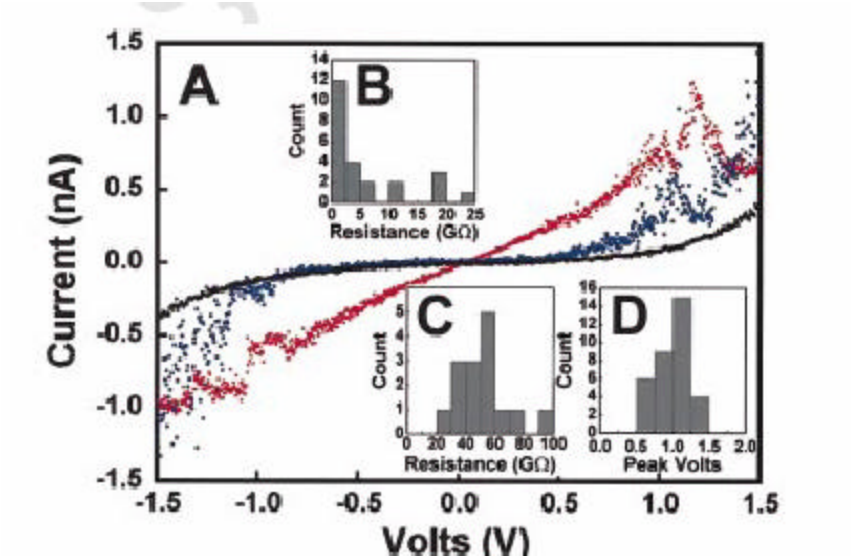
Conducting AFM Probes of Inserted Nitro OPE Molecule



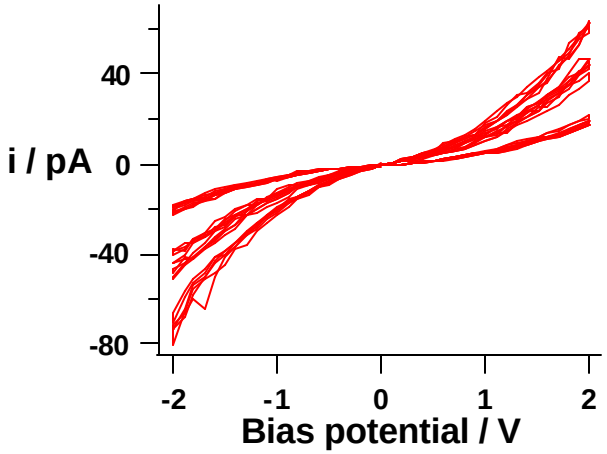
Au–S–molecule–S–Au junction in alkanethiolate matrix

Full contact simulates 2-terminal device

Results: Nitro-OPE in C12S- SAM



Lindsay et al, APL, 81, 2002



Bjordefors, Daniel, Allara

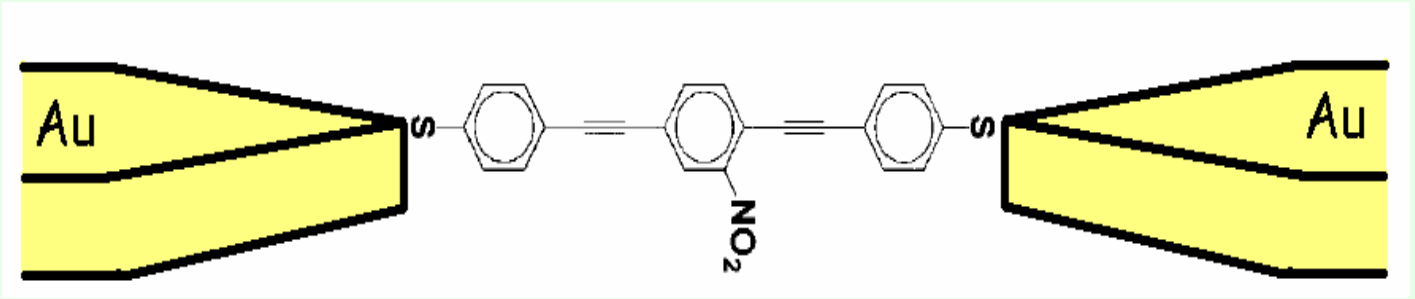
- ~2 nm nanoparticles
- measurement under toluene solvent
- integral i ratios → 1 molecule
- very weak NDR at ~1-1.5 V
- no NDR with simple OPE
- currents ~500-1000 pA

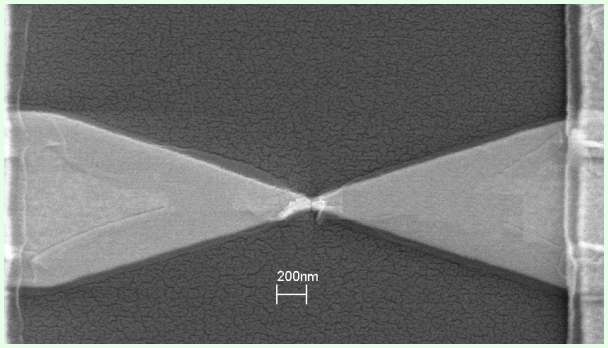
- ~2-5 nm nanoparticles
- measurement in air or Ar
- integral i ratios → 1 molecule
- no NDR 0 — ± 5 V
- no NDR with simple OPE
- currents ~50-100 pA

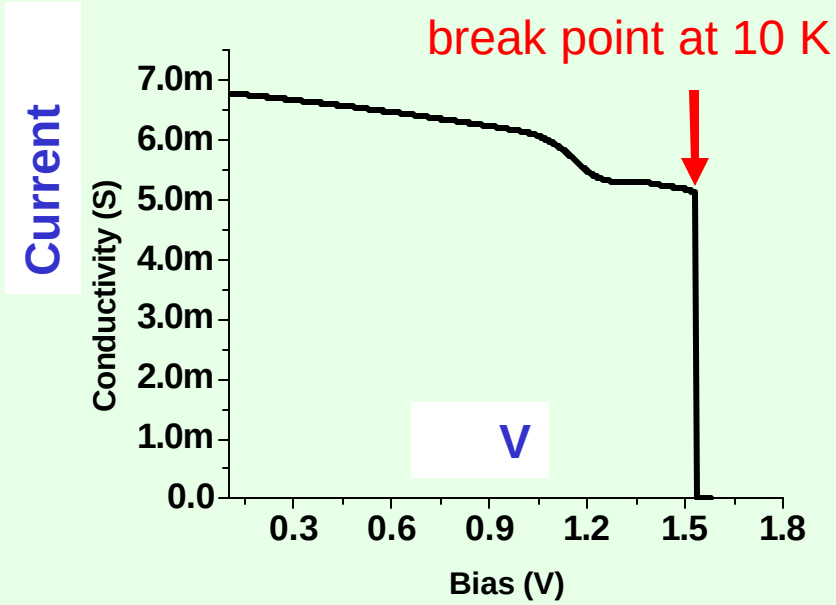
Conclusion: NDR extremely sensitive to surrounding matrix and environment

Single molecule devices

nano-Junction Molecule Devices -- Fabrication





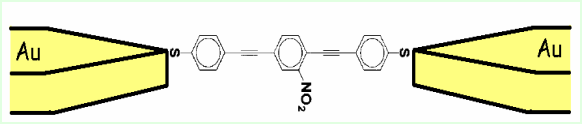


1. e-beam fab Au nano-wires between contact pads
2. Form SAM on Au surface
3. Apply V at 10 K --- wire breaks causing nm-scale gap; molecules bridge gap by thermal motion
4. ~10% junctions show molecules bridged; typically ~1-3 molecules

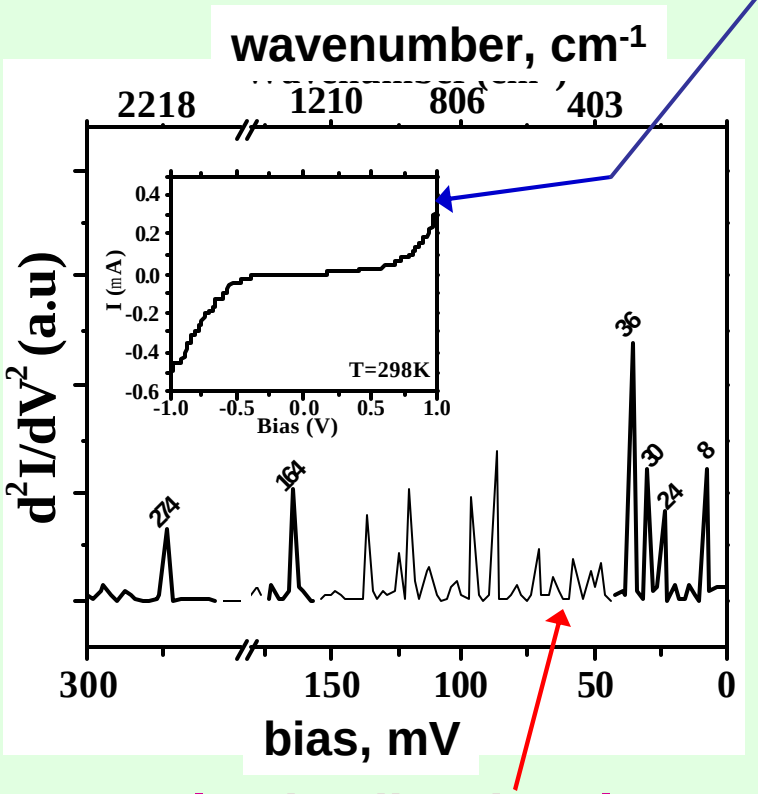
[Park, Lim, Park, Alivisatos, McEuen, APL, 75, 301–303 (1999)]

Selzer, Allara, Mayer, Cabassi (submitted)

nano-Junction Molecule Devices -- I-V Data



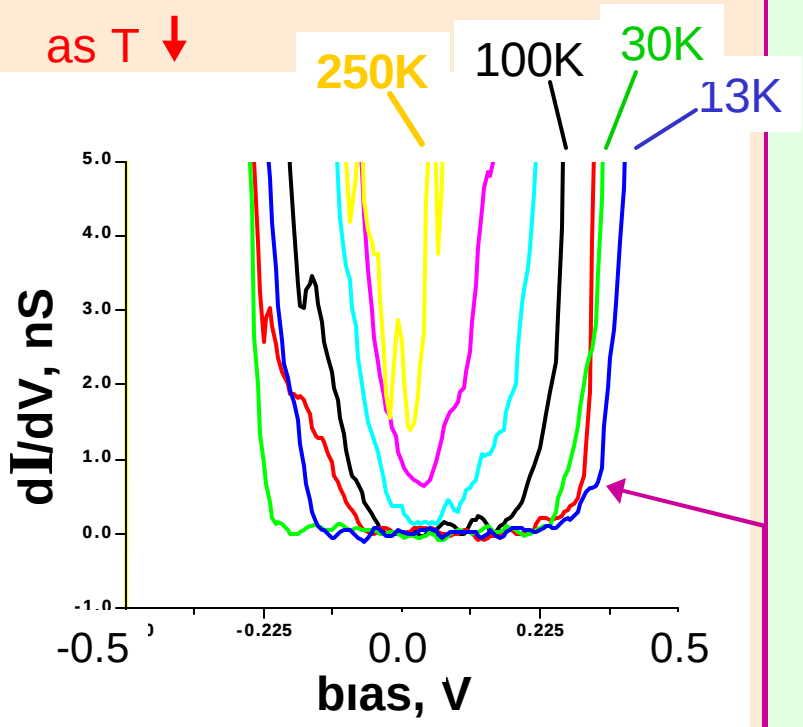
~0.3 mA at 1 V (~3 MW);
expected value of 1 molecule



Inelastic vibrational loss spectra at 13 K;
- **proves molecule in gap**

Conductivity *vs* 1/T

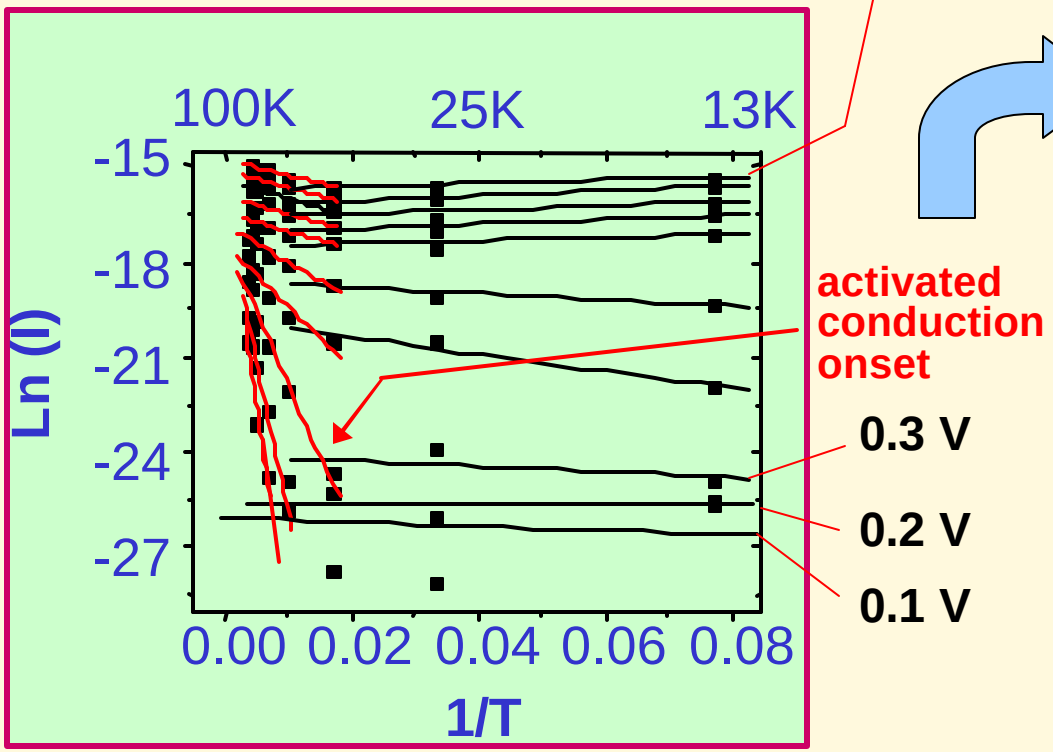
threshold V ↑
as T ↓

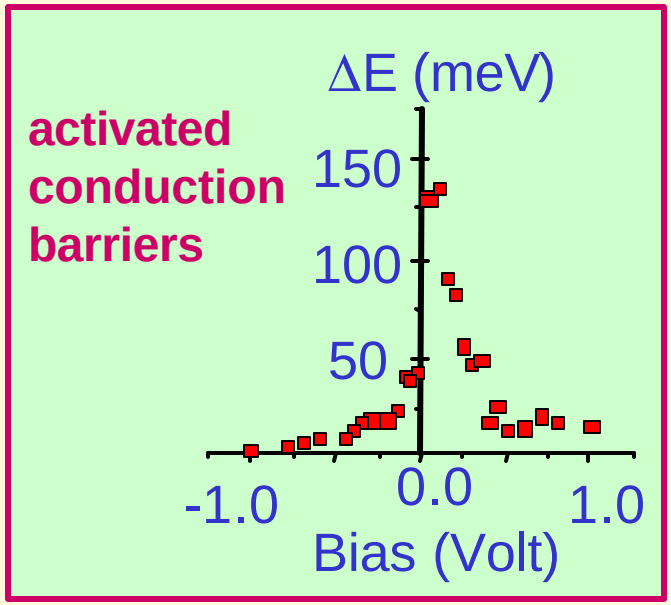


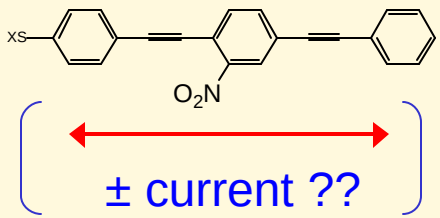
sharp increase in dI/dV:
- **onset of new conduction channel**

nano-Junction Molecule Devices -- T-Dependence

Ln(I) vs 1/T at different V's







hopping conduction ↘ 40 K:

- **internal molecular barriers**

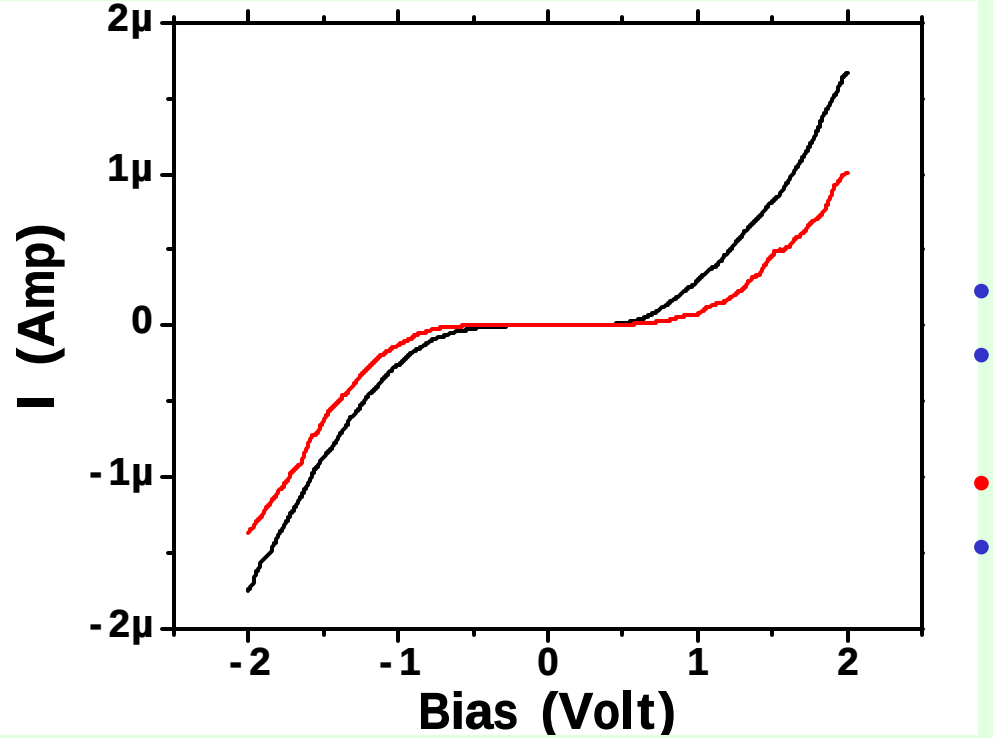
hopping onset T ¯ as bias V -:

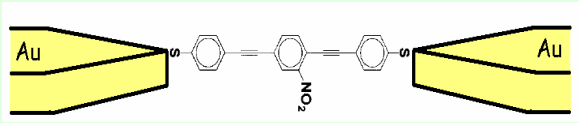
- **vibrational scattering "heats" molecule - opens barriers**

DE ® 0 V ↘ |±0.5 V|

- **internal molecular E fields?**

No NDR or Switching Effects

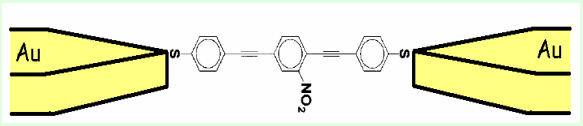




- 2 different devices in graph
- repeatable I-V curve forms device to device
- never see NDR or Switching
- devices destroyed on sweeps to ±5 V

nano-Junction Molecule Devices -- Summary

- **Through molecule e^- tunneling**
  (Inelastic tunneling vibrational spectrum)
- **Individual molecule devices**
  (expected values of tunneling current)



- **≻40 K activated hopping intramolecular conduction**
  (V-dependent barrier from T dependence)
  - **Vibrational scattering heats molecule**
  - **increased conduction via activated conformational transitions?**

- **Monotonic I-V behavior out to ~±5 V ---**
  no NDR - switching effects on repeated cycling
  - **Previous nanopore devices (≻10^3 molecules) show NDR (Reed et al)**

Conclude NDR-switching is function of molecular packing

Switching-NDR Mechanism(s)??

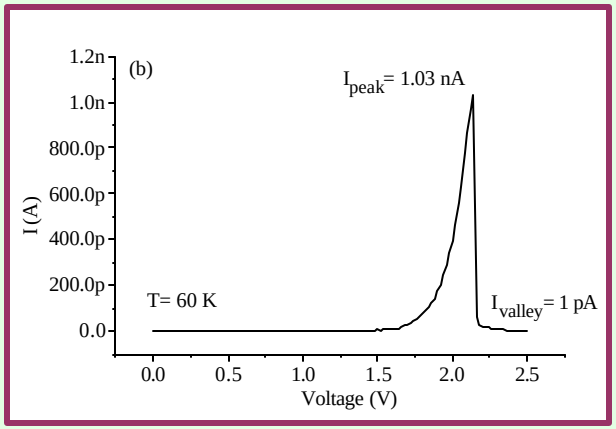
Ring Rotation **?**

Nitro Rotation **?**

Concerted Motions **?**

Bond Scission **?**

Molecule tilt **?**



Theoretical Approaches vary:

Seminario *et al.*, *J. Am. Chem. Soc.* 120, 3970 (1998).

Seminario *et al.*, *J. Am. Chem. Soc.* 122, 3015 (2000).

Di Ventra *et al.*, *Phys. Rev. Lett.* 86, 288 (2001).

Kornilovitch, Bratkovsky, *Phys. Rev. B* 64, 195413 (2001).

Cornil, Karzazi, Bre´das, JACS, 2002, 124, 3516-3517

Taylor, Brandbyge, Stokbro, arXiv:cond-mat/0212191 v1 9 Dec 2002

Overall Conclusion:

- **effects extremely sensitive to surrounding matrix and environment**
- **predictive theory missing**

A Conformational Locking Mechanism? --- Recent DFT Theory Calculations

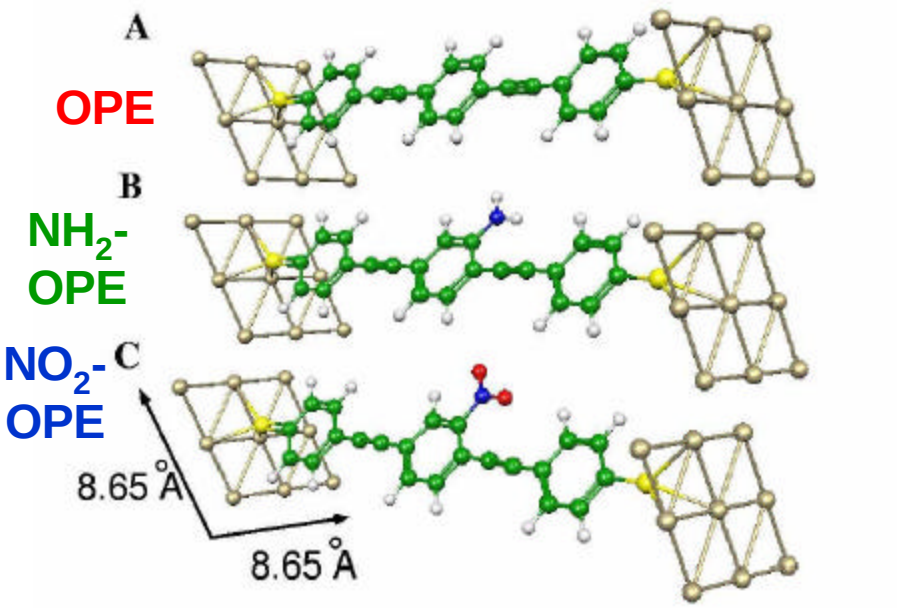
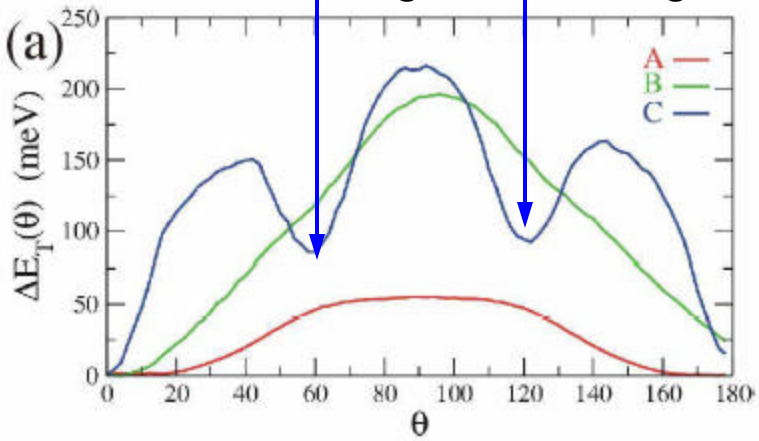
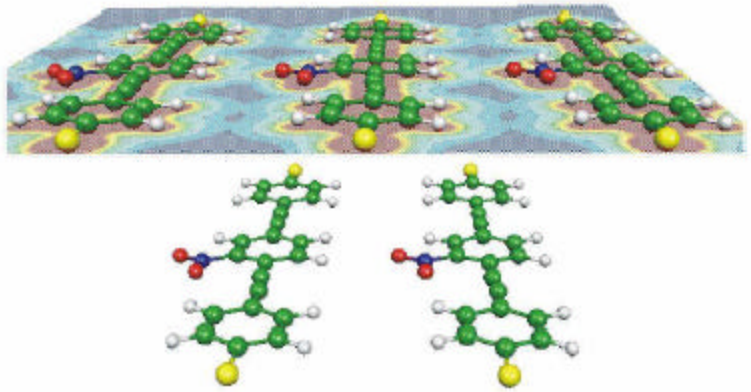


FIG. 1: Geometry of monolayers A, B, and C connected with two Au (111) surfaces. Color codes: C(green), H(white), O(red), N(blue), S(yellow), Au(gold).

NO_2-OPE uniquely shows minima at 60° ring rotation

ΔE vs middle ring rotation angle





NDR-Switching Mechanism:
V excitation of conformational rotation to New conductance state
- locking via intermolecular matrix effects??

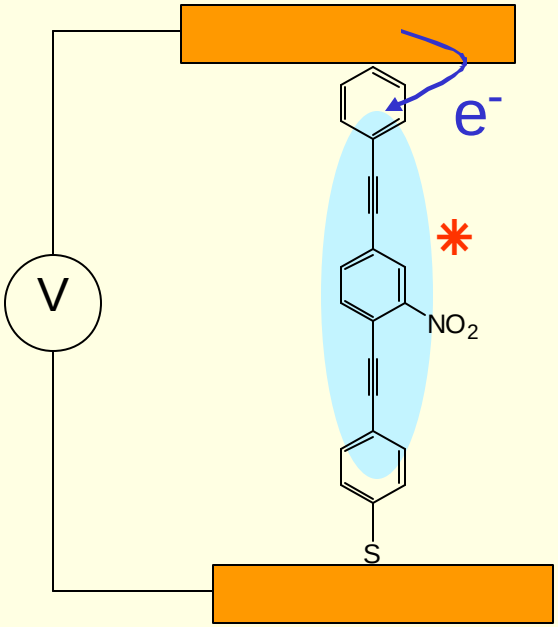
K. Stokbro et al,
arXiv:cond-mat/0212191 v1 9Dec 2002

Planar Devices: Molecular Level Design & Testing Issues

- molecules
- bottom contacts
- self-assembly
  - molecular geometry
  - chemistry
- matrix effects in molecule switching
- electron injection states
- top contact metallization issues

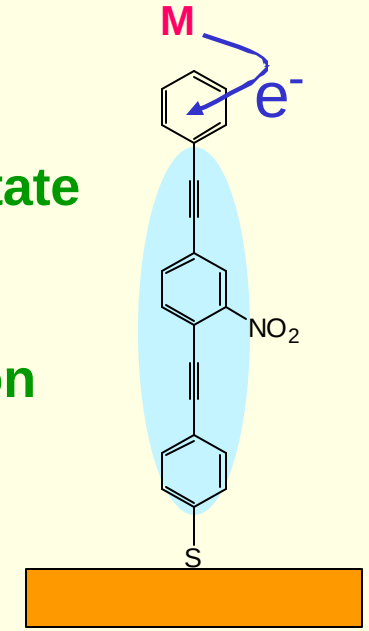
One-Electron Injection States:

- Important in switching?
- Can be made chemically?

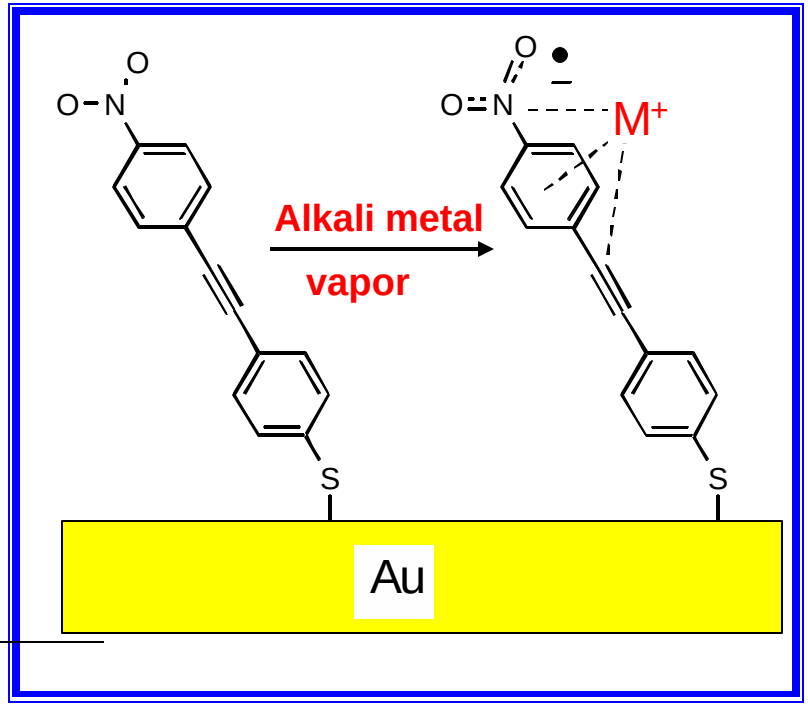


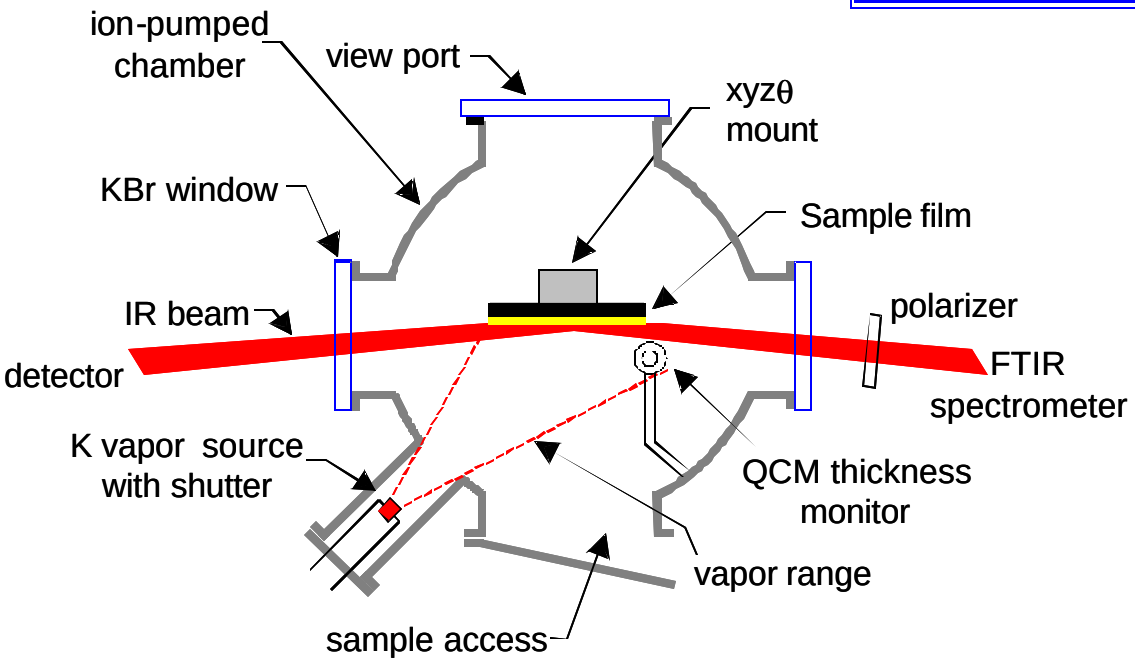
e-injection state stabilized by conformational "locking"?

e-injection state stabilized by M^+ charge compensation

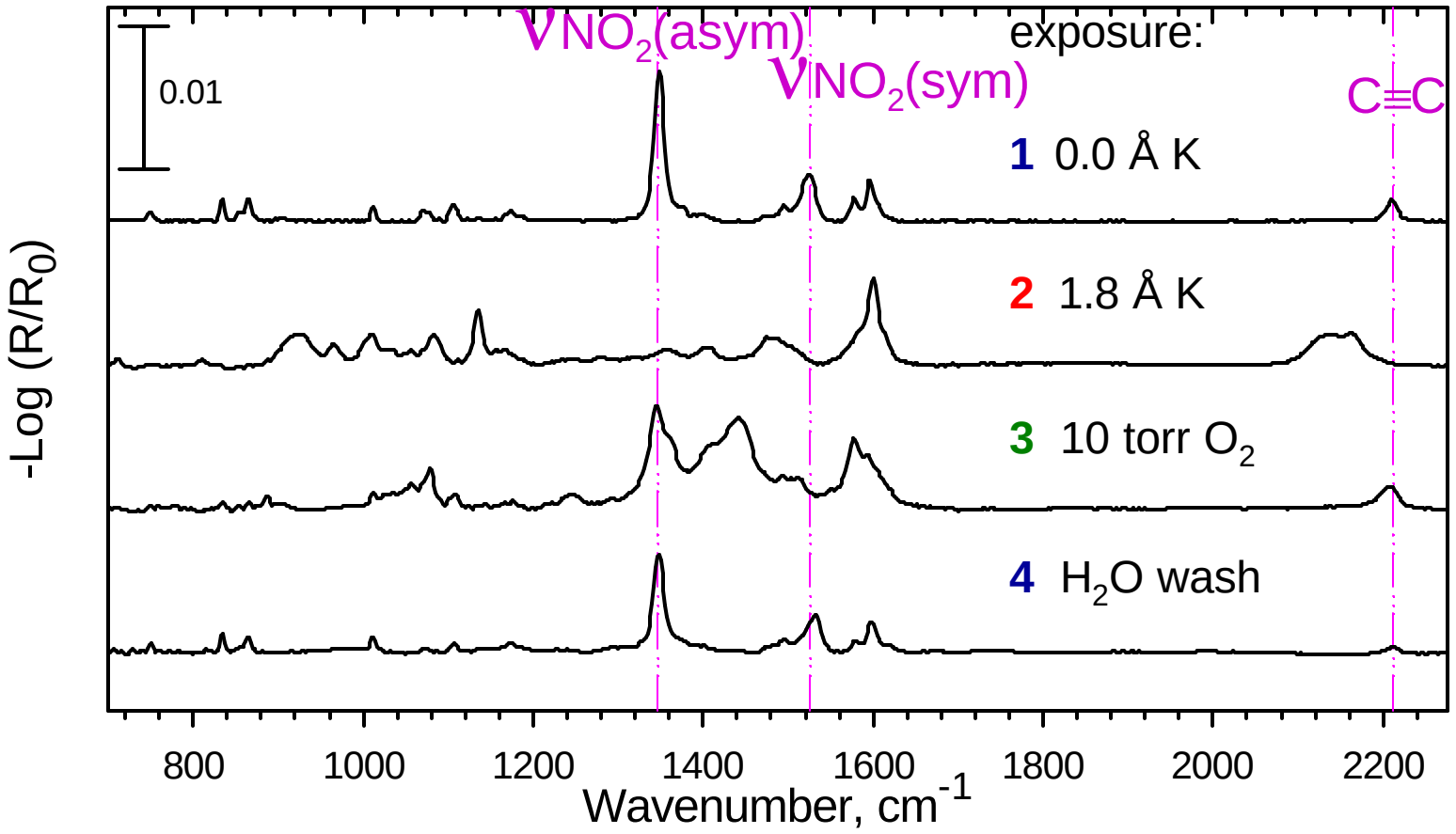


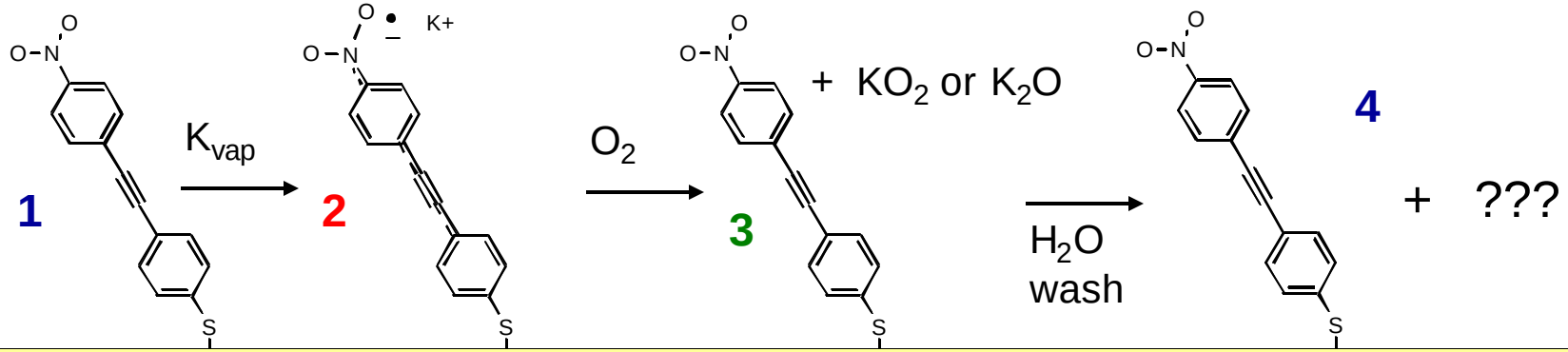
- Make SAMs of -NO_2 containing molecules
- Dose with alkali metal atoms (K and Li) in UHV
- Track chemical changes by vibrational spectroscopy
- Possible route to spin ½ array?

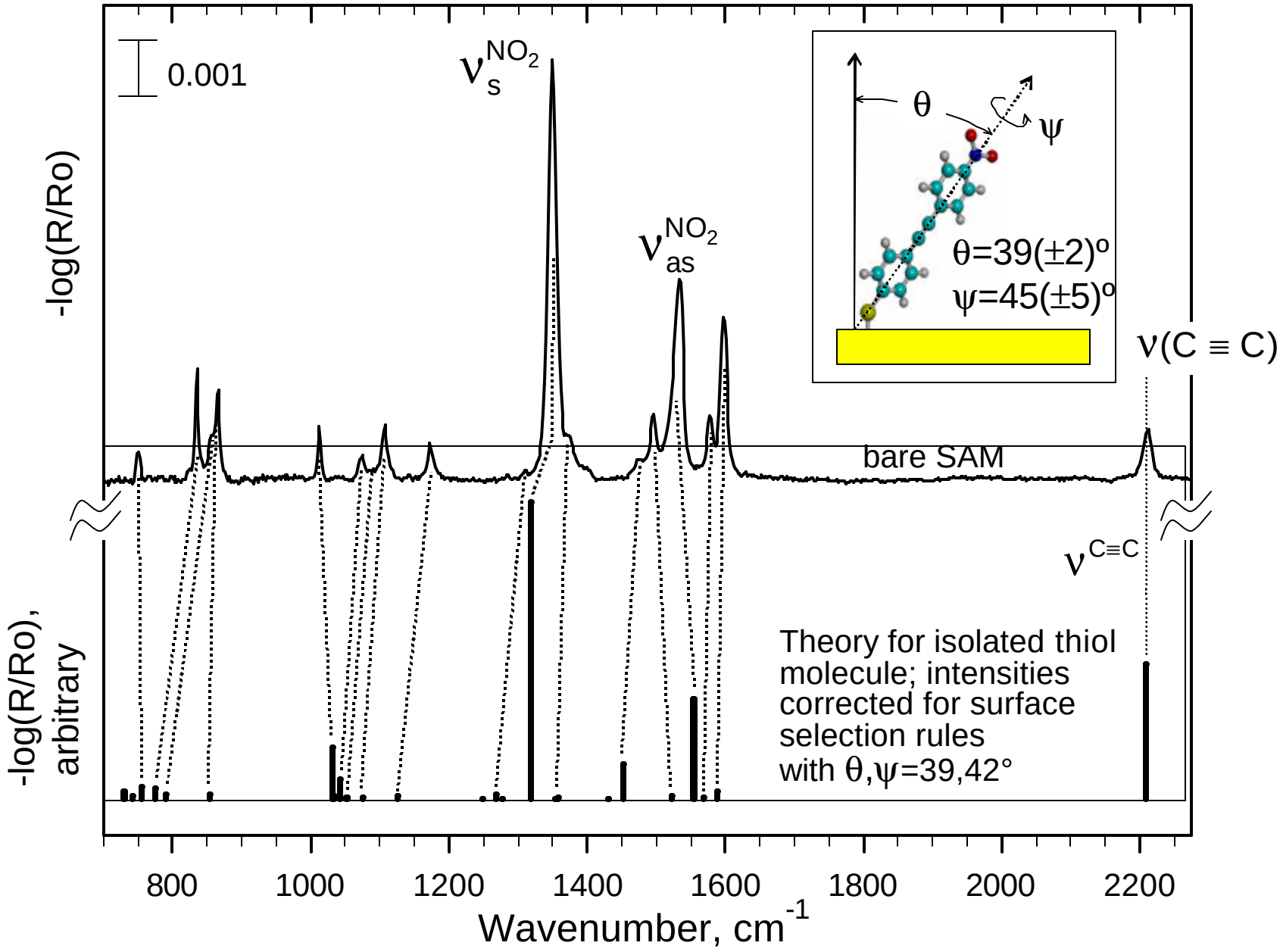

O
O
N
O
N
M+
Alkali metal
vapor
S
S
Au


ion-pumped
chamber
view port
xyzθ
mount
KBr window
Sample film
IR beam
polarizer
detector
FTIR
spectrometer
K vapor source
with shutter
QCM thickness
monitor
vapor range
sample access

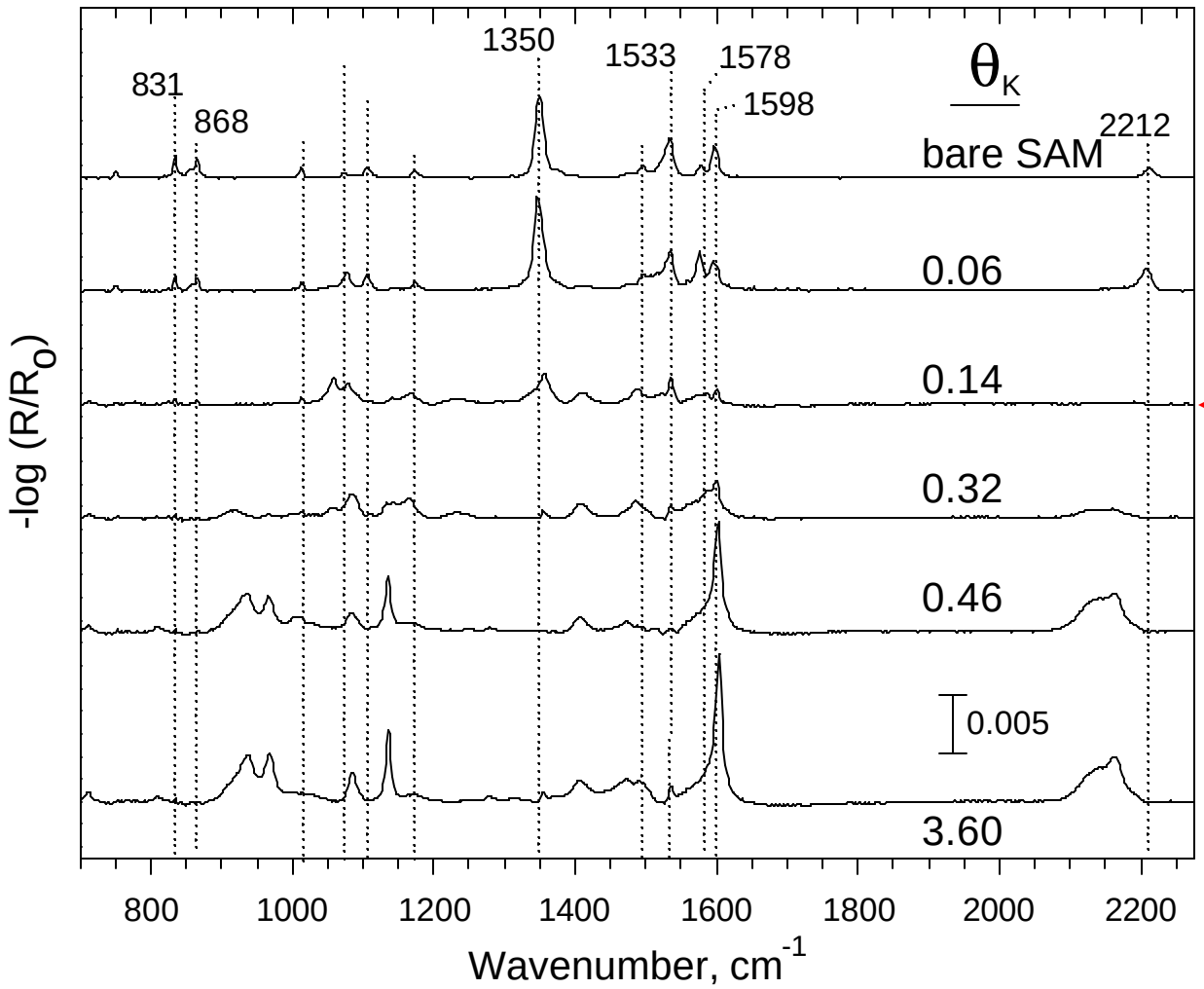
1-electron states exist & mostly reversible (2-electron states also)





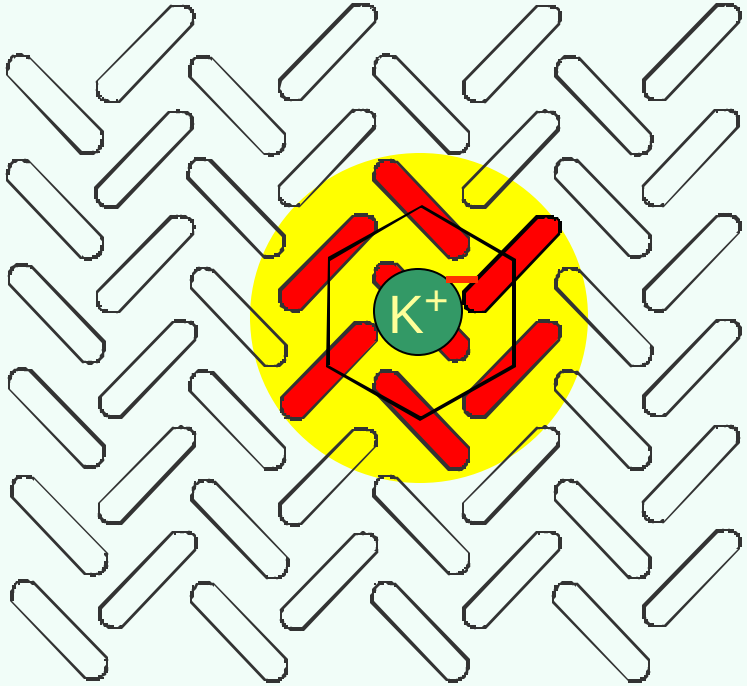

0.001
$\nu_s^{NO_2}$
$\nu_{as}^{NO_2}$
$\nu^{C\equiv C}$
$\nu(C \equiv C)$
θ
ψ
θ=39(±2)°
ψ=45(±5)°
bare SAM
-log(R/Ro)
-log(R/Ro), arbitrary
Theory for isolated thiol molecule; intensities corrected for surface selection rules with θ,ψ=39,42°
800
1000
1200
1400
1600
1800
2000
2200
Wavenumber, cm^{-1}

1-electron states exist & mostly reversible (2-electron states also)

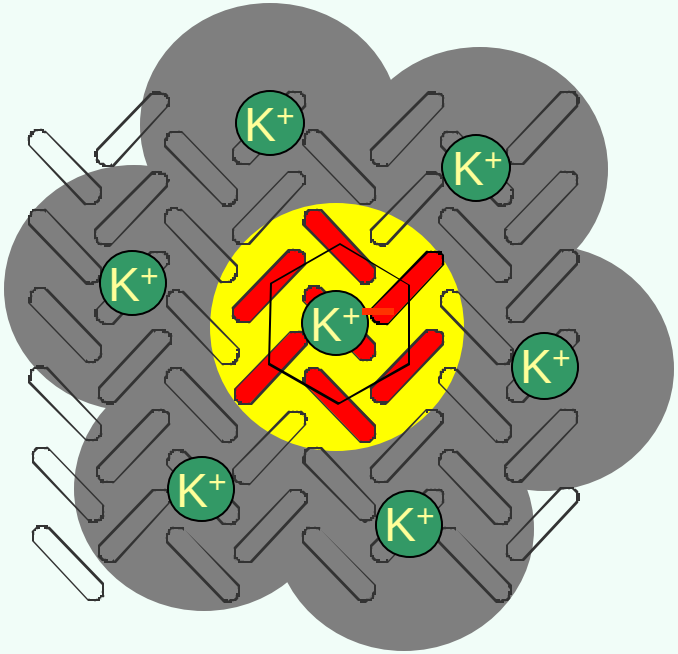


~ complete collapse of initial spectral features by ~1 K per 7 SAM molecules*

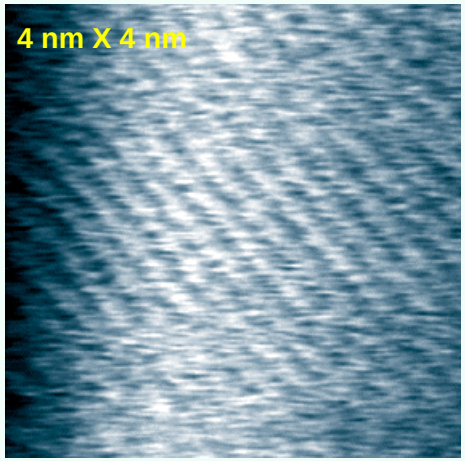
* Sticking coefficient = 0.80-0.90



e⁻ delocalized over NN shell??



Repulsive lattice?? (K/graphite)

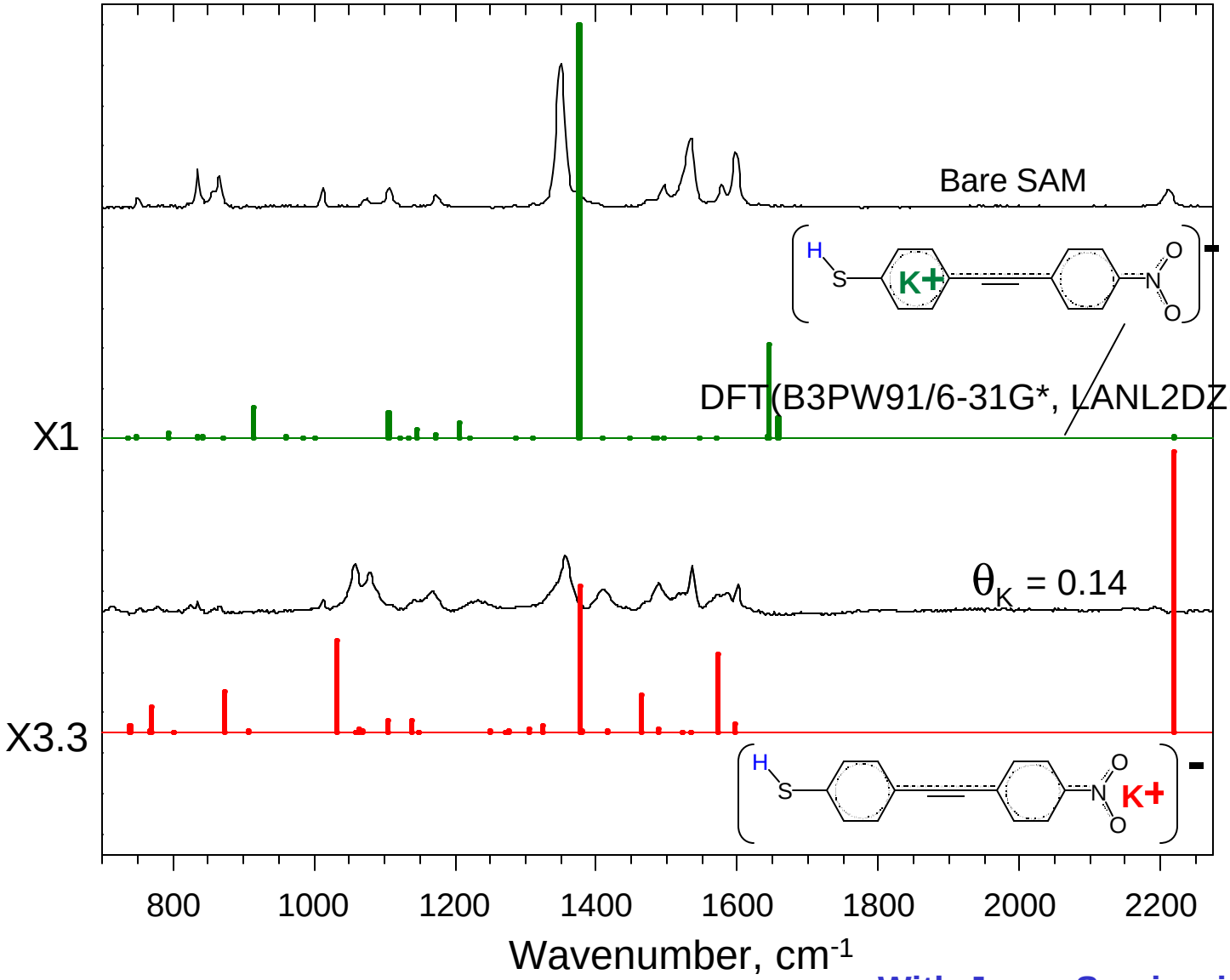


contact AFM
4 nm X 4 nm

Bare SAM: Complex lattice -- not a simple $(\sqrt{3}x\sqrt{3})$

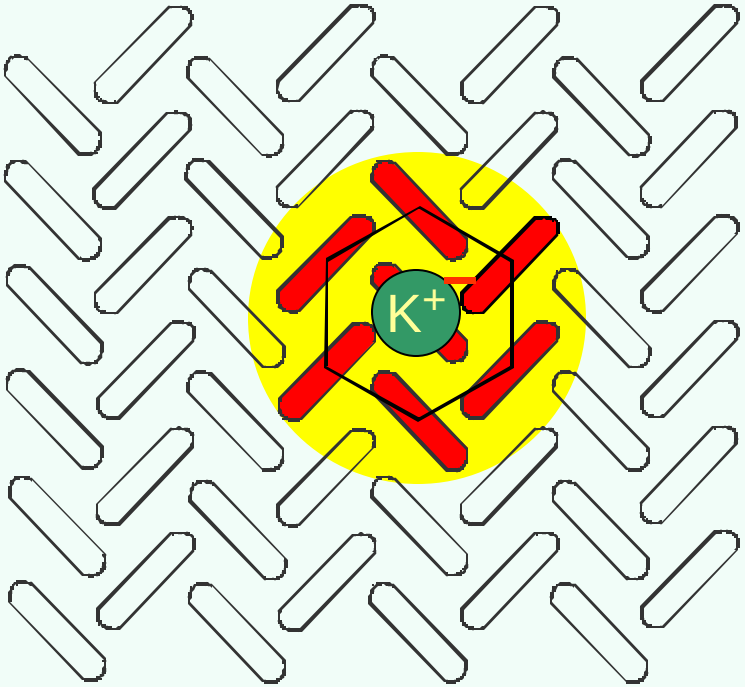
DFT calculations of K + 1 Molecule show poor fits to spectra

- HF/(3-21G, 6-31G*); B3PW91/6-31G* level; isolated molecule
- Mode intensities corrected for known surface orientation in SAM



top location best fit

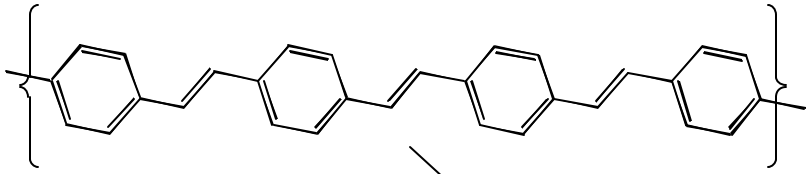
With Jorge Seminario (US Carolina)



- Results suggest e^- delocalized among nearest neighbors
- Similar delocalization in molecule switching?
- Possible electron spin lattice?

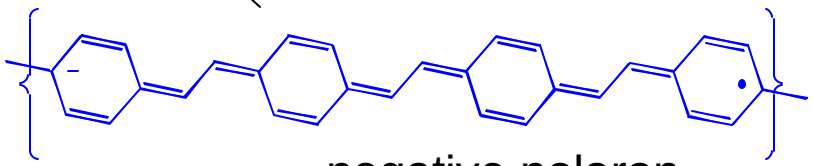
Conductance Control via Doping

Bulk



s = ~10^{-11} Ω^{-1} cm^{-1}

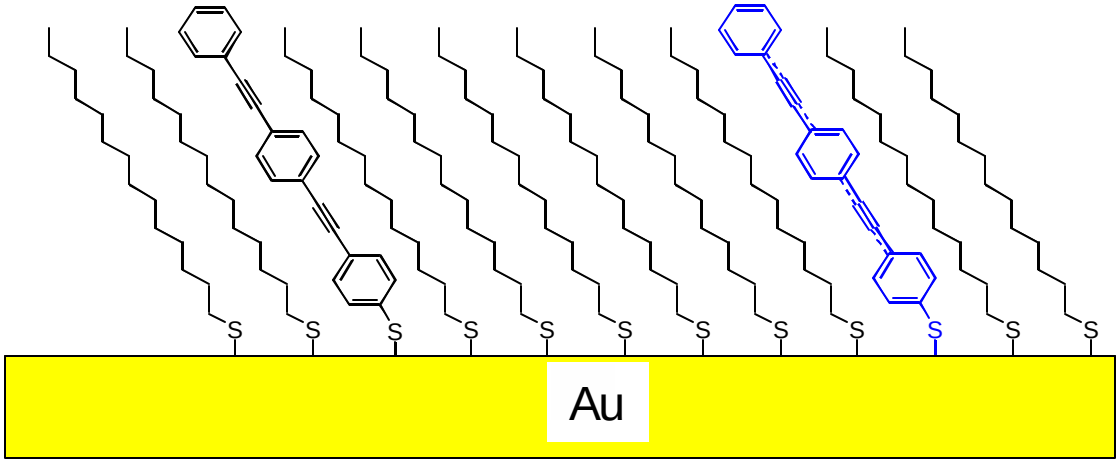
e^- donors



negative polaron

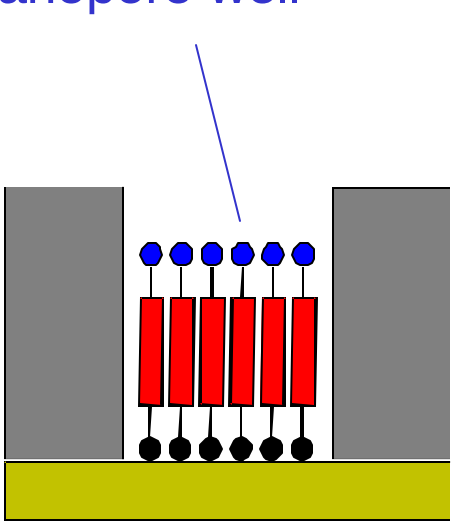
s = 3 Ω^{-1} cm^{-1}

SAM?

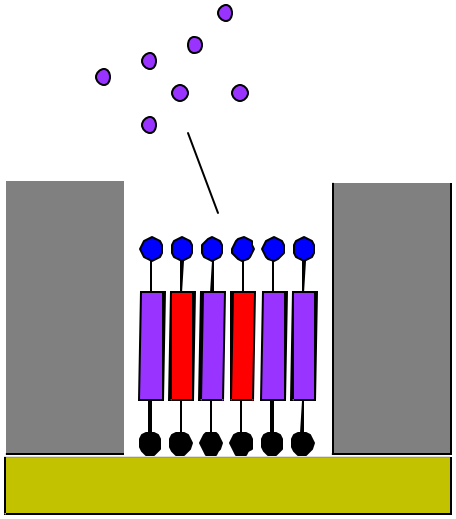


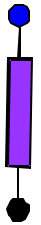
Doping: A Potential Strategy for Dramatic Changes in Molecular Wire Electronic Responses

self-assemble oligomers
in nanopore well

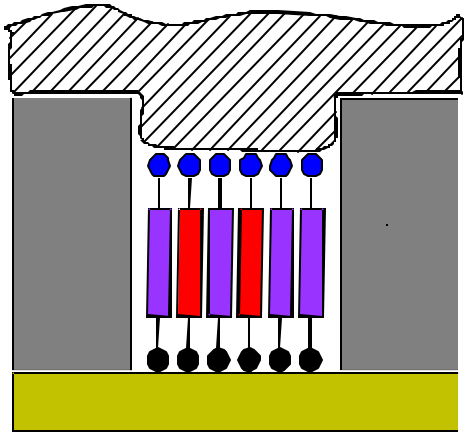


K vapor dose

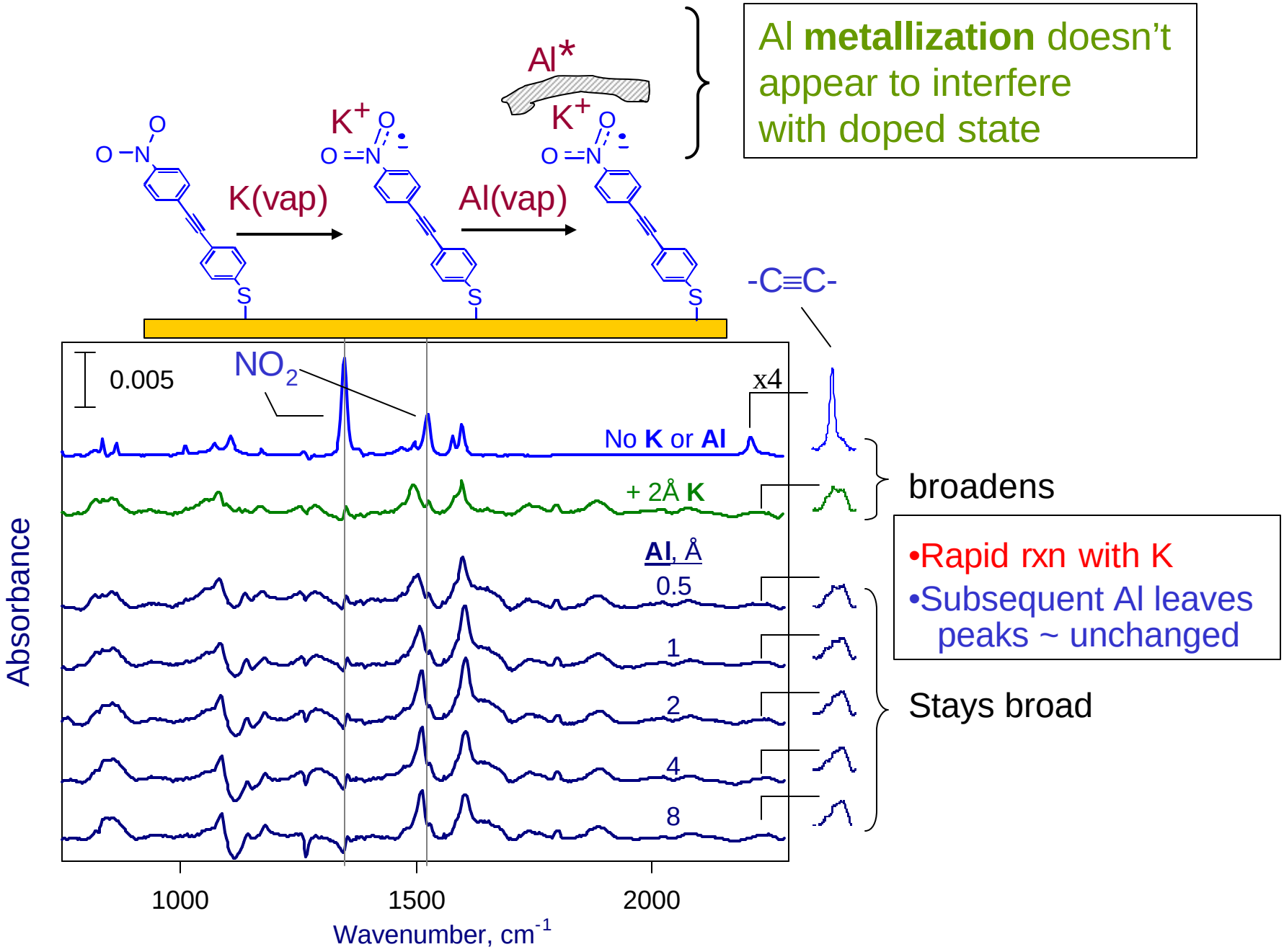




enhanced conductivity oligomer



metal contact deposition


Al metallization doesn't appear to interfere with doped state
Al*
K+
K+
K(vap)
Al(vap)
-C≡C-
0.005
NO2
x4
No K or Al
+ 2Å K
broadens
Al, Å
0.5
1
2
4
8
•Rapid rxn with K
•Subsequent Al leaves peaks ~ unchanged
Stays broad
Absorbance
1000
1500
2000
Wavenumber, cm-1

Rationale for A Molecular Electronics Technology

I-V Behavior of Molecules

Potential Applications and Device Types

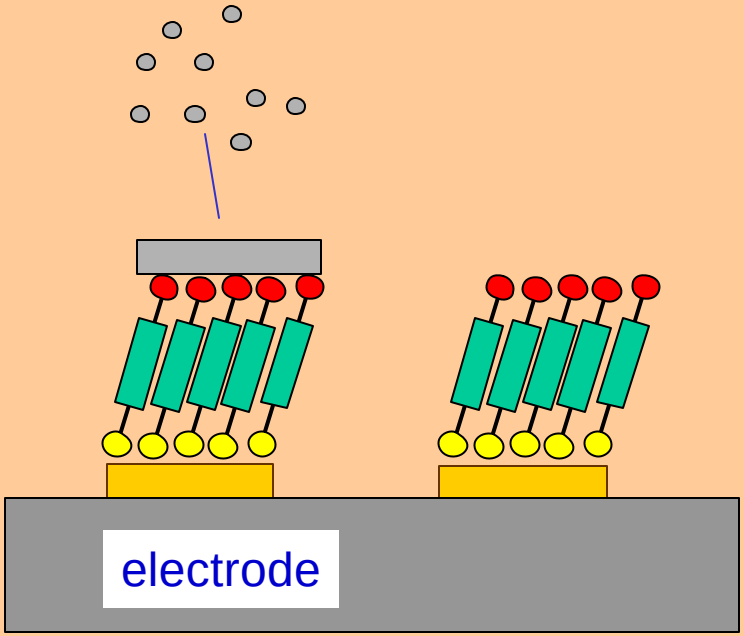
Manufacturability Issues

Planar Devices : Molecular Level Design & Testing Issues

- molecules
- bottom contacts
- self-assembly
  - molecular geometry
  - chemistry
- **matrix effects in molecule switching**
- electron injection states
- **top contact metallization issues**

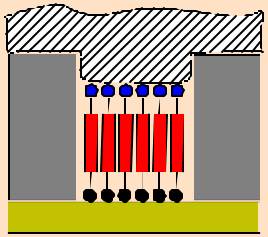
Conclusions and Perspectives

Contact Metallization



Top contacts: the major bottleneck in molecular electronics?

Metallization Issues



Hybrid:
Self-Assembly
+
Traditional Fab

Deposited metal contact

design molecule terminal group for interface control

short

junction

*** junction?**
***degradation?**

host SAM matrix

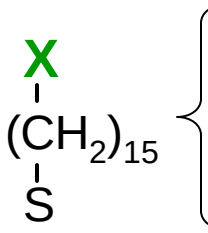
- **metal-molecule chemistry**
- **shorts**

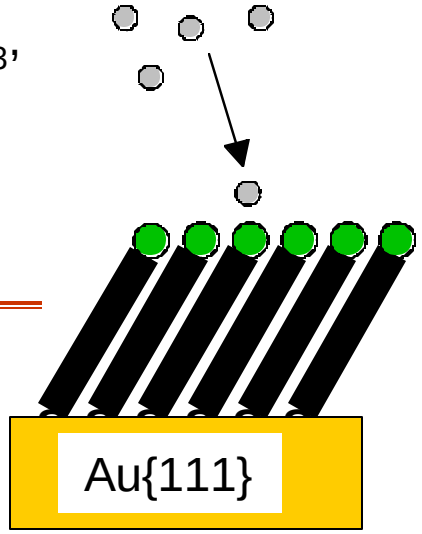
new interlayer

Experimental Approach:

- Multi-technique *in-situ* (real time) analysis: incisive characterization
- SAMs as precision model organic surfaces

X = CH_3, CO_2CH_3, CO_2H, OH, OCH_3, phenyl, NO_2, etc.





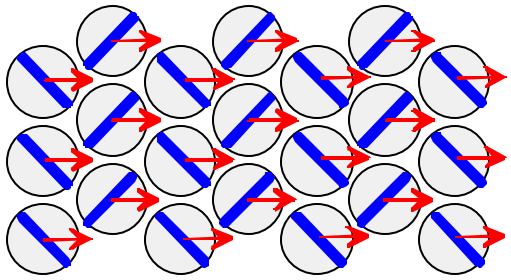
metal - molecule interface

well-defined monolayer

bonding ↔ morphology

electronic states

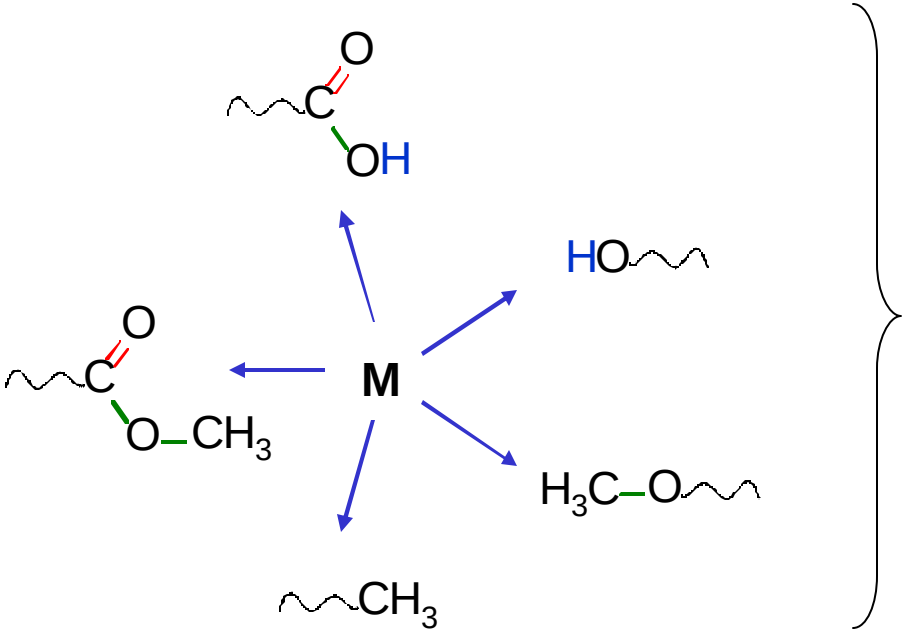
$(\sqrt{3}x\sqrt{3})$,R30° superlattice



IRS
XPS
Spectros. Ellips.
ToF-SIMS
(AFM)

Choosing organic groups with representative chemical features

Metal vapor + Typical O-functional groups



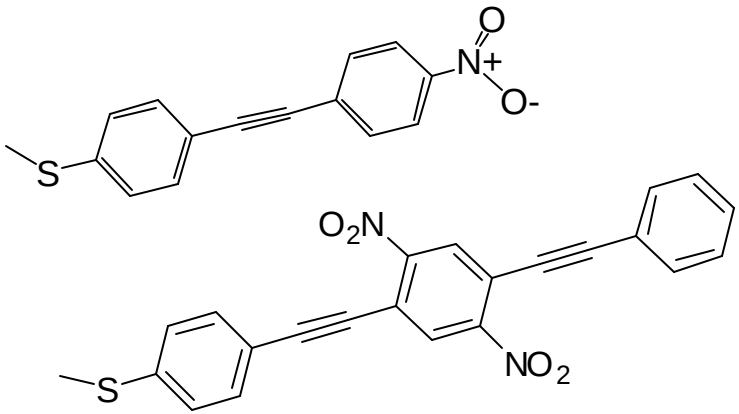
π-bonds

σ-bonds

hydroxylic H

hydrocarbon H

Metal vapor + Aromatic-Conjugated Structures



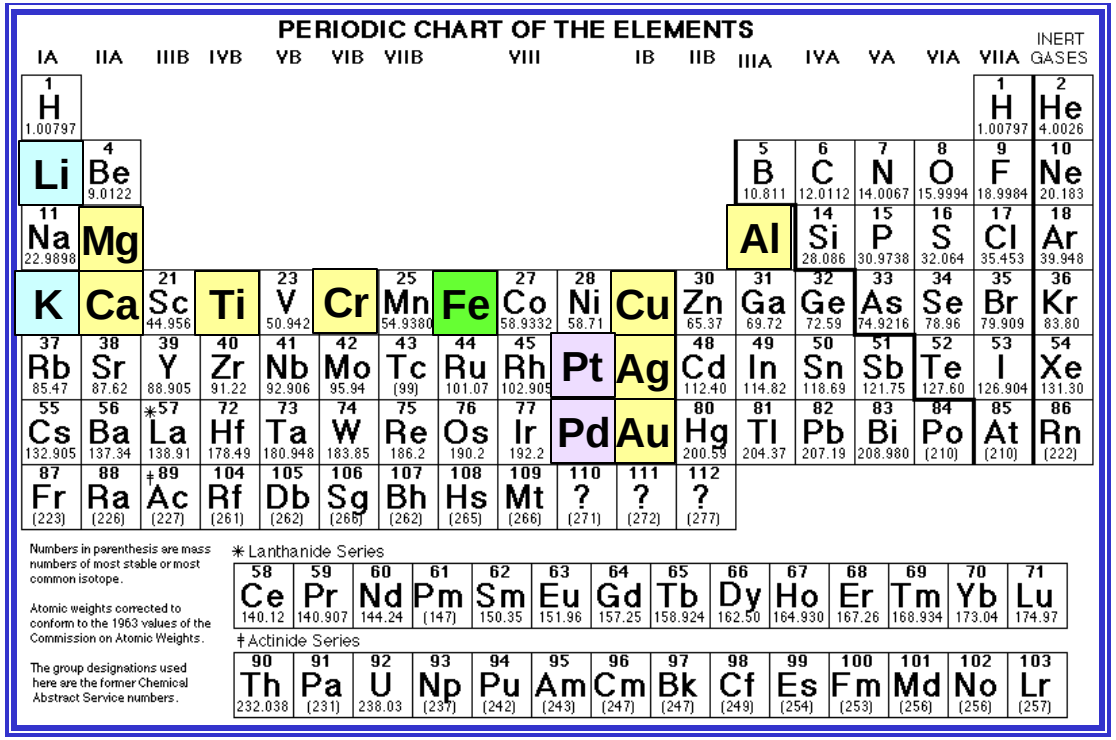
π-bonds

σ-bonds

hetero atoms

aromatic H

Choosing metals and predicting behavior

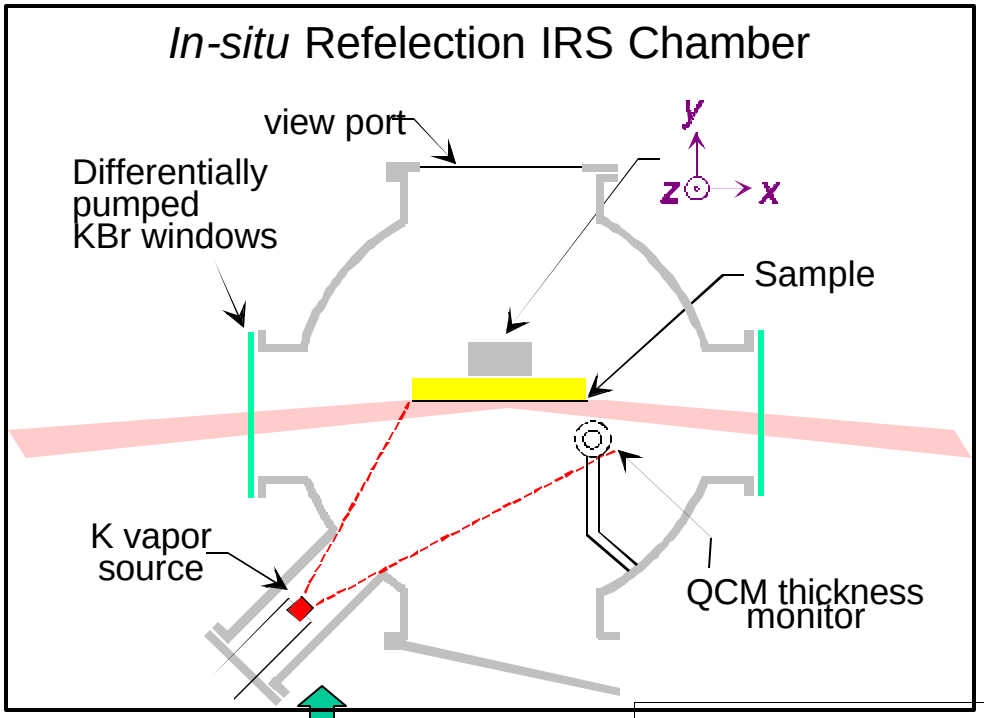


done ✓ In progress

Poor predictions of metal-organic Interfaces from standard chemical knowledge

Standard Oxidation Potentials (V)

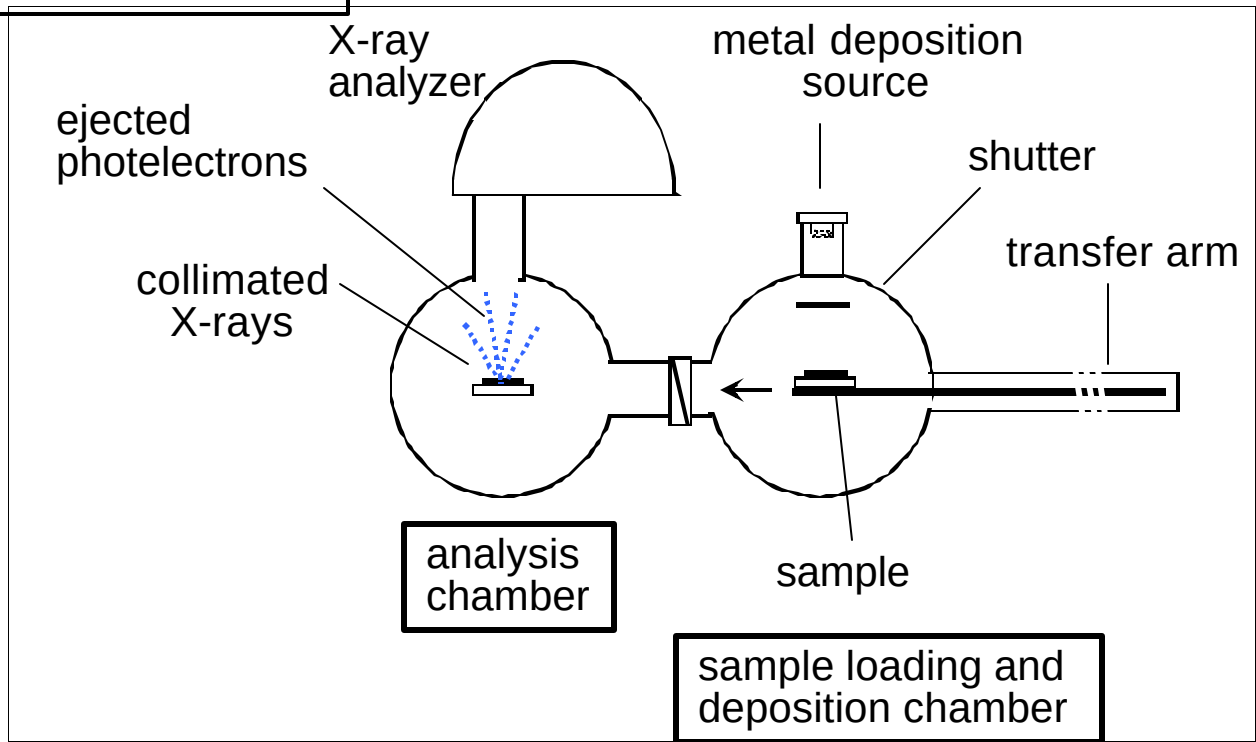
$Li \rightarrow Li^{+}$	3.05
$K \rightarrow K^{+}$	2.93
$Ca \rightarrow Ca^{+2}$	2.87
$Mg \rightarrow Mg^{+2}$	2.37
$Al \rightarrow Al^{+3}$	1.66
$Ti \rightarrow TiO^{+2}$	0.86
$Cr \rightarrow Cr^{+3}$	0.74
$Fe \rightarrow Fe^{+2}$	0.44
$H_2 \rightarrow H^{+}$	0
$Cu \rightarrow Cu^{+2}$	-0.34
$Ag \rightarrow Ag^{+}$	-0.80
$Pd \rightarrow Pd^{+2}$	-0.99
$Pt \rightarrow Pt^{+2}$	-1.20
$Au \rightarrow Au^{+}$	-1.68



Examples of Tools Used For Molecular Surface/ Interface Characterization

In-situ Infrared Spectrometer Analysis System

In-situ X-Ray Photoelectron Spectrometer Analysis System



Al + **X**$(CH_2)_{15}S$-/Au{111} SAM

Example of Results for the case of IRS Analysis

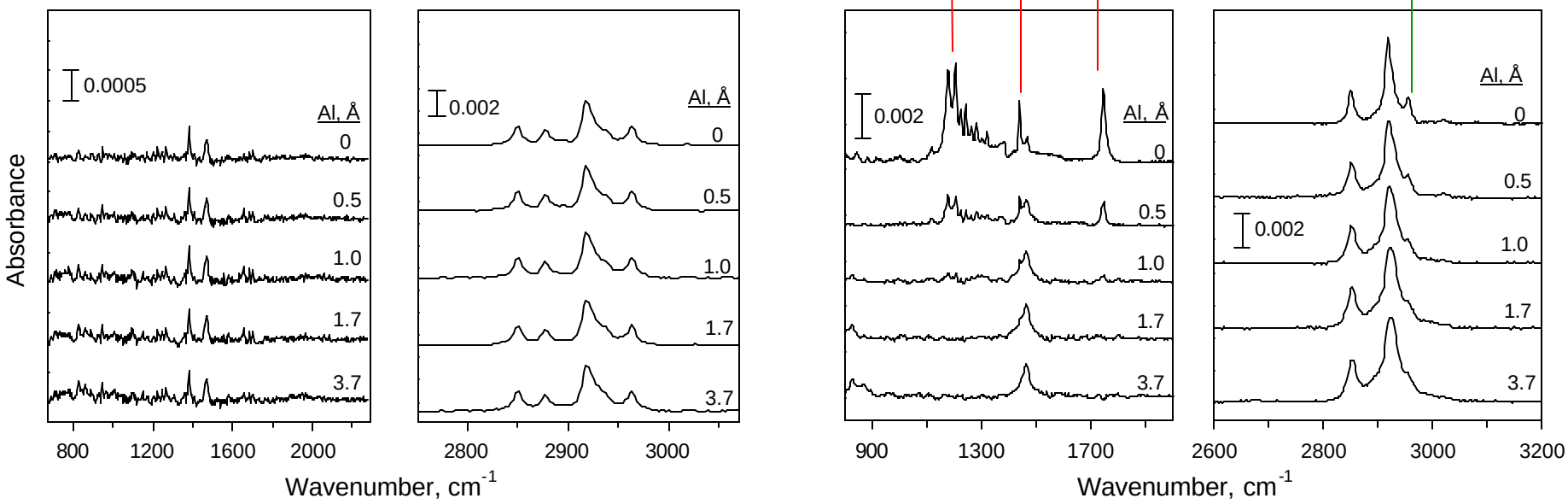
X = CH_3

* no reaction with adsorbate
* chains remain conformationally ordered

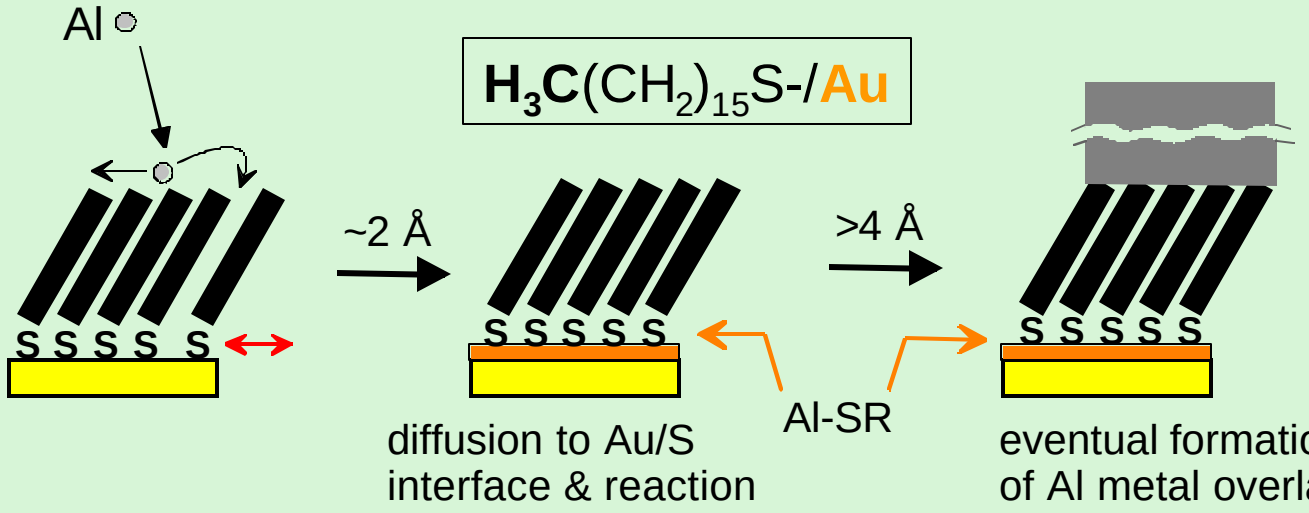
X = CO_2CH_3

* -CO_2CH_3 unit reacted by 0.5 - 1 Å Al (~ 1.0 Al per molecule)
* chains show some conformational disordering

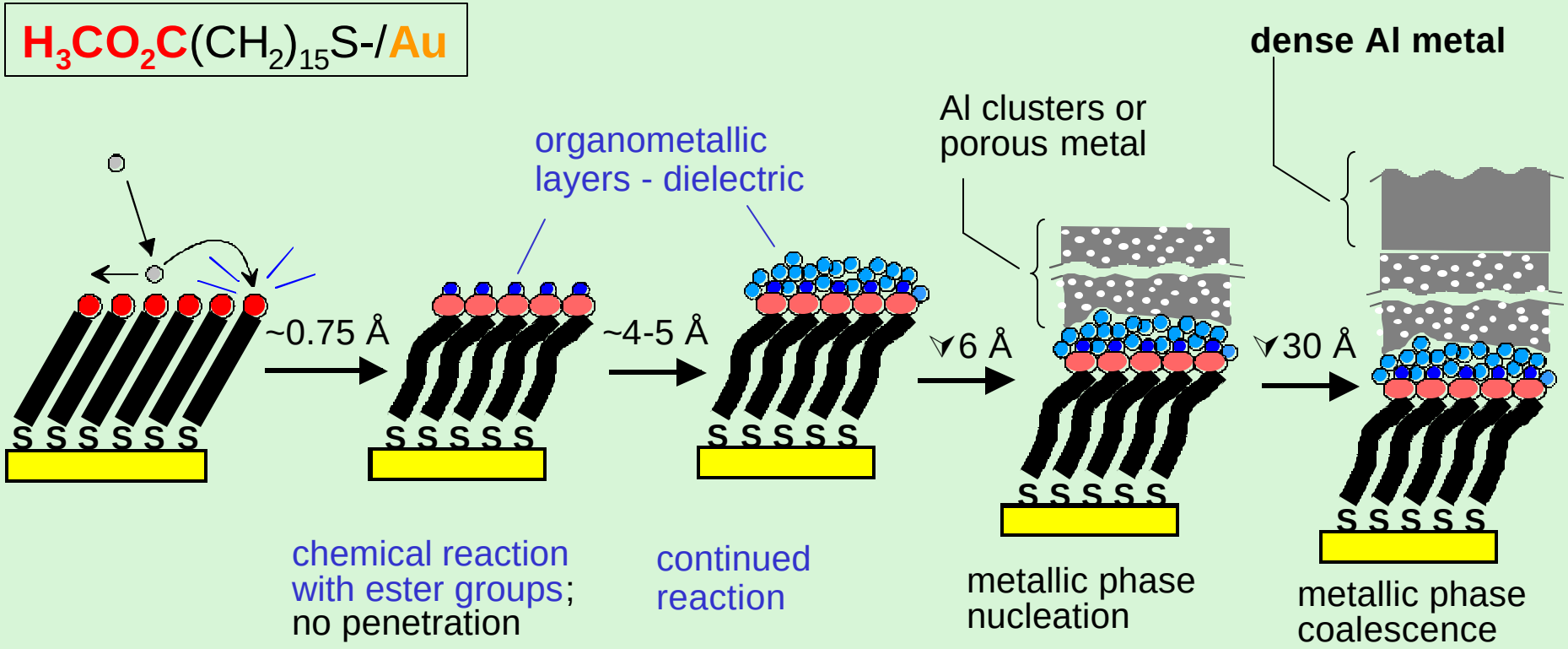
CH_3 in -CO_2CH_3 not lost



Interface Evolution: Al Deposition on -CH_3 & -CO_2CH_3 Terminated SAMs

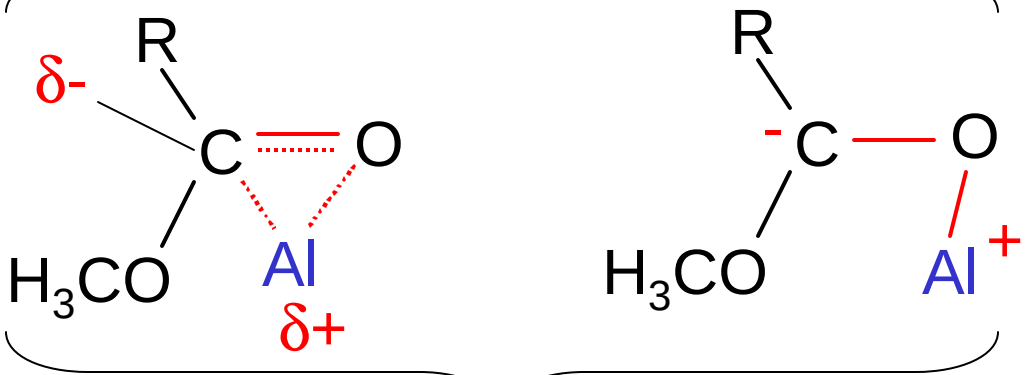


Hooper, Fisher, Konstadinidis, Jung, Nyugen, Opila, Collins, Winograd, Allara, *JACS*, *121*, 8052(1999)



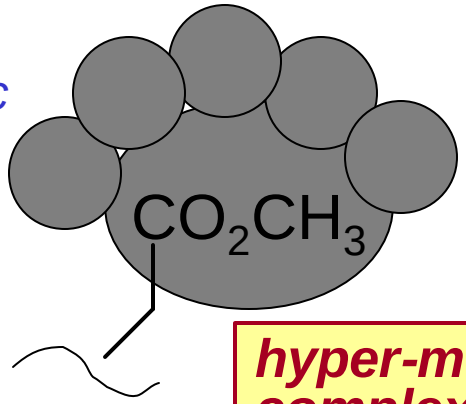
Reactive SAMs Can Exhibit Complex Overlayer Chemistry

1 Al

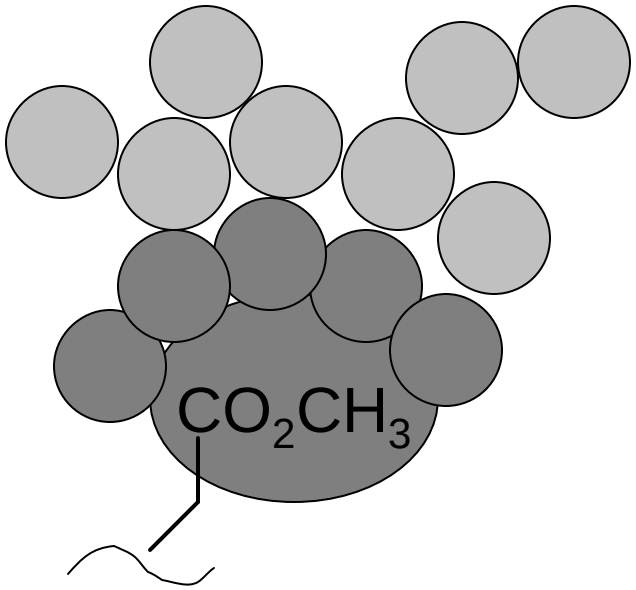


4 Al

nonmetallic phase



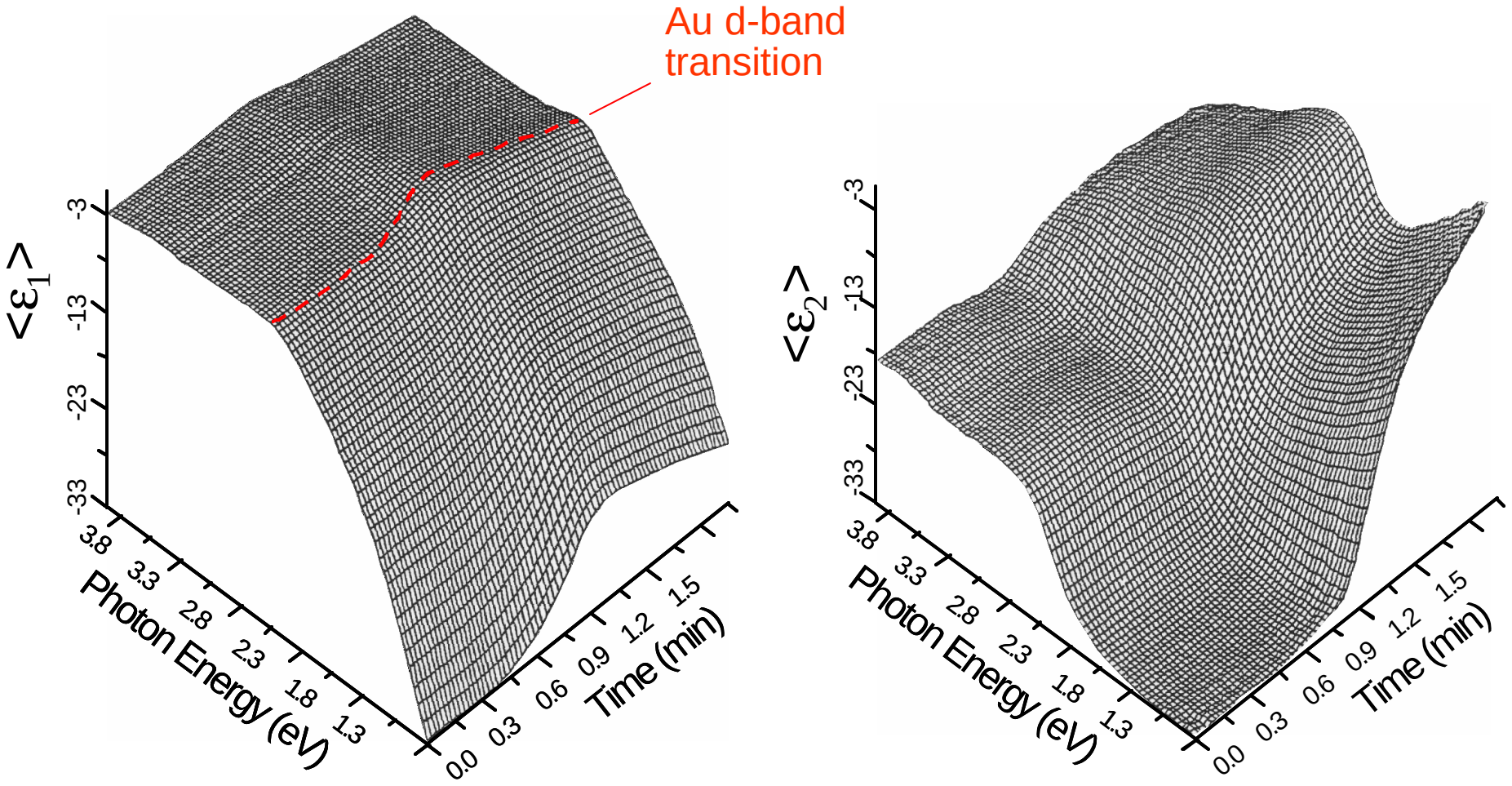
more Al



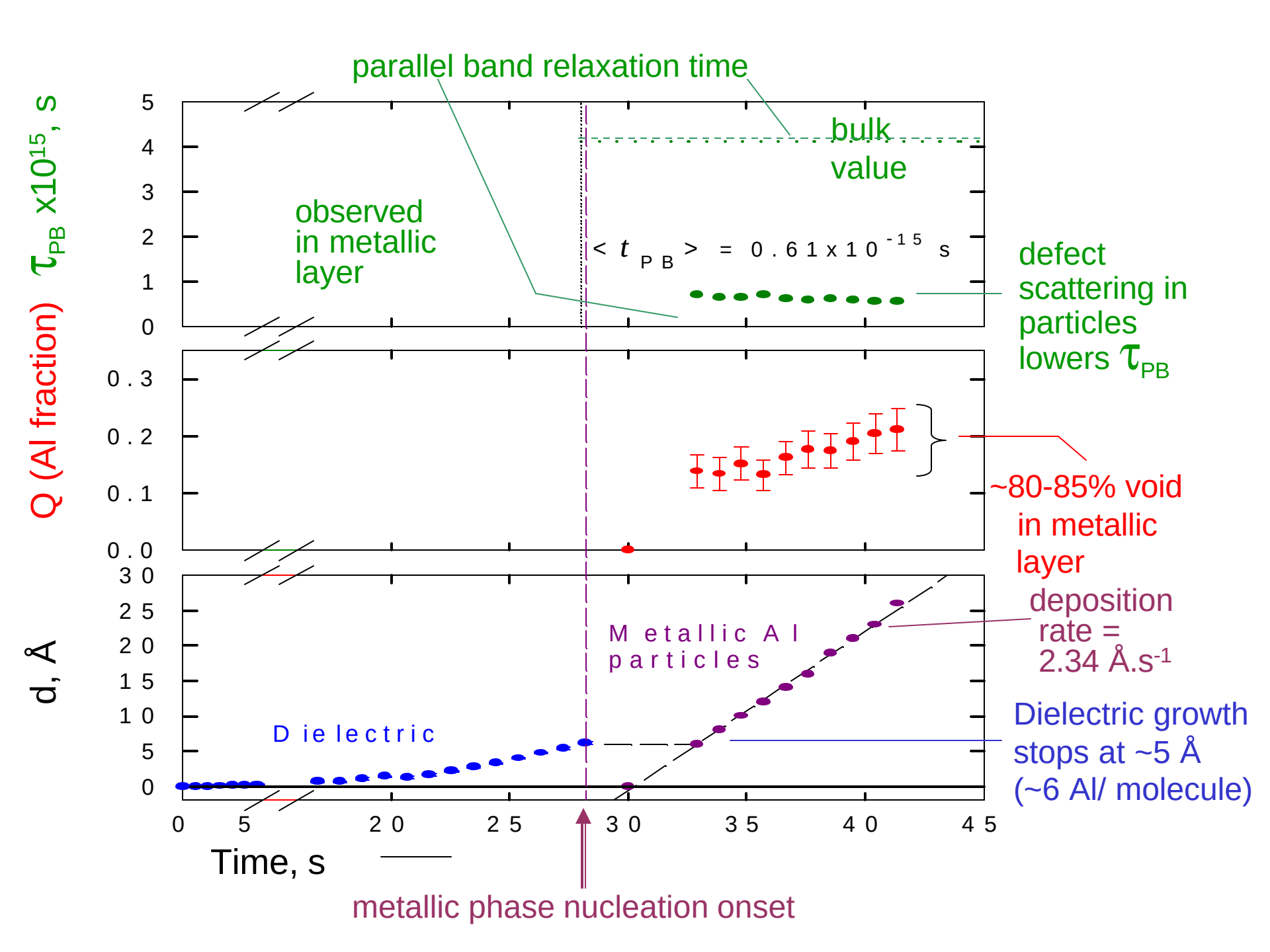
metallic phase nucleation

hyper-metal complex

Spectroscopic Ellipsometry: Psuedo Dielectric Function Spectra



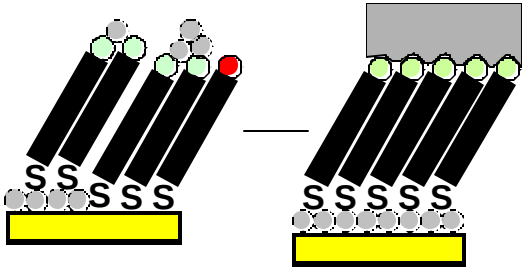
- 100 Ψ,Δ spectra
- 83 data points
- Real time spectra
  - data collection + transfer in ~ 1 s


parallel band relaxation time
bulk value
observed in metallic layer
< t PB > = 0.61 x 10 -15 s
defect scattering in particles lowers τPB
~80-85% void in metallic layer
deposition rate = 2.34 Å.s-1
Dielectric growth stops at ~5 Å (~6 Al/ molecule)
Metallic Al particles
Dielectric
metallic phase nucleation onset
Time, s
Q (Al fraction)
τPB x10^15, s
d, Å
0
1
2
3
4
5
0.0
0.1
0.2
0.3
0
5
10
15
20
25
30
0
5
20
25
30
35
40
45

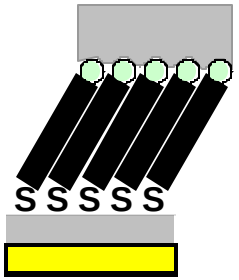
Unreactive thiolate SAMs Allow Metal Atom Penetration

Al. Cu, Ag, Au + $AuS(CH_2)_{16}OCH_3$

- **Al**
  - **penetration stops at 1 adlayer at Au/S interface**
  - ***weak solvation* by $-OCH_3$**
  - **overlayer film**

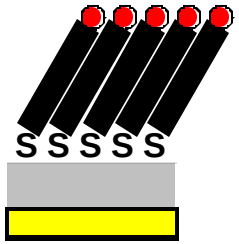


- **Cu, Ag**
  - **continuous penetration**
  - **weak *solvation* by $-OCH_3$**
  - **overlayer film**



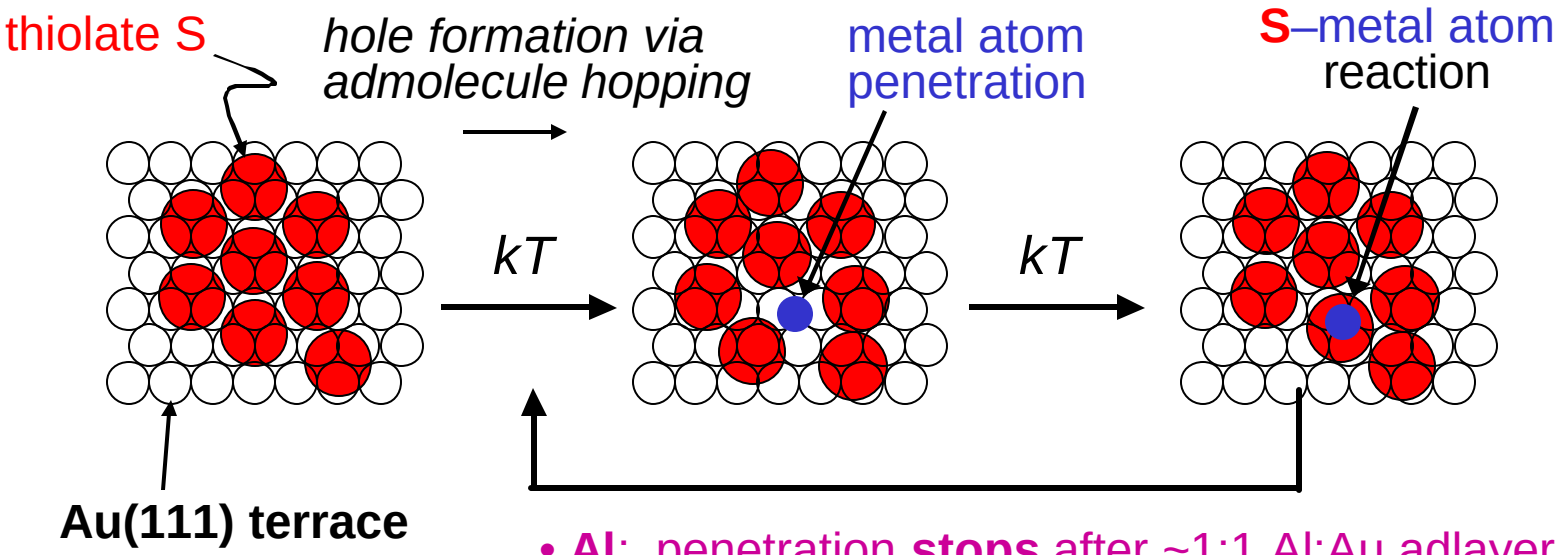
- **Au**
  - **continuous penetration**
  - **no solvation by $-OCH_3$**
  - **no overlayer film**

(*floating SAM*)

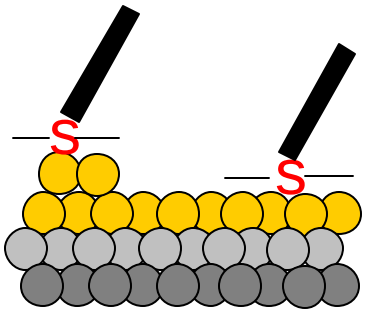


underlying mechanism????

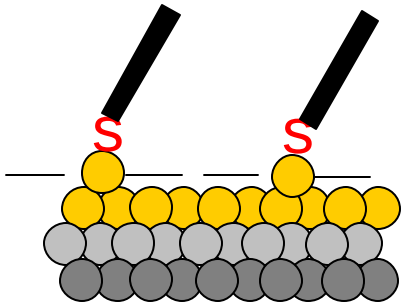
Penetration Depends on Metal-Thiolate Species Diffusion



- **Al**: penetration **stops** after ~1:1 Al:Au adlayer
- **Cu, Ag**: penetration **continues** at all coverages
- **Au only penetrates (floating SAM)**



S atom diffusion

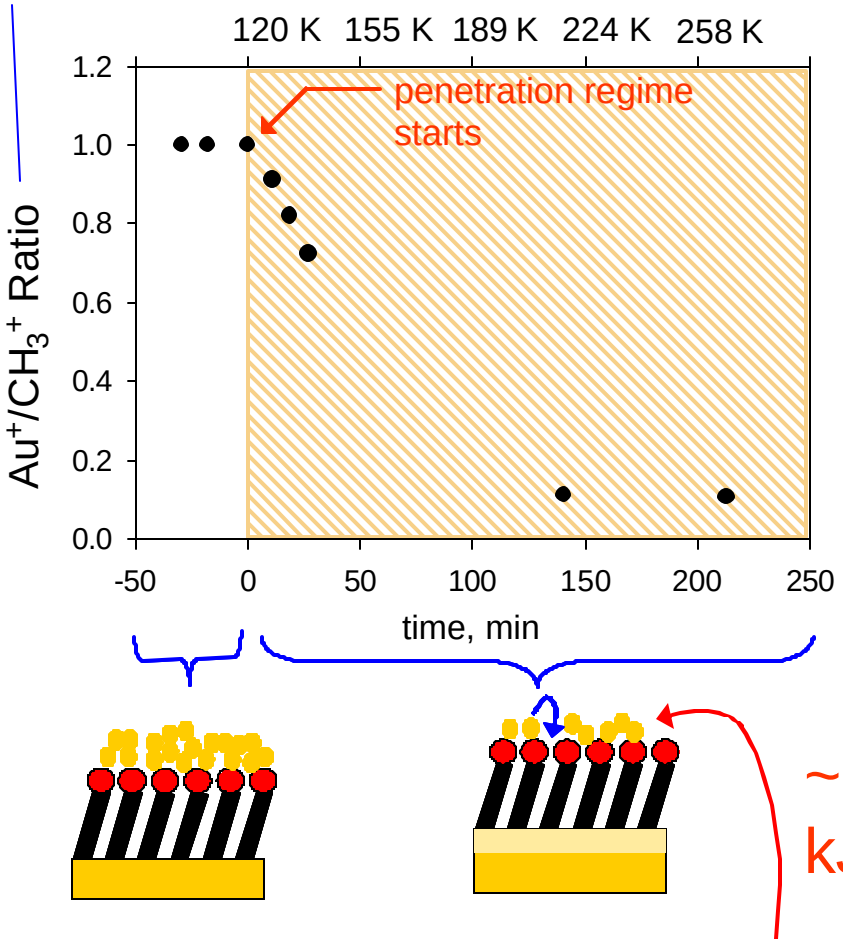


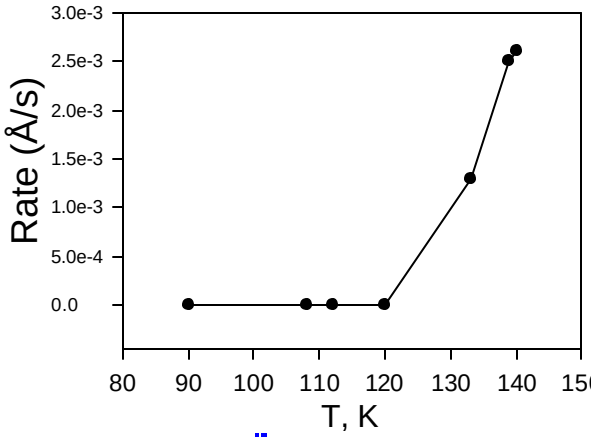
metal-S diffusion

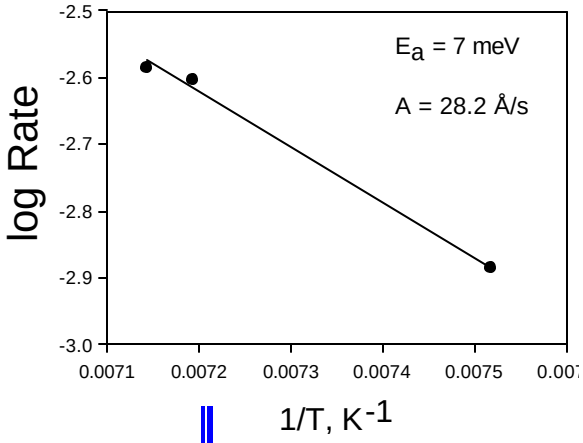
DFT calculations of thermochemistry supports metal-thiolate admolecule diffusion

ToF-SIMS Measurement of T Dependence of Au Penetration Rate In a H_3CO-Terminated C16S- SAM/Au{111}

Au+/CH_3 signals decrease as Au overlayer decreases

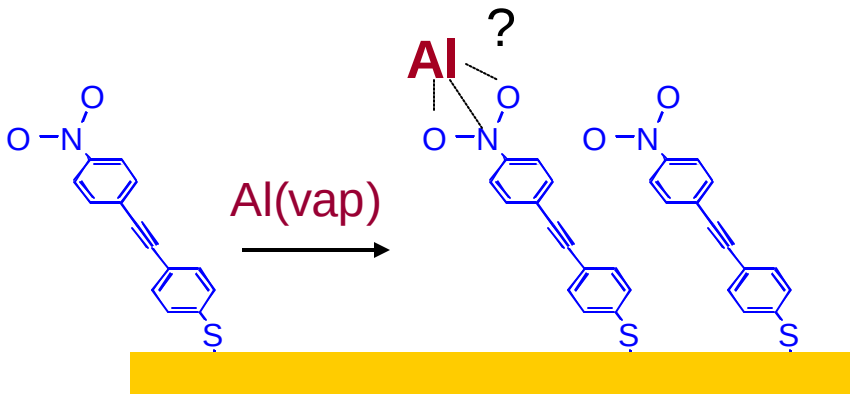




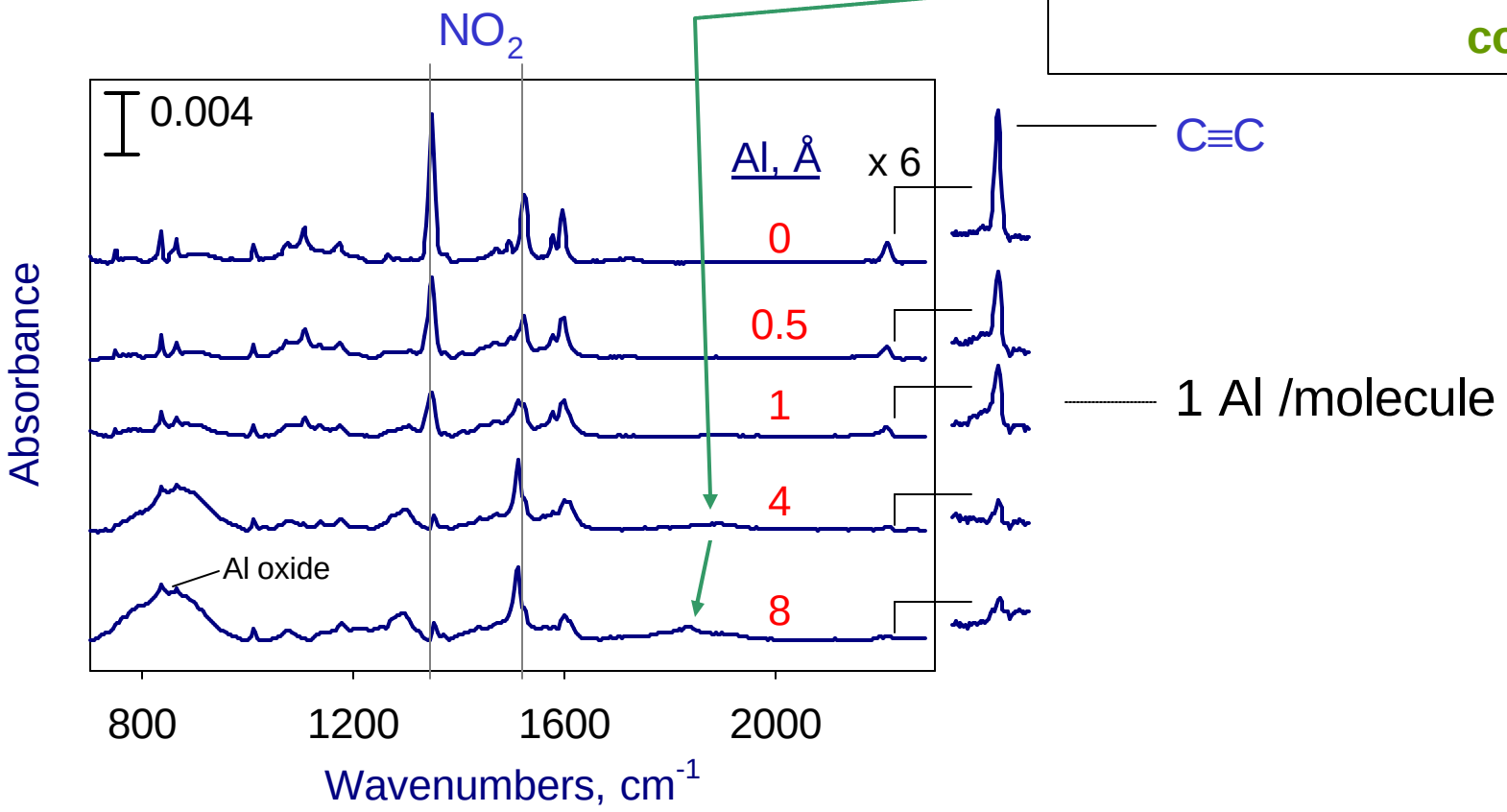


$$\log(\text{rate}) = A \cdot \exp(-E^*_{\text{penetration}}/RT)$$

(Haynie, Uppili, Allara, Winograd, in preparation)



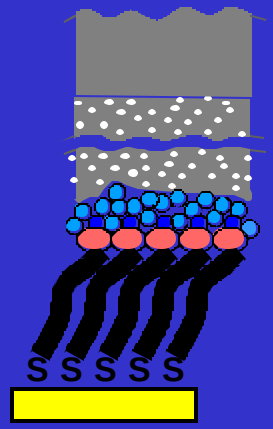
- Al perturbs NO_2 but does not consume
- C°C diminishes but stays sharp
- Formation of Al---C ° C complex?



Top Contact Metallization ----Conclusions

- Metal-organic contacts --- unexpected complexities

- Effects on device behavior remain uncorrelated



- Extraordinarily fine control of the metal-molecule interface is possible via fine tuning of chemistry and process dynamics

Rationale for A Molecular Electronics Technology

I-V Behavior of Molecules

Potential Applications and Device Types

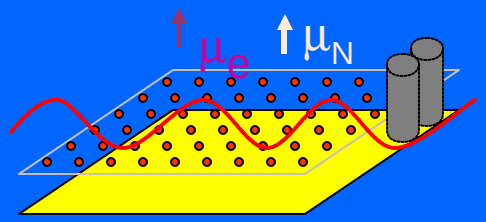
Manufacturability Issues

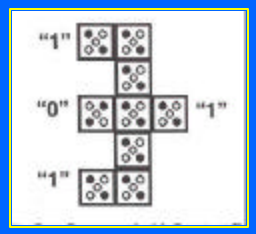
Selected Issues in Single Molecule Devices

Planar Devices: Molecular Level Design & Testing Issues

Conclusions and Perspectives

Molecular Q-Dot Quantum Computers





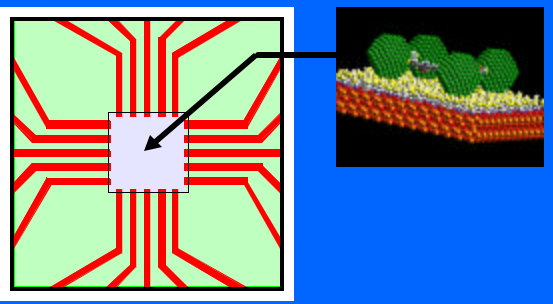
Molecular Q-Dot Cellular Automata Computers

smaller

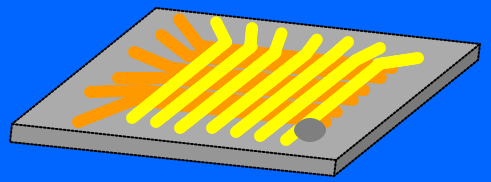
Molecular Electronics

new capabilites

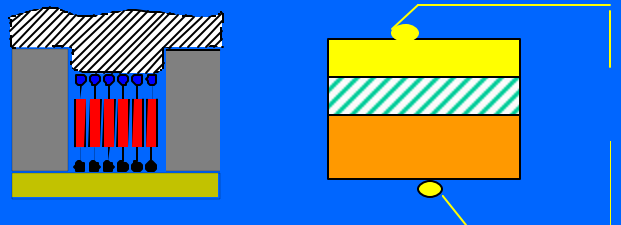
Molecule-*n*-Particle Logic Blocks



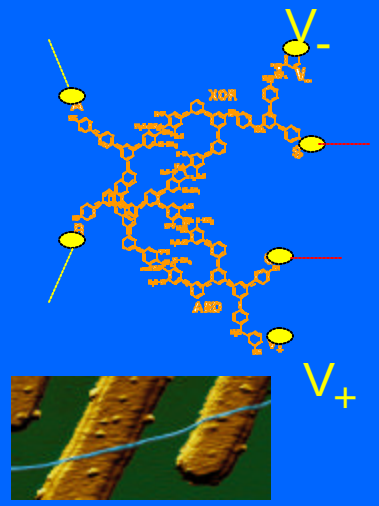
Crossbar Devices
- M3
- *nano*-mechanical



Metal/Molecule/Metal (planar M3) Switching & Memory Components



Single Molecule Logic Devices
- nanotubes
- large molecules



Transitioning: Lab Bench to Manufacturing

- 10-100 nm size
- lab bench processing

→

- standard lithography scale
- high yield throughput
- high reliability
- high throughput testing diagnostics

Major Apparent Current Challenges

- **scale up of device area**
  - **minimize shorts**
  - **maximize contact stability**

→

- **Top Metallization**
  - **metal**
  - **deposition method**

↓

- **Molecule Deposition**
  - **optimum molecule for desired device function**
  - **active layer composition (matrix effects)**
  - **solvents, etc. (dense films)**
  - **post-deposition cleaning (clean top contact surface)**
  - **thermal / chemical stability for post-deposition processing**

- **Parallel with Si-based electronics:**
  step changes often linked to *laborious* materials/chemistry developments

- Surface Characterization/Spectroscopy
- Molecular self-organization
- Organometallic chemistry
- Molecular Surface Science
- Nanofabrication