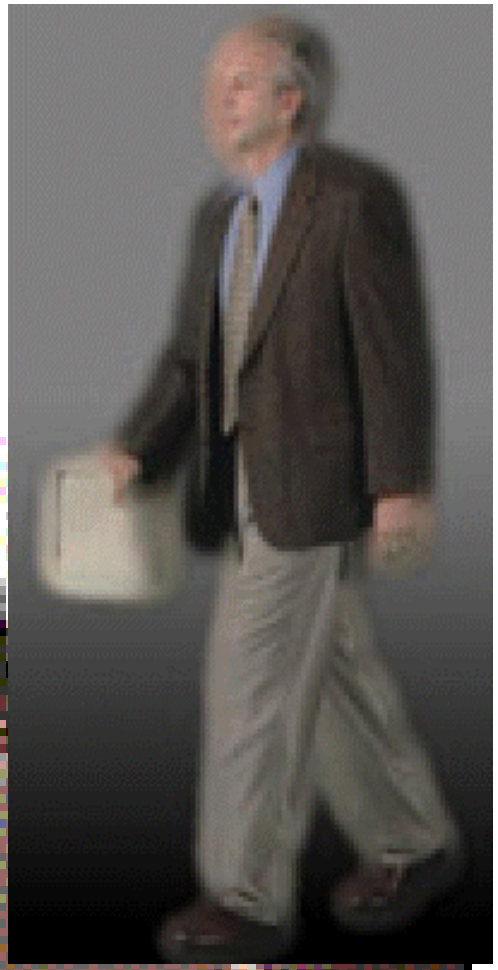
UC Riverside

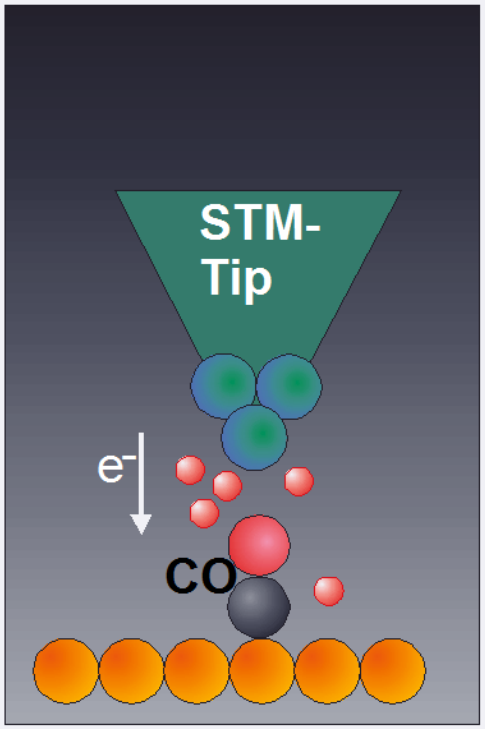
Dynamics at the Single-Molecule Scale

Ludwig Bartels

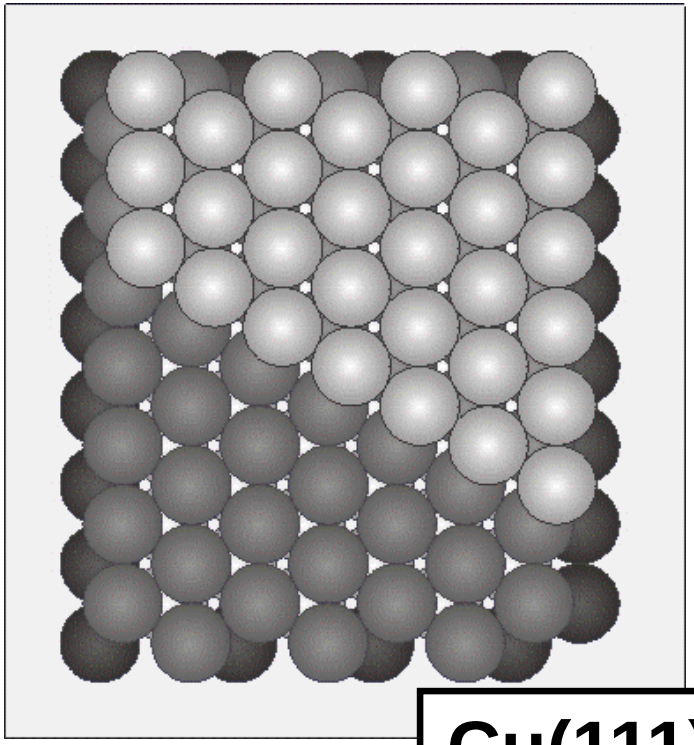
- Introduction
- Dynamics of Organic-Metal Linkers
  - Dynamics of Benzenethiol on Cu(111)
- Dynamics-Based Molecular Functionality
  - Walking Molecules and Molecule Carriers
- Acknowledgements



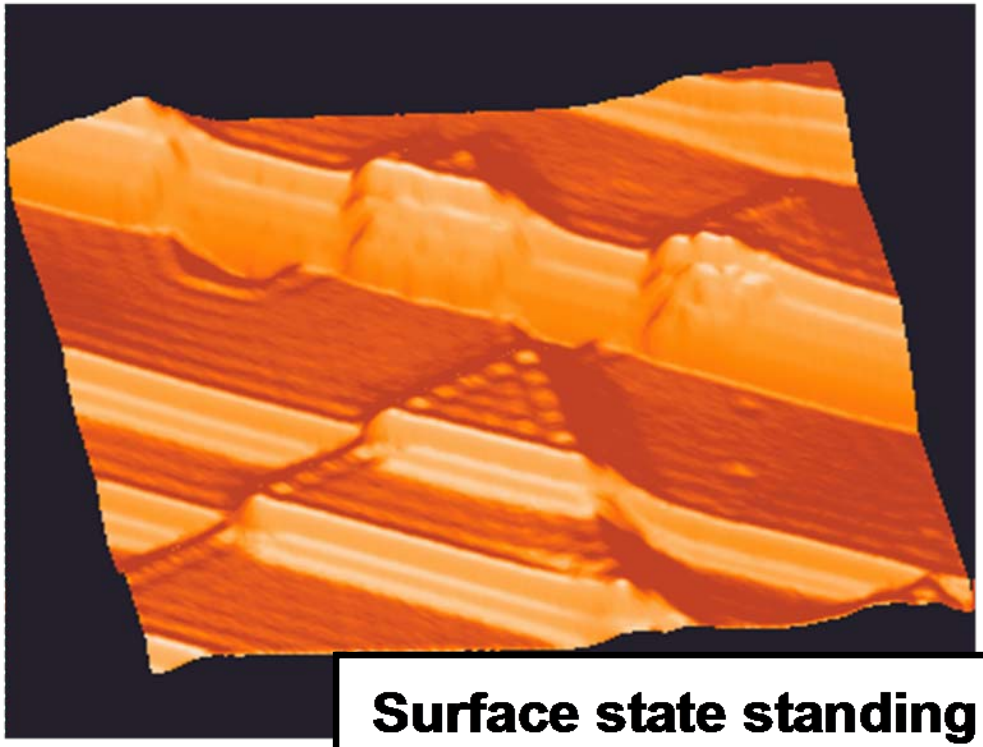
Bergmann Symposium, Dresden, Nov. 08



Field: 0-5V/nm
Current Density: 0-10^8 A/cm²
Distance: 7Å
Tip Speed: 0-10μm/s
Time Resolution: 10μs-Days
Spatial Resolution: 1pm

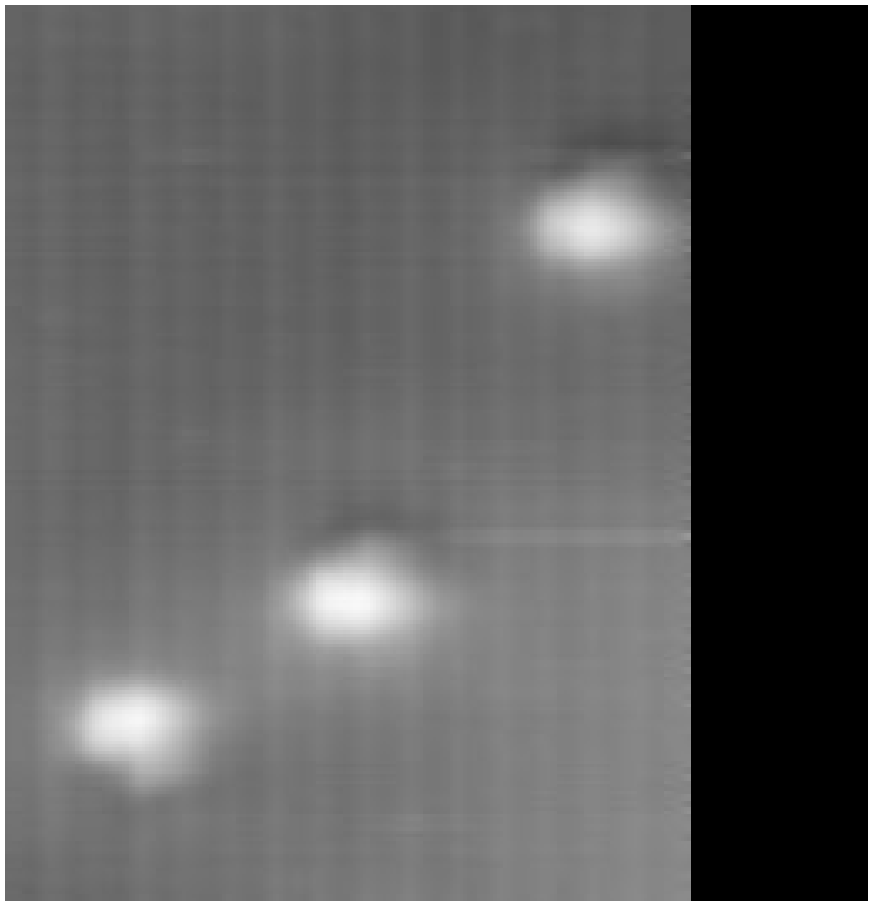


Cu(111)

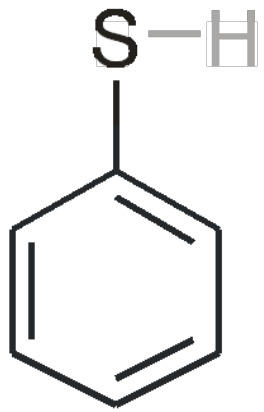


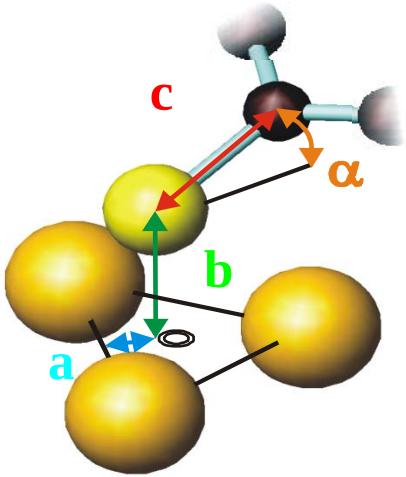
Surface state standing waves oscillations

Benzenethiolate (after H Abstraction)



T = 59 K, 40 sec/frame

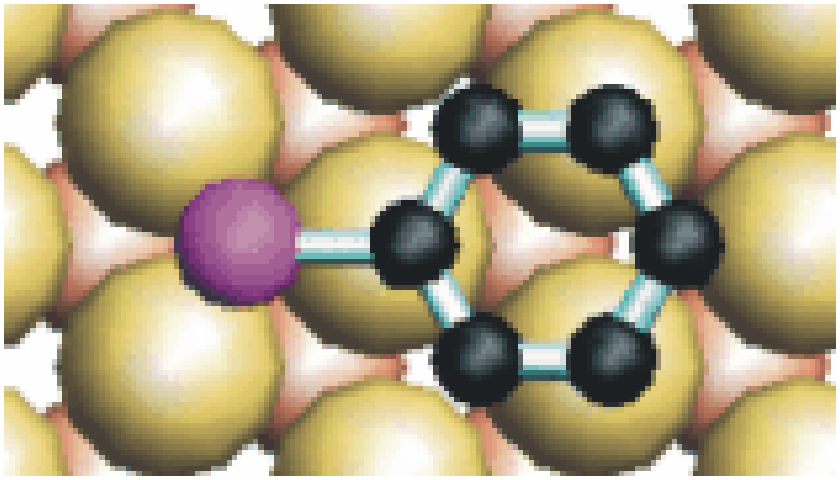


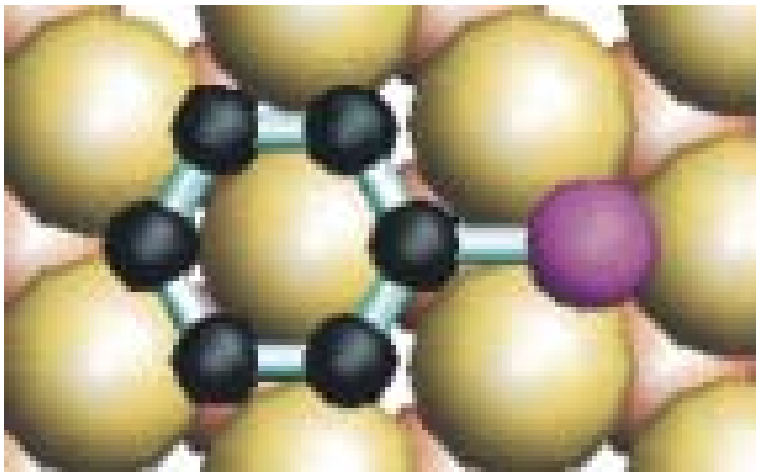


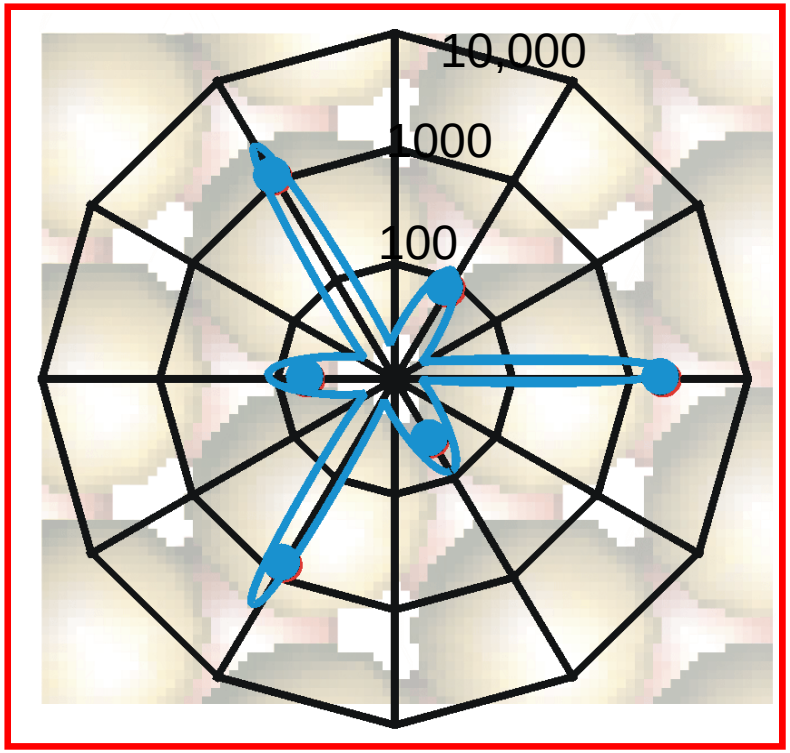
α =25°
a =0.59Å
b =1.97Å
c =1.80Å

Wong et al, JACS **126**, 7762 (2004), APL

Surface Configuration

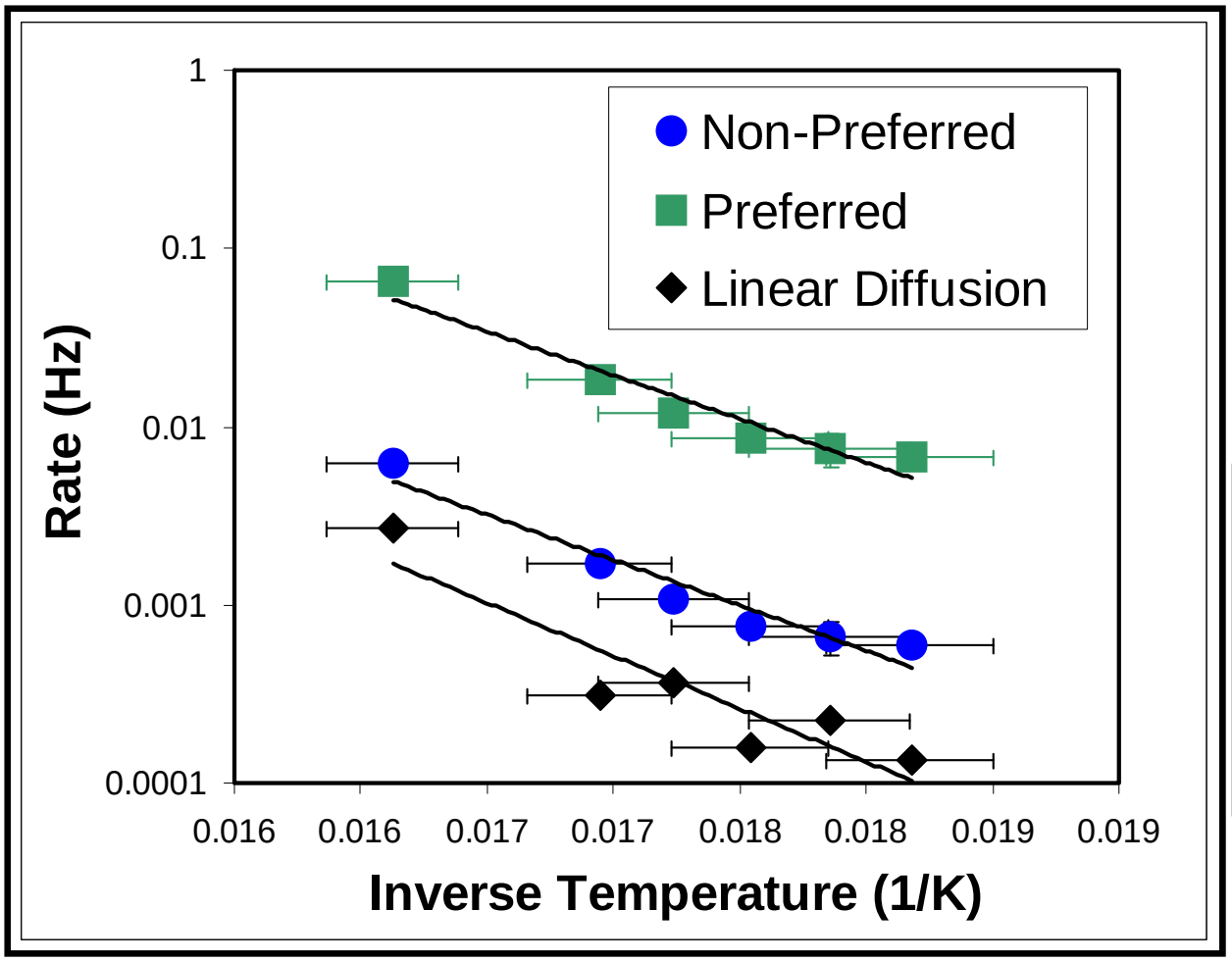






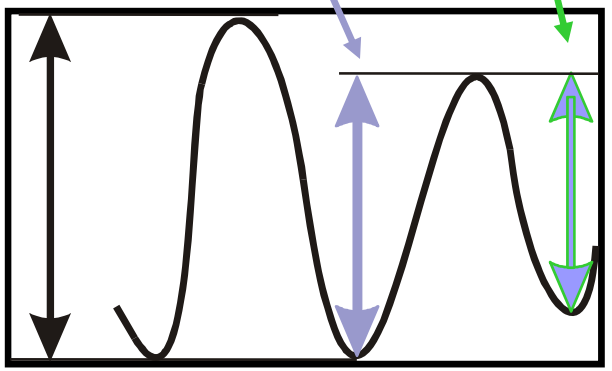
Radial axis in logarithmic scale

Potential Barriers



Preferred Rotation
0.12 eV

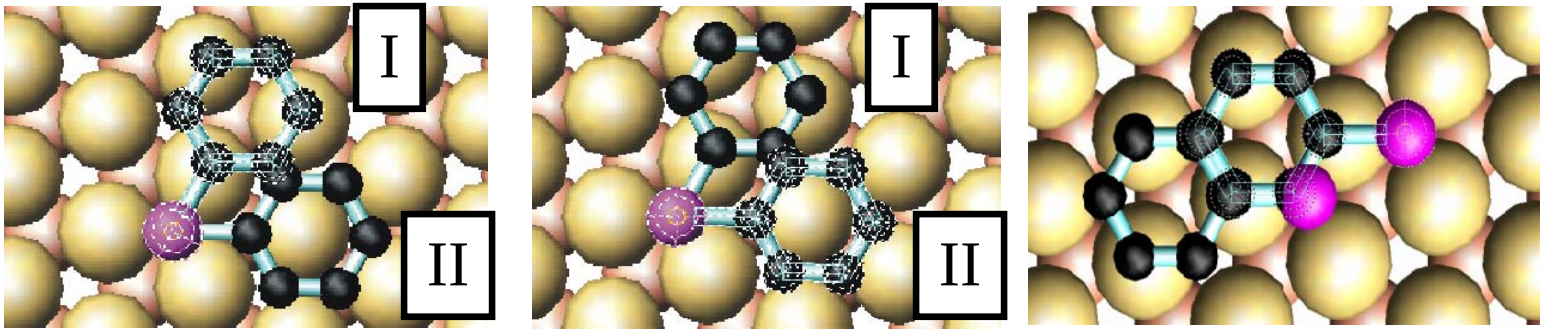
Non-Preferred
Rotation
0.13 eV

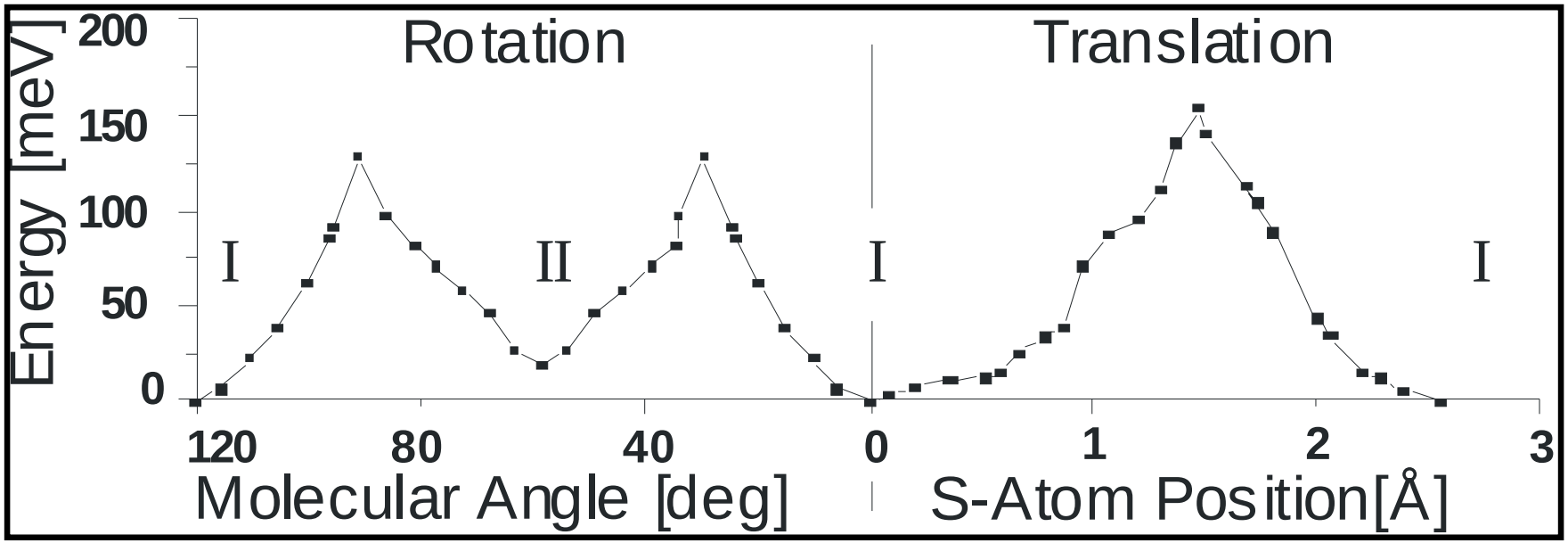


Linear Diffusion
0.15 eV

Prefactor ~ 10^8 Hz

DFT Calculations



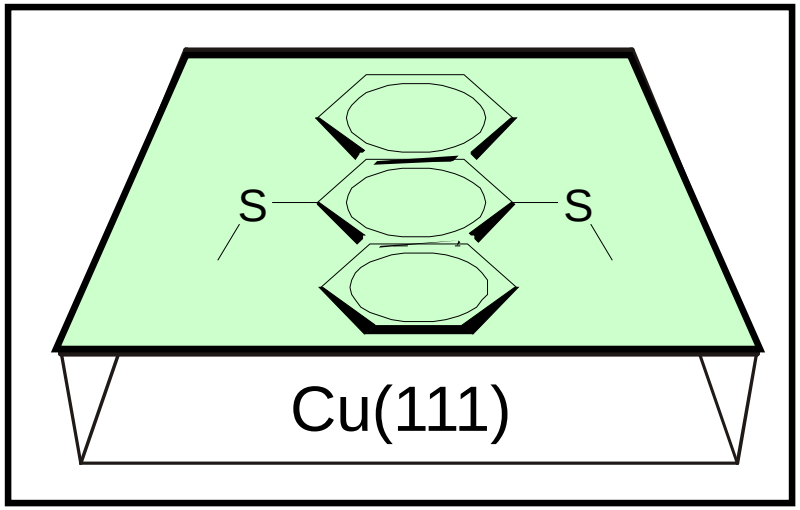


APL **88**, 183106 (2006)

With T.S. Rahman of UCF

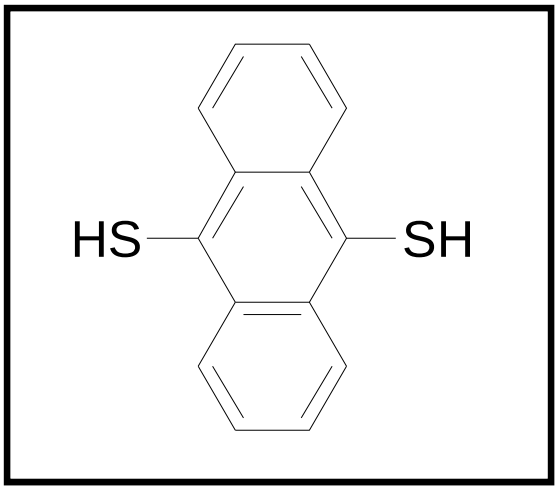
Benzenethiol rotates.

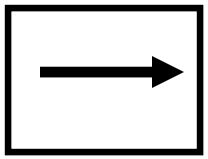
Can a second substrate anchor prevent rotation ?

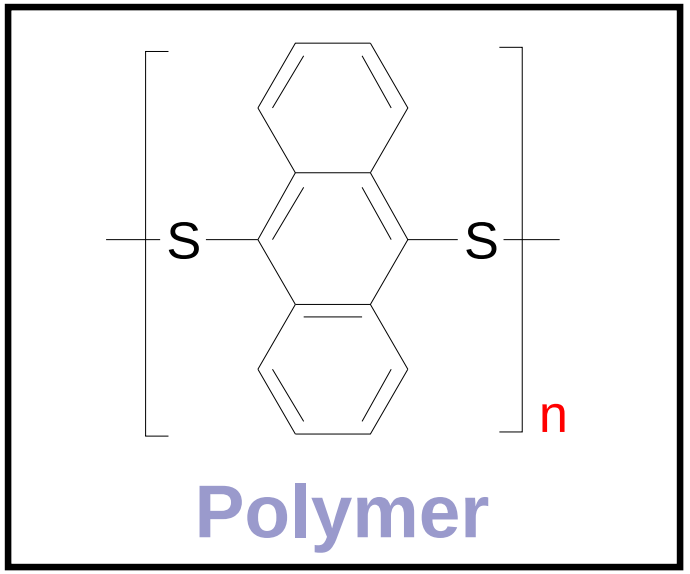


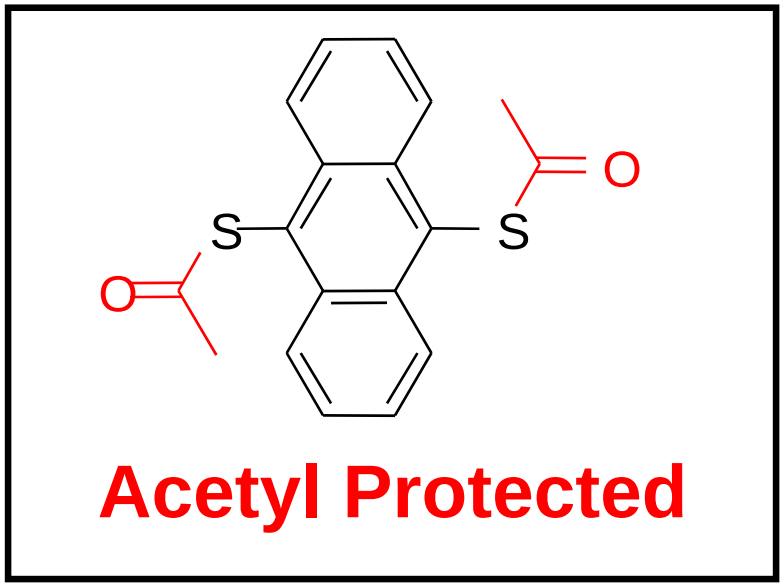
Protection of Thiols

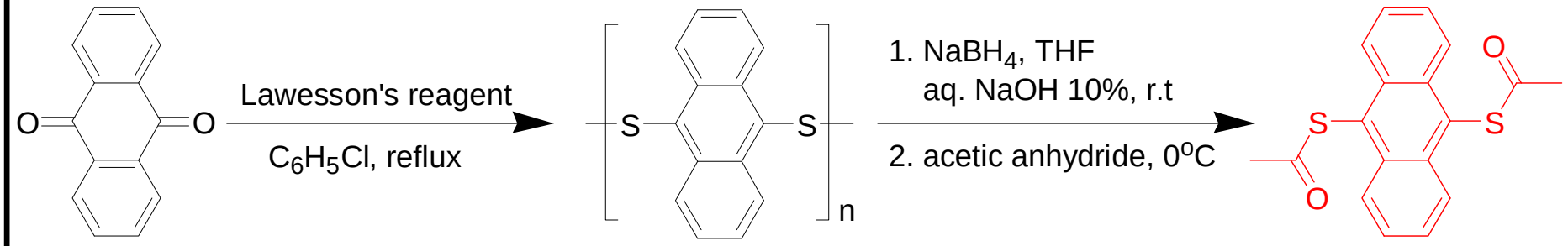
(Thermal) Deposition

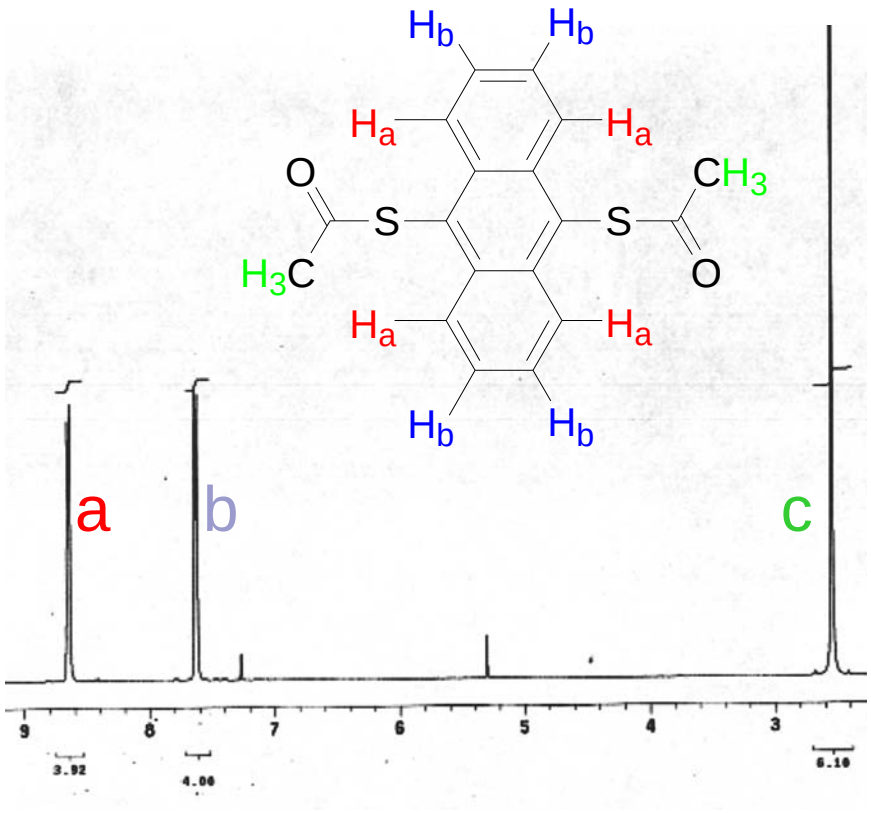


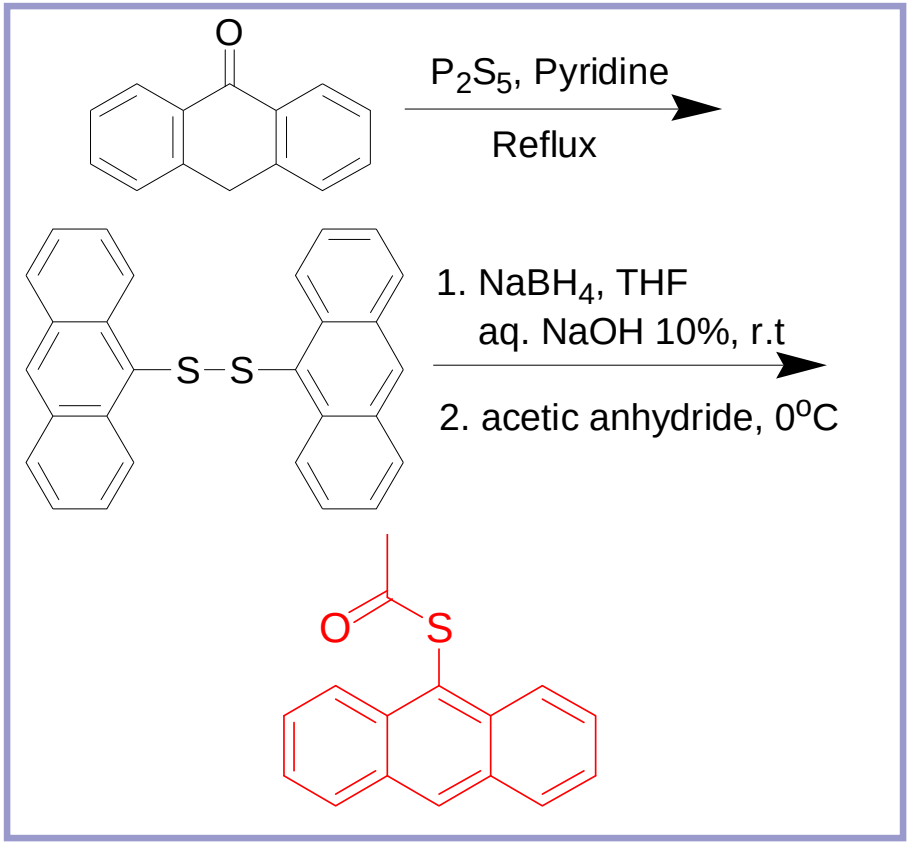




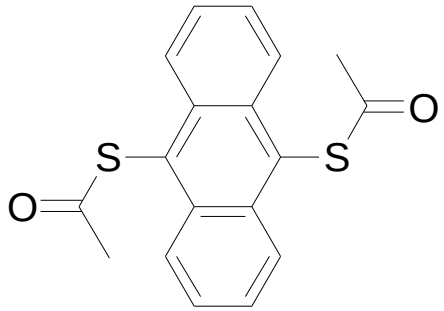



Lawesson's reagent
C_6H_5Cl, reflux
1. $NaBH_4$, THF
aq. NaOH 10%, r.t
2. acetic anhydride, 0°C
n


H_b
H_a
CH_3
H_3C
a
b
c


P_2S_5, Pyridine
Reflux
1. $NaBH_4$, THF
aq. NaOH 10%, r.t
2. acetic anhydride, 0°C

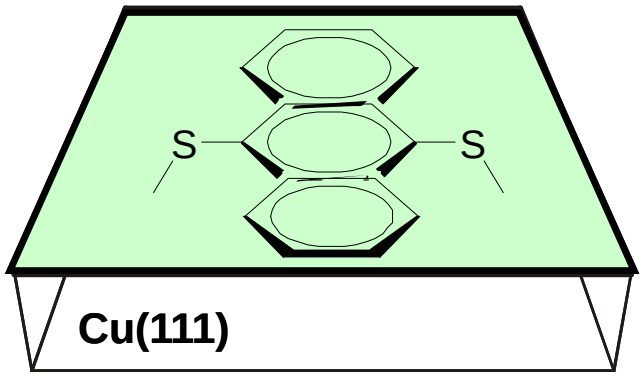
9,10-dithioanthracene



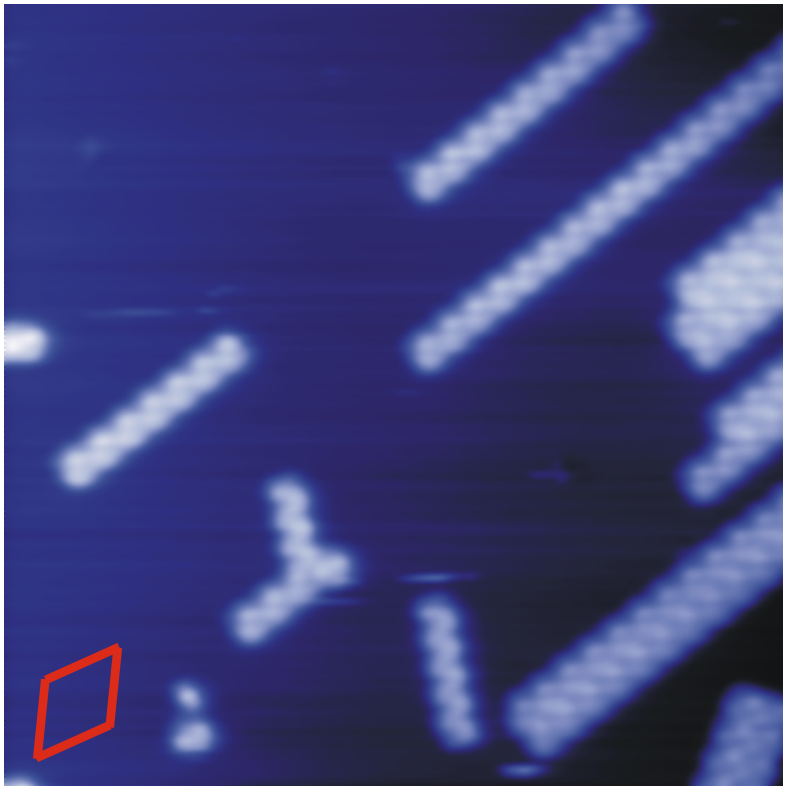
Acetyl protected

Deposition

Annealing



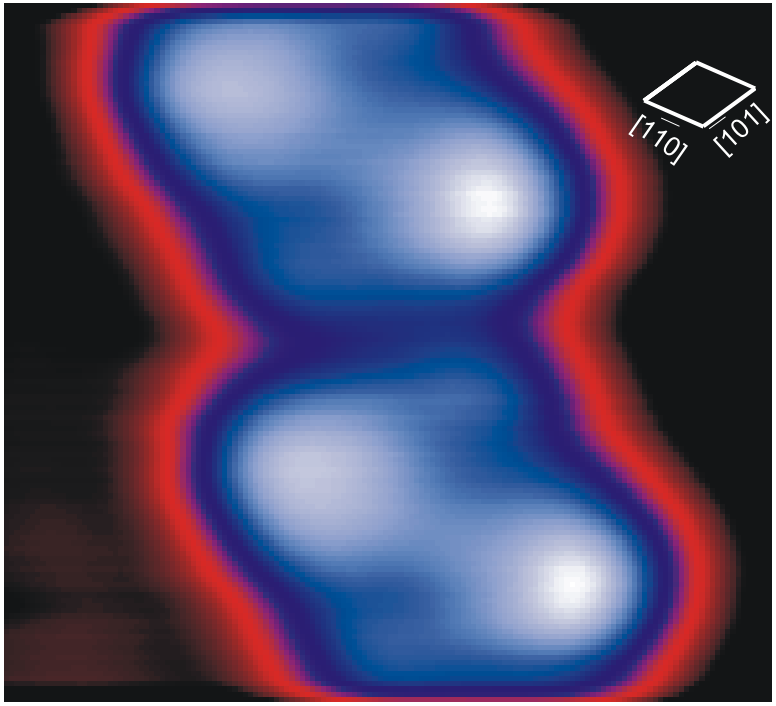
Unprotected

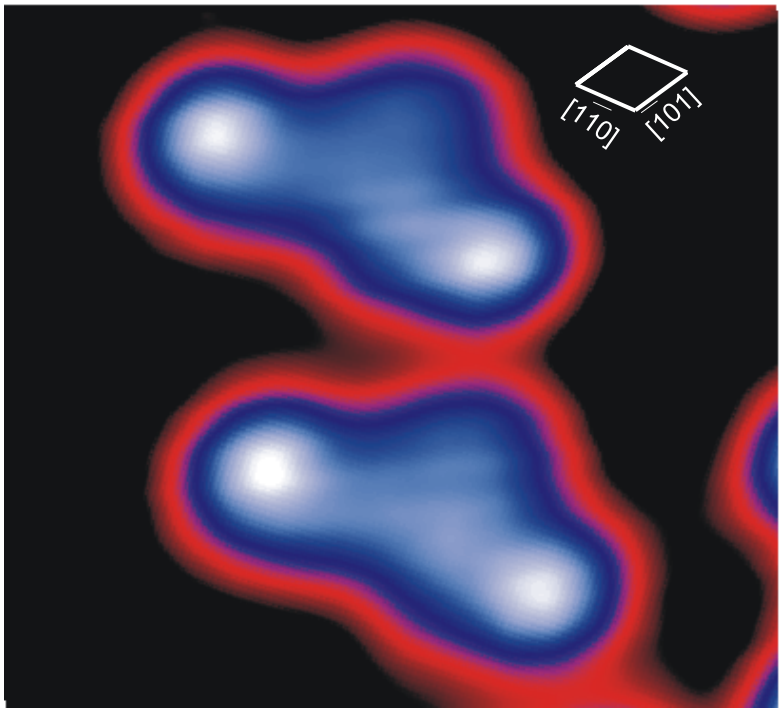


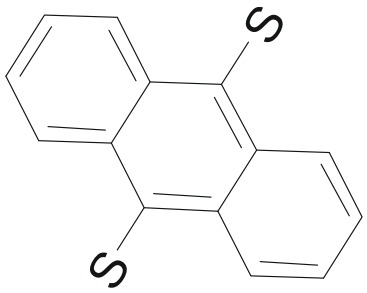
U=-1.7V, I=110pA, 230x230Å, T=80K

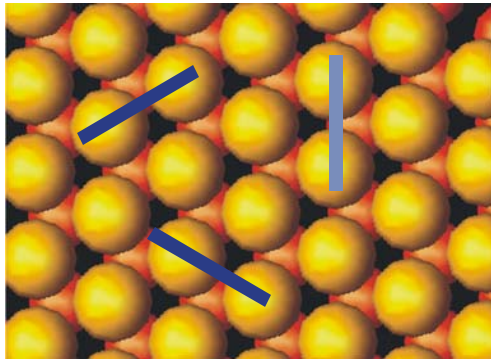
Molecular Rows

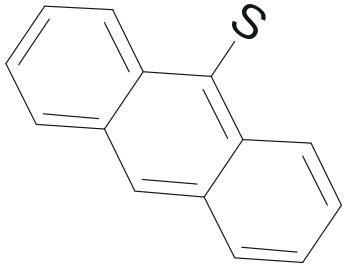
Adsorption Geometry



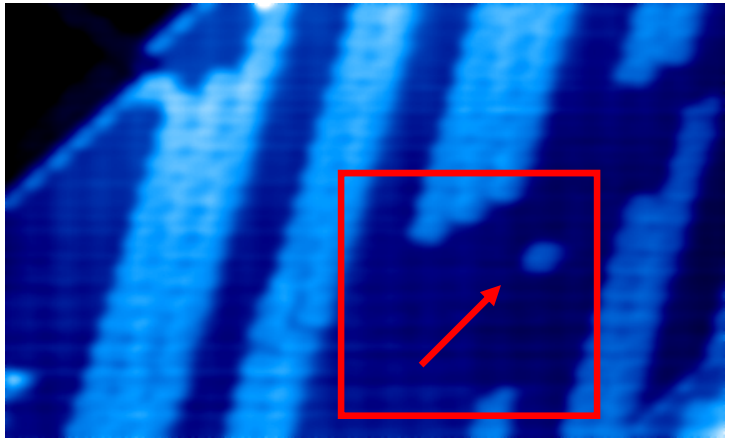




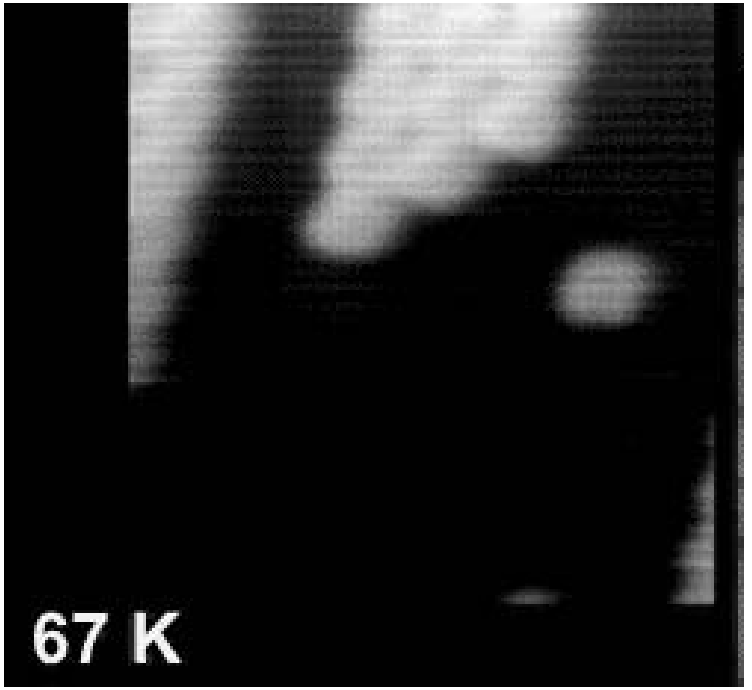




Aromatic Moiety Parallel to Substrate High Symmetry Axes

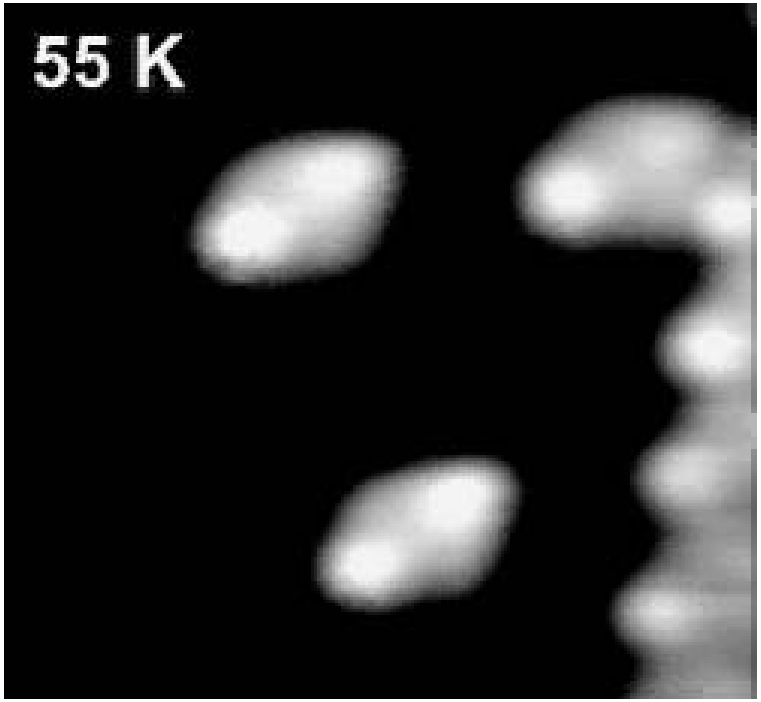


U=-2.0V, I=56pA, 237x143Å, T=67K



U=-2.0V, I=56pA, 81x81Å, T=67K,
Scan rate = 10.9sec per image frame

1D Diffusion on 6fold Symmetric Substrate

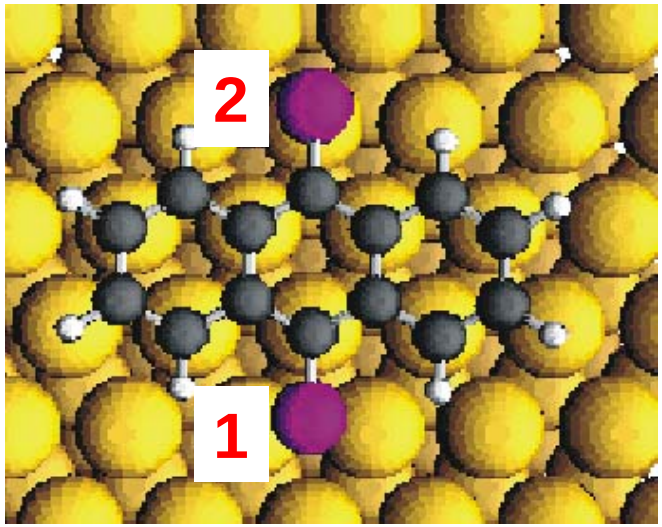


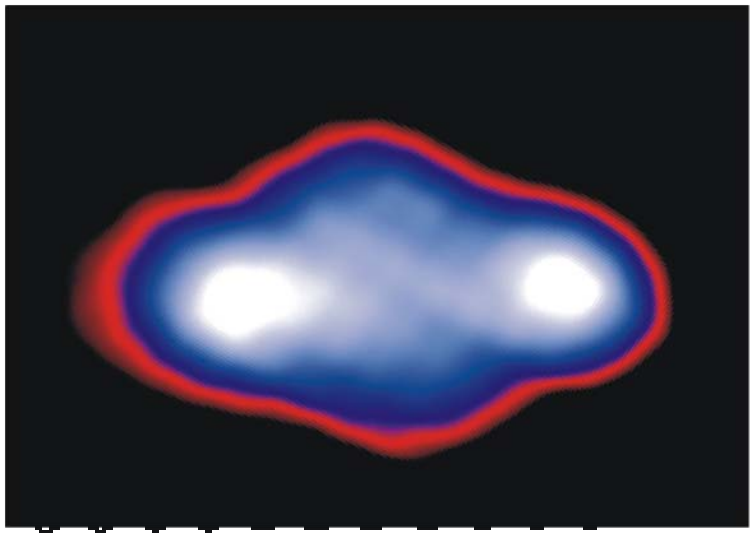
U=-3.0V, I=80pA,
48x48Å, T=55K,
Scan rate = 55 sec per image

Two Adsorption Minima

Optimal Anthracene Adsite

Sulfur 2 on-top, Anthracene aligned

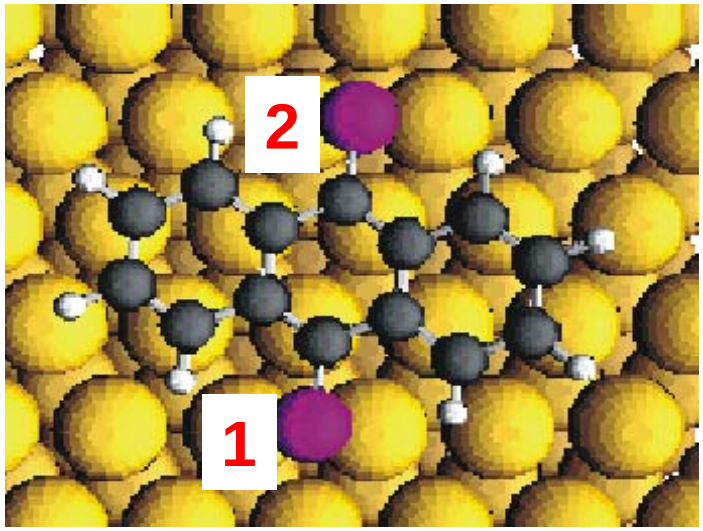


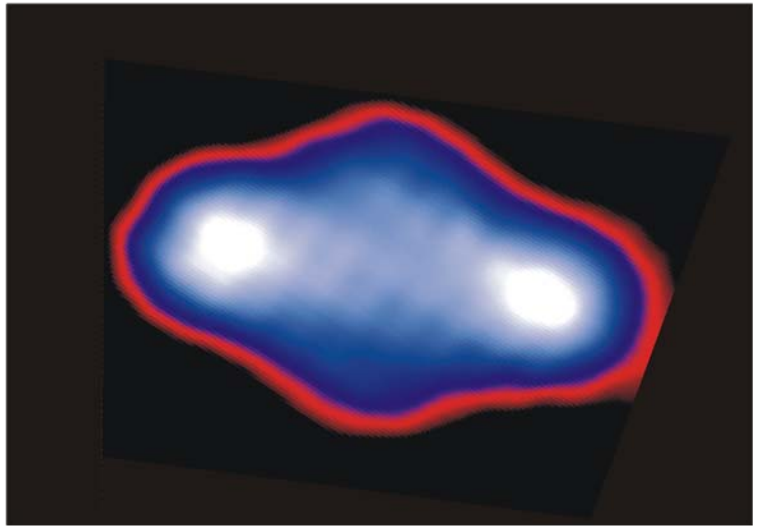


Wan, L. *et. al Langmuir*, **13**, 7173 (1997)

Optimal Sulfur Adsite

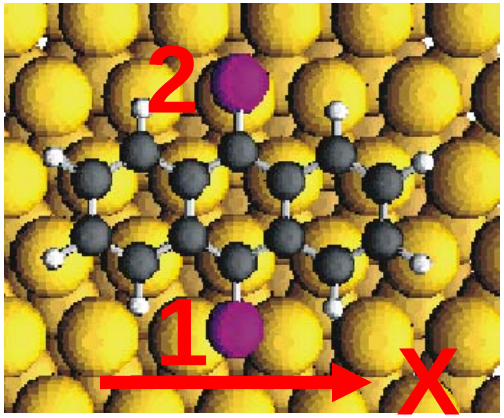
Sulfur 2 bridge, Anthracene misaligned

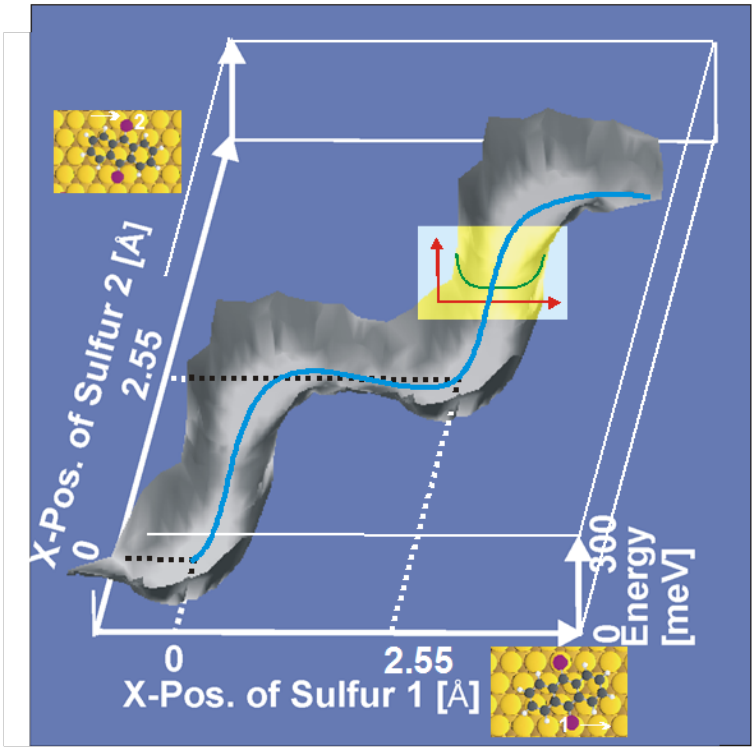


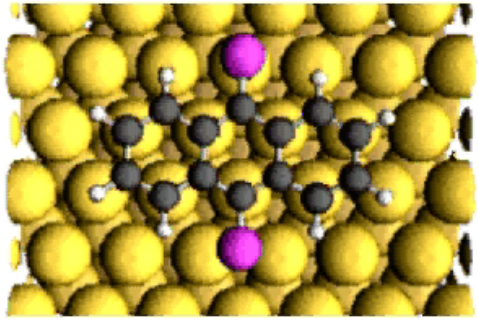


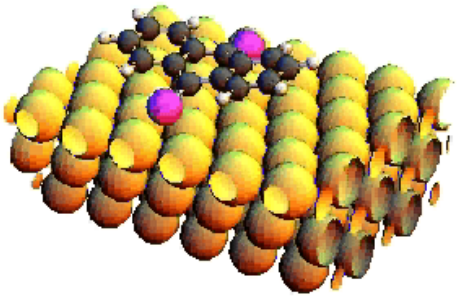
Wong, K. *et. al. Langmuir,* **20**, 4406 (2004)

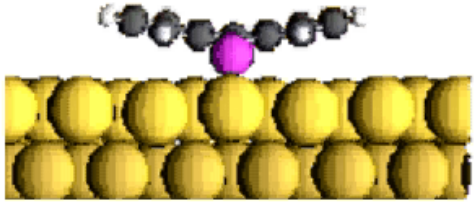
Potential Energy Surface

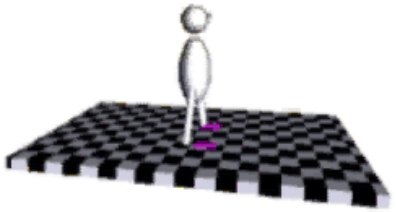




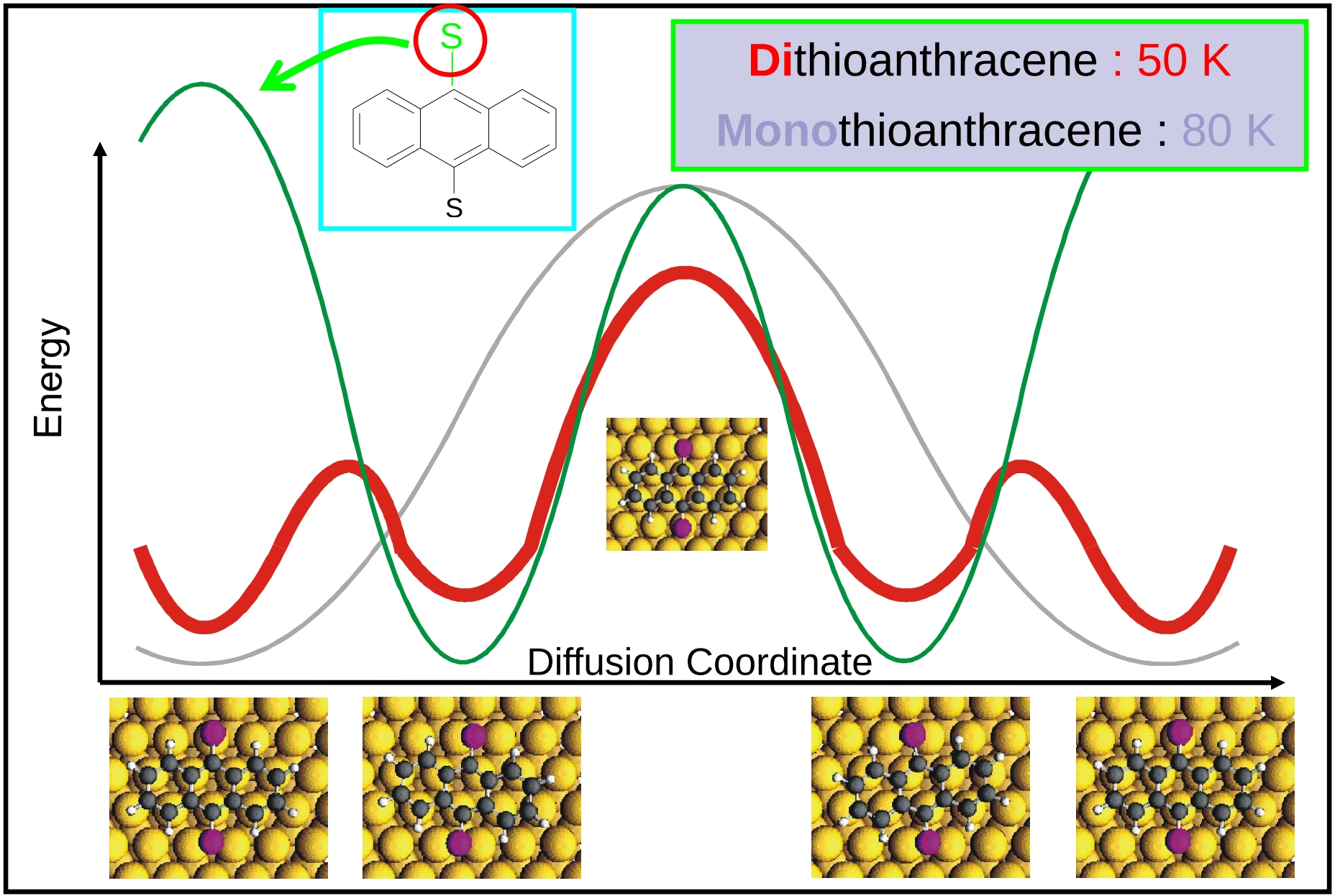


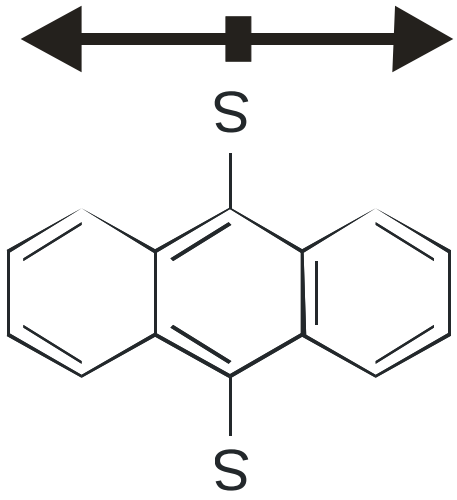




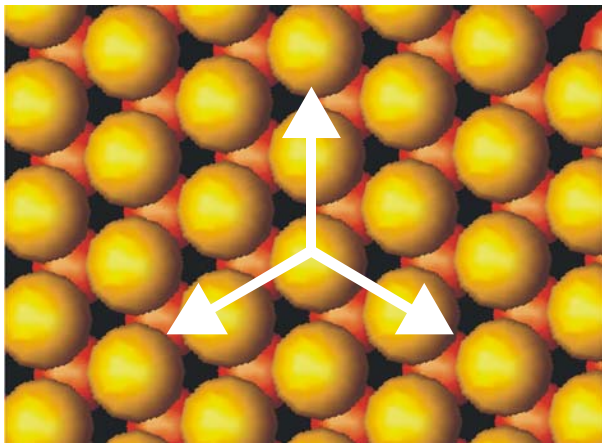


Kwon et al., Phys. Rev. Lett. **95**, 166101
AIP '*Top Physics Stories from 2005*'

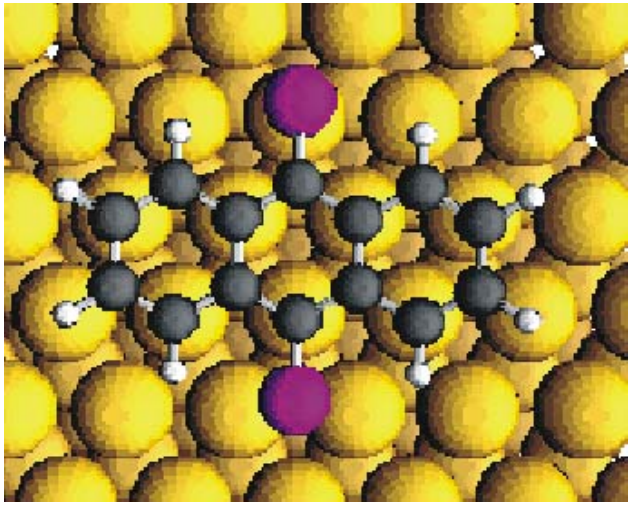

S
S
Dithioanthracene : 50 K
Monothioanthracene : 80 K
Energy
Diffusion Coordinate



2-fold symmetric adsorbate

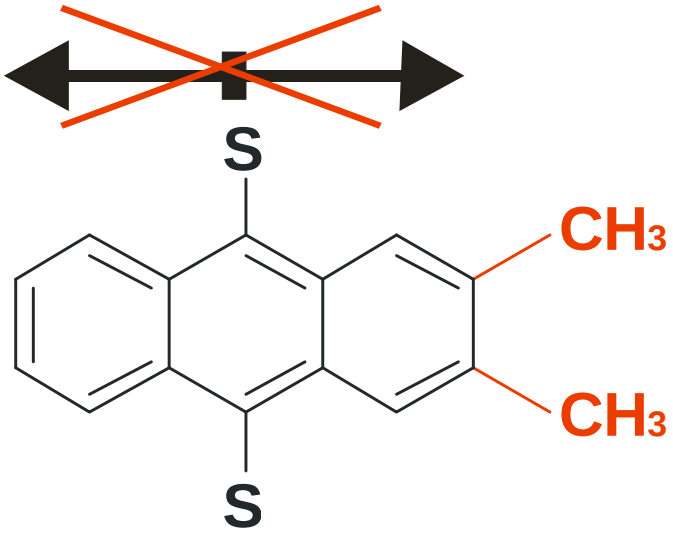


3-fold symmetric substrate

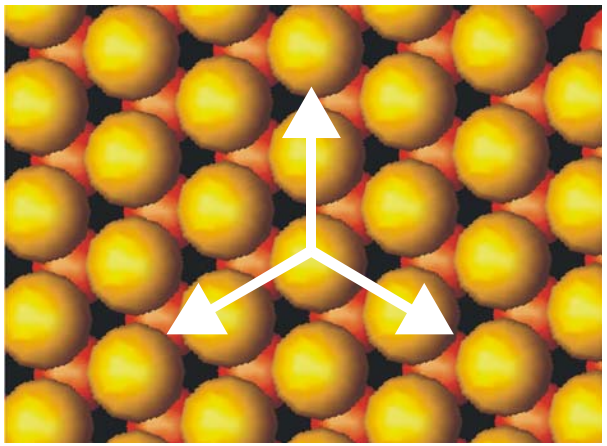


2-fold symmetric system

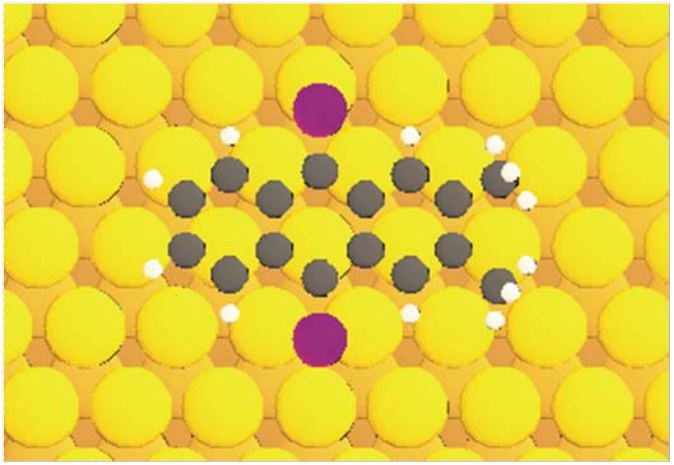
Uniaxial Motion



(rot.) asymmetric adsorbate

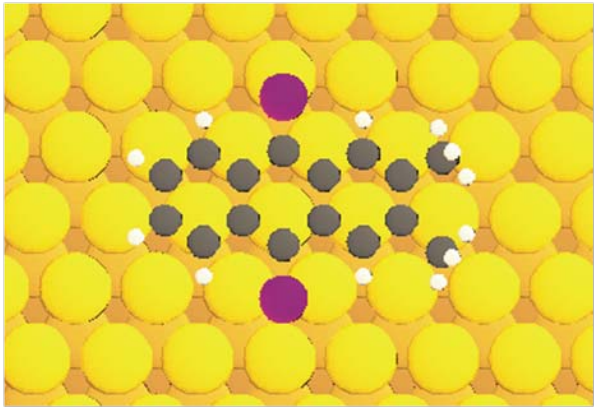


3-fold symmetric substrate



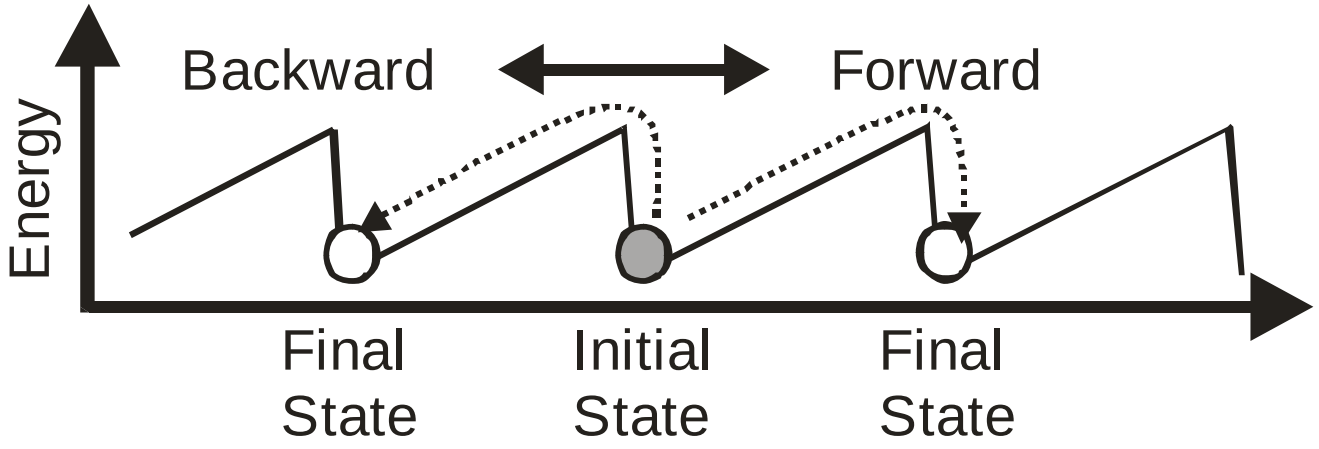
asymmetric system

Movement only in one Direction ???



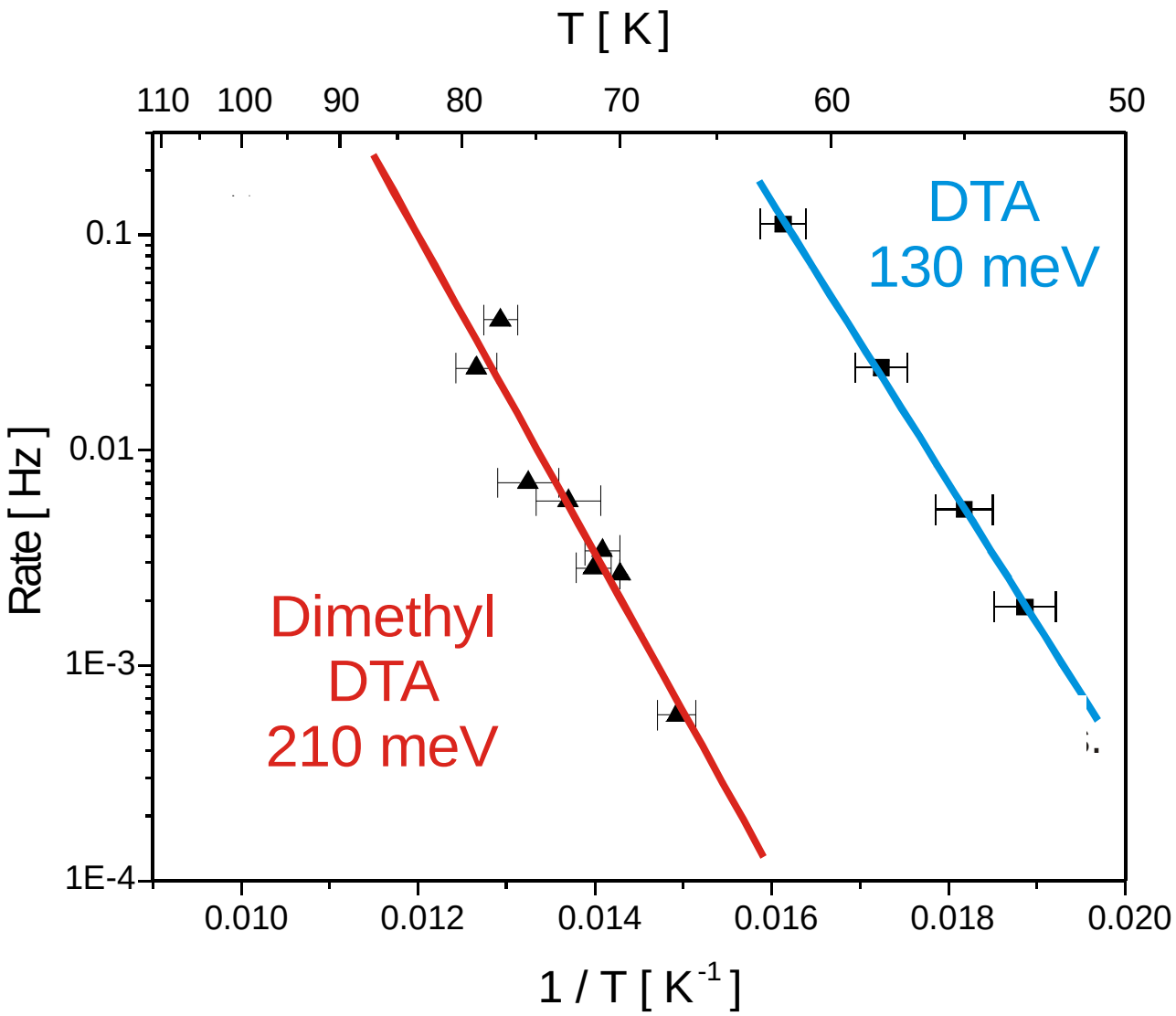
Asymmetric System

Movement only
in one
Direction ???

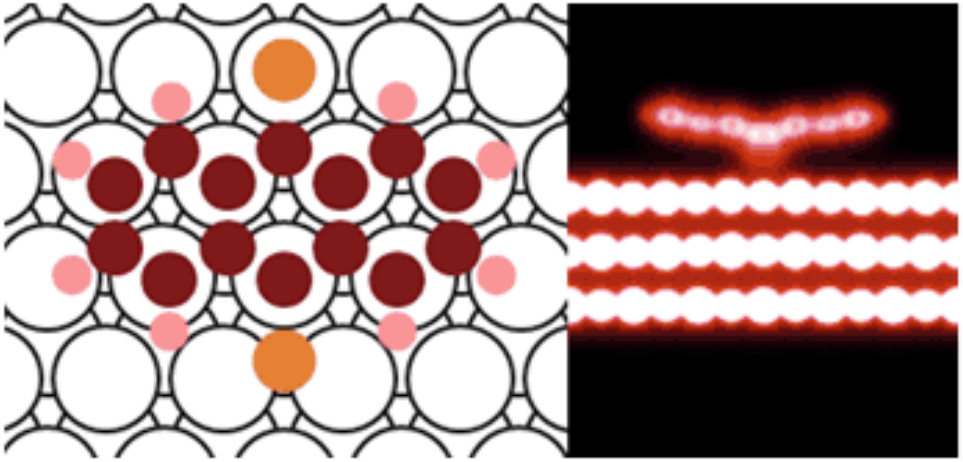


Does Methyl-Substitution really have any Effect on the Potential ?

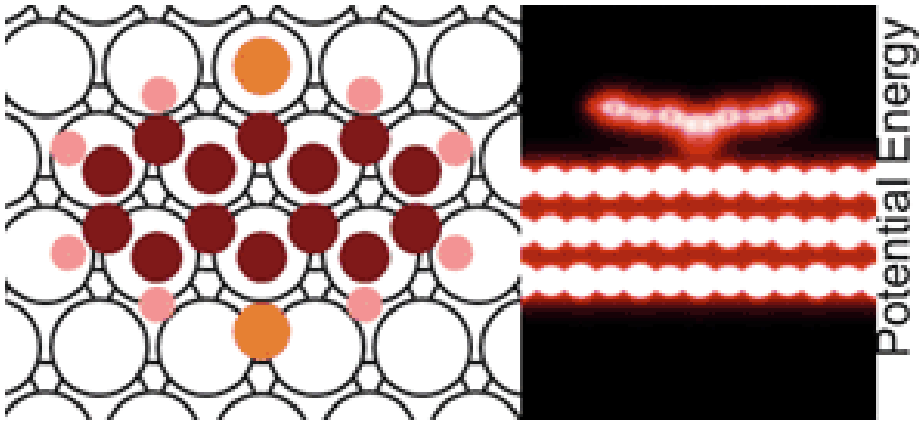
Methyl-Substitution has an Impact !

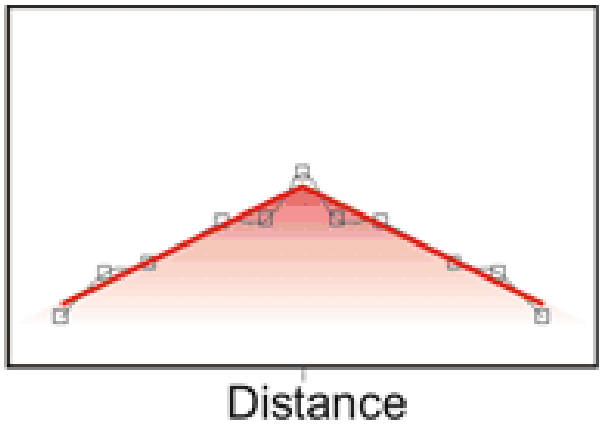


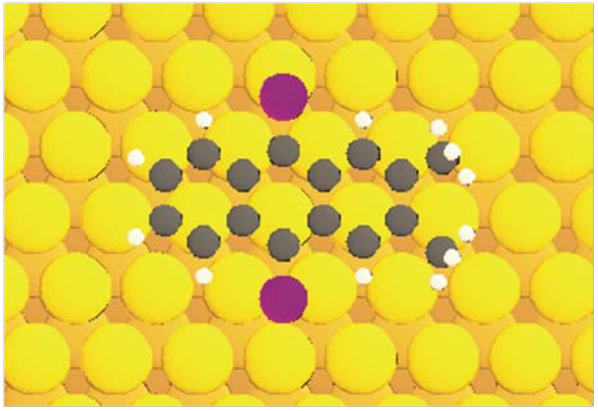
Methyl-Substitution



Methyl-Substitution

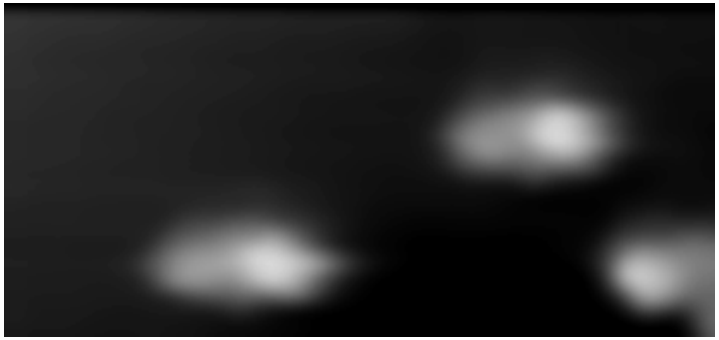






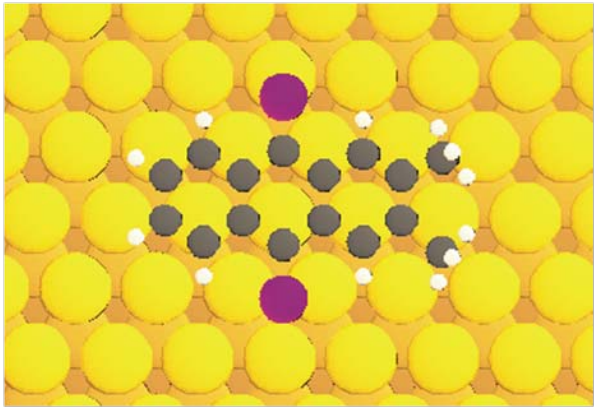
Asymmetric System

Movement only
in one
Direction ???



No !

Microscopic
Reversibility
Directly Observed

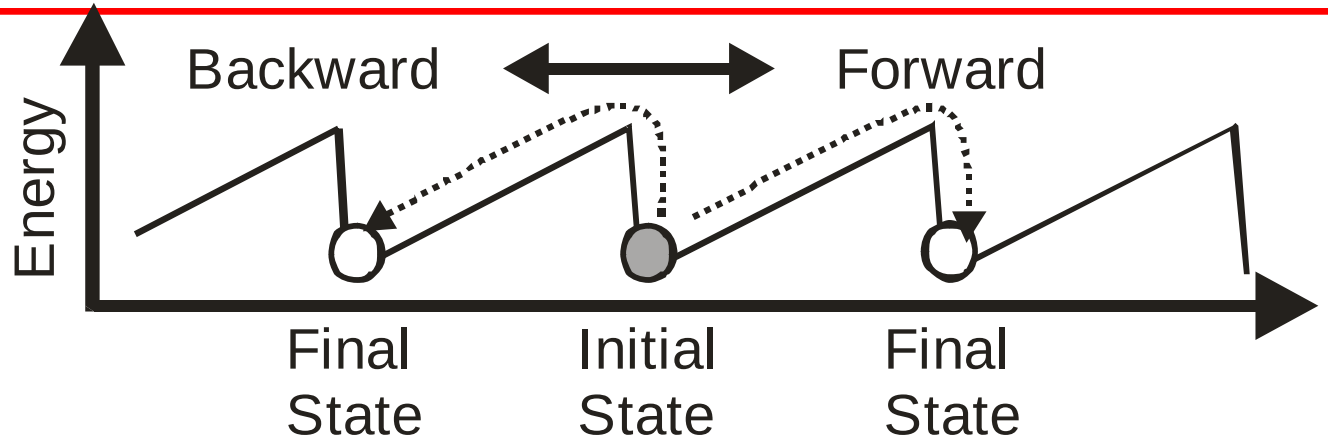


Asymmetric System

Movement only in one Direction ???

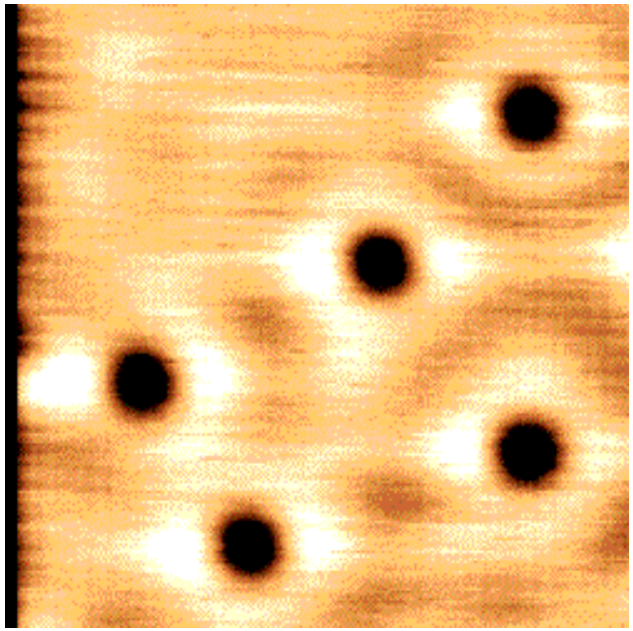
The Principle of Microscopic Reversibility / Time Inversion Symmetry

In equilibrium the number of particles moving in each direction along any one pathway is identical.

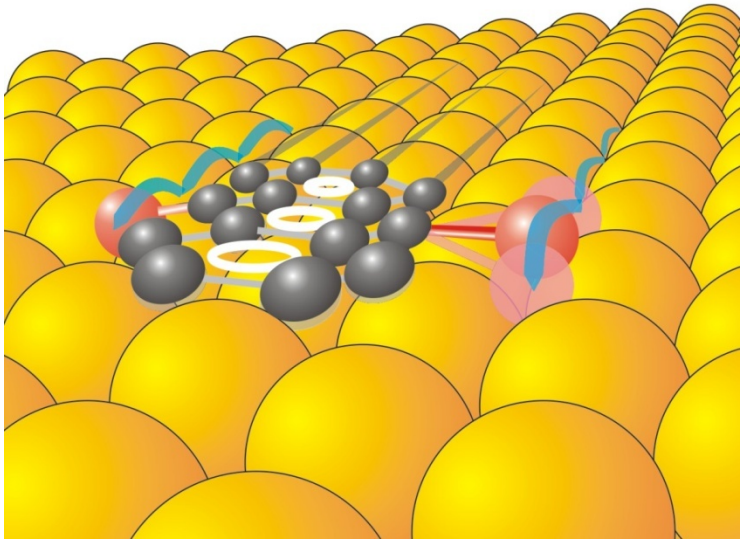


Can we utilize DTA's linear motion for linear transport of small molecules at surfaces ?

CO

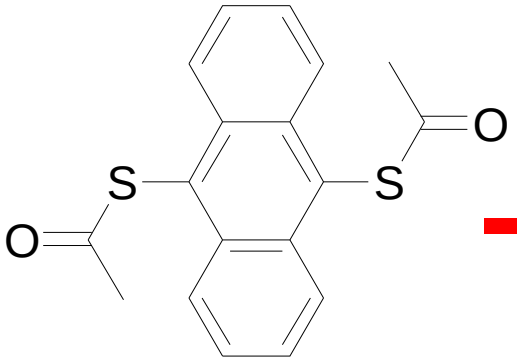


DTA

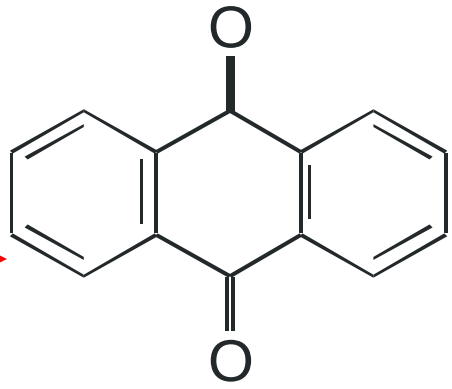


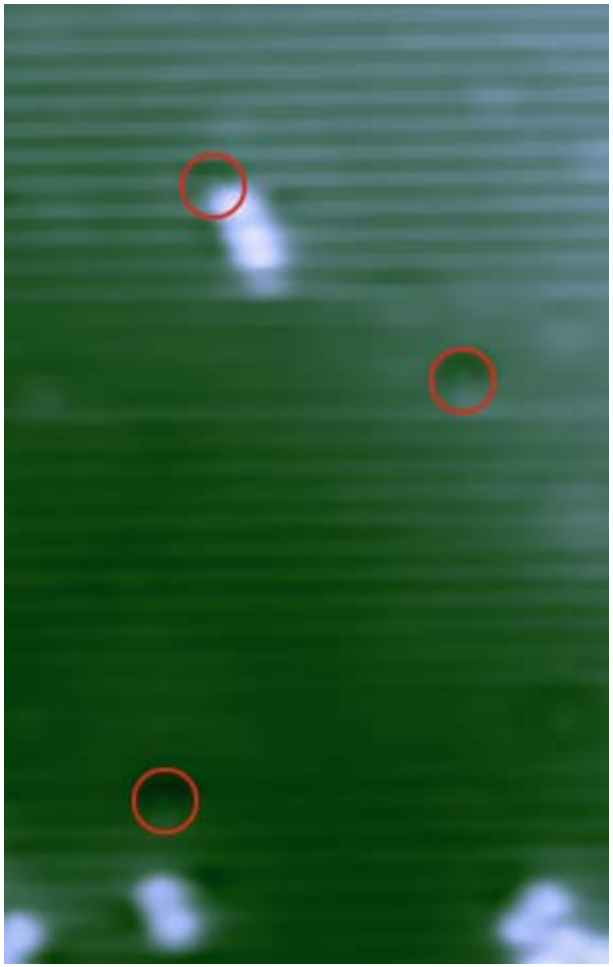
Anthraquinone

DTA

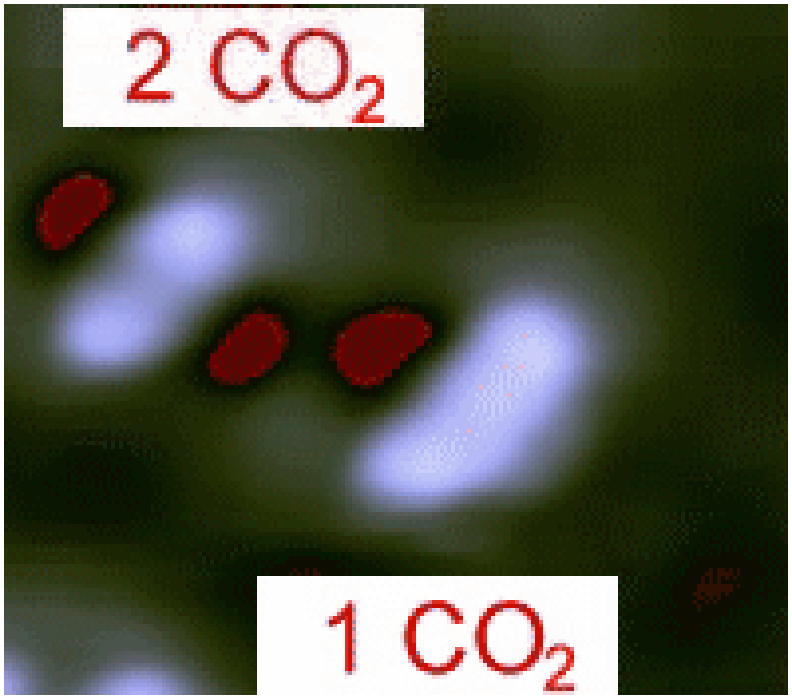


Anthraquinone





22 K



55 K

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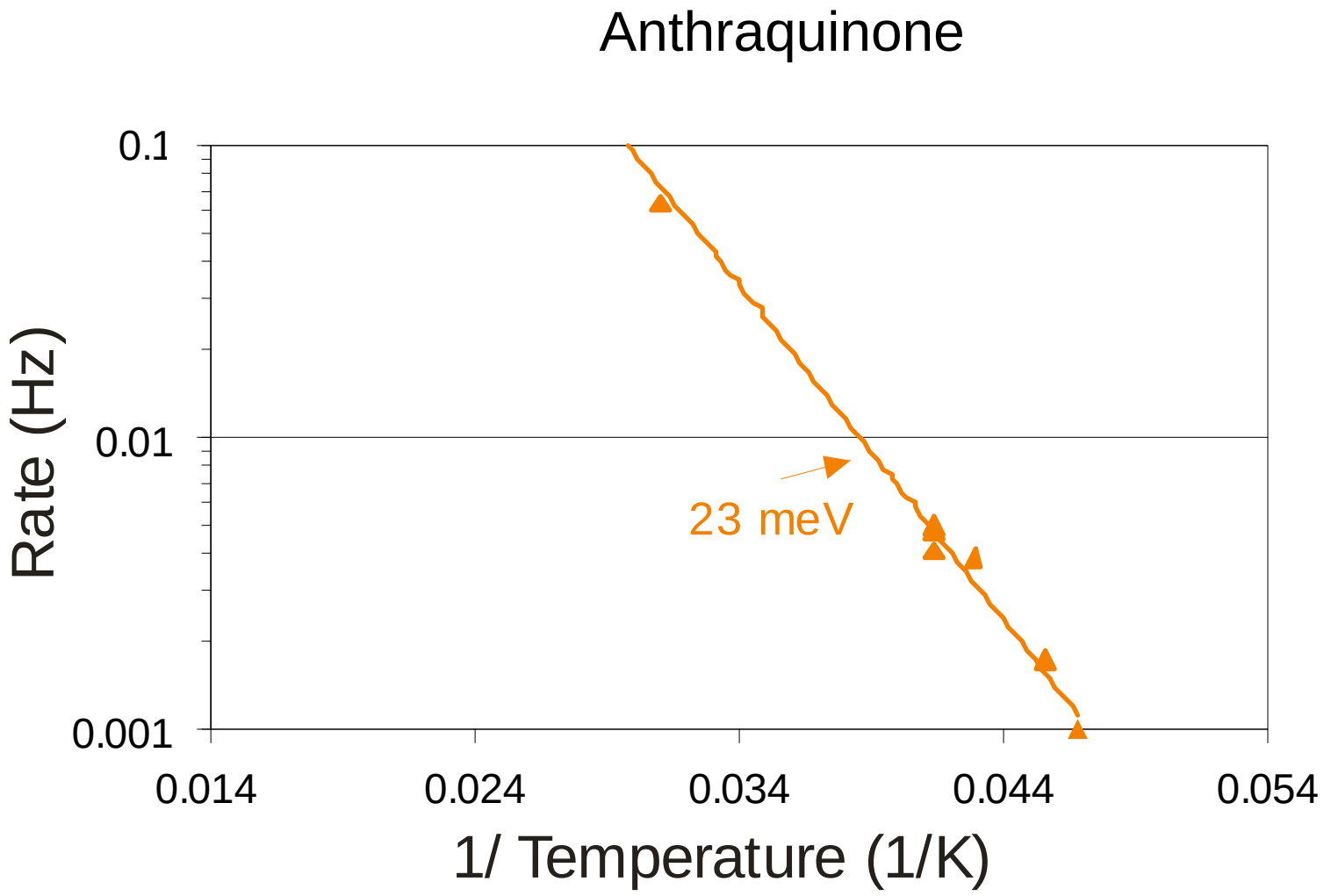
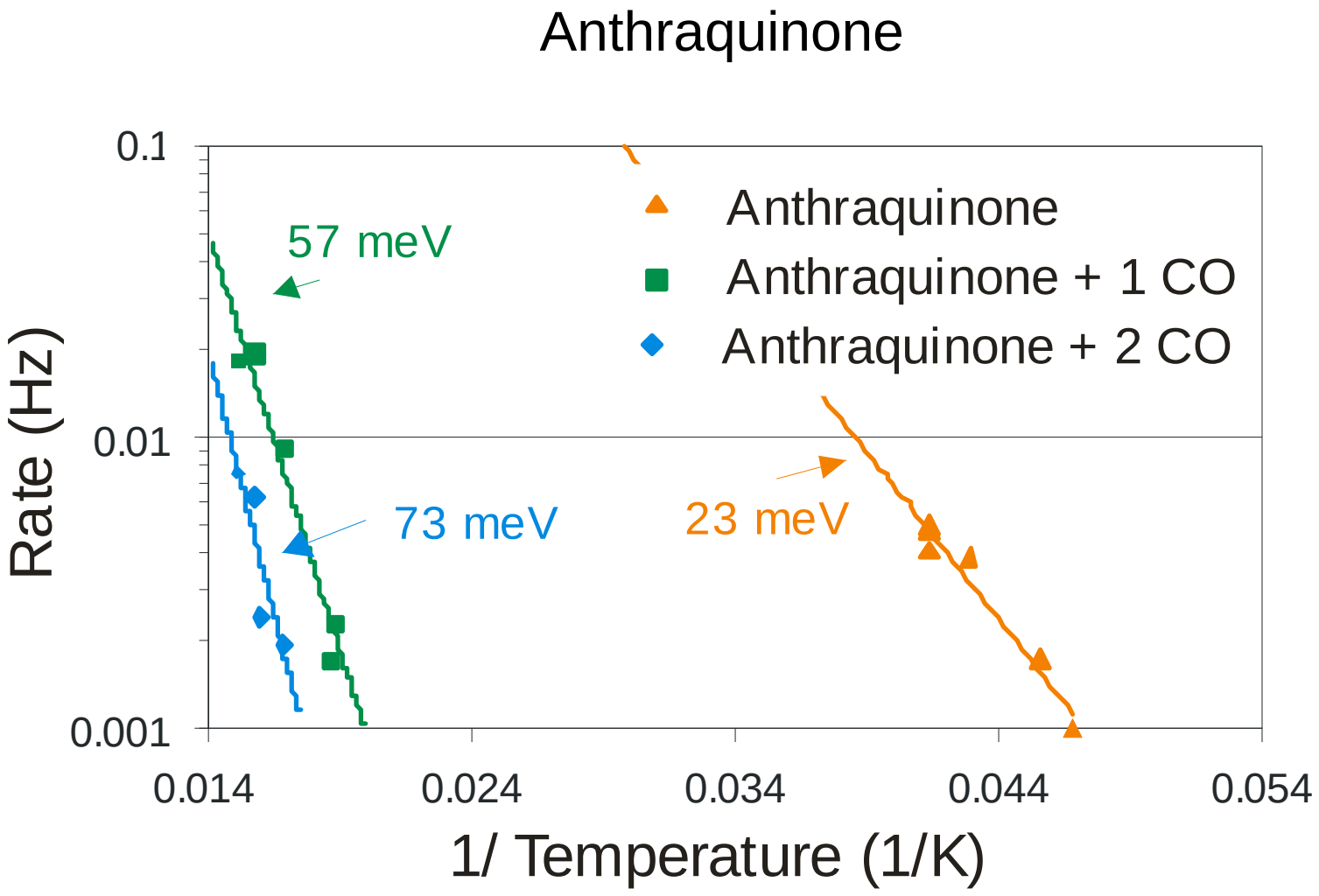
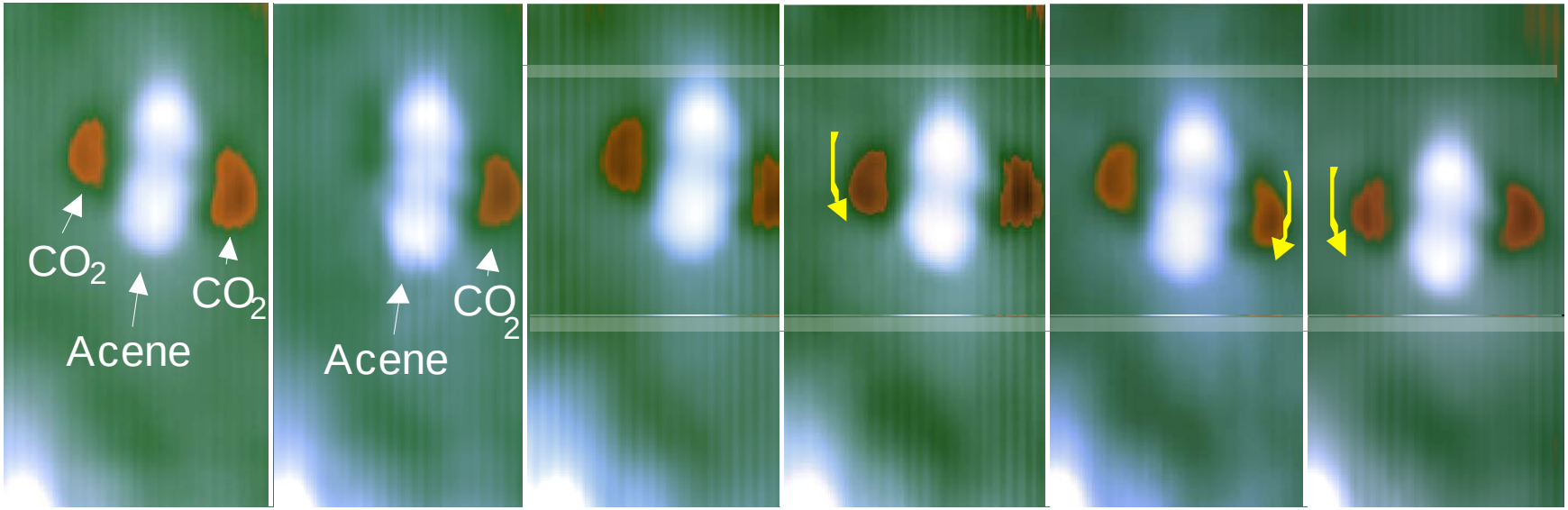


Very Low Temperature Process : approx. 20 K



Loading Slows the Molecule Down



CO_2 Unloading

CO_2 Reloading

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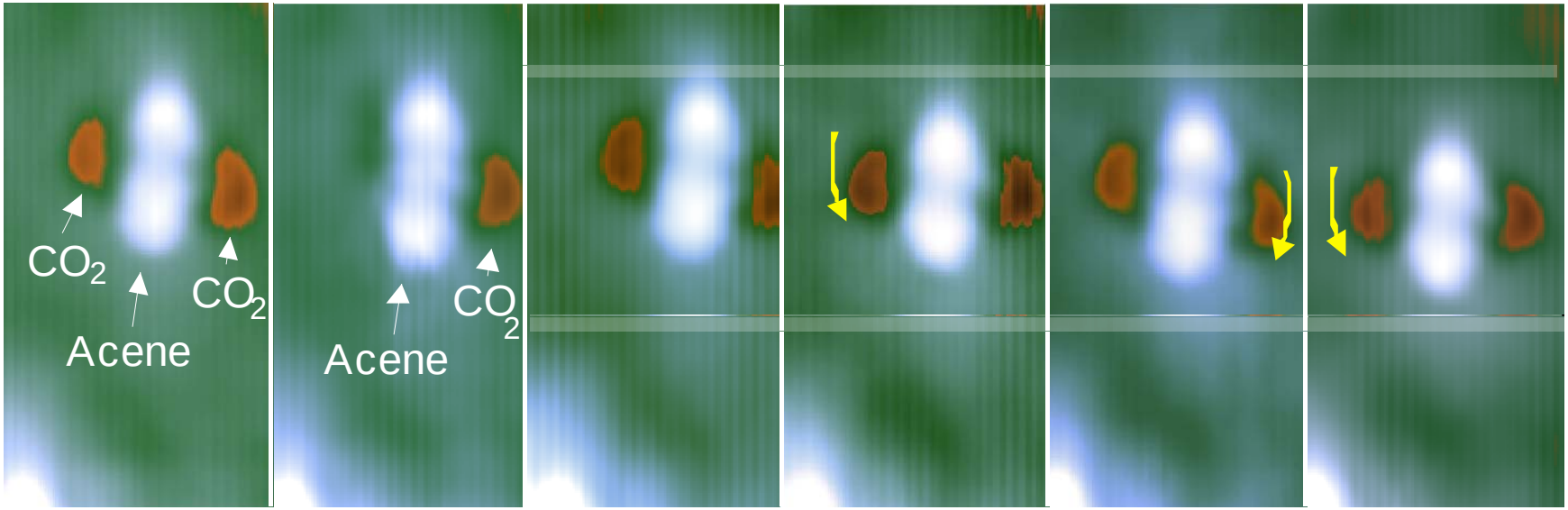

Step-By-Step
Motion

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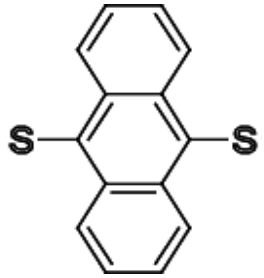
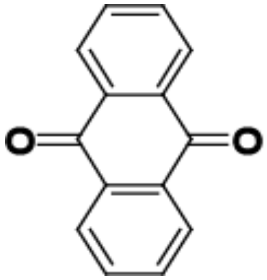
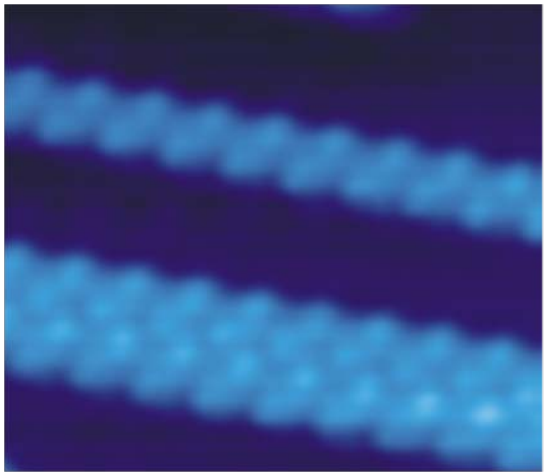
Molecular Rows

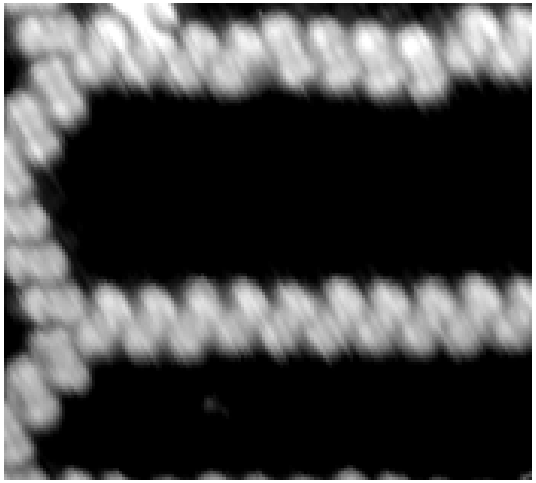


9,10-Di-thioanthracene

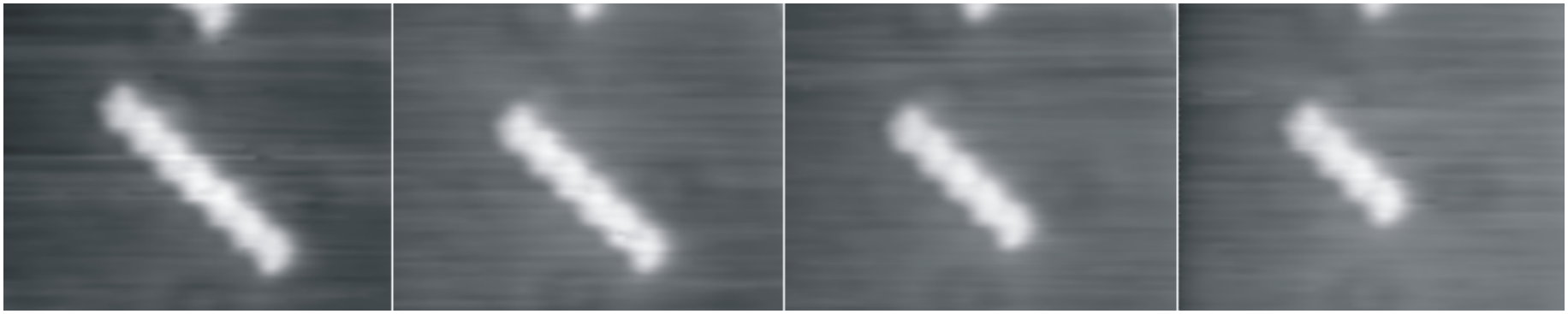


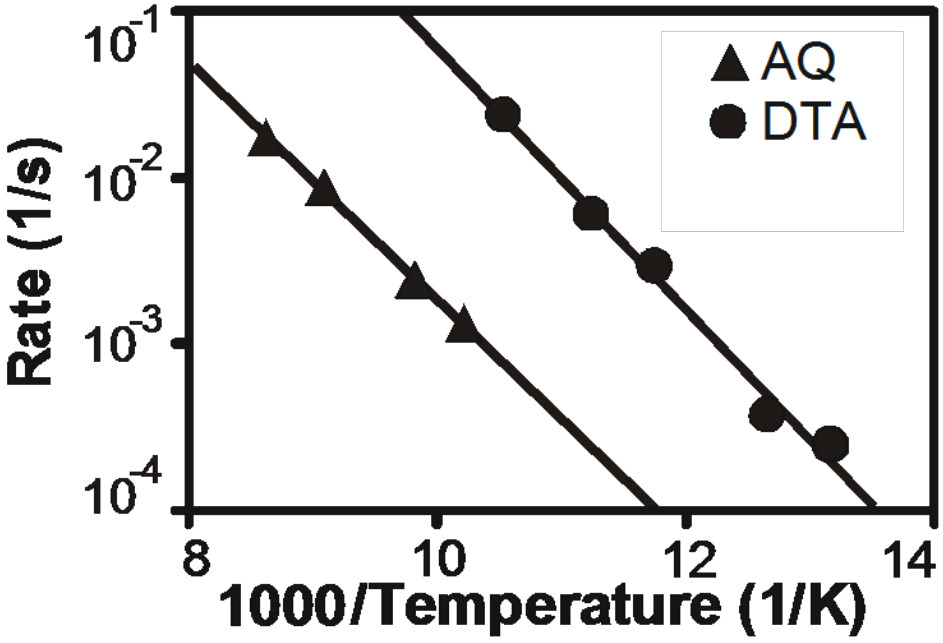
9,10-Anthraquinone





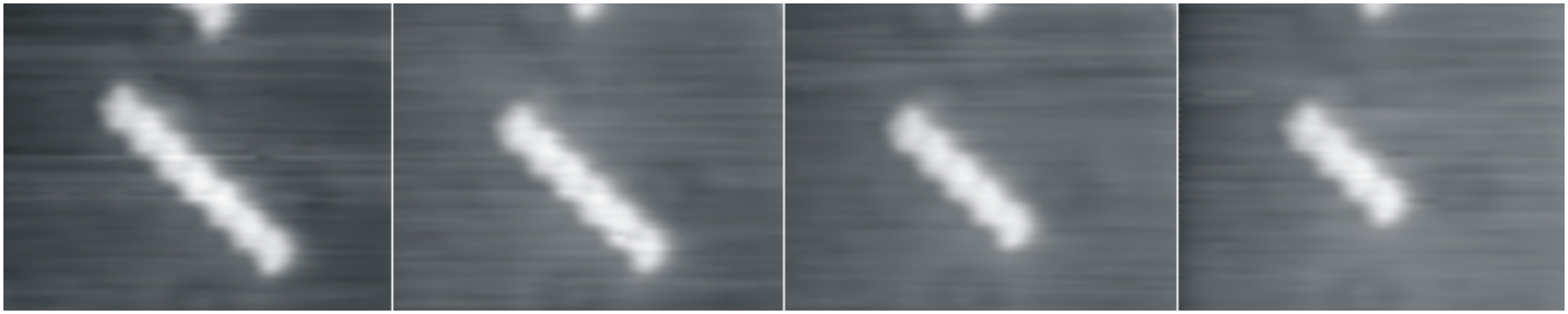
Thermal Disintegration of DTA Row

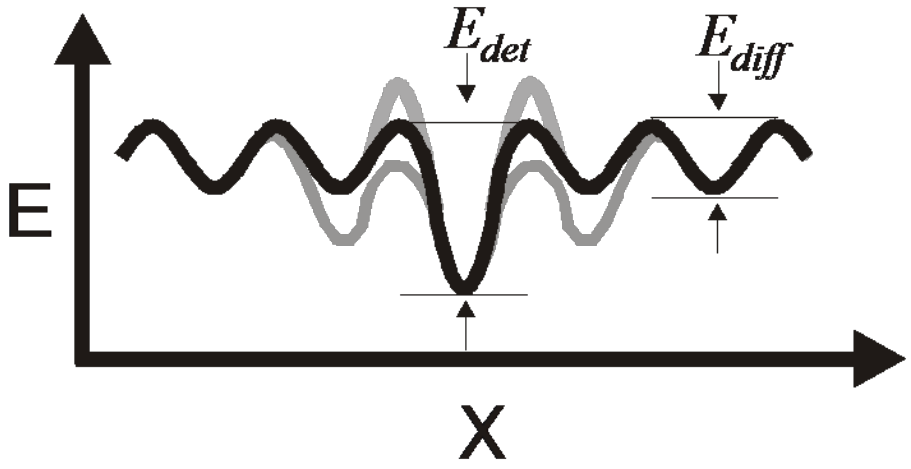


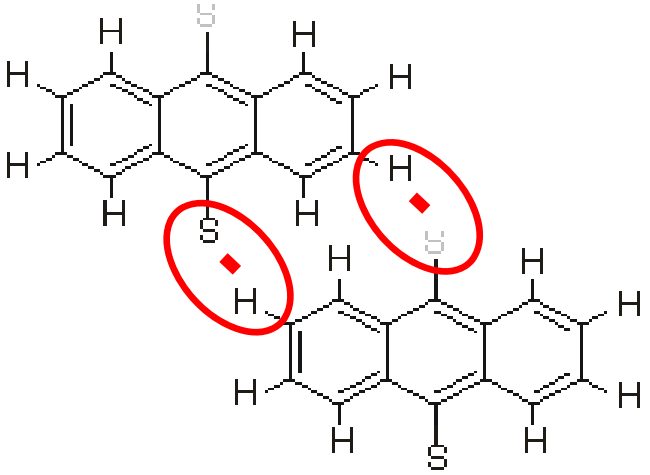


130 meV
160 meV

Thermal Disintegration of DTA Row





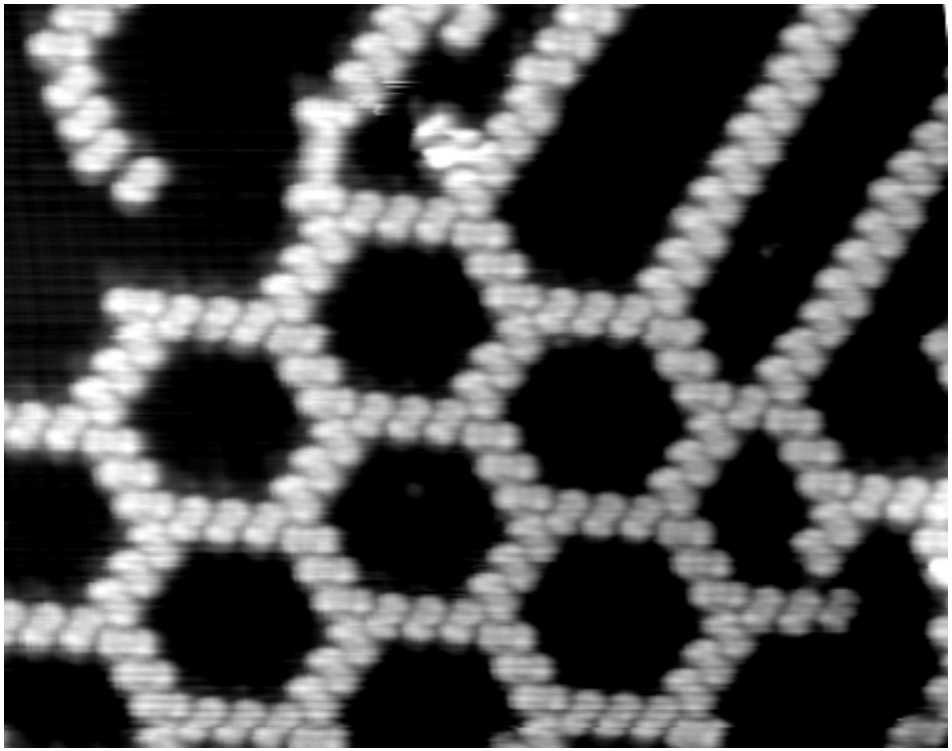


Anthraquinone 50 meV
DTA 20 meV

JACS **129**, 12056 (2007)

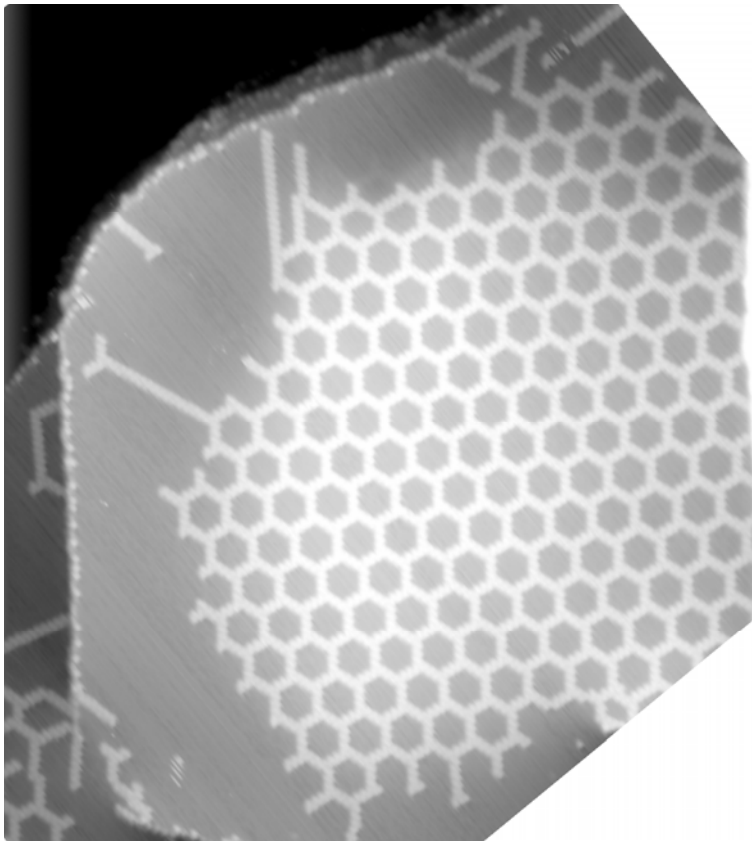
Anthraquinone

Anthraquinone



At medium coverages, honeycomb patterns emerged alongside molecular rows …

Anthraquinone-d8



…, which grow into very extended and well-ordered films

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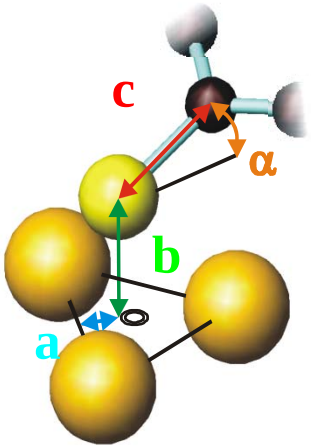
T. Einstein, Univ. Maryland

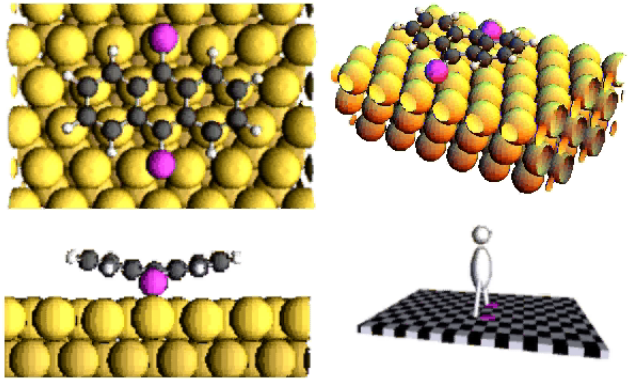
Office of Basic Energy Sciences

National Science Foundation
WHERE DISCOVERIES BEGIN

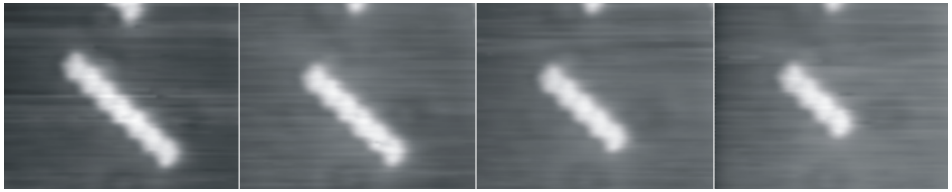


α =25°
a=0.59Å
b=1.97Å
c=1.80Å

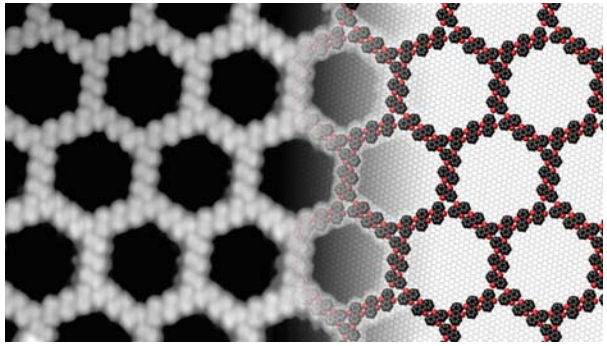
Benzenethiol Dynamics
JACS **126**, 7762 (2004)



Encoded Surface Dynamics
Phys. Rev. Lett. **95**, 166101 (2005)
Science **315**, 1391 (2007)



Probing Fundamental Chemistry
JACS **129**, 12056 (2007)
JACS, online ASAP



Supramolecular Assembly
Science **313**, 962 (2006)