Probing Interface Reactions by STM:

Molecular Dynamics on the Angstrom Scale

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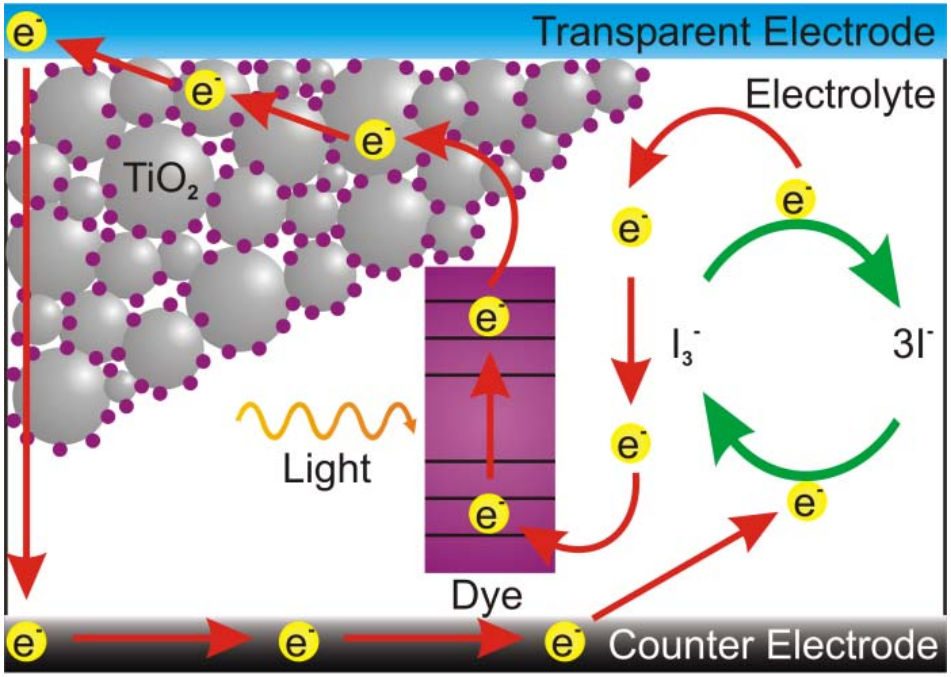
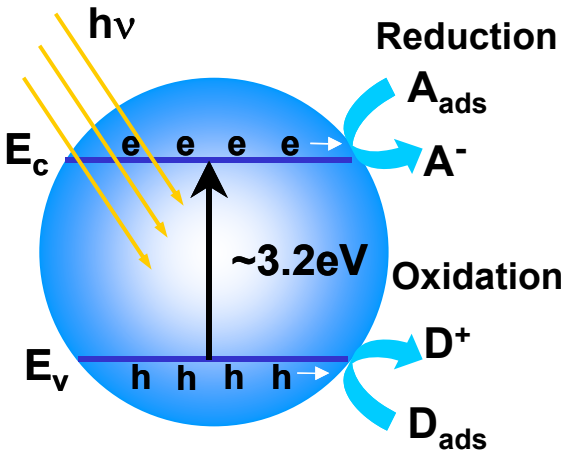
Outline

- Motivation: Why do we study interface?
- Adsorption Geometry of Large Molecules on TiO_2(110)
- Tip-Induced Reaction
- Making Oriented Nanocrystal TiO_2

Motivation: Why do we study the interface?



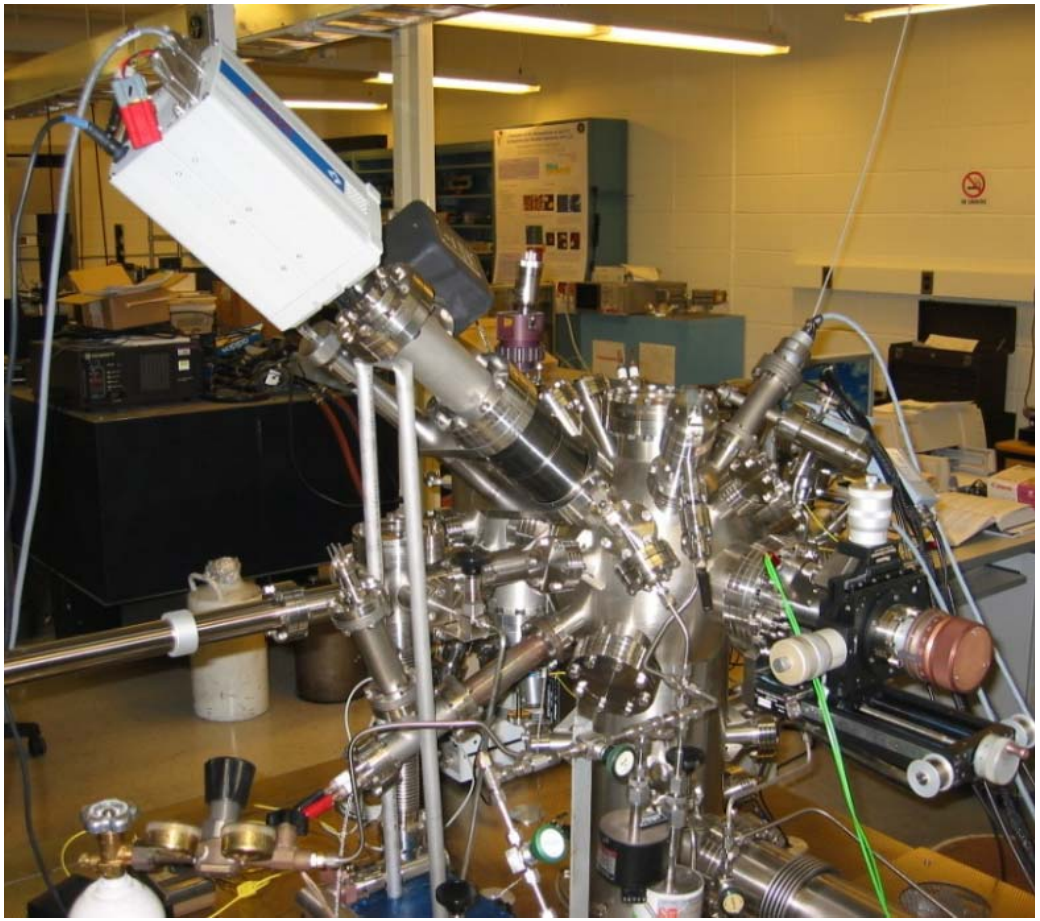


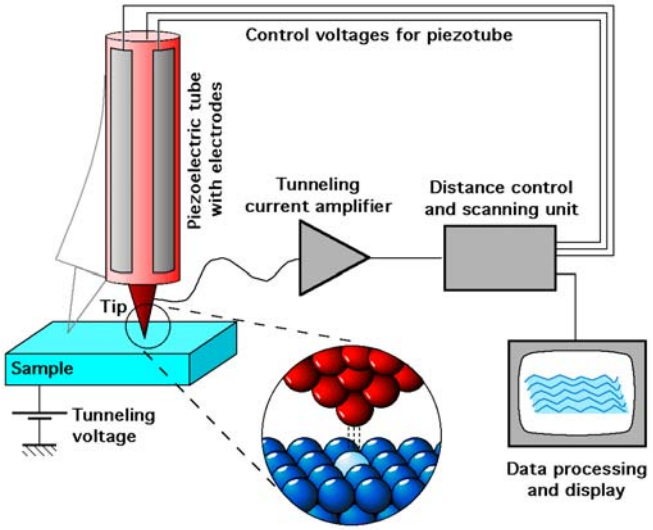
Graetzel Cell

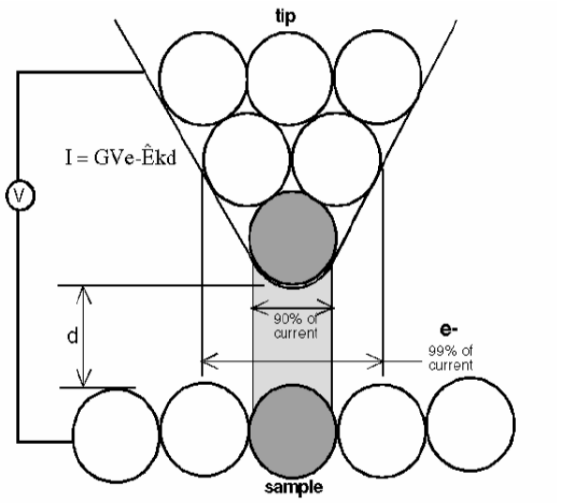
- ***Role of molecular conformation***
- ***Molecular "fit" on surface***
- ***Undesired (or desired) molecular reactions adsorbates***
- ***Implications for transfer efficiency***

Surface— adsorbate interface plays very important role!

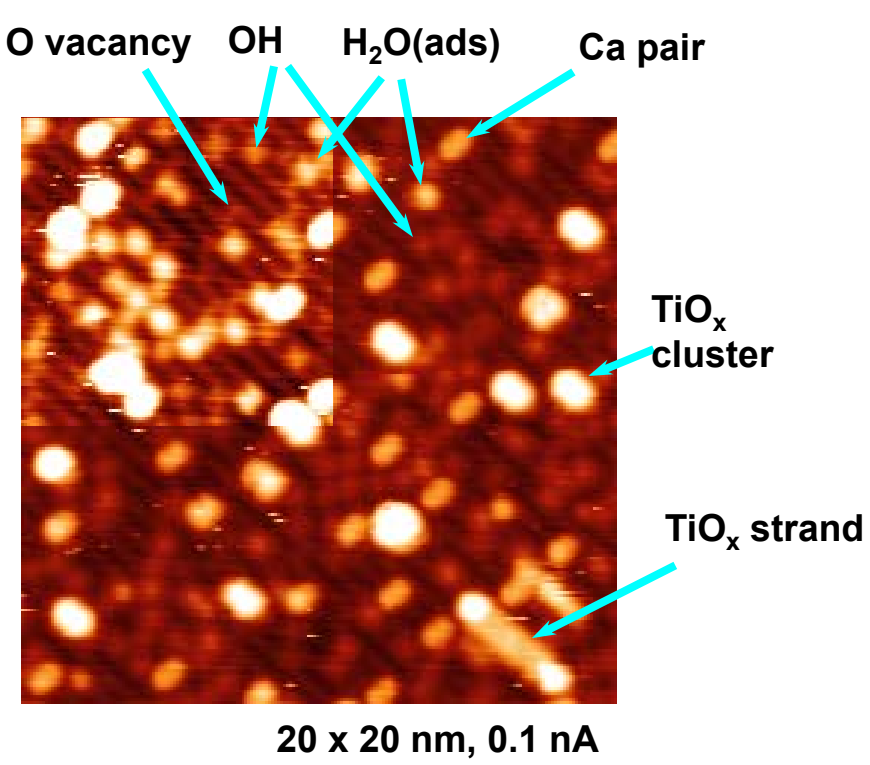
Research tool: Scanning Tunneling Microscope (STM)



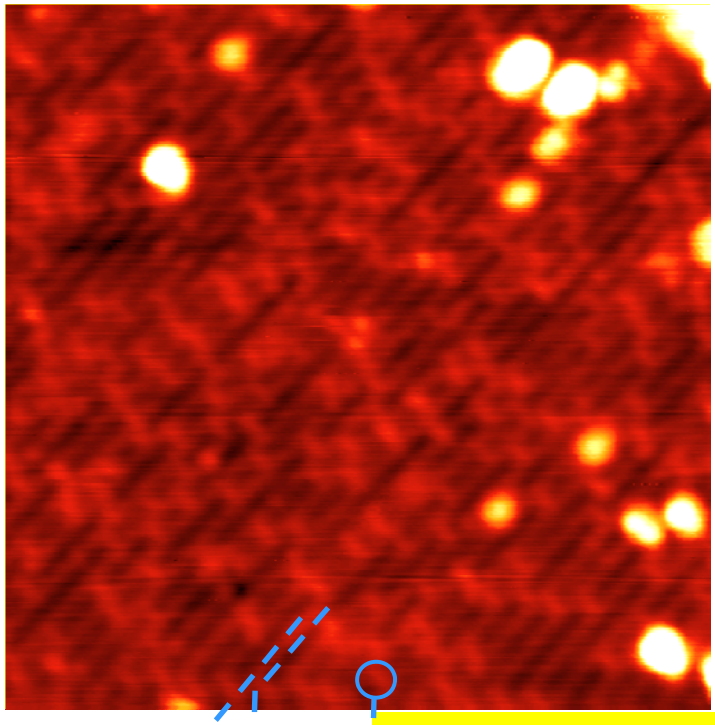




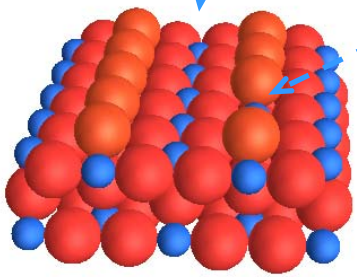
STM of clean TiO_2(110)



20 x 20 nm, 0.1 nA



20 x 20 nm, 1.0 nA



Bridging oxygen vacancies: 18 %

- **Rutile(110) surface:**
  - **Most thoroughly studied surface**
  - **Relatively easy to prepare**

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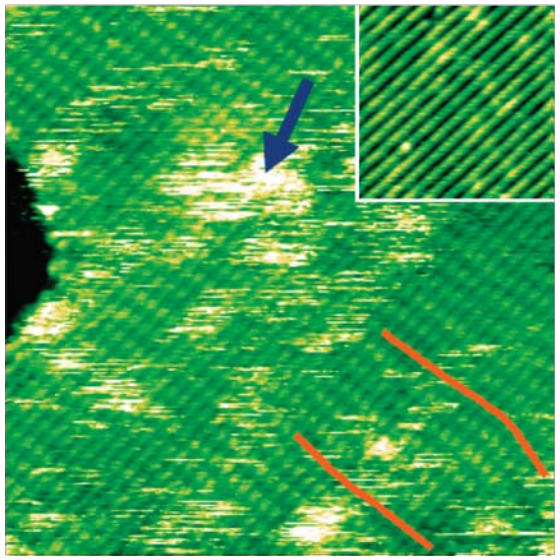
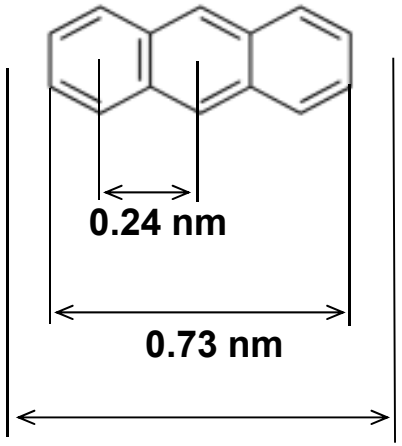
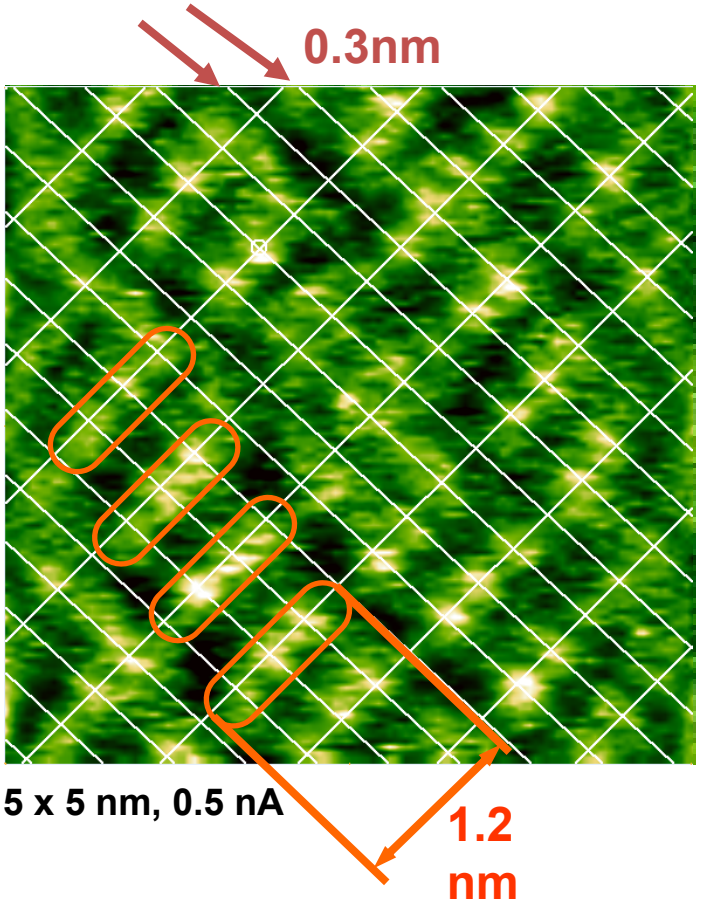
STM of 1ML Adsorbed Organic Molecules

Anthracene





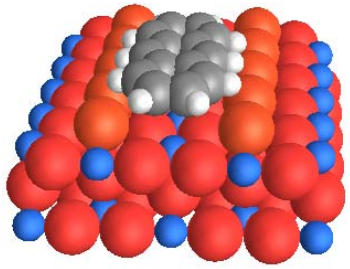


Sample at 300K

30 x 30 nm, 1.4 nA

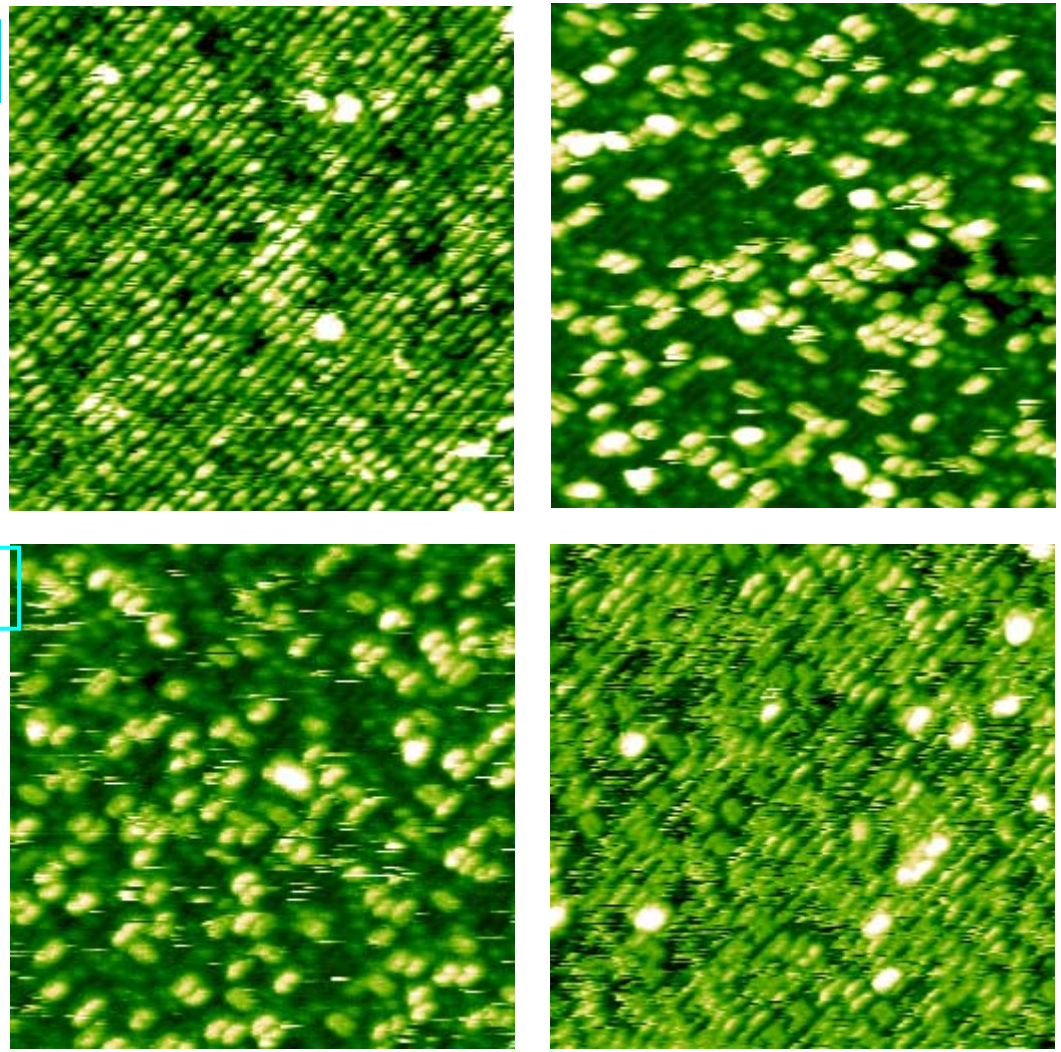
5 x 5 nm, 0.5 nA

- **Anthracene molecules aligned along $Ti^{(5)}$ rows**
- **Form quasi-periodic pattern with 1.2 nm period – Mol. length**
- **Electrostatic interaction (repulsive along and attractive across rows) responsible for surface pattern – due to surface puckering**

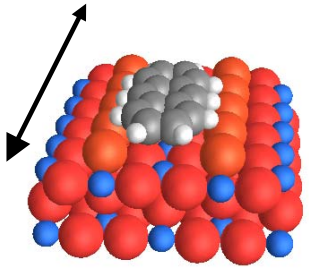


STM of adsorbed organic molecules

Anthracene (0.17 ML)



- Anthracene molecules are *mobile* along the atomic rows of TiO_2(110)

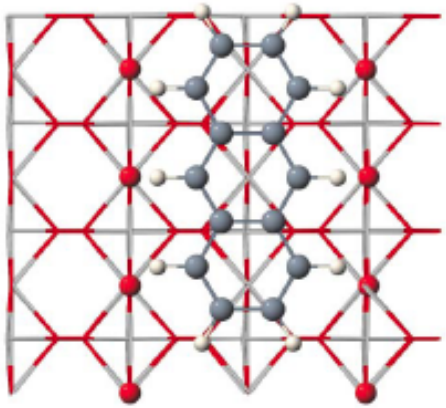


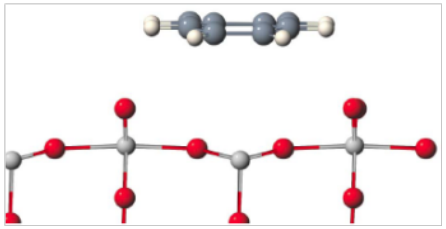
30 x 30 nm, 50 pA

DFT Calculations - Adsorption Geometry

Configuration A

E_{ads} = -1.2 eV

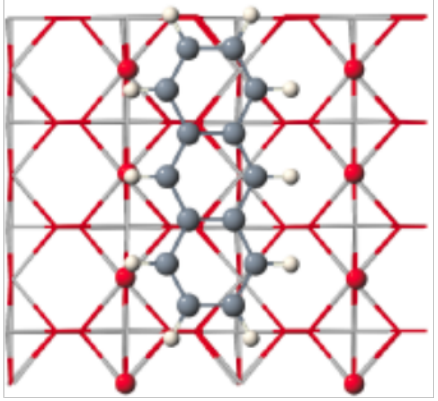


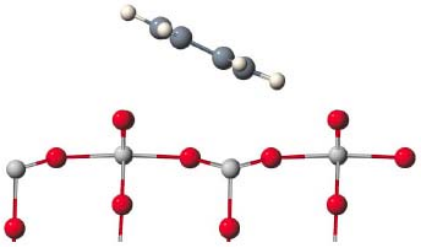


Configuration B

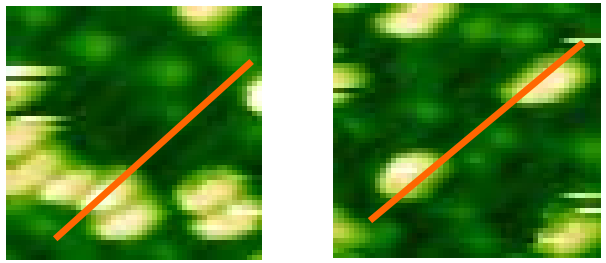
Most Favorable

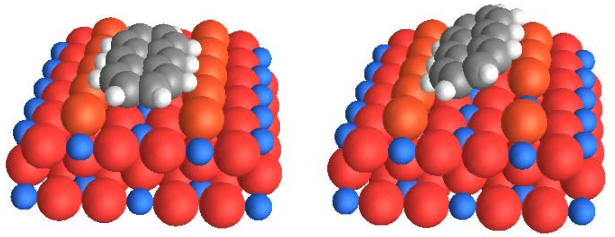
E_{ads} = -1.5 eV





Anthracene - 135 K





Compare with NEXAFS study

S. Reiss et al., *J.Chem.Phys.* (2002) 116, 7704

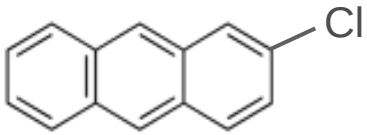
From TPD experiments

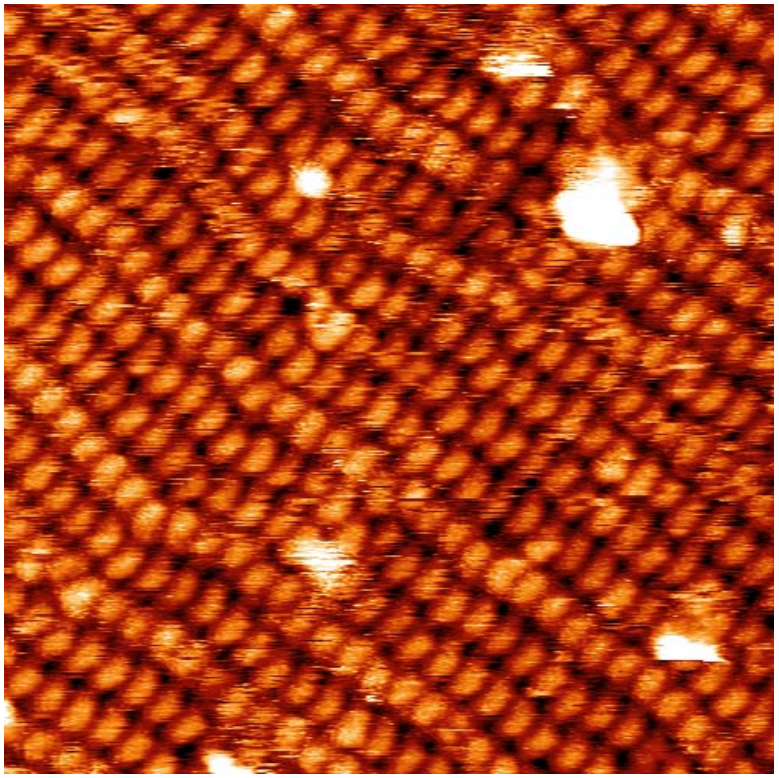
E_{ads} = 0.9 eV

Calculation by N. Aaron Deskins – Worcester Polytechnic Institute

STM of adsorbed organic molecules

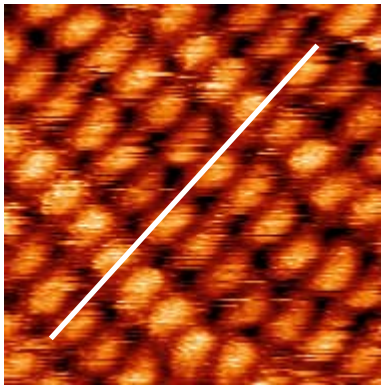
2-Chloroanthracene (1ML)

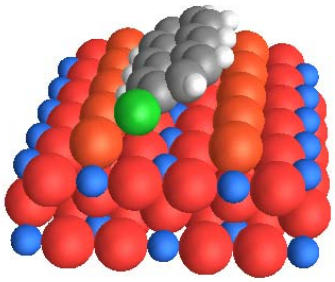




RT

20 x 20 nm, 0.1 nA





- 2-Chloroanthracene molecules also aligned along $Ti^{(5)}$ rows
- As with anthracene, electrostatic interaction responsible for surface pattern
- Chlorine causes permanent tilting

Outline

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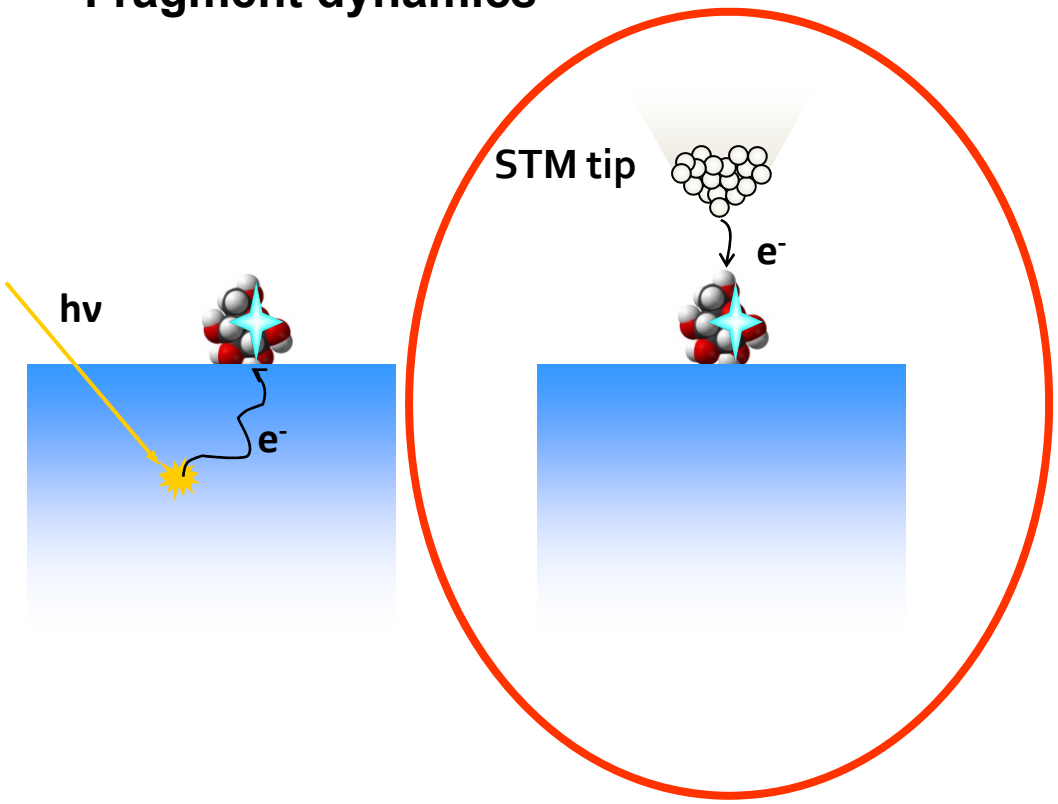
Examine electron transfer reactions via tip-induced charge injection, i.e. from STM tip to adsorbed molecule

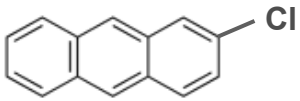
– Controlled energy of the electrons

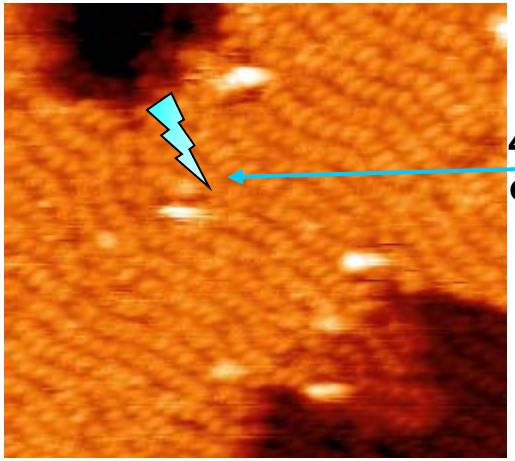
– Localized to site and molecular state

– Fragment dynamics



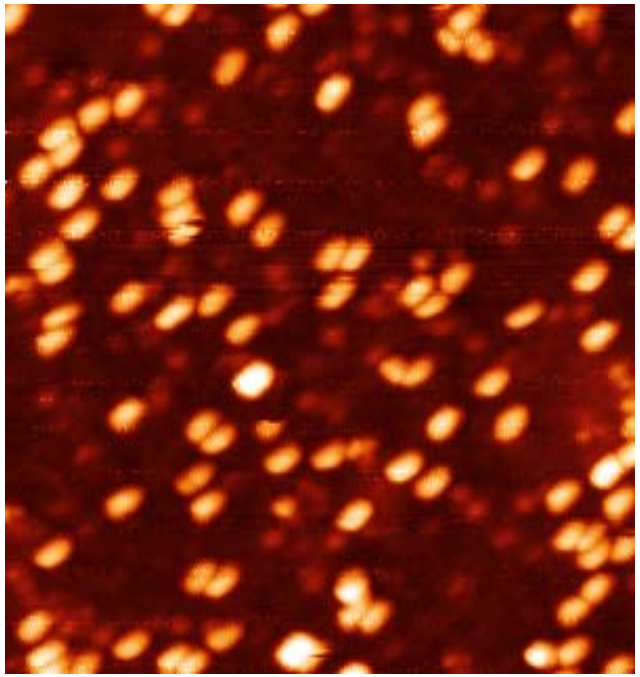
Voltage pulse from STM tip





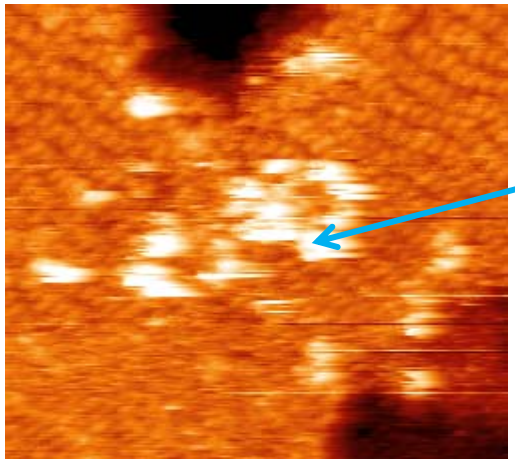
4 V pulse, 5 ms,
o feedback

2-chloroanthracene
coverage:
1 ML
0.1 ML



135 K

30 x 30 nm, 20 pA



~ 0.8 nm

RT

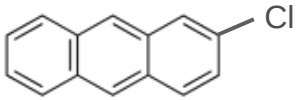
25 x 20 nm, 0.2 nA

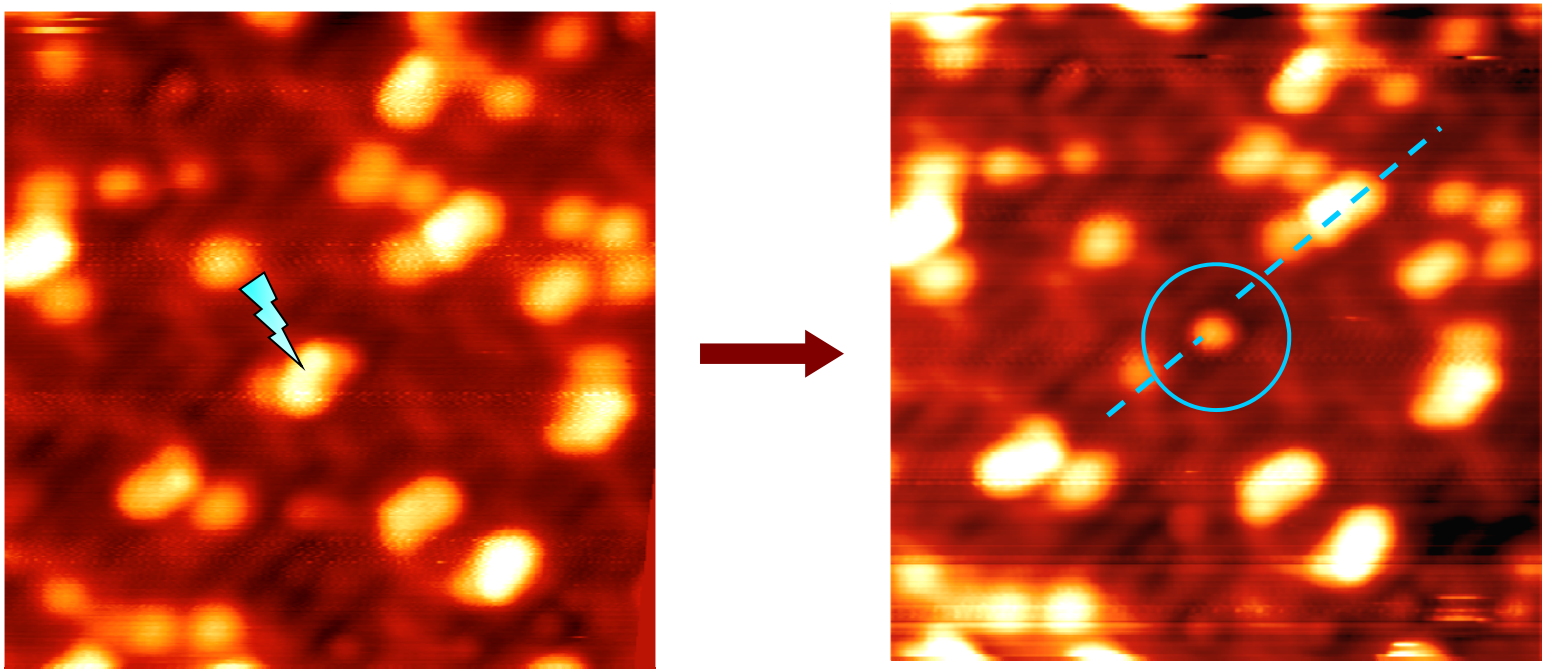
Preferable conditions for single-molecule reaction studies:

- Low surface concentration
- Cryogenic temperatures

Voltage pulse from STM tip

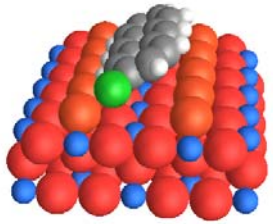
2-Chloroanthracene

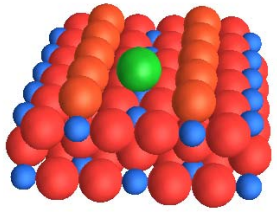




135 K

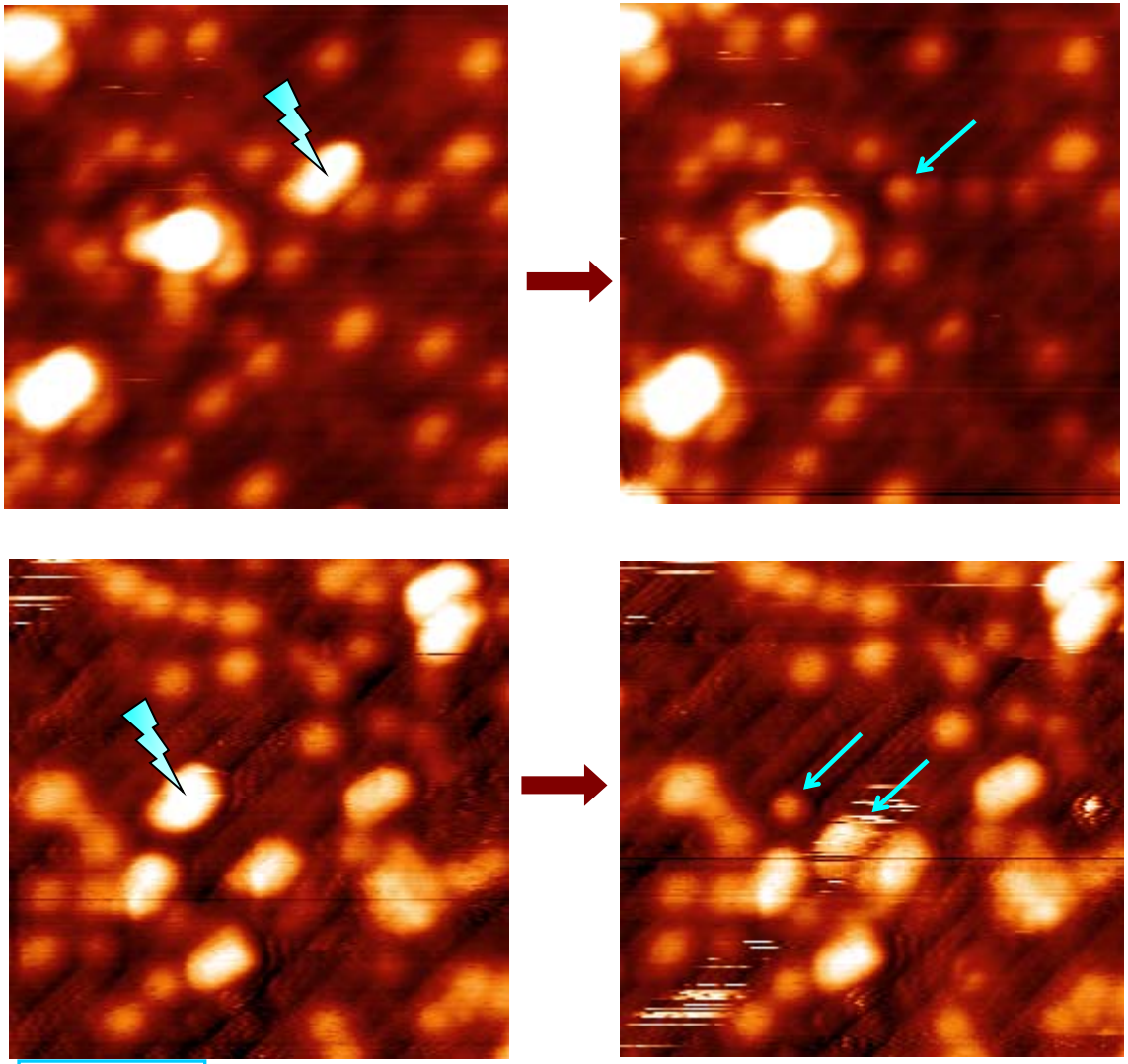
10 nm, 20 pA





- **Dissociation event detected!**
- **Adatom X sits on Ti$^{(5)}$ rows**

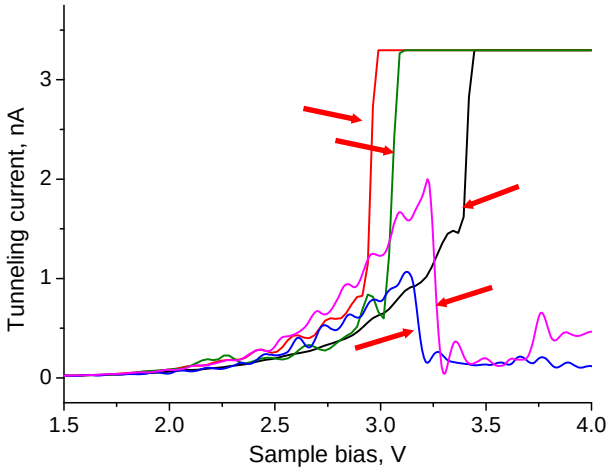
Voltage pulse from STM tip



135 K

10 x 10 nm, 20 pA

Reaction pulse I(V)



2-Chloroanthracene dissociation voltage statistics:

V = + 3.1 ± 0.3 V

(16 observations)

Observations on Fragment Dynamics

- **Desorption of the molecule also occurs ~ 50%**
- **Reactions**
  - **Low cross-section**
  - **Cl remains bonded in place – image forces**
  - **Anthracenyl ejected: surface, tip, vacuum. Estimated anthracenyl adsorption energy ~ estimated kinetic energy.**

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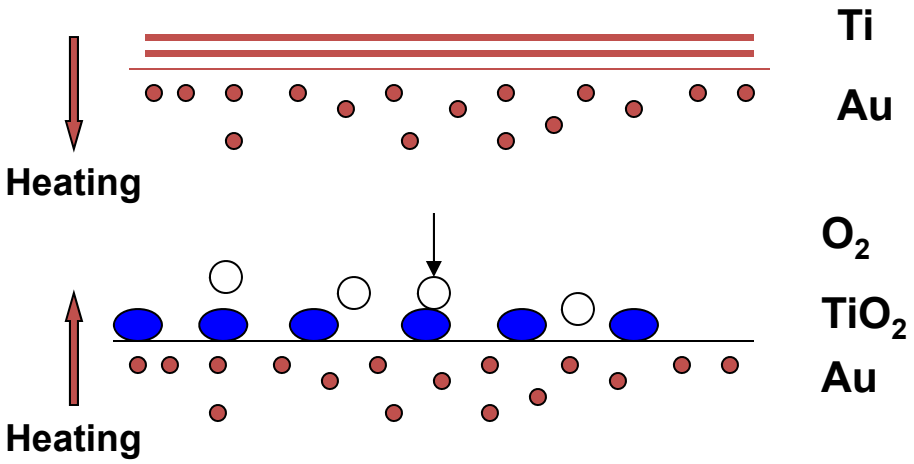
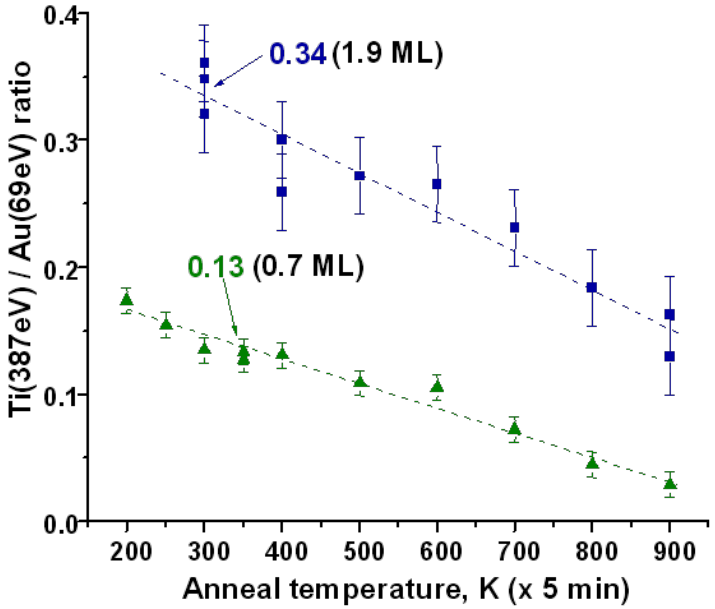
Nanoparticles

In Situ Growth
STM Nanocrystallography
Reactivity

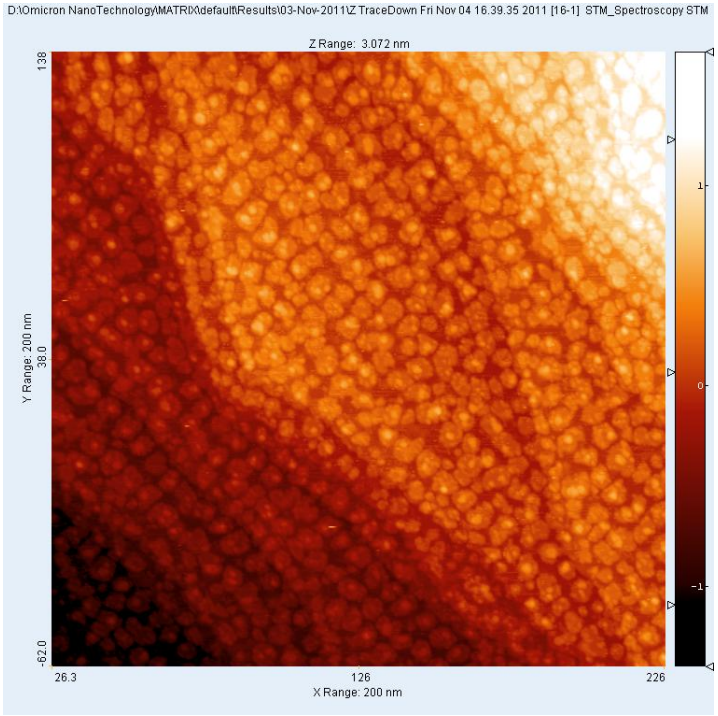
Surface-Alloy Growth





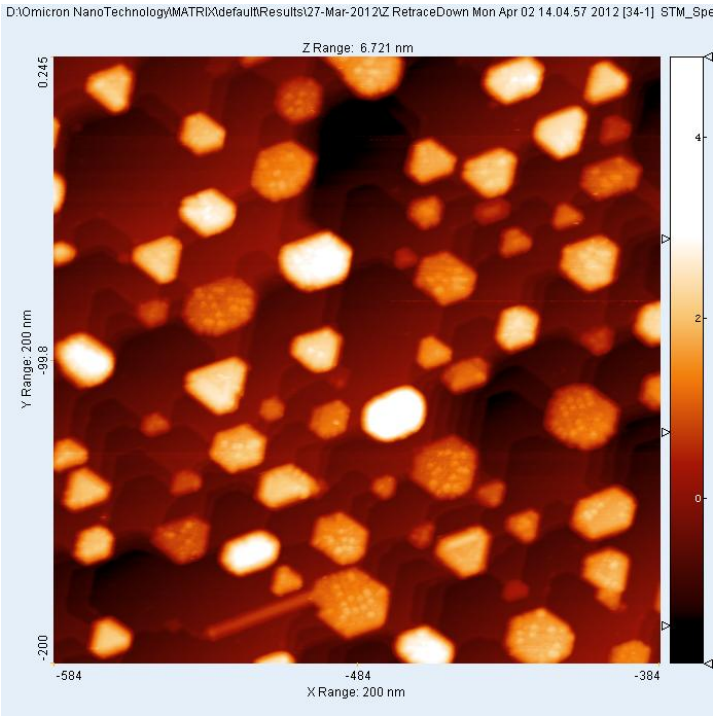
- Ratio Ti 387eV and Au 69eV Auger signals after annealing
- 900K forms surface alloy

Overview of nano TiO_x crystals



200nm x 200nm

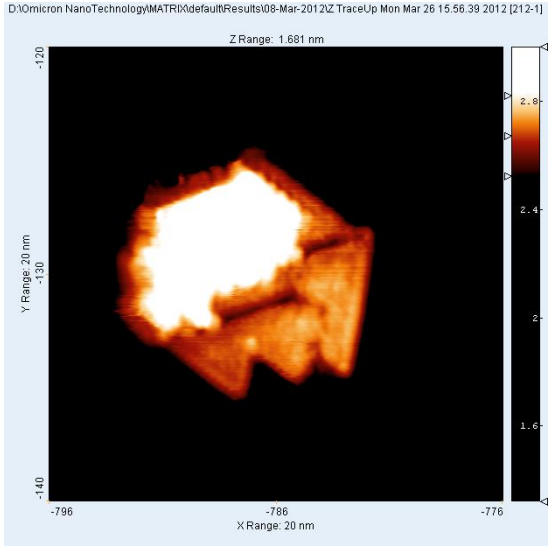
Ti islands on Au (111) substrate

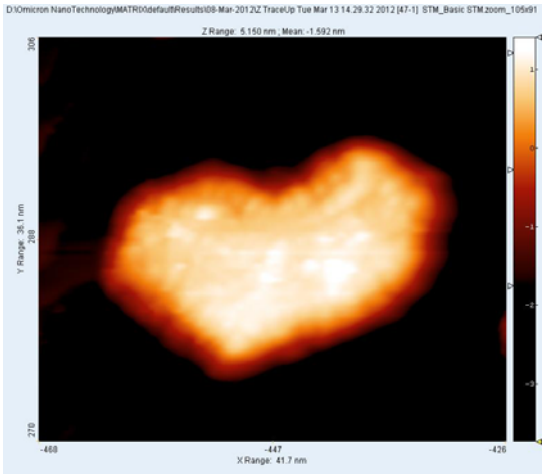


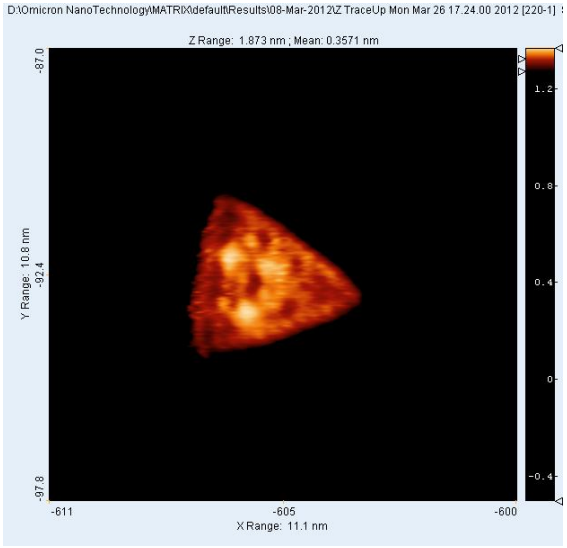
200nm x 200nm

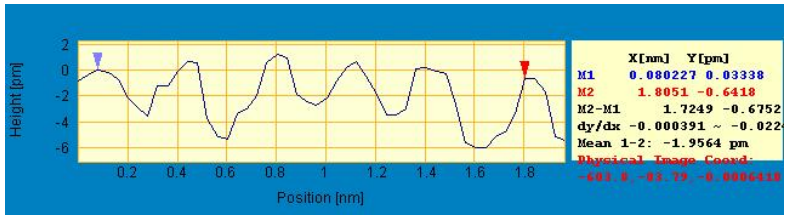
TiO_x crystals on Au (111) substrate

Representative Crystals





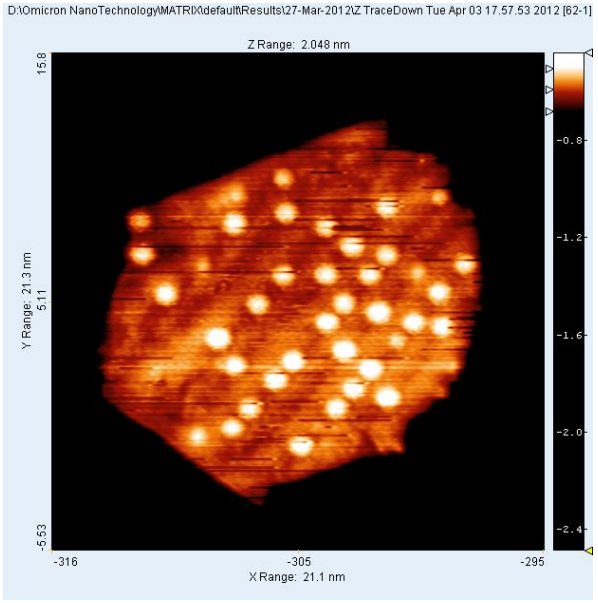


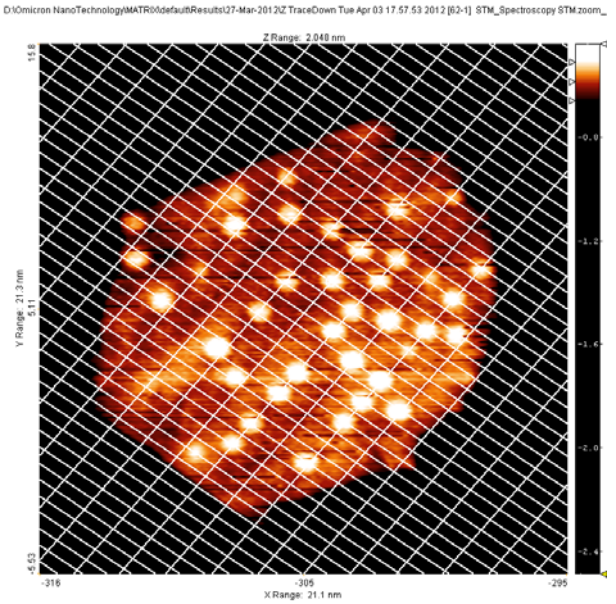


Atom spacing is 0.31nm compared to Au substrate atom spacing 0.29nm

Strong interaction with the substrate!

Unit cell of nano TiOx crystals





Au adtoms sitting on surface?

a = 0.5 nm

b = 1.2 nm

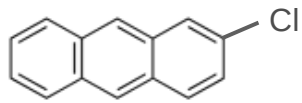
Conclusions

- **Molecular adsorbed phases and motion on TiO_2 (110) surfaces.**
- **2-Chloroanthracene single-molecule dissociation events by current pulse from STM tip**
  - **Dissociation energy of +3.1 ± 0.3 eV.**
  - **Dissociation mechanism**
- **UHV nanocrystals synthesized for dynamics.**

Acknowledgements

- ✓ Thanks to Prof. Osgood for the guidance in research
- ✓ Thanks to Denis and Yang Lou, a great pleasure working with you.
- ✓ Thanks to Stan, Figo, Vincent for all supports and useful discussions.

Voltage pulse from STM tip

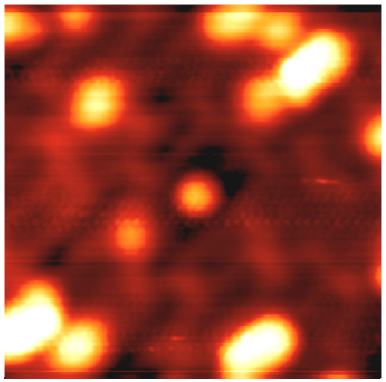


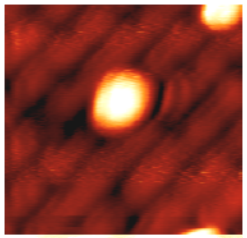
Bias + 1.5V

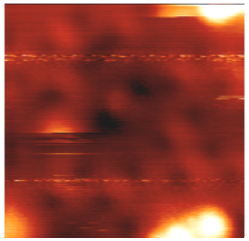
– 1.5V

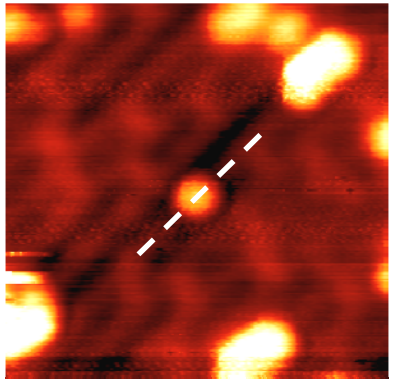
+ 2.5V

+1.5V







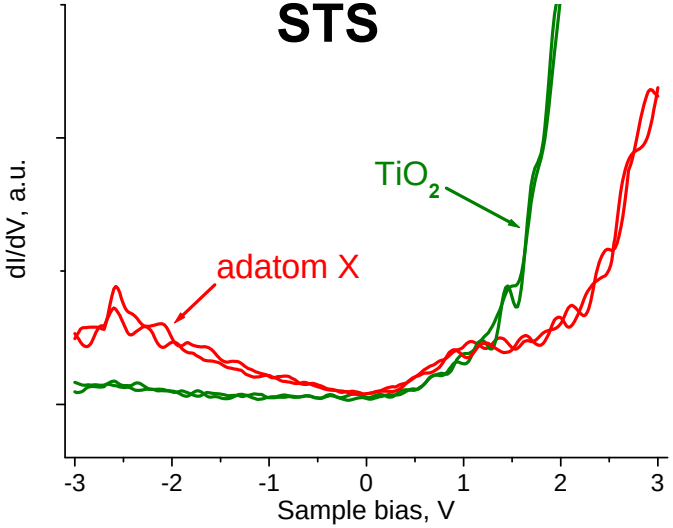


Very stable

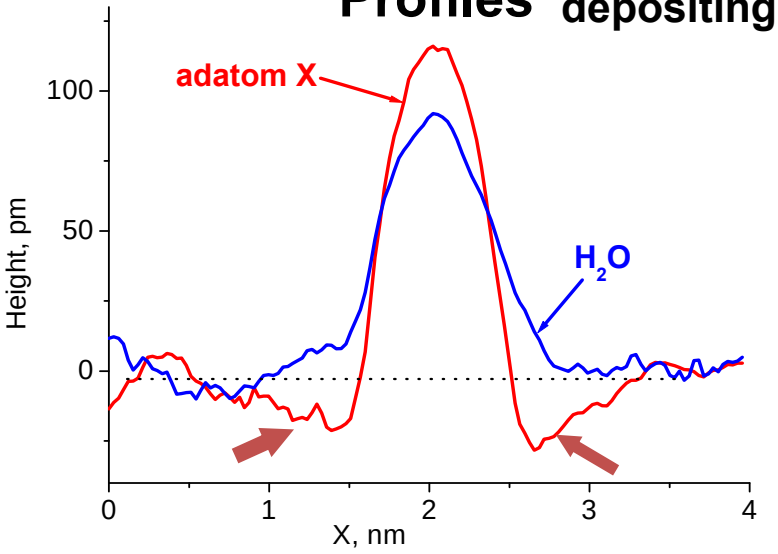
7 x 7 nm, 20 pA

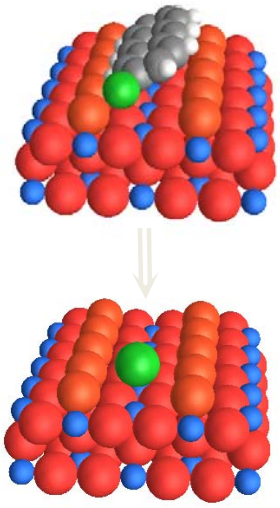
2-Chloroanthracene dissociates depositing Cl atom

STS



Profiles





- Negative charge

Dissociation Mechanism: DEA

Gas-Phase Dissociation by Electron Attachment

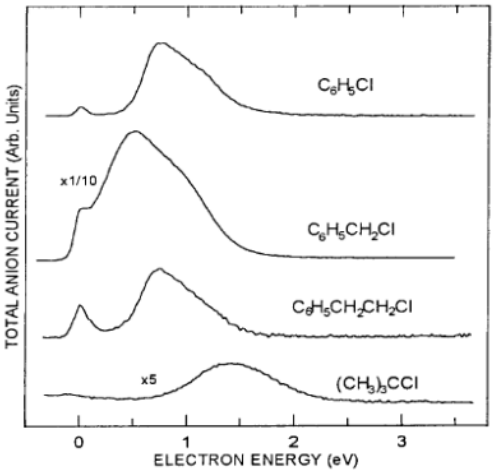


Figure 2. Total anion current, as a function of the incident electron energy, in chlorobenzene, benzyl chloride, (2-chloroethyl)benzene, and *tert*-butyl chloride.

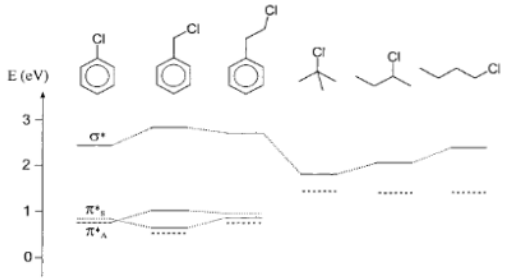
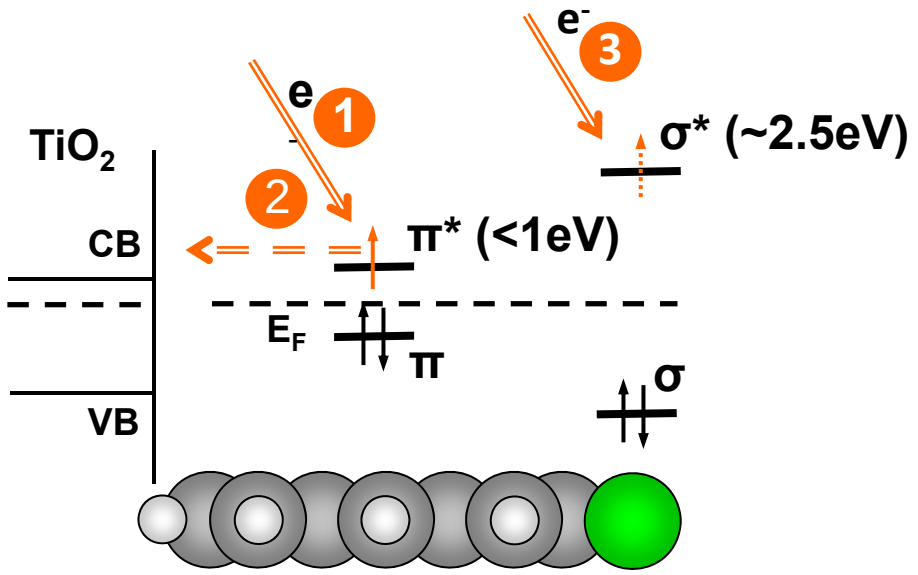


Figure 3. Diagram of the resonance energies measured in the ET spectra (full lines) and of the peak energies measured in the DEA spectra (dashed lines).



- **Dissociation is caused by electron attachment**
- **Because of surface proximity the lifetime on π* orbital is very short**
- **Dissociation caused by electrons tunneling directly into C-Cl σ* orbital**

Modelli A., Venuti M., *J.Chem.Phys.A* (2001) 105, 5836