Advances in Single Molecular (STM) Chemistry

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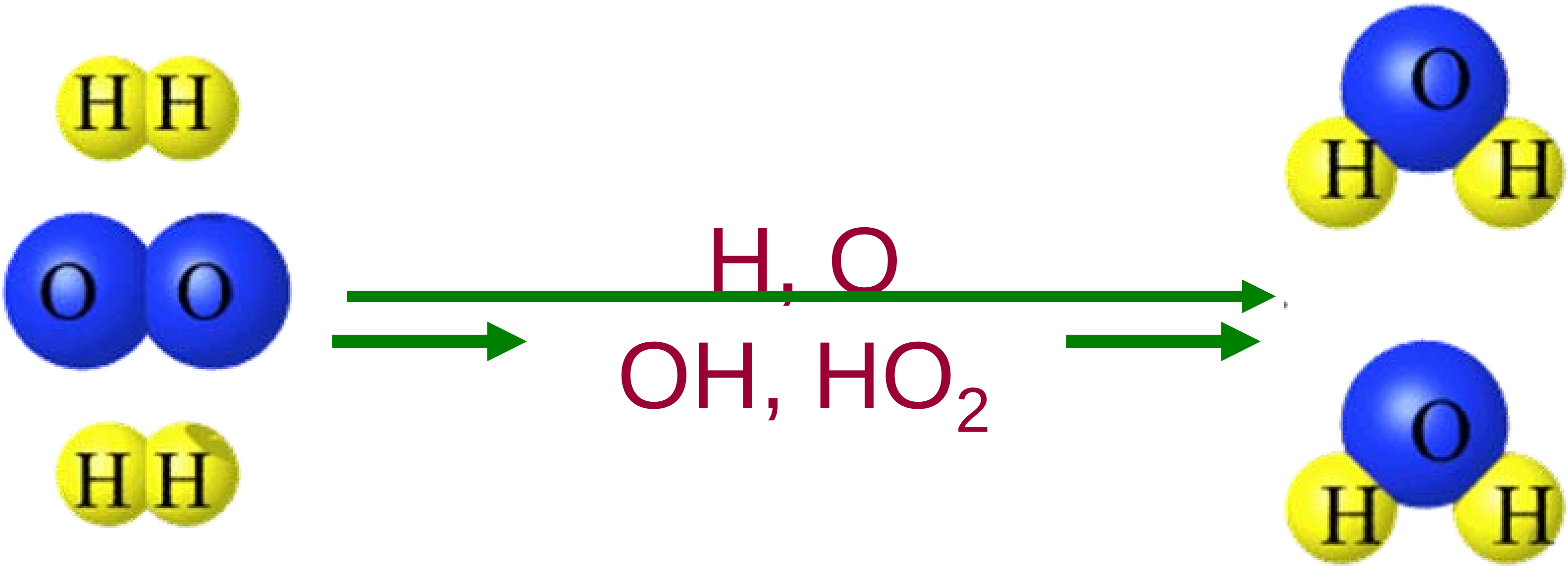
Why Single Molecular Chemistry?

$$2H_2 + O_2 \rightarrow 2H_2O + ENERGY$$

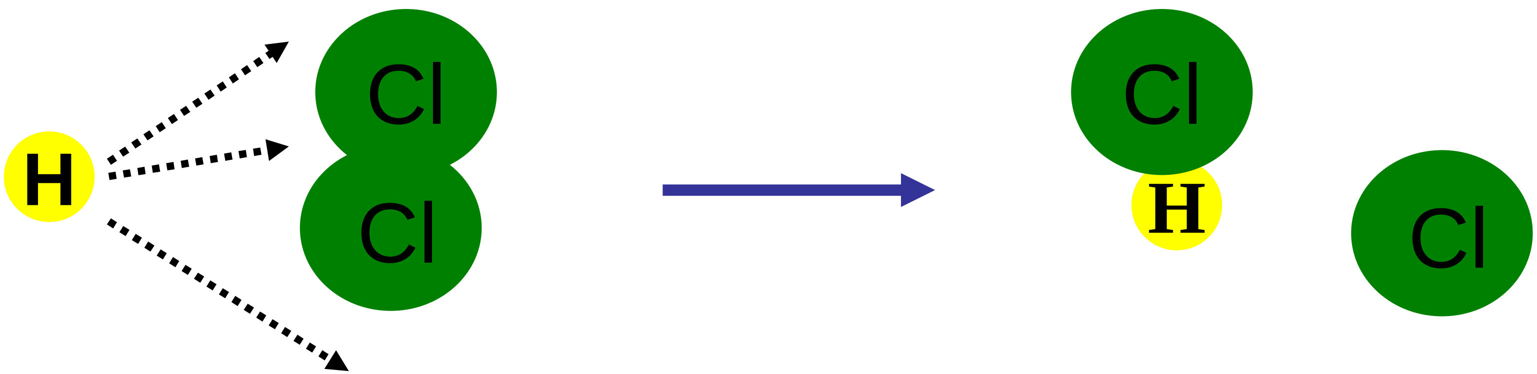
Overall reaction



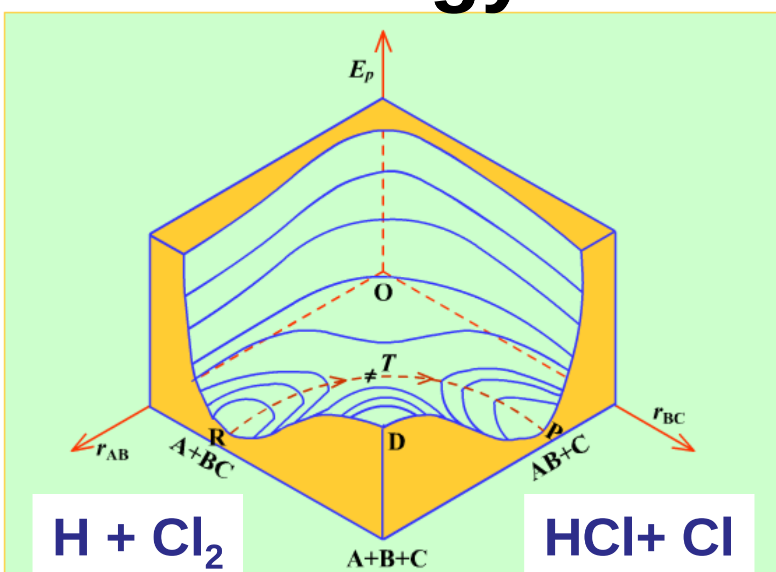
Chemistry: 行易 知難

Elementary Reaction

$H + Cl_2 \rightarrow HCl + Cl$



Potential Energy Surface



Introduction and Outline

Toward ultimate chemistry with

√ **(a) <10^{-8} m spatial resolution,**

- Single-molecule imaging
- Single-bond characterization
- Control of single-molecule reactions

(b) <10^{-14} s time resolution?

femtosecond chemistry

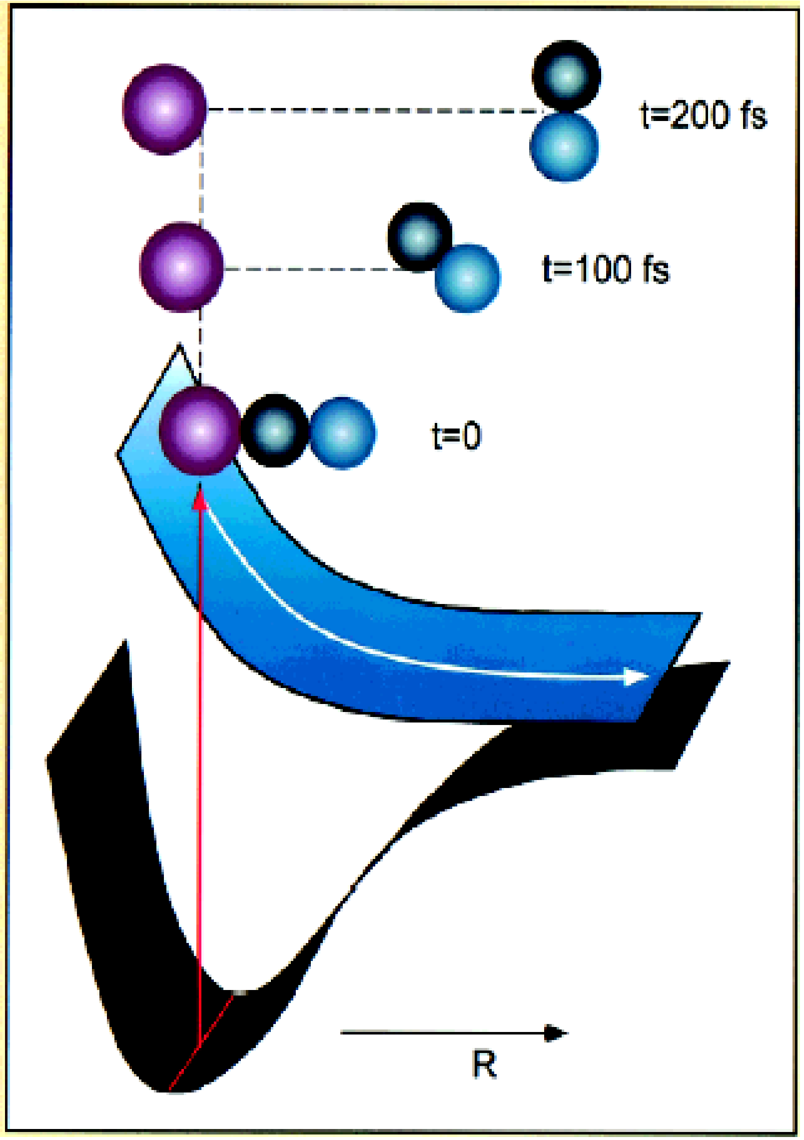
(c) both (a) and (b)

Are you dreaming?

√ **Chemical dynamics derived from STM**

1. Abstraction reaction
2. Adsorption mechanism

Dynamics: follow a chemical reaction



Types of surface chemical reactions

1. corrosion reactions:

etch: $Cl_2 + Si = SiCl_2$

2. crystal growth reactions

PVD : $Ag(g) \rightarrow Ag(s)$

MBE : $Ga(g) + As(g) \rightarrow GaAs(s)$

CVD : $SiH_4(g) + 2O_2(g) \rightarrow SiO_2(s) + 2H_2O(g)$

3. catalytic reactions

exchange reaction : $H_2\ (g) + D_2\ (g) \rightarrow 2HD(g)$

recombination reaction : $H_{ad} + H_{ad} \rightarrow H_2\ (g)$

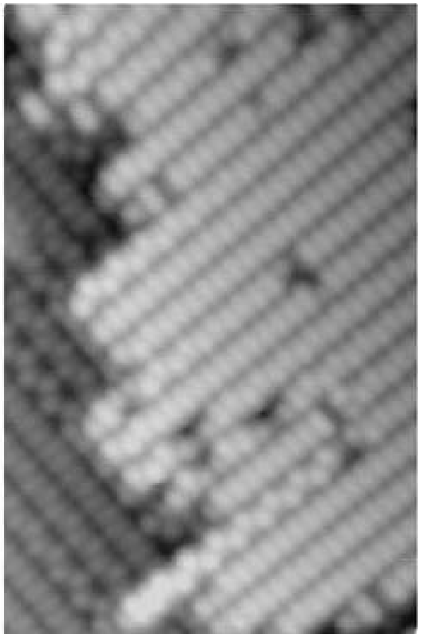
unimolecular decomposition reaction

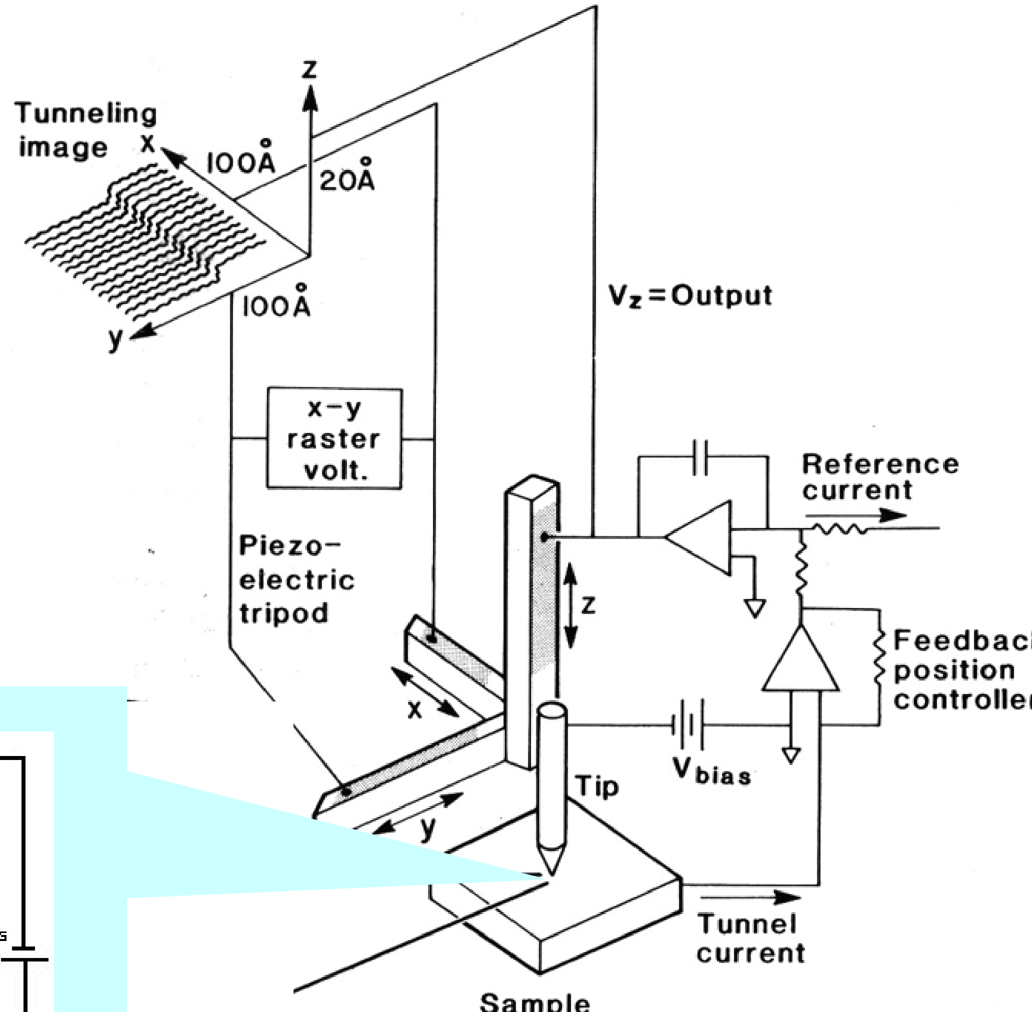
$$N_2O\ (g) \rightarrow N_2(g) + O_{ad}$$

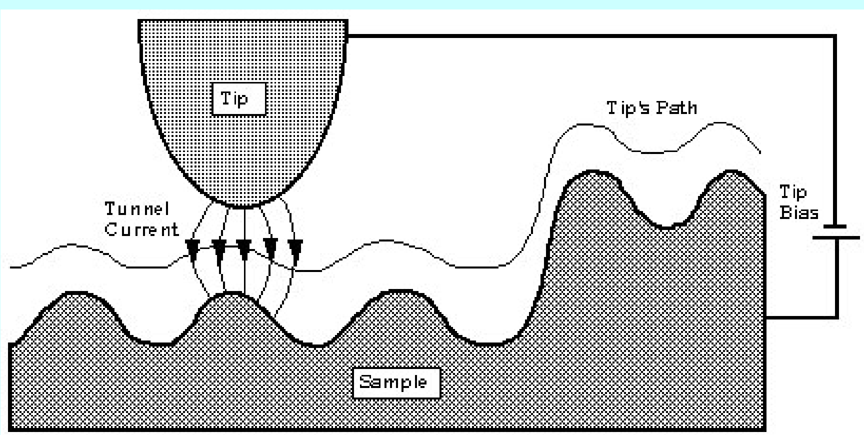
bimolecular reaction

$$CO\ (g) + O_2(g) \rightarrow CO_2(g)$$

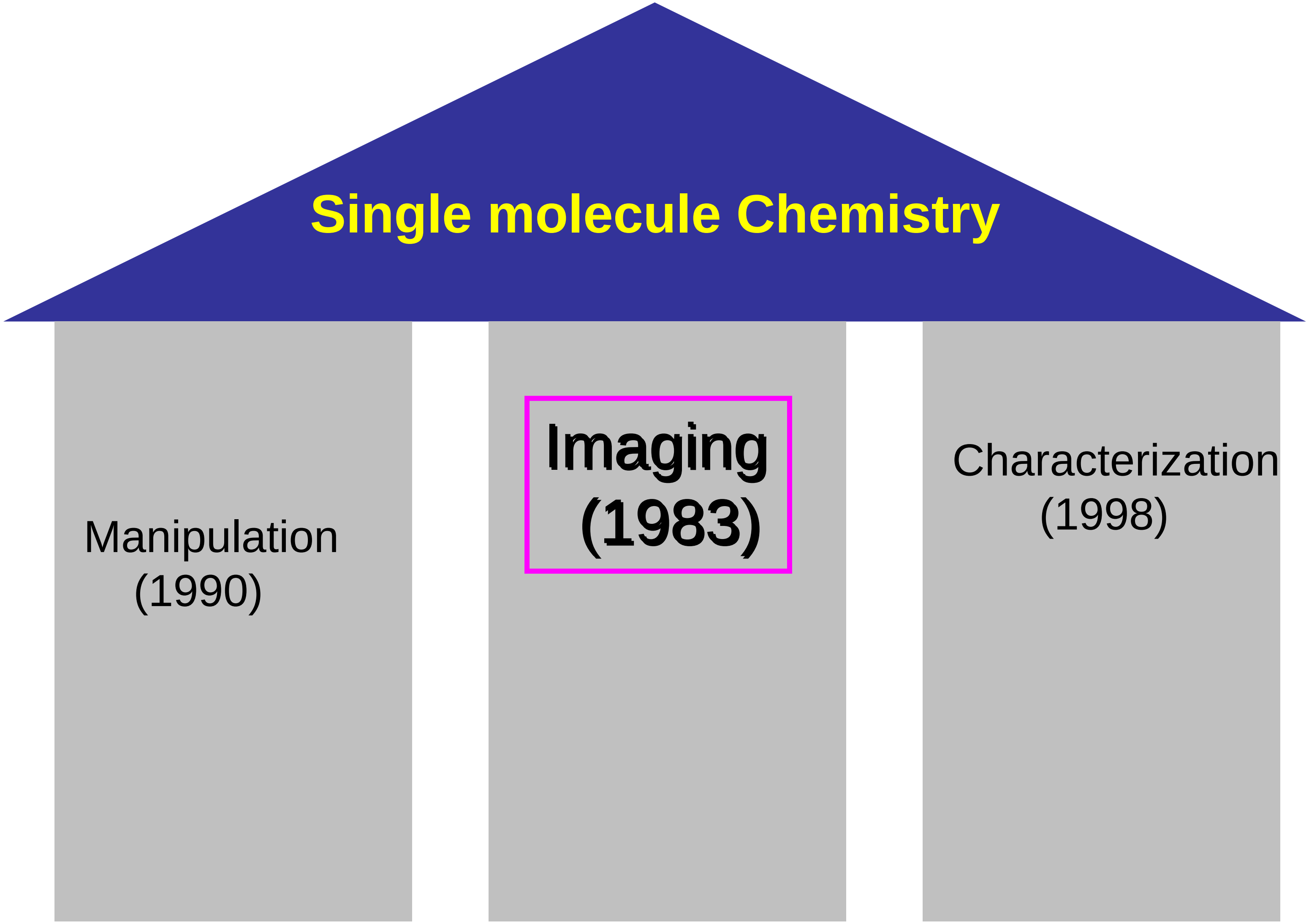
Scanning Tunneling Microscopy



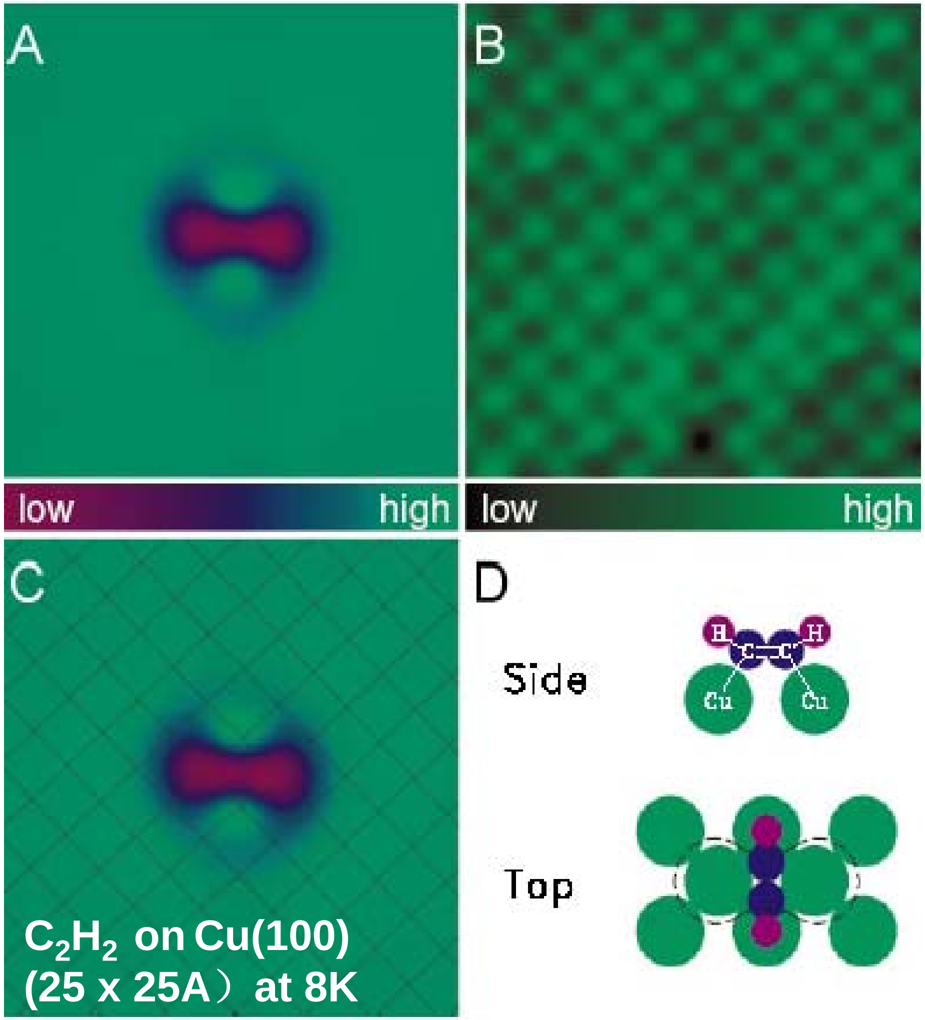




Three Pillars in STM

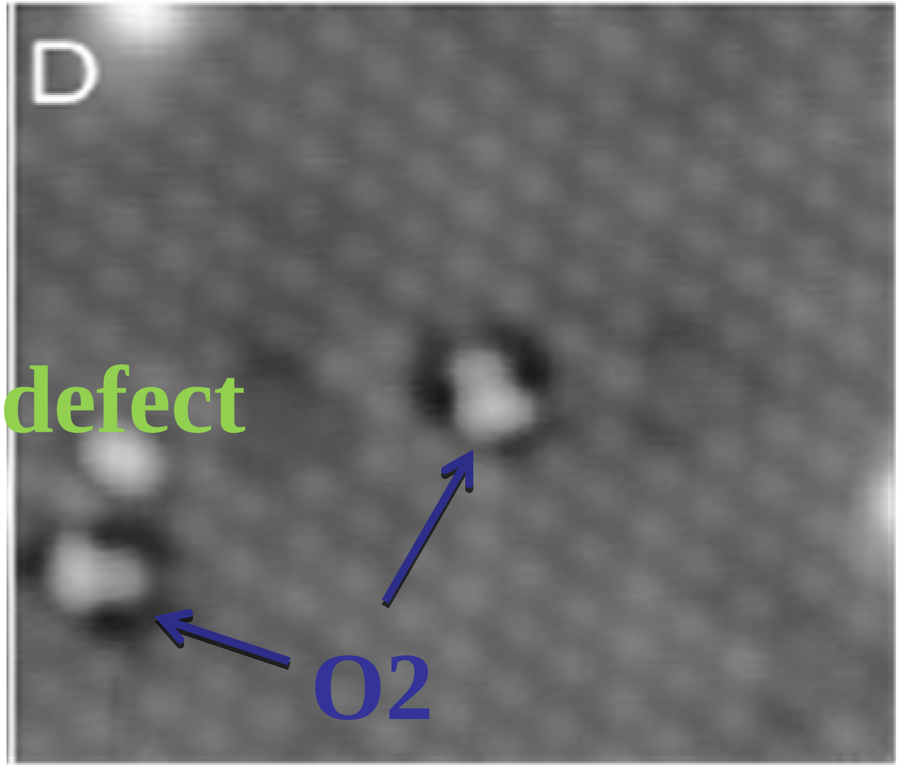


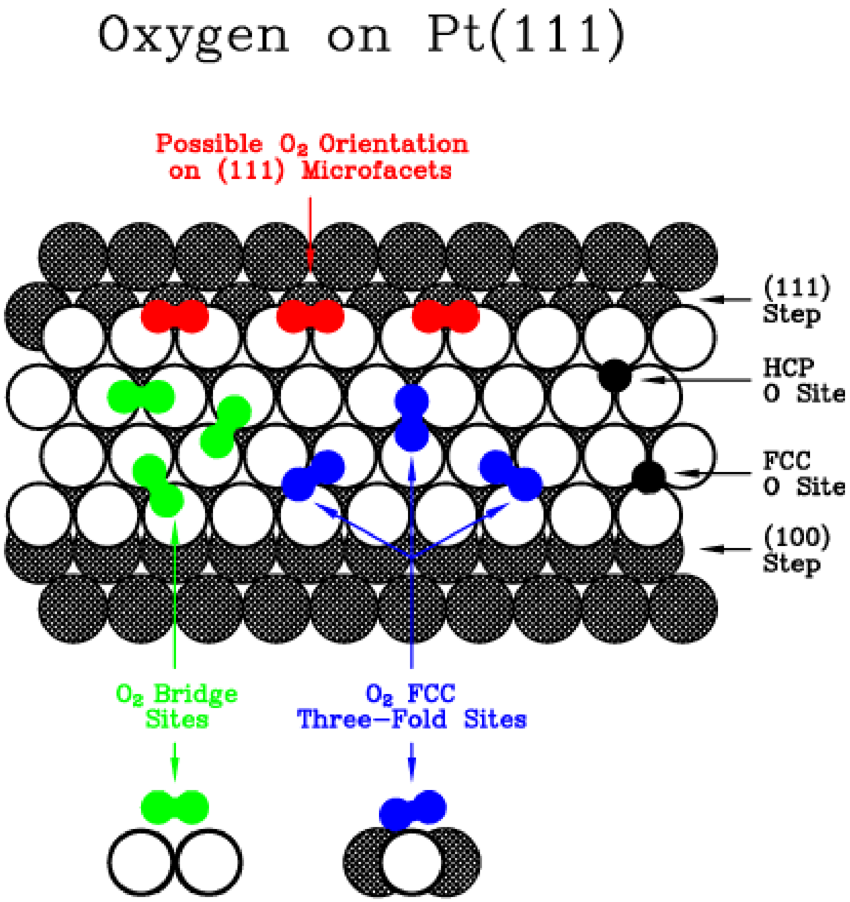
Acetylene 乙炔



B. C. Stipe, M. A. Rezaei,W. Ho, Science 280(1998)1732

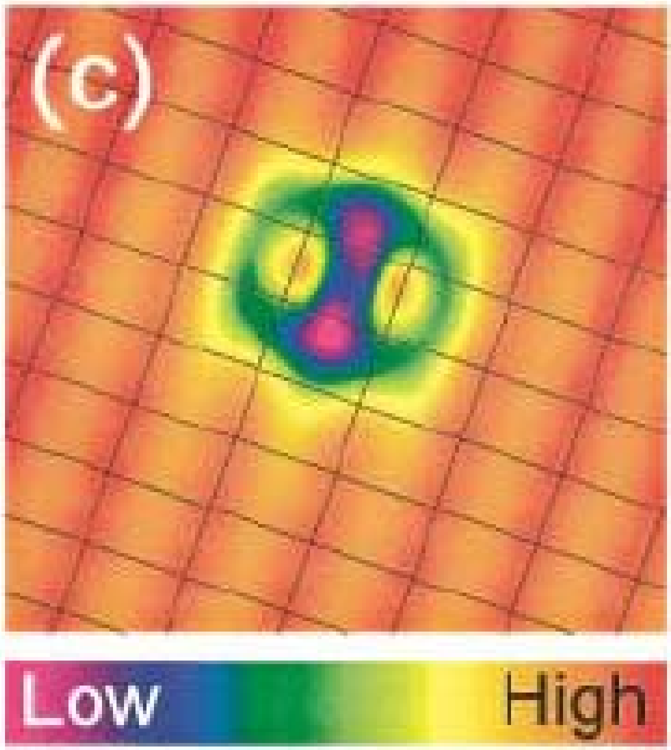
O_2 on Pt(111) at 8 K





Ho etc.

O_2 on Ag(110) by CO-tip

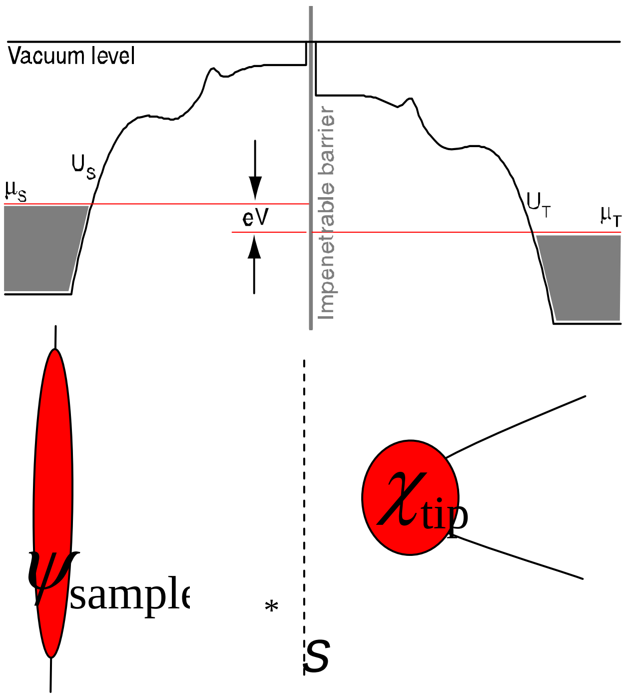


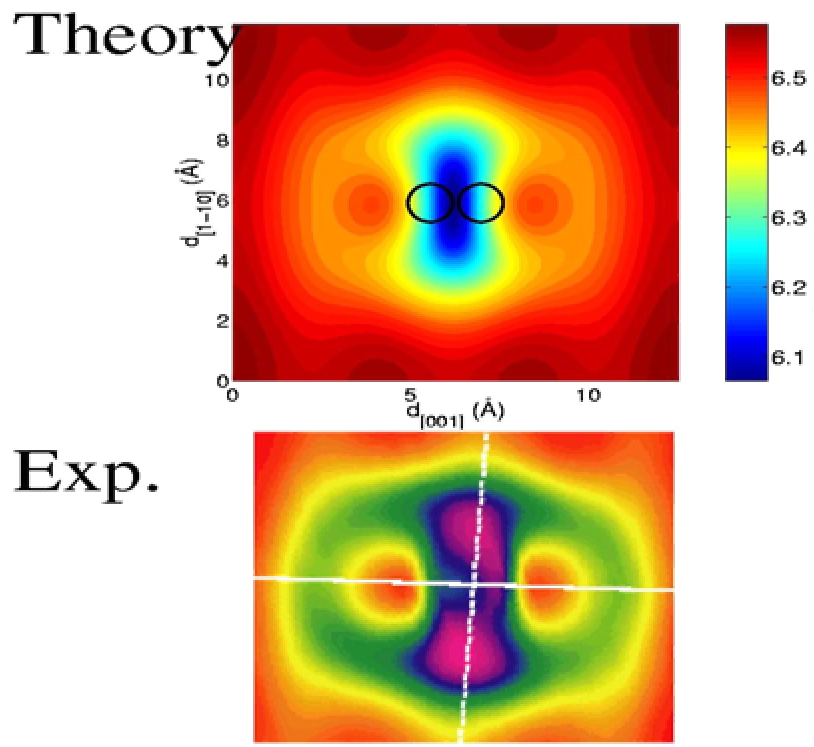
What are all those bumps?

What kind of information is contained in the STM image ?

* Hahn, Lee, and Ho, Phys. Rev. Lett. **85**, 1914 (2000)

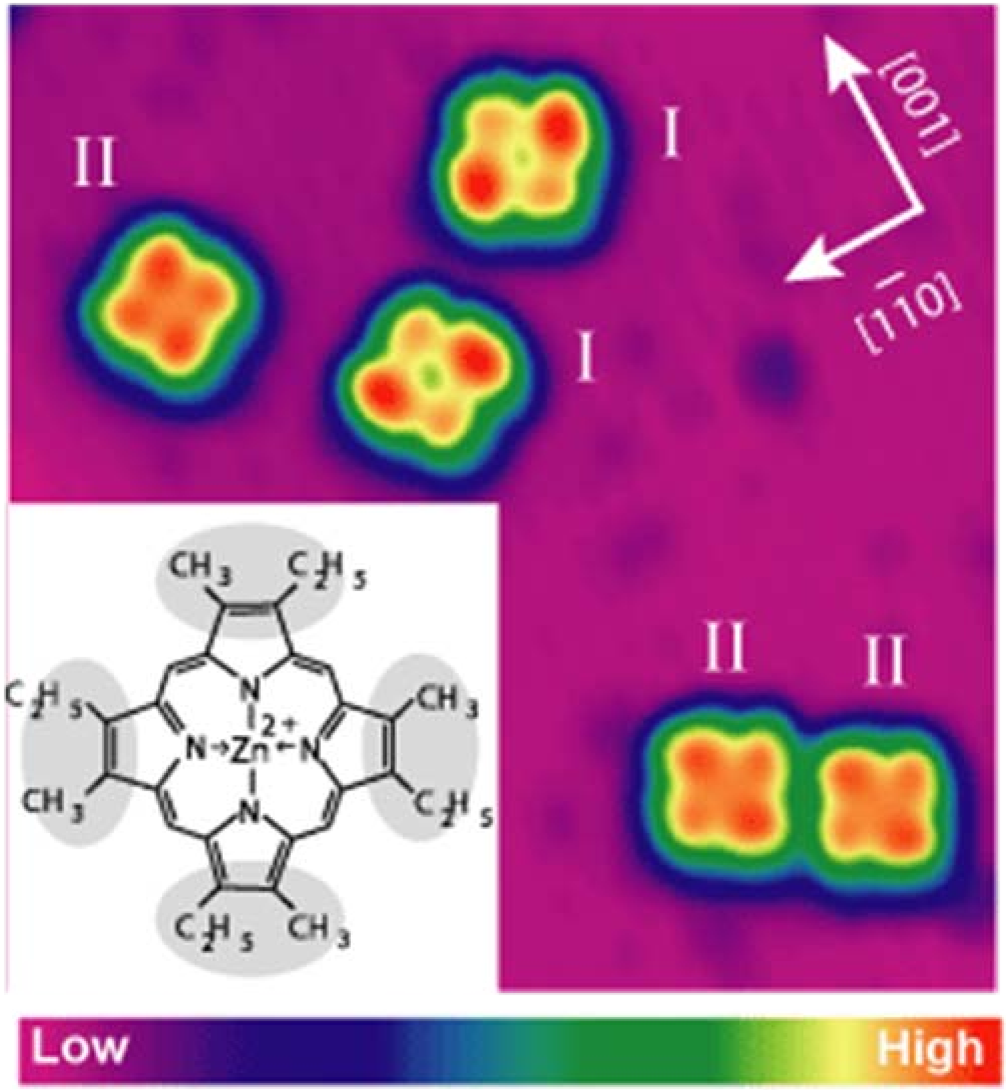
LDOS from LDA vs. STM images: O_2/Ag(110)





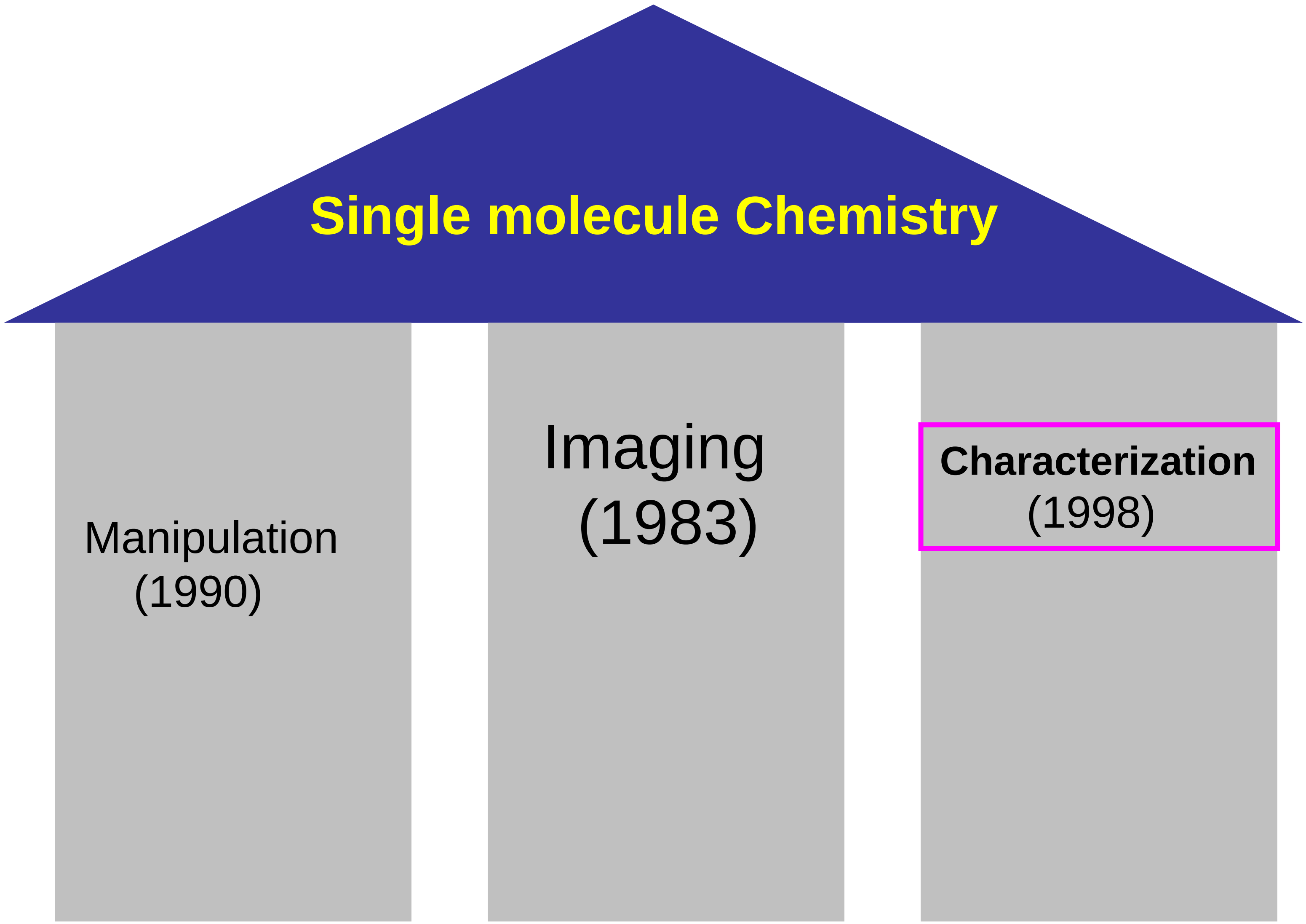
Protrusions derive from an anti-bonding molecular state and not from the nuclear positions

Large molecule: Zn(II) Etioporphyrin

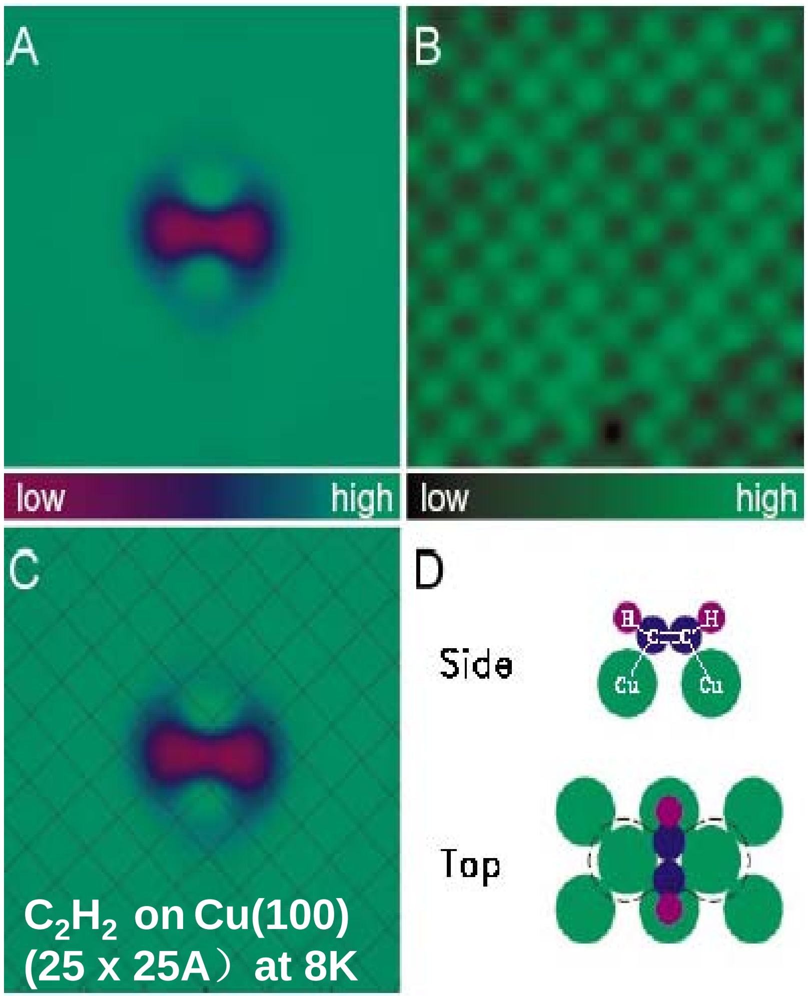


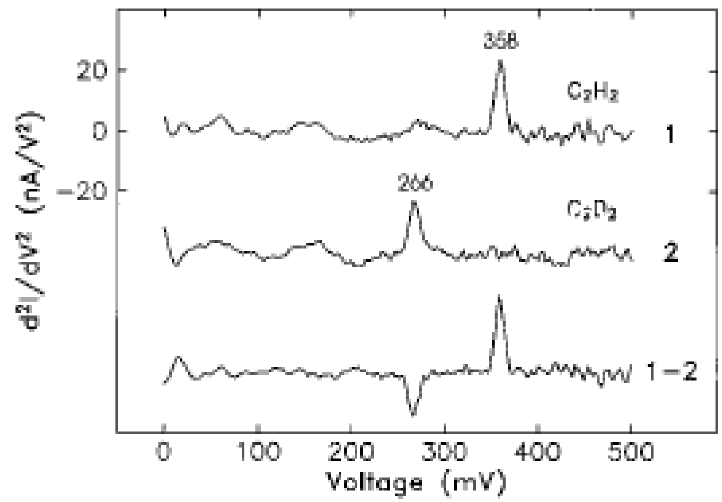
Ho etc.

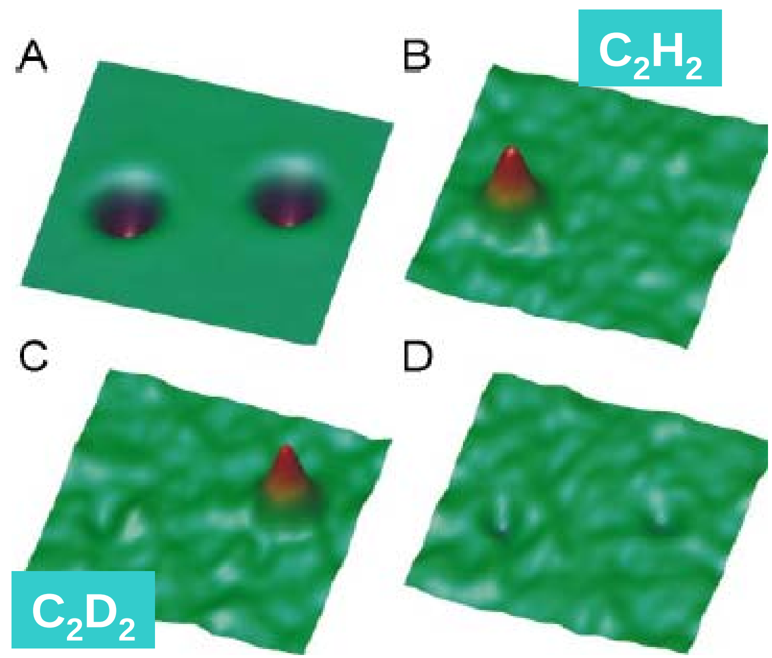
"Second Pillar"



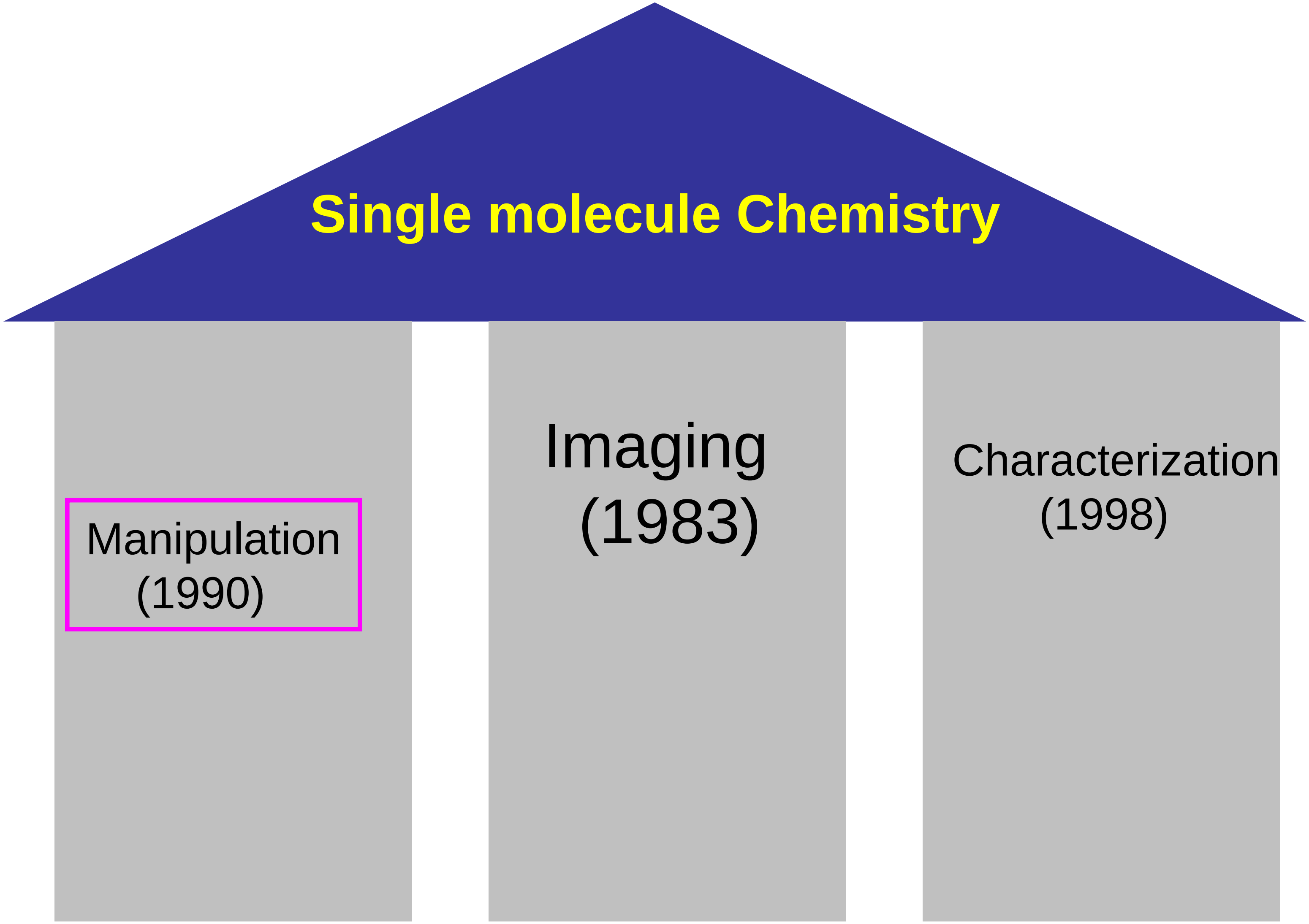
Isotope identification



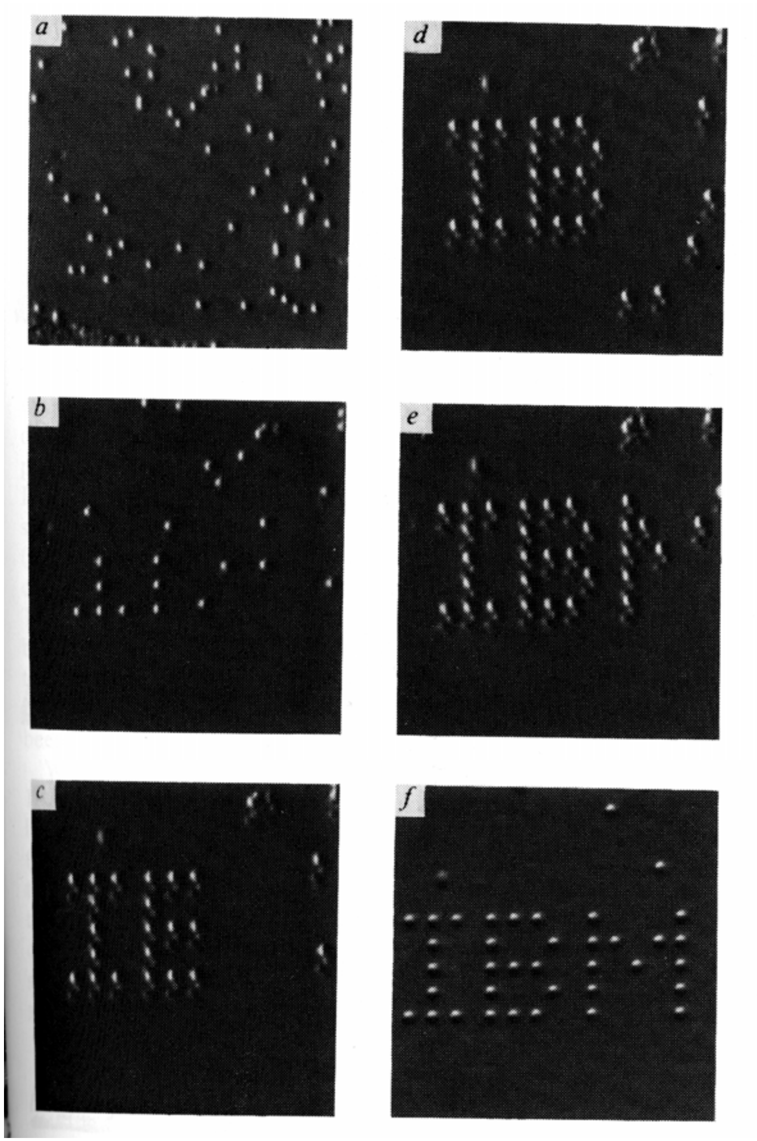




“Third Pillar”



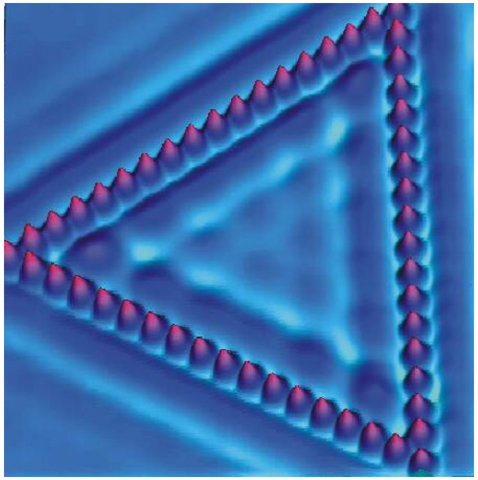
First Controlled Atomic Manipulation*

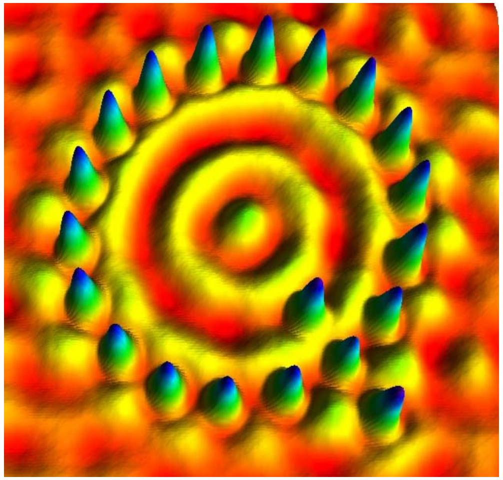


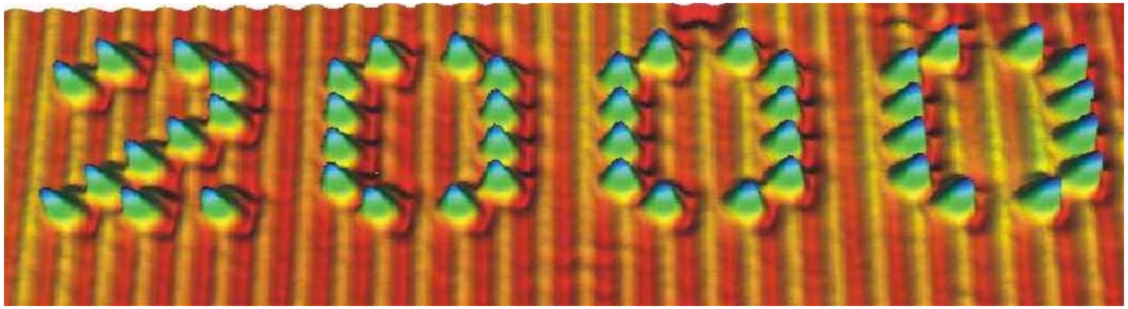
- **Xe adsorbed on Ni(110) at 4K**
- **Xe dragged by direct tip surface interaction**

*Eigler & Schweizer, Nature **344** 524 (1990)

Manipulating Atoms and Molecule

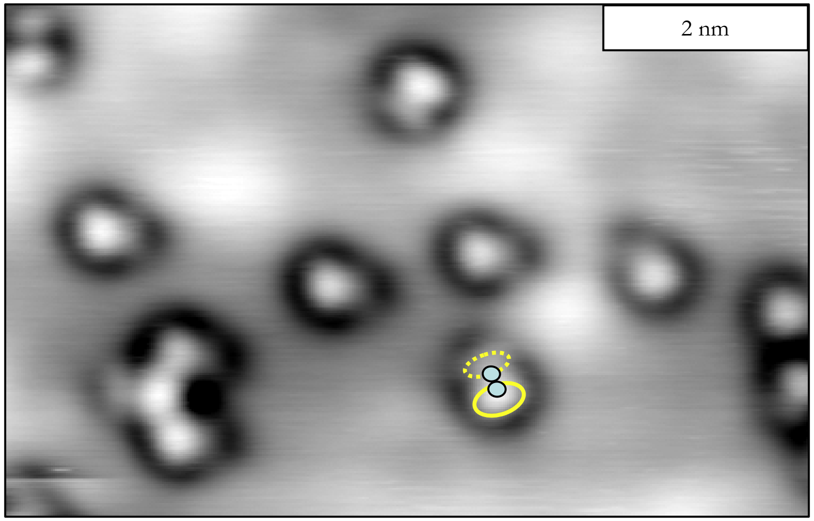






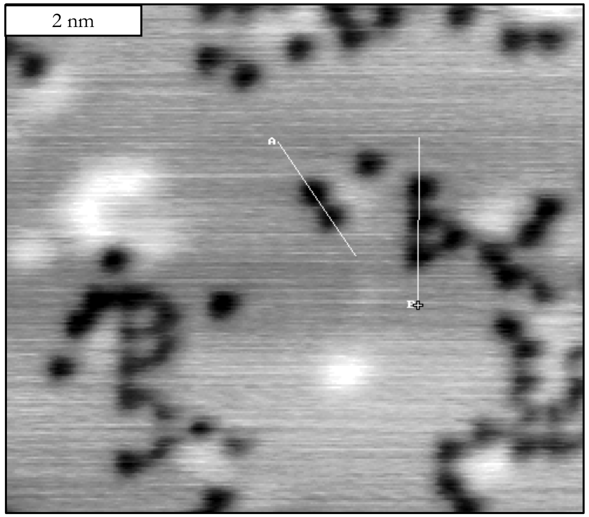
Dissociation of O2 by e- injected by the tip

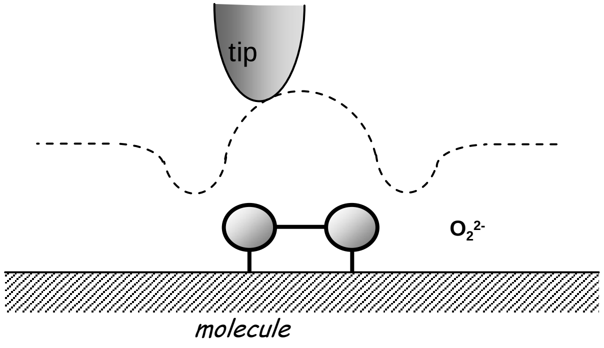
Molecular oxygen on Pd(111) at 30K

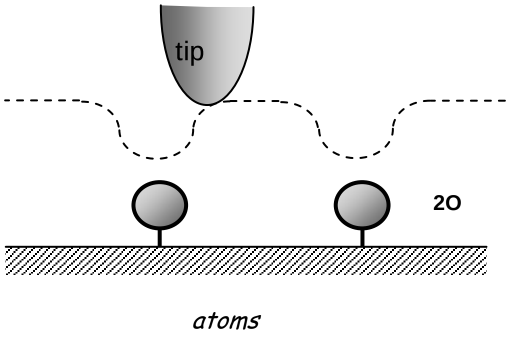


Tunnel current increased from 1 to 10 nA

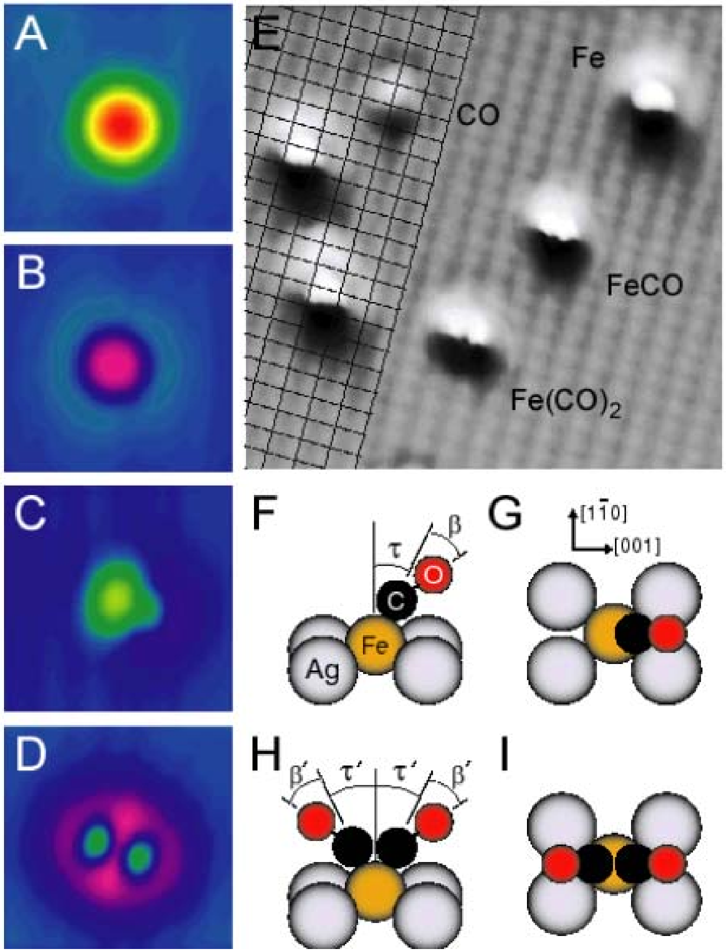
Atomic oxygen







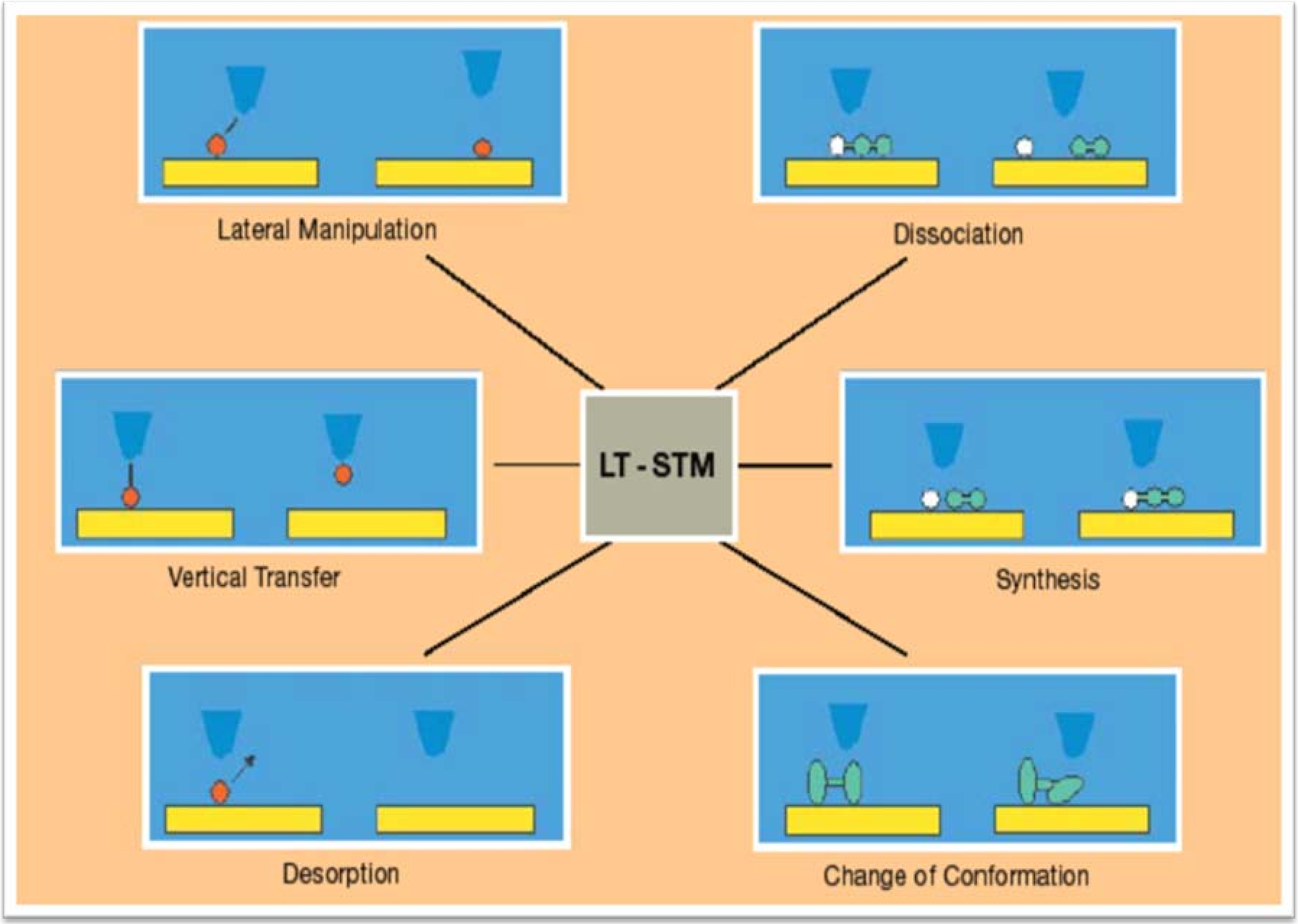
Single molecule synthesis



Formation of single inorganic complexes

H.J. Lee and W. Ho, Science **286**, (1999)

STM Manipulation processes



Introduction and Outline

Toward chemistry with

√ (a) <10^{-8} m spatial resolution,

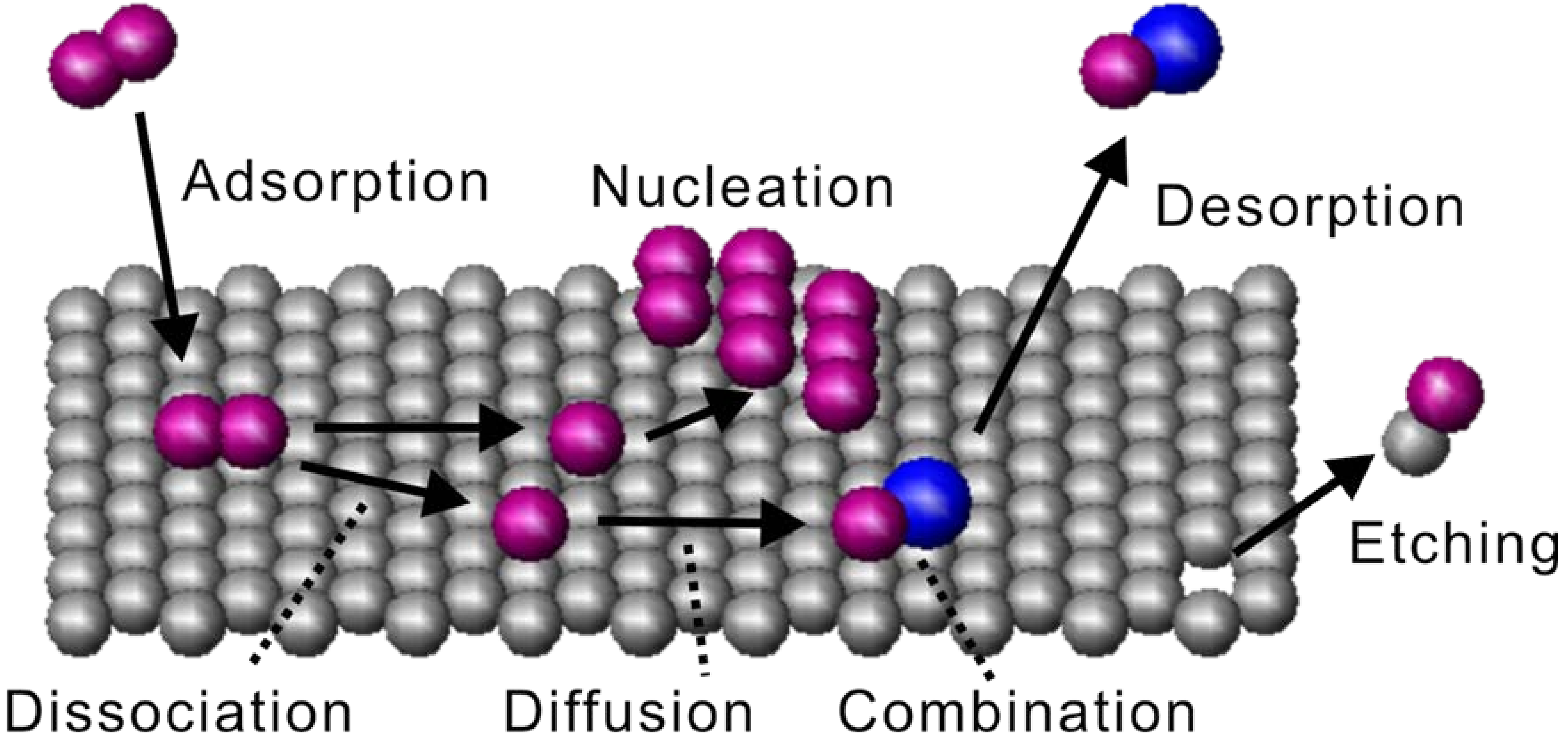
- Single-molecule imaging
- Single-bond characterization
- Control of single-molecule reactions

Chemical dynamics derived from STM

√ 1. Abstraction reaction

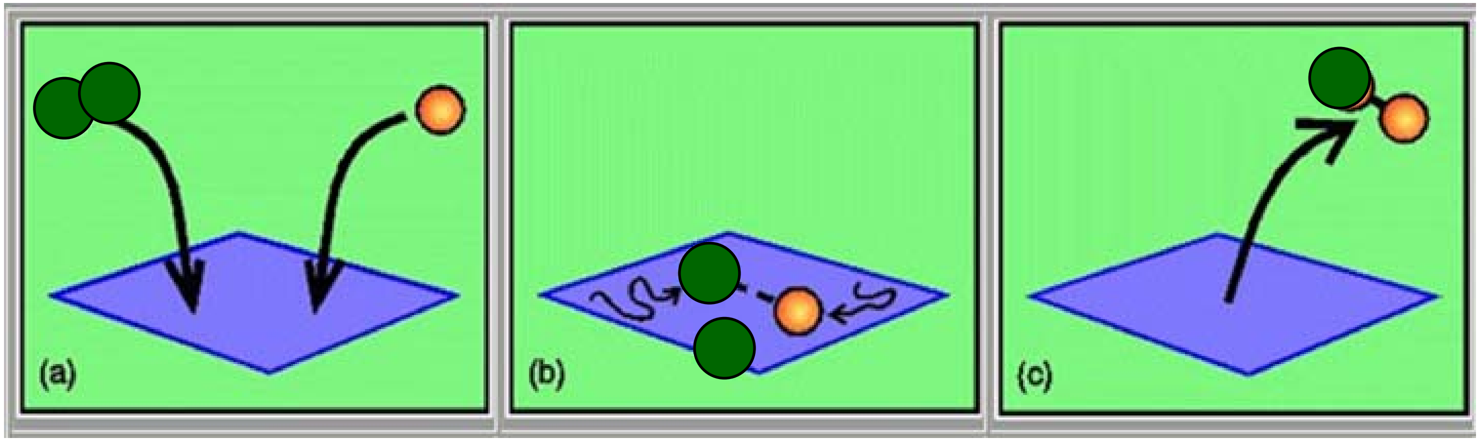
2. Adsorption mechanism

Surface reactions

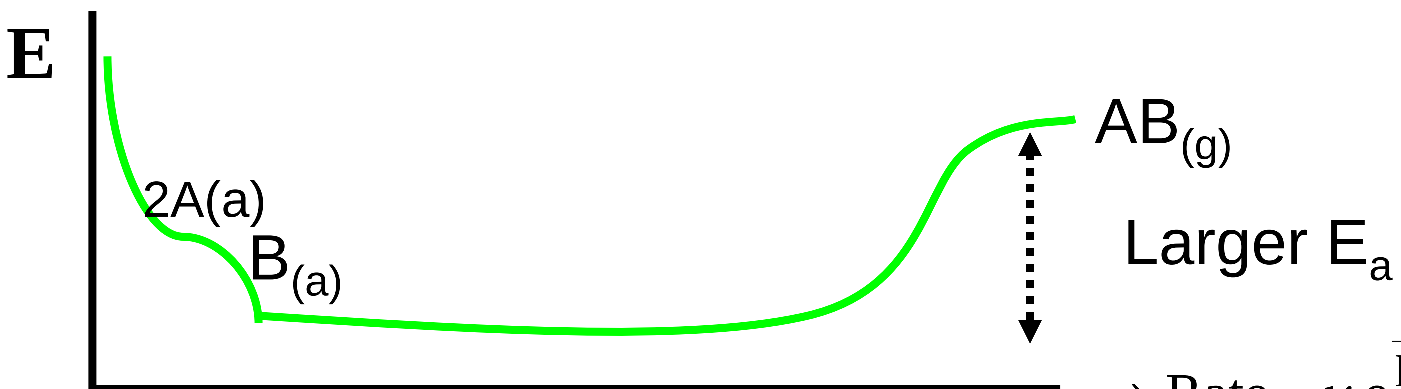


A textbook surface catalytic reaction

$A_{2(g)} + B_{(g)} \rightarrow A_{(a)} + B_{(a)} \rightarrow AB_{(g)}$



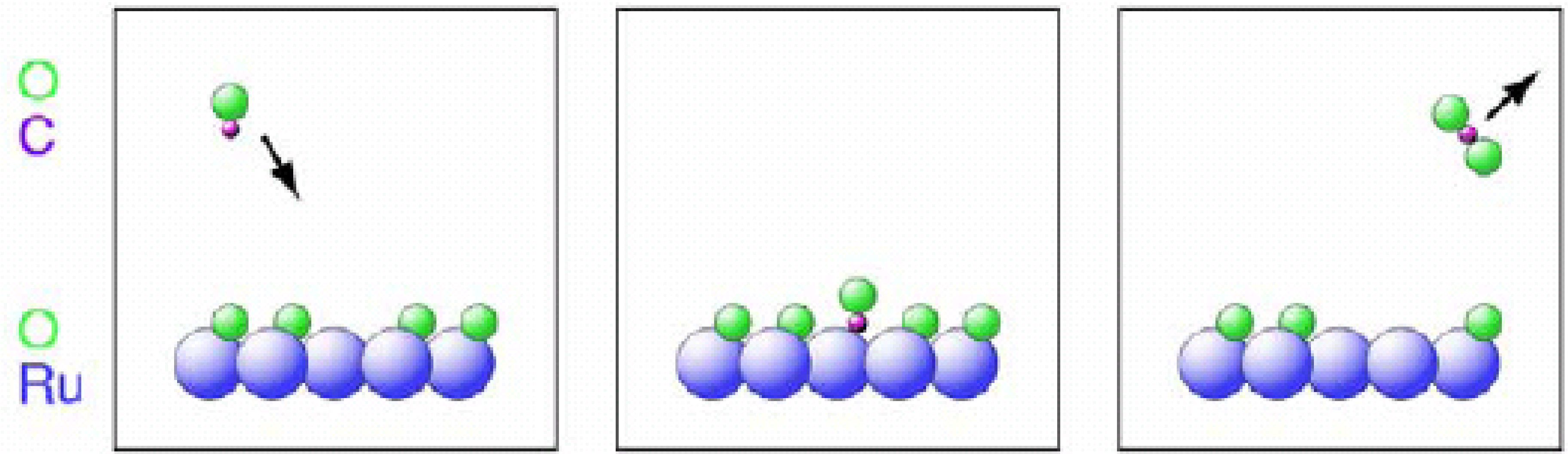
Langmuir-Hinshelwood Mechanism (LH)

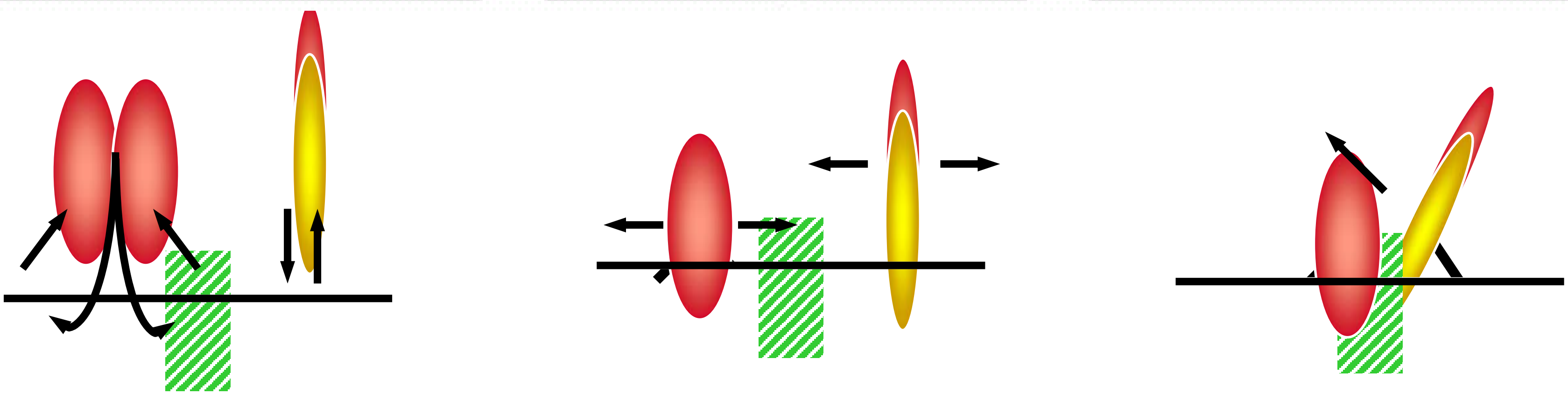


$$\Rightarrow \text{Rate} = \nu\, e^{\frac{-E_a}{k_B T}} \text{ small}$$

LH example

$CO + O_2 \rightarrow CO_2$

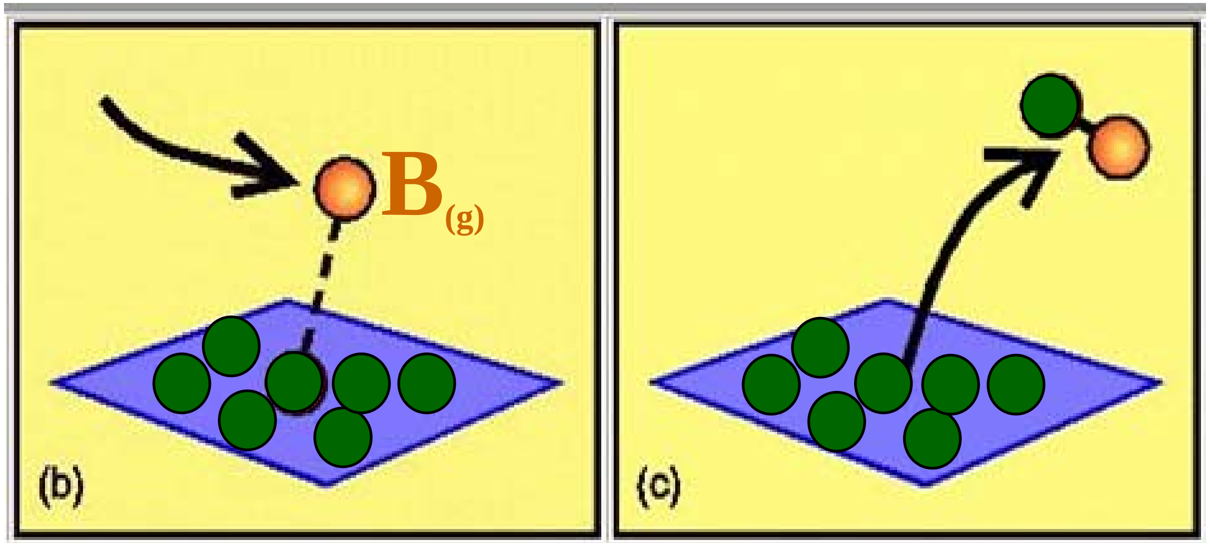


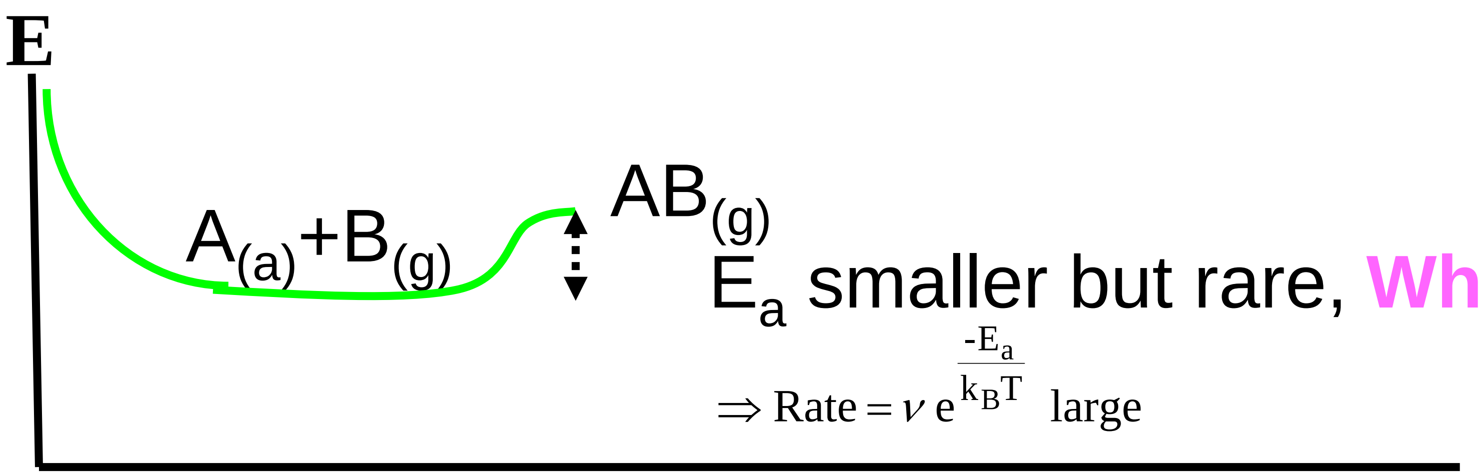


Catalytic reaction of the 2nd kind :

Eley-Rideal Mechanism (ER)

$A_{2(g)} \rightarrow A_{(a)} + B_{(g)} \rightarrow AB_{(g)}$



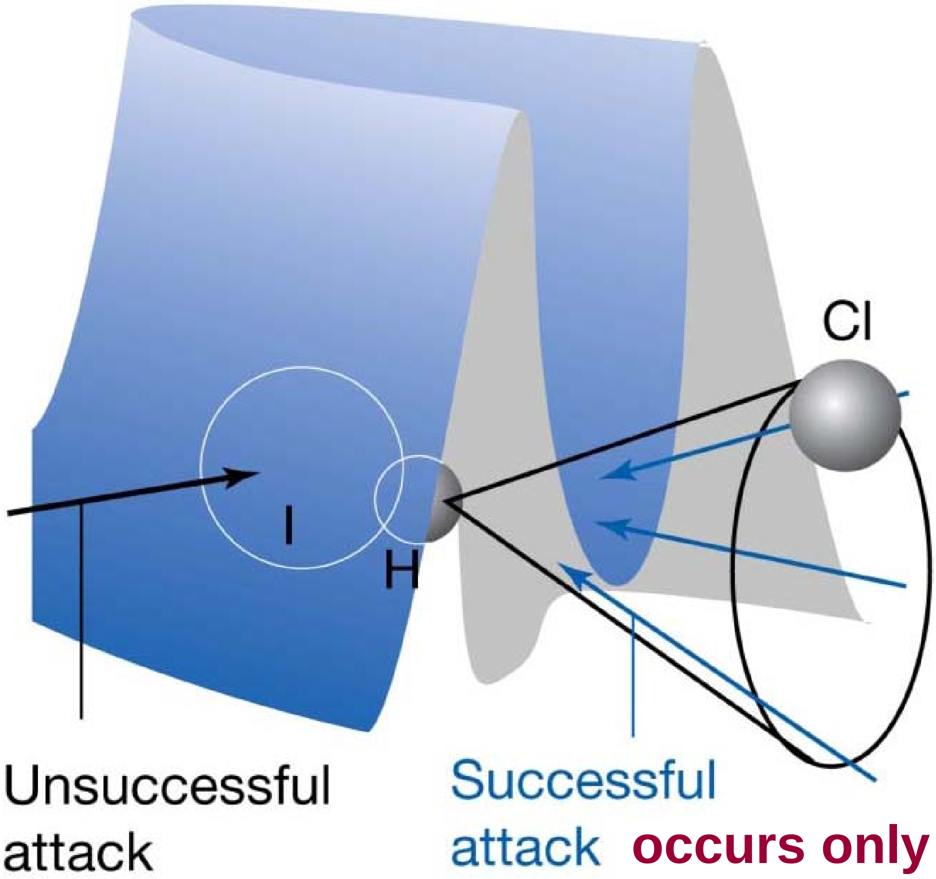


E_a smaller but rare, **Why?**

$$\Rightarrow \text{Rate} = \nu\, e^{\frac{-E_a}{k_B T}} \text{ large}$$

Modeling successful approach of Cl to HI

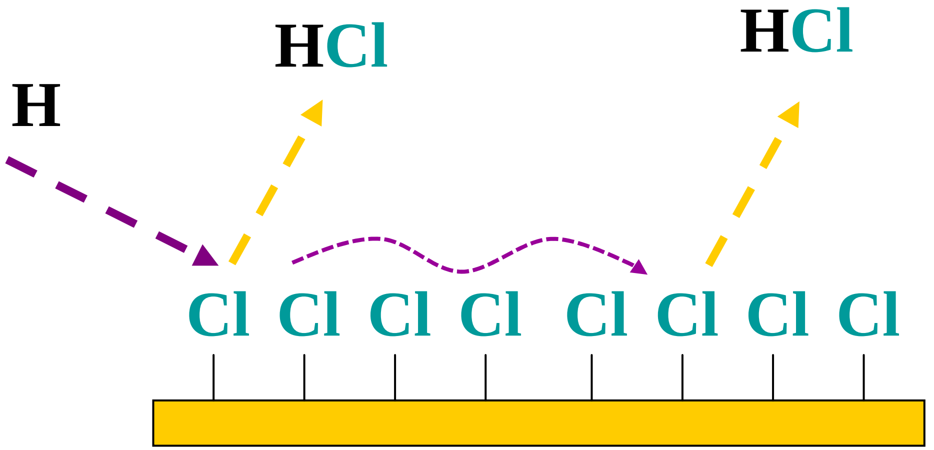
IH + Cl → HCl + I



occurs only when Cl approaches within a cone surrounding the H atom

Cl extraction by H on Au(111)

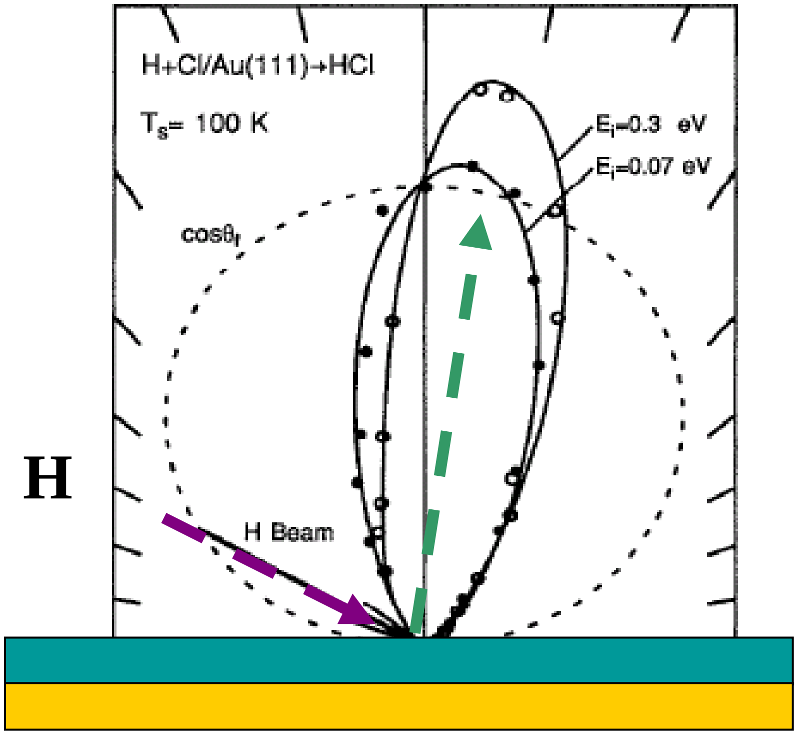
$$H_{(g)} + Cl_{(a)} \rightarrow HCl_{(g)}$$

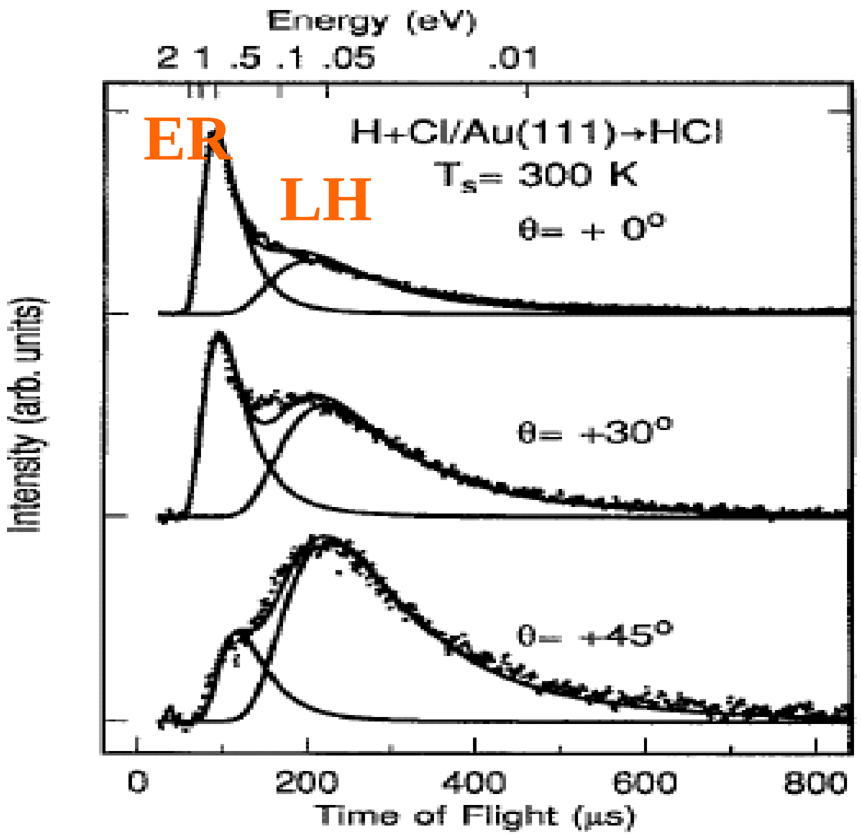


ER or not ER

How to tell?

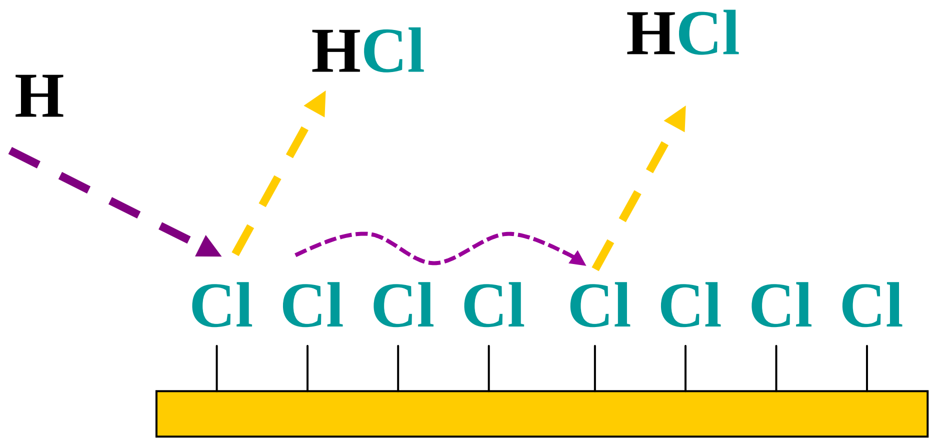
Rettner's approach:
Probing the gas product





Question: Details of LH events?

Our approach: examining the surface



Are reaction sites random or not random?

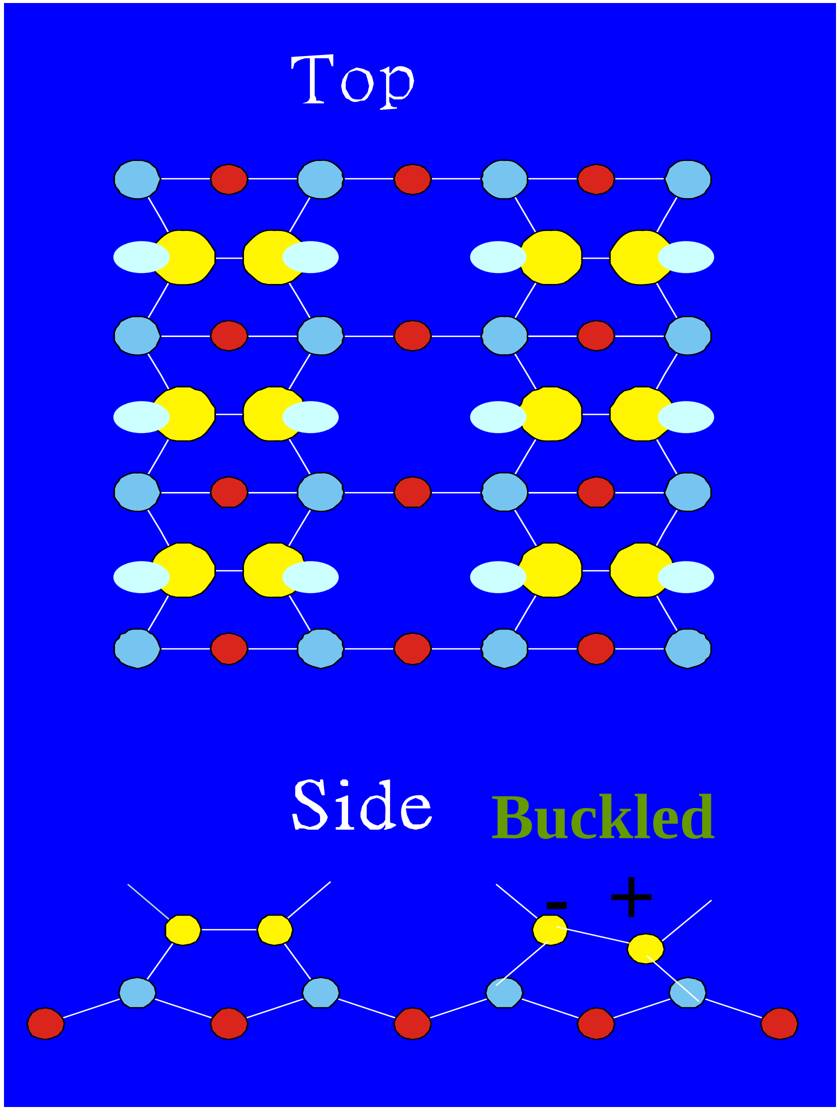
Raindrops on the windshield

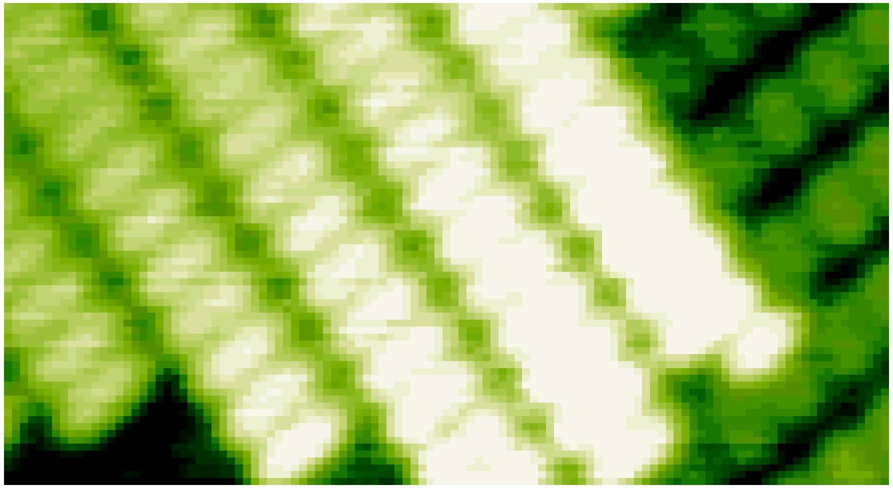
ER

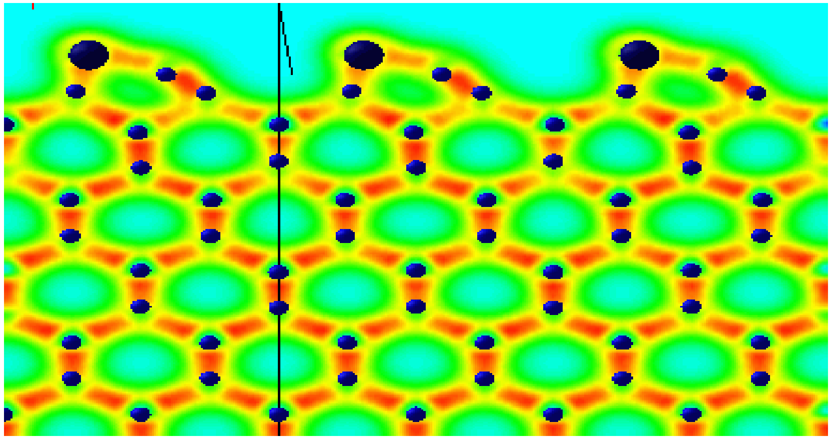
or

not ER ?

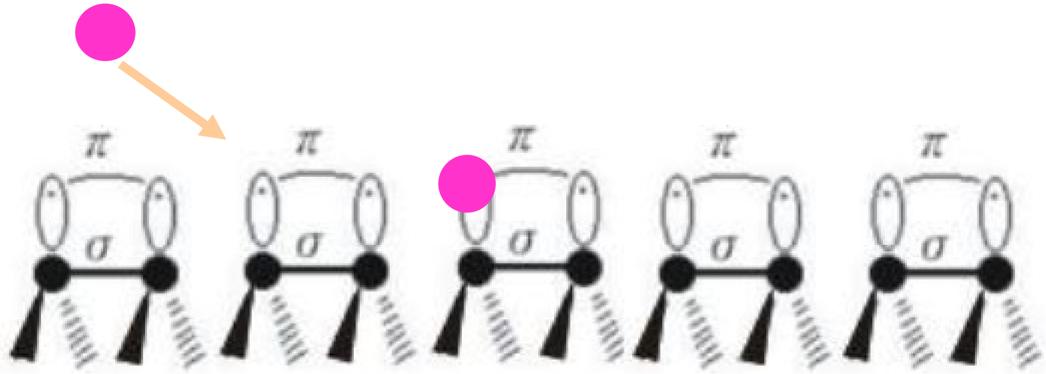
Dangling bonds (DBs) of Si(100)-2×1

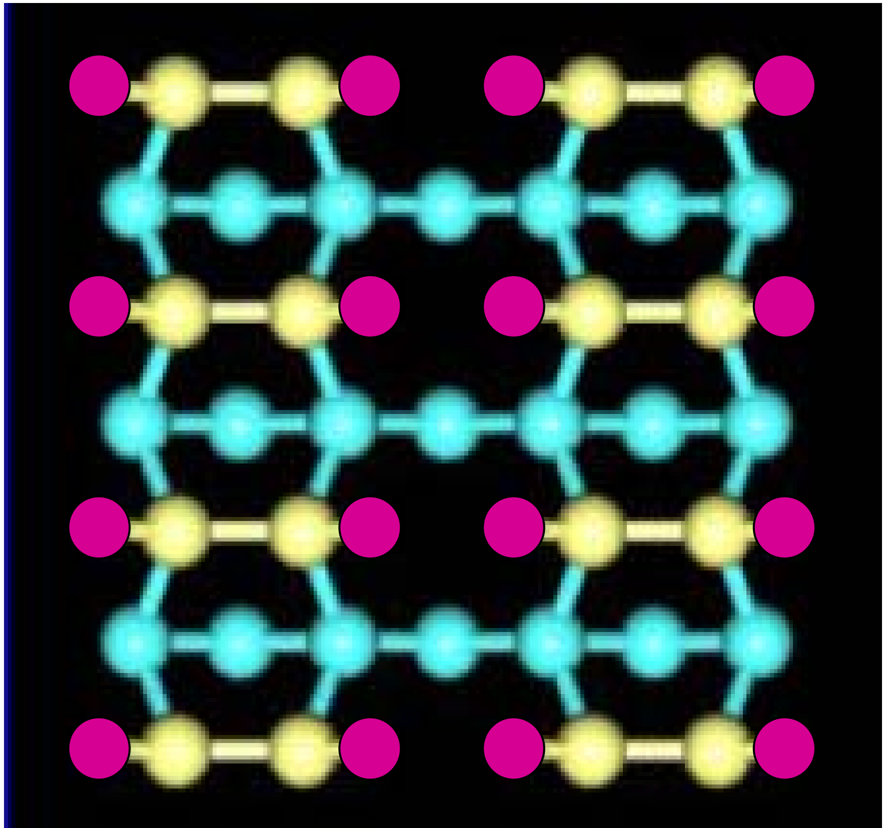


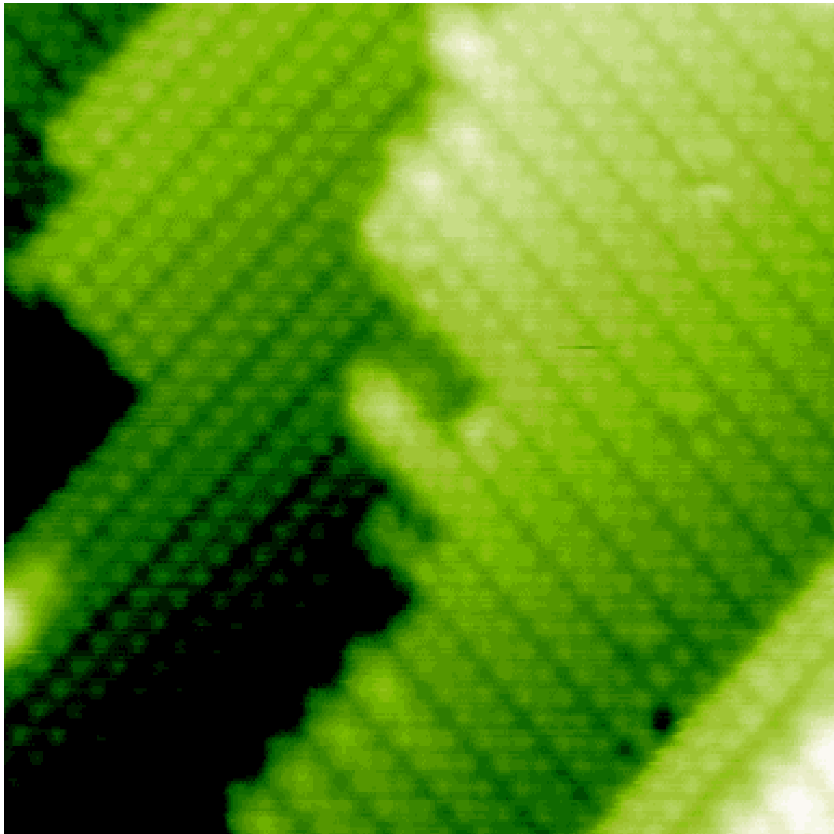




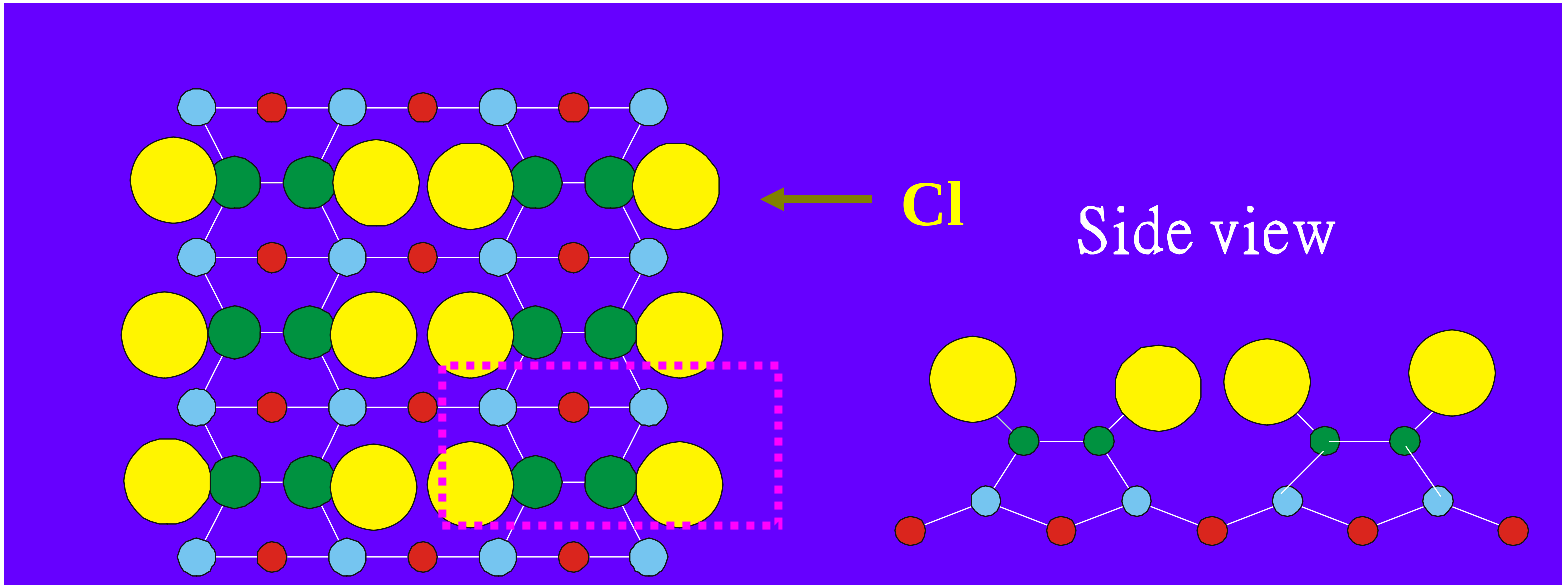
Atomic Hydrogen termination of DBs

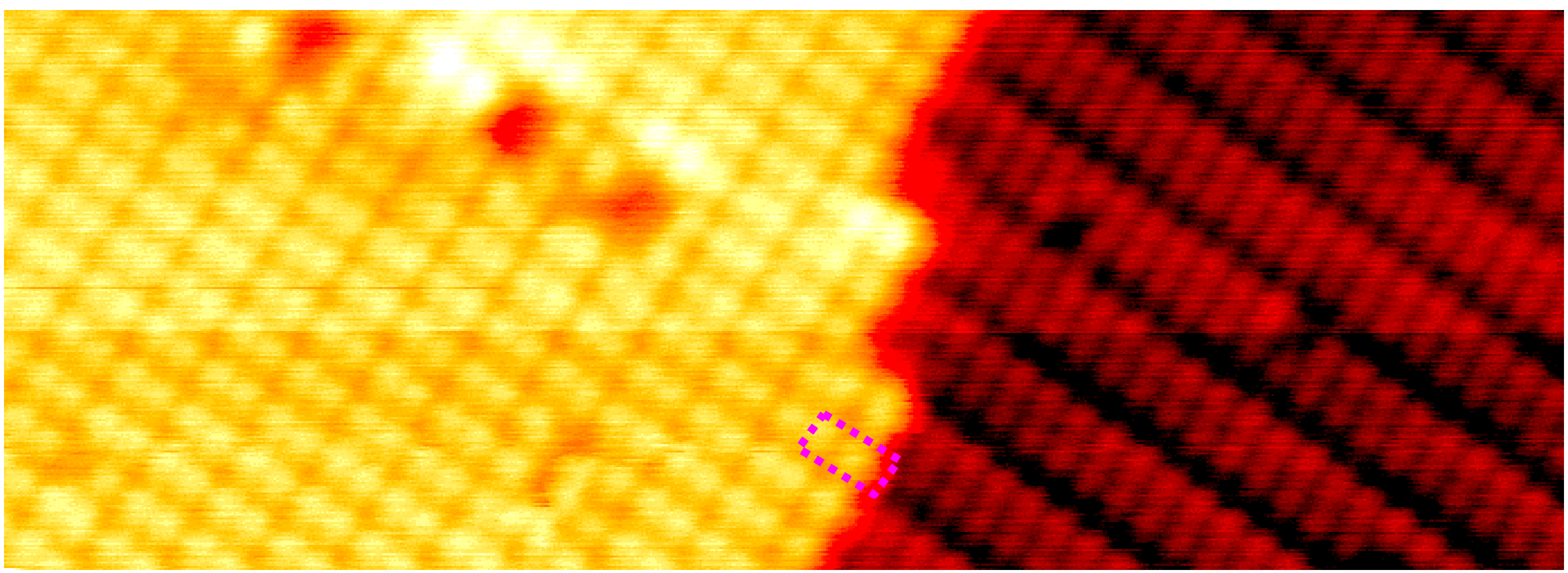






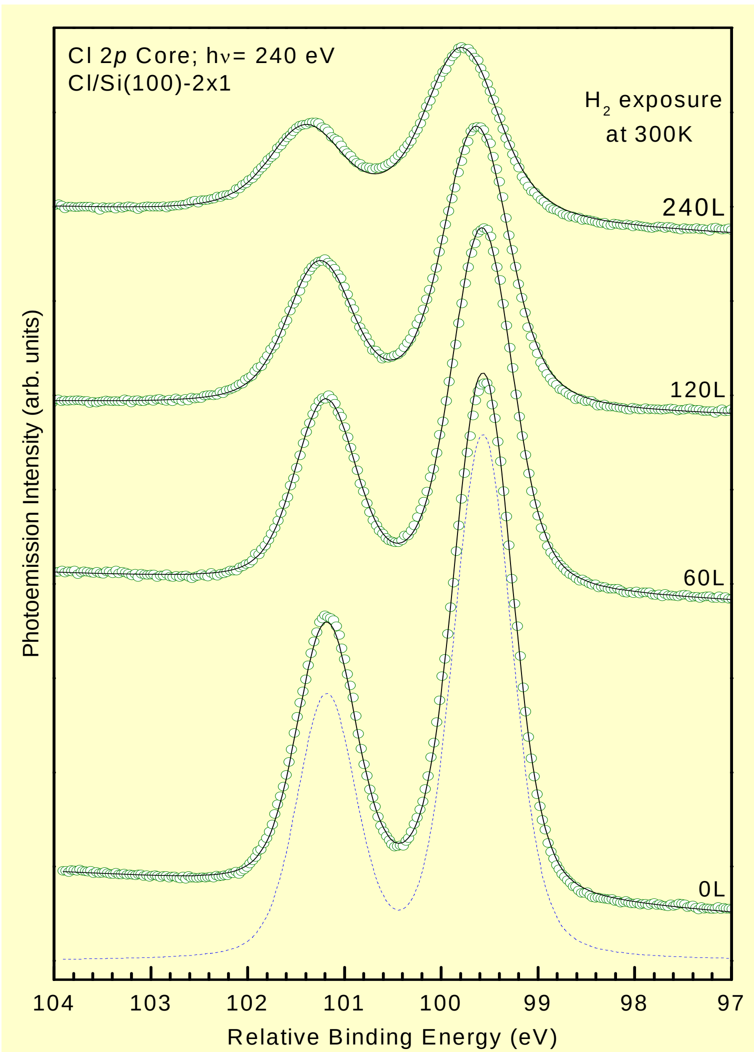
Cl termination of DBs on Si(100)

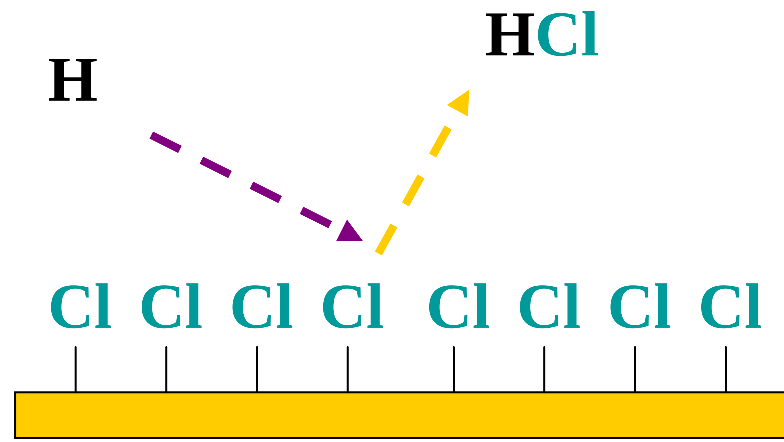




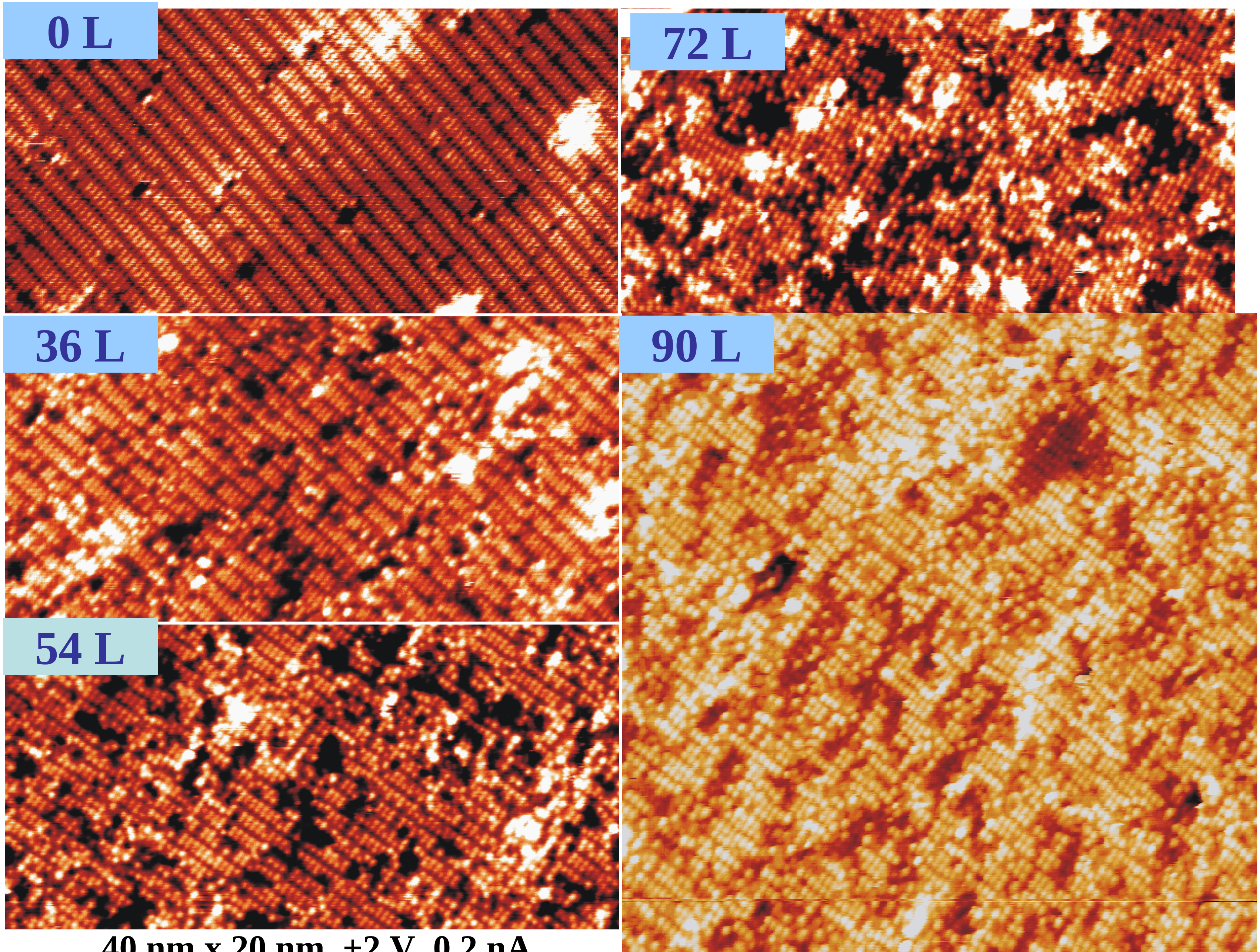
Cl extraction by H atomic beam

$$H_{(g)} + Cl_{(a)} \rightarrow HCl_{(g)}$$





H bombardment on Cl/Si(100)-2x1

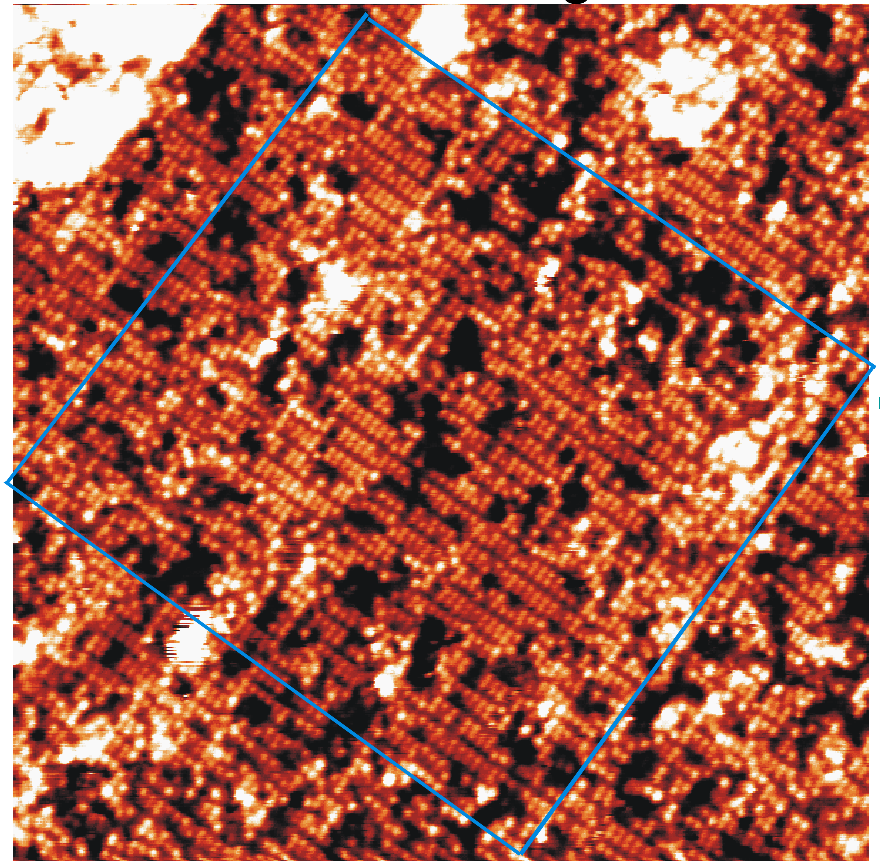


40 nm x 20 nm, +2 V, 0.2 nA

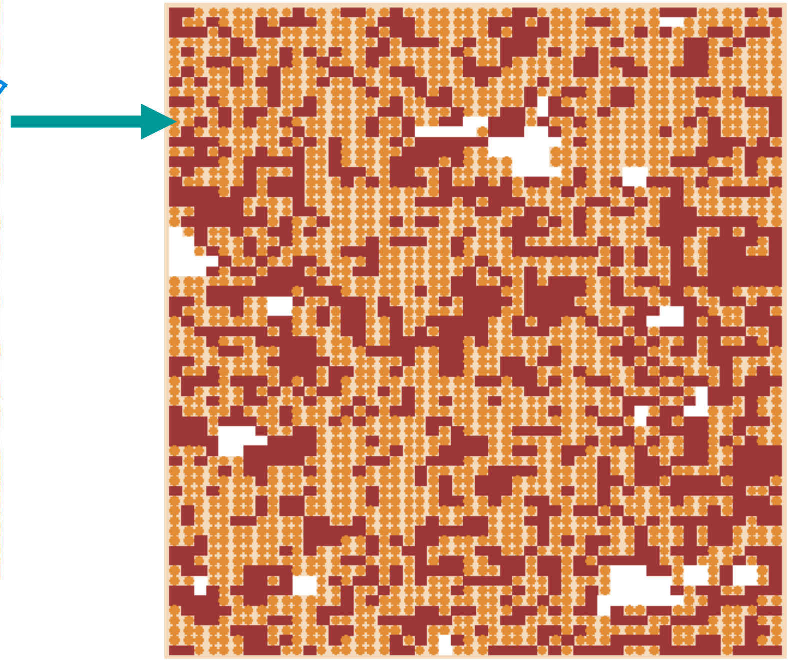
Random or not random

Analysis is not trivial

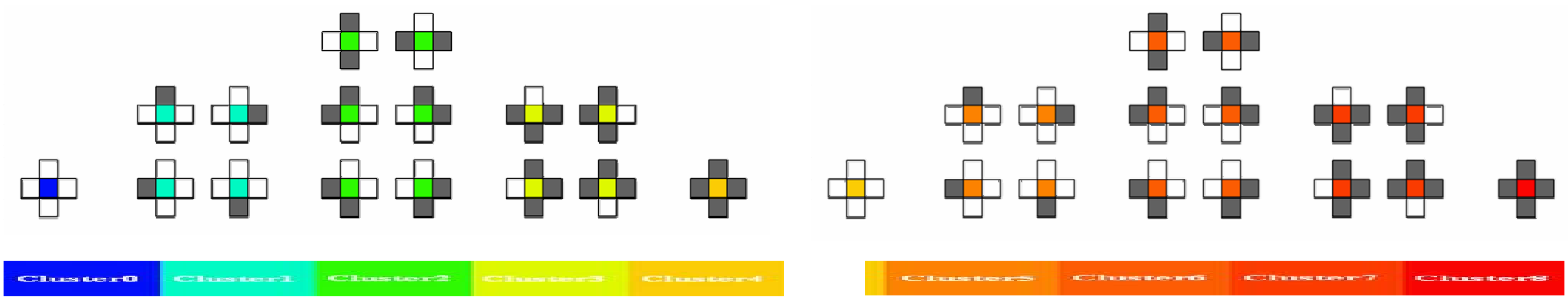
54 L H-atom dosage

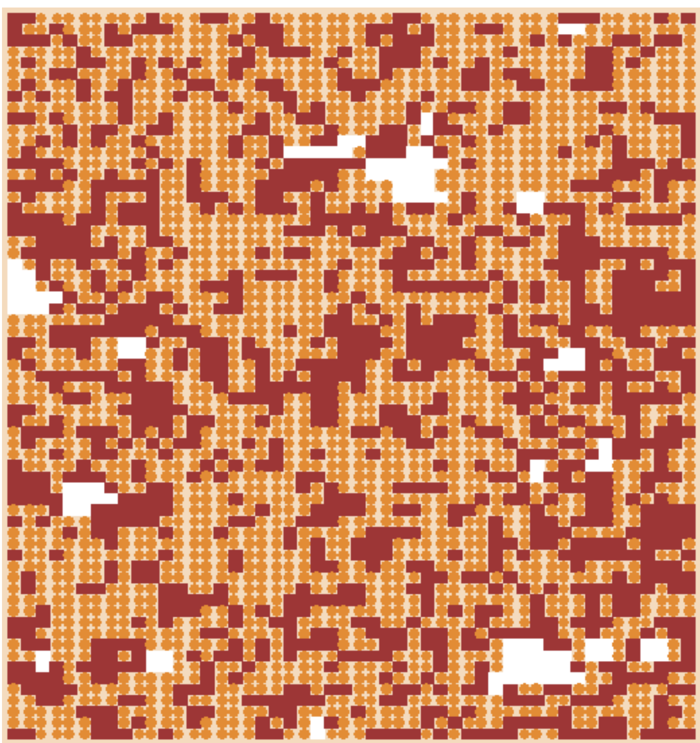


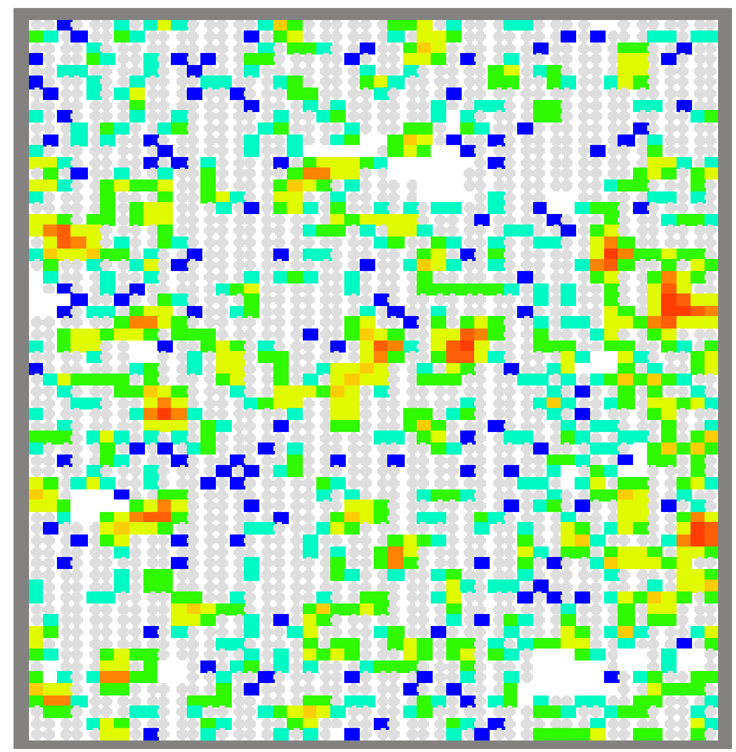
digitization



Classifying Reaction Sites

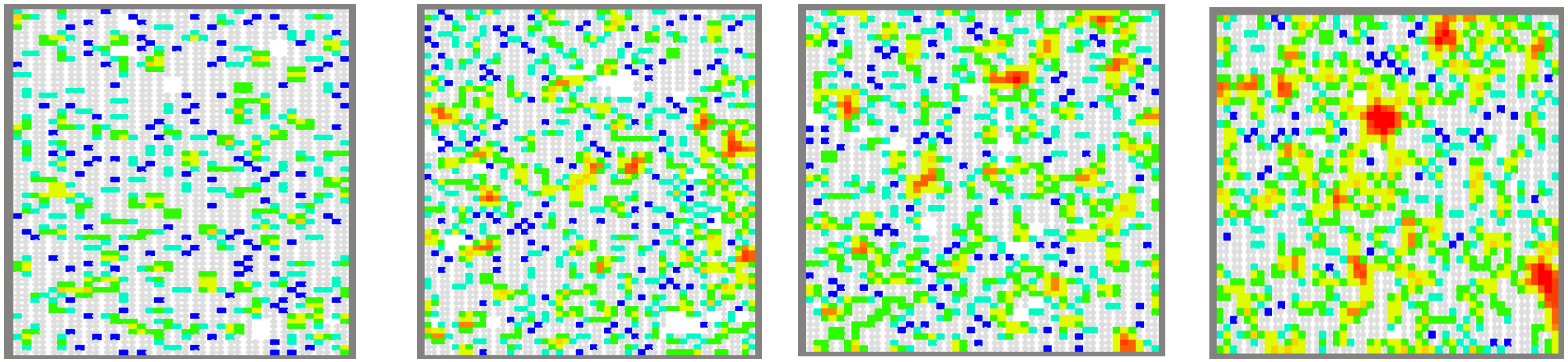






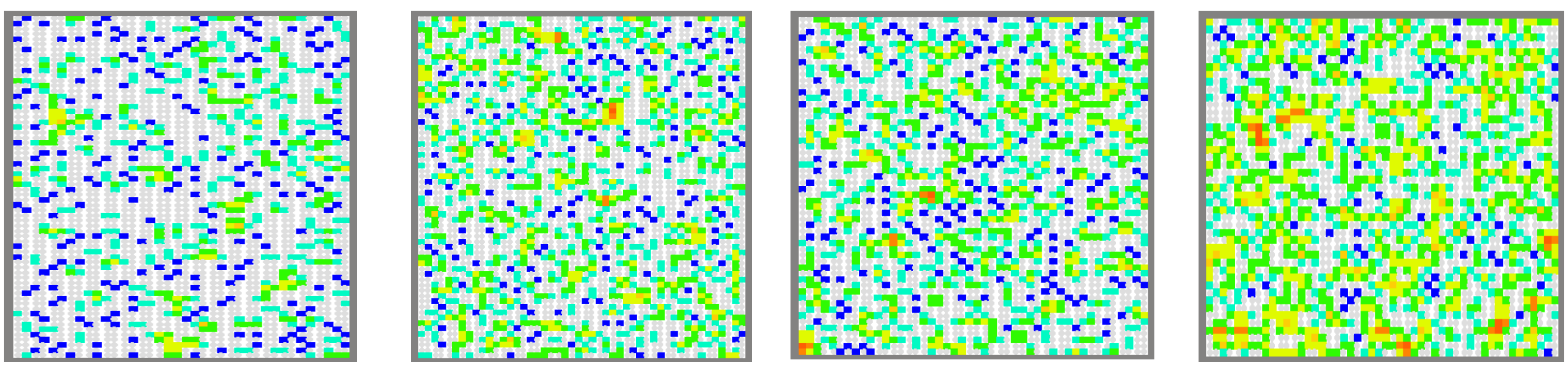
Comparison

STM Data

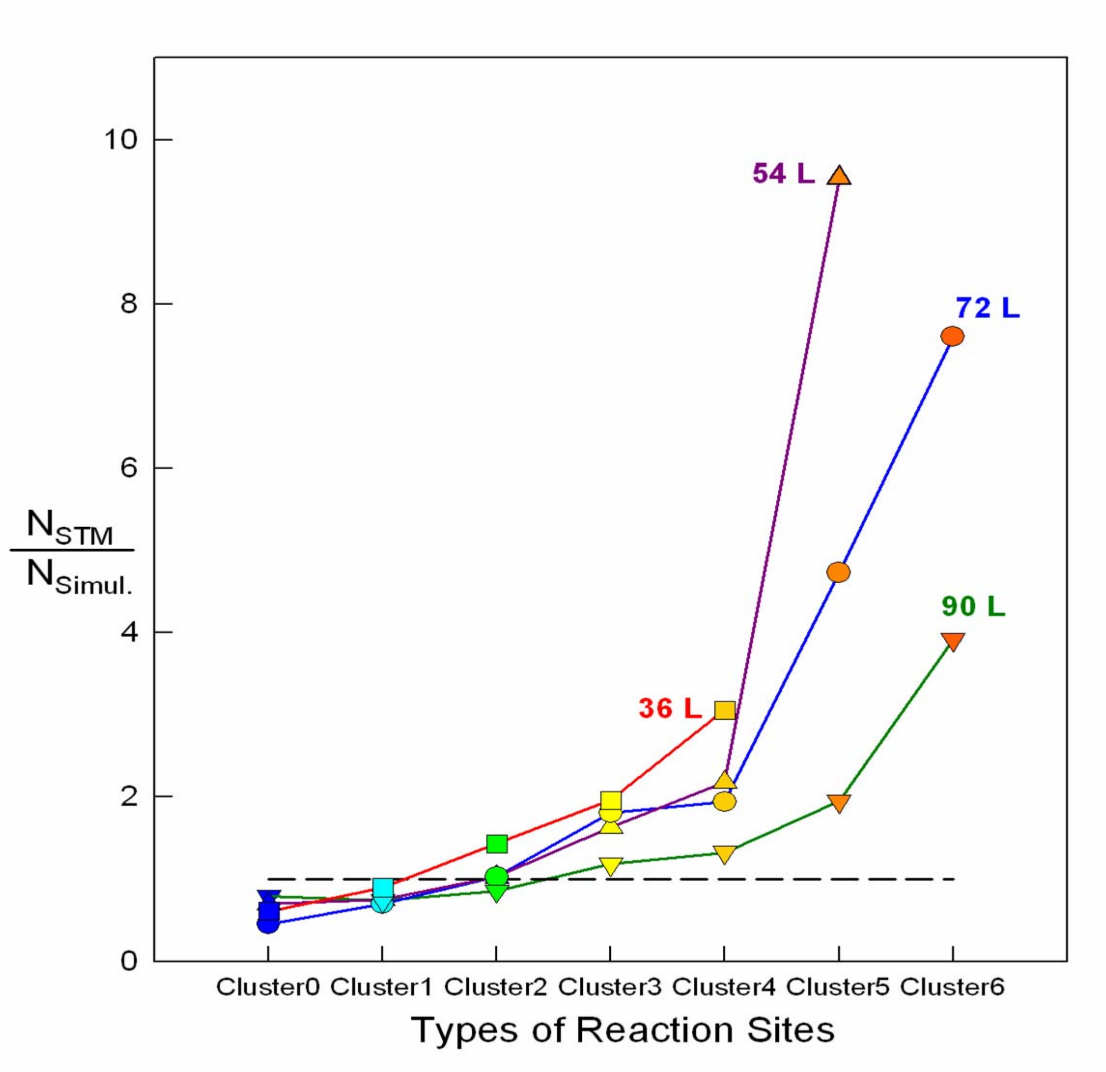


36 L 54 L 72 L 90 L

Simulation

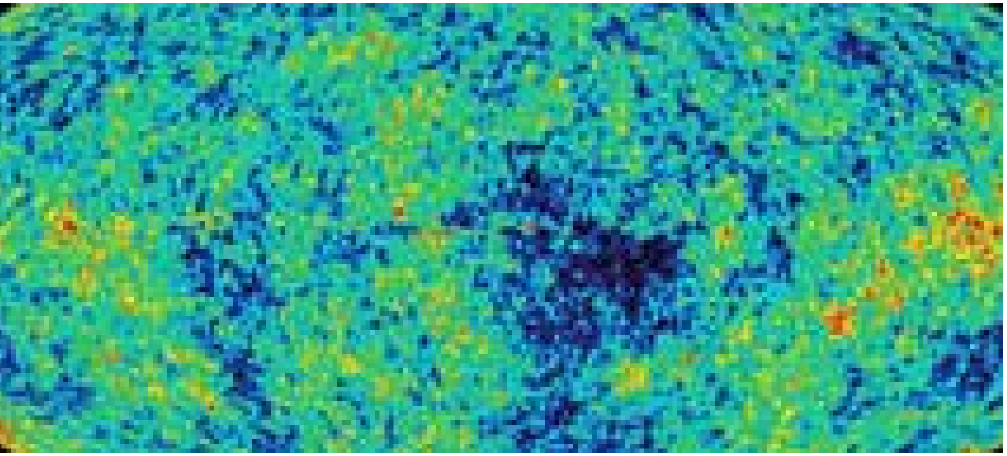


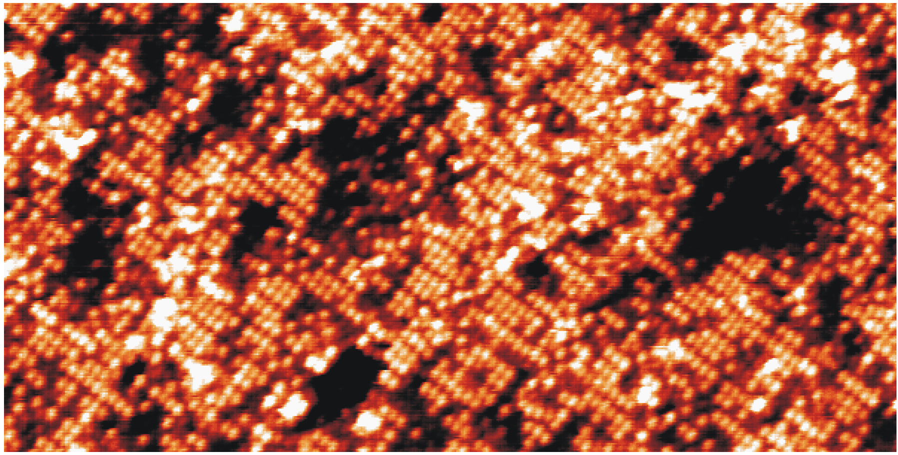
Comparison



10
8
6
4
2
0
$\frac{N_{STM}}{N_{Simul.}}$
54 L
72 L
90 L
36 L
Cluster0 Cluster1 Cluster2 Cluster3 Cluster4 Cluster5 Cluster6
Types of Reaction Sites

Cosmology vs. Surface Sci.

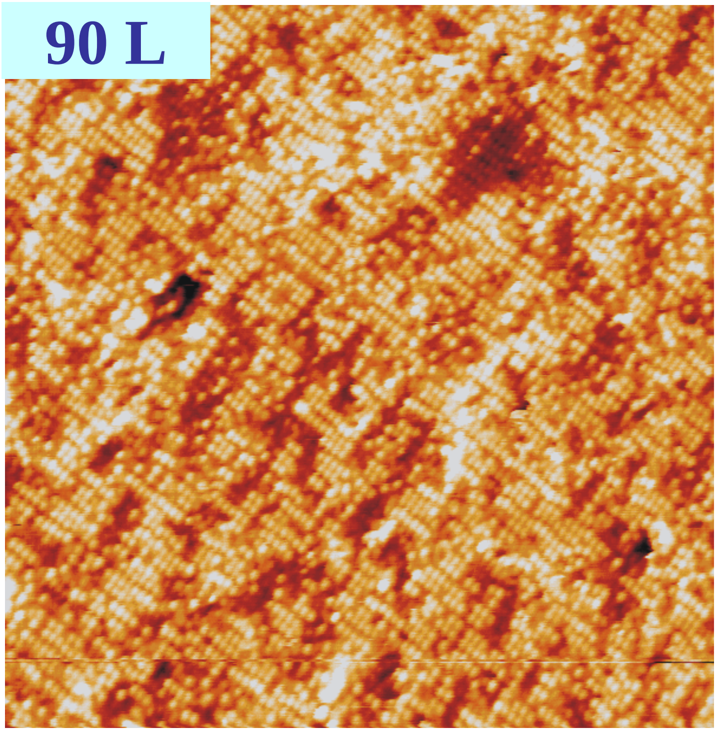


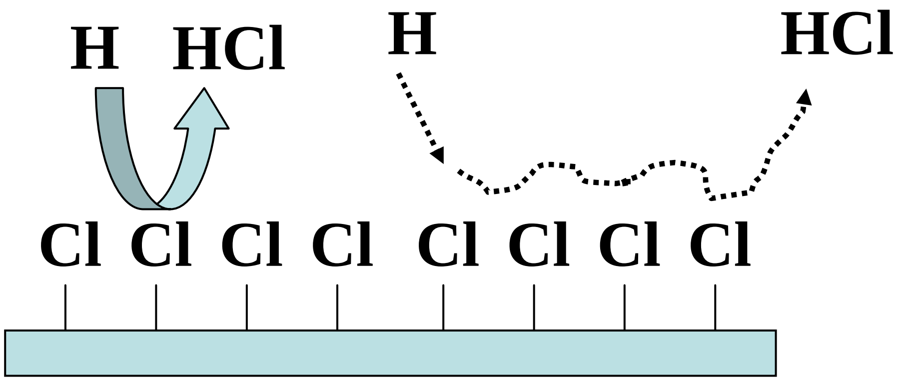


Time scale: 10^{18} : 10^{-12}

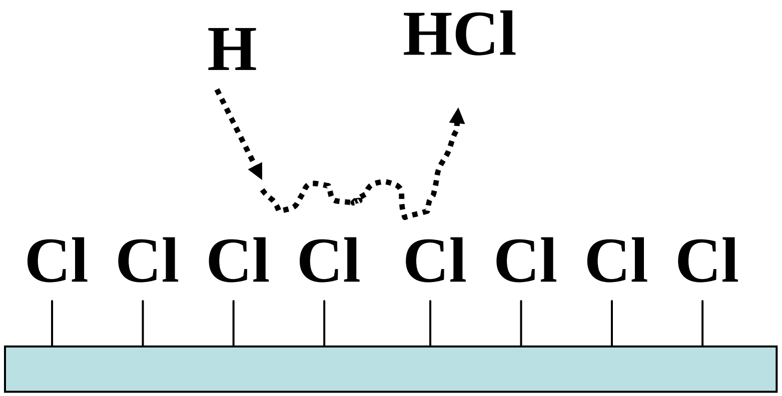
Size scale: 10^{26} : 10^{-8}

Summary: **Hot atom mechanism plays an important role.**





ER or not ER ?



Hot atom

Introduction and Outline

Toward chemistry with

√ (a) <10^{-8} m spatial resolution,

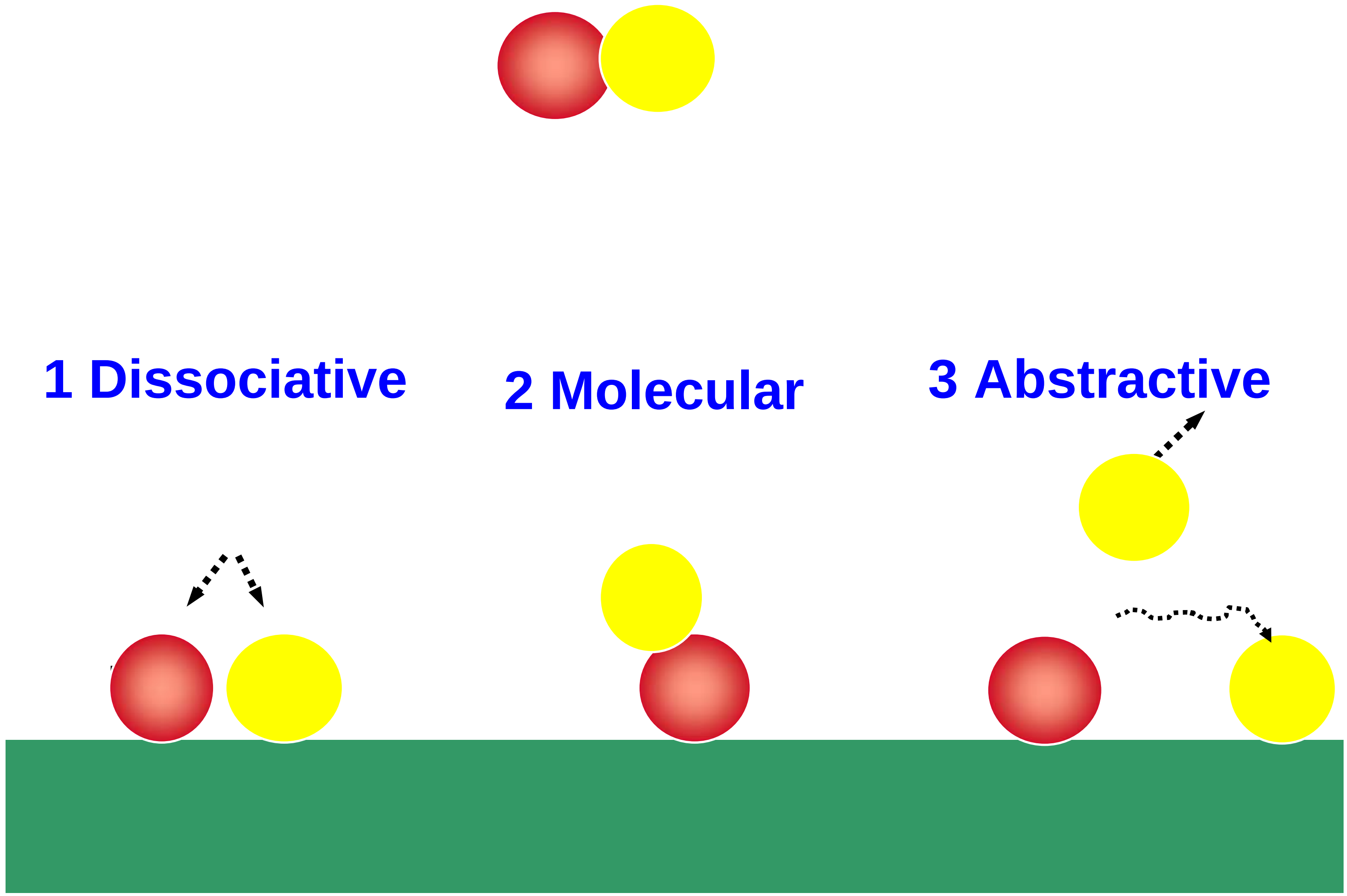
- Single-molecule imaging
- Single-bond characterization
- Control of single-molecule reactions

Chemical dynamics derived from STM

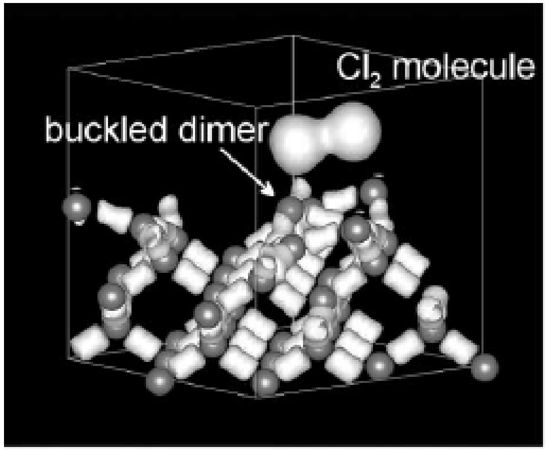
1. Abstraction reaction

√ 2. Adsorption mechanism

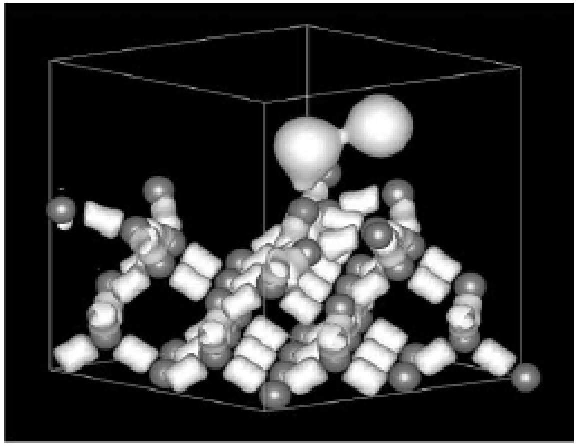
Three mechanisms of Diatomic Adsorption



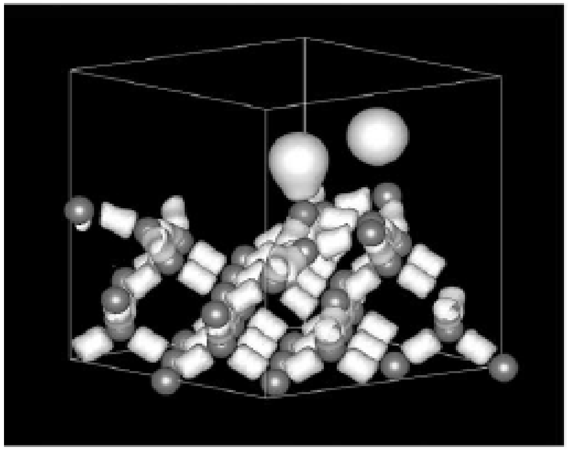
First-principles Molecular dynamics simulation



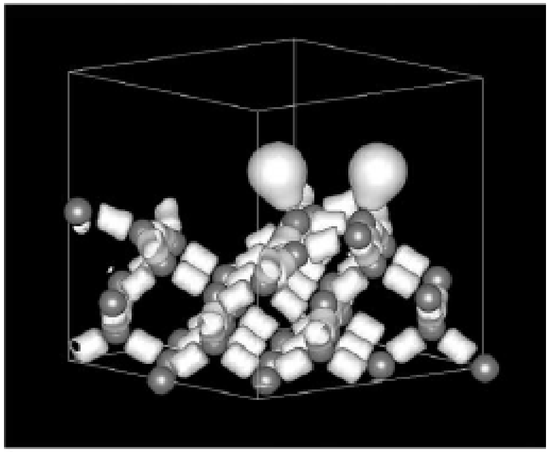
(a) 0 psec



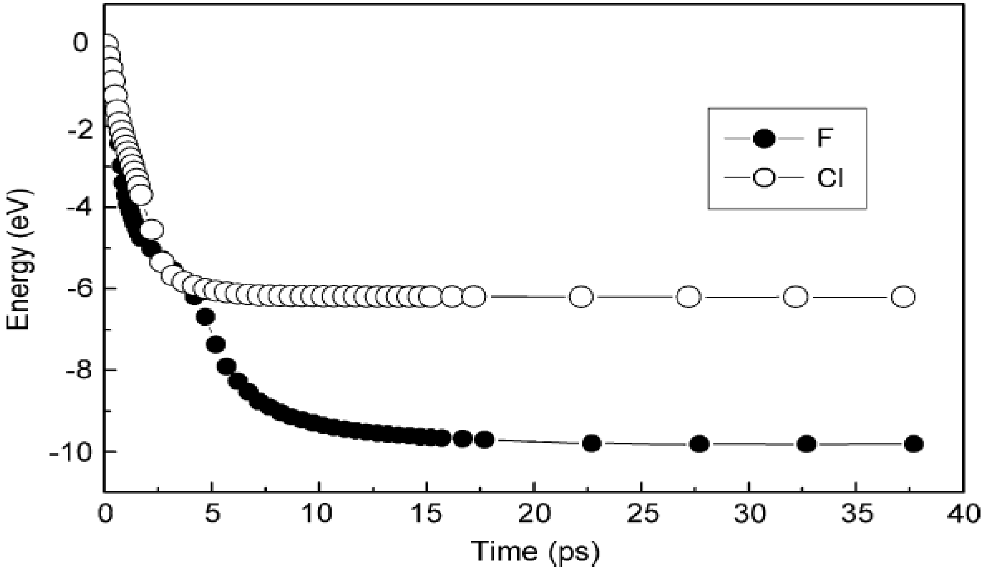
(b) 0.6 psec



(c) 1.3 psec



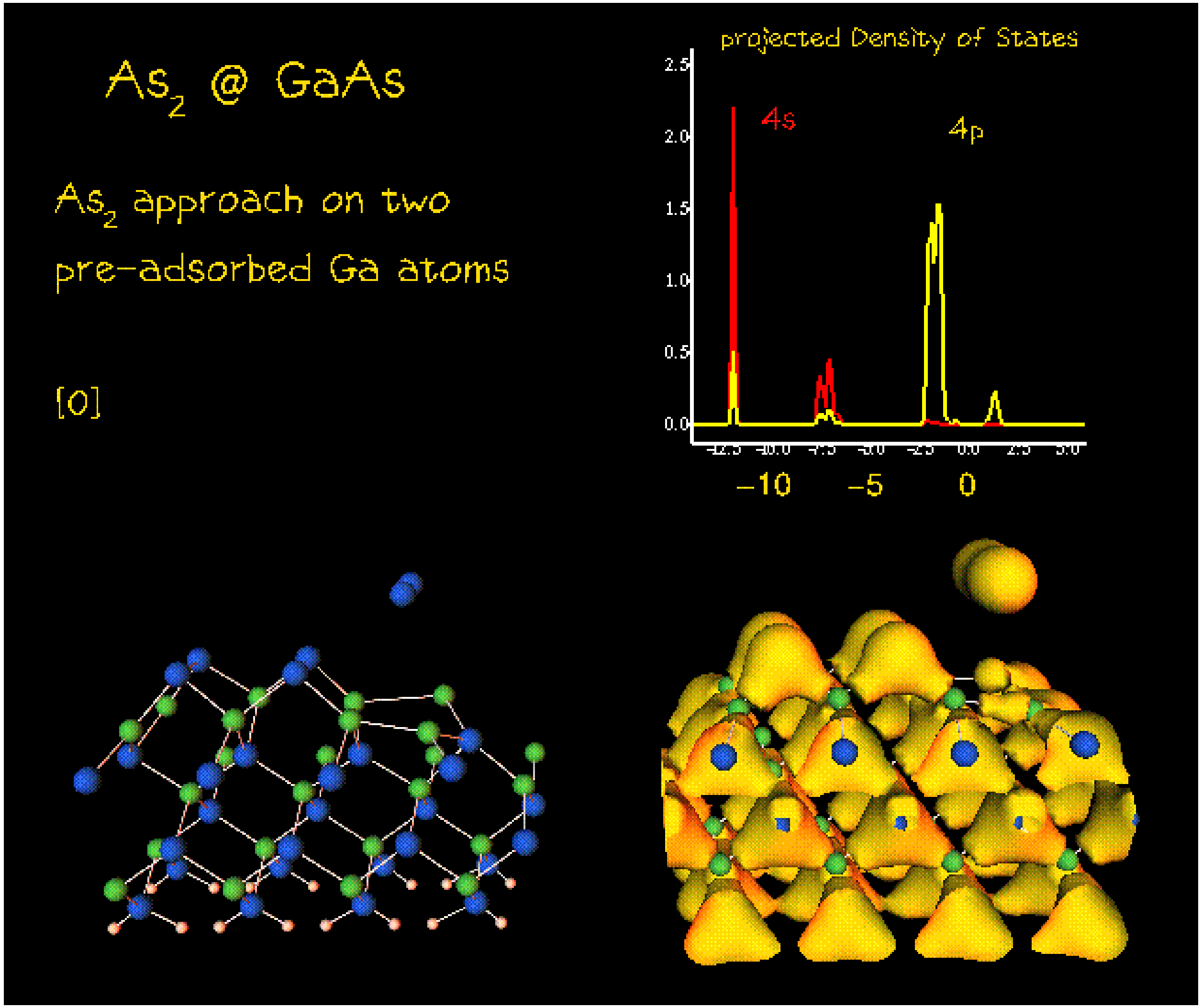
(d) 16.2 psec



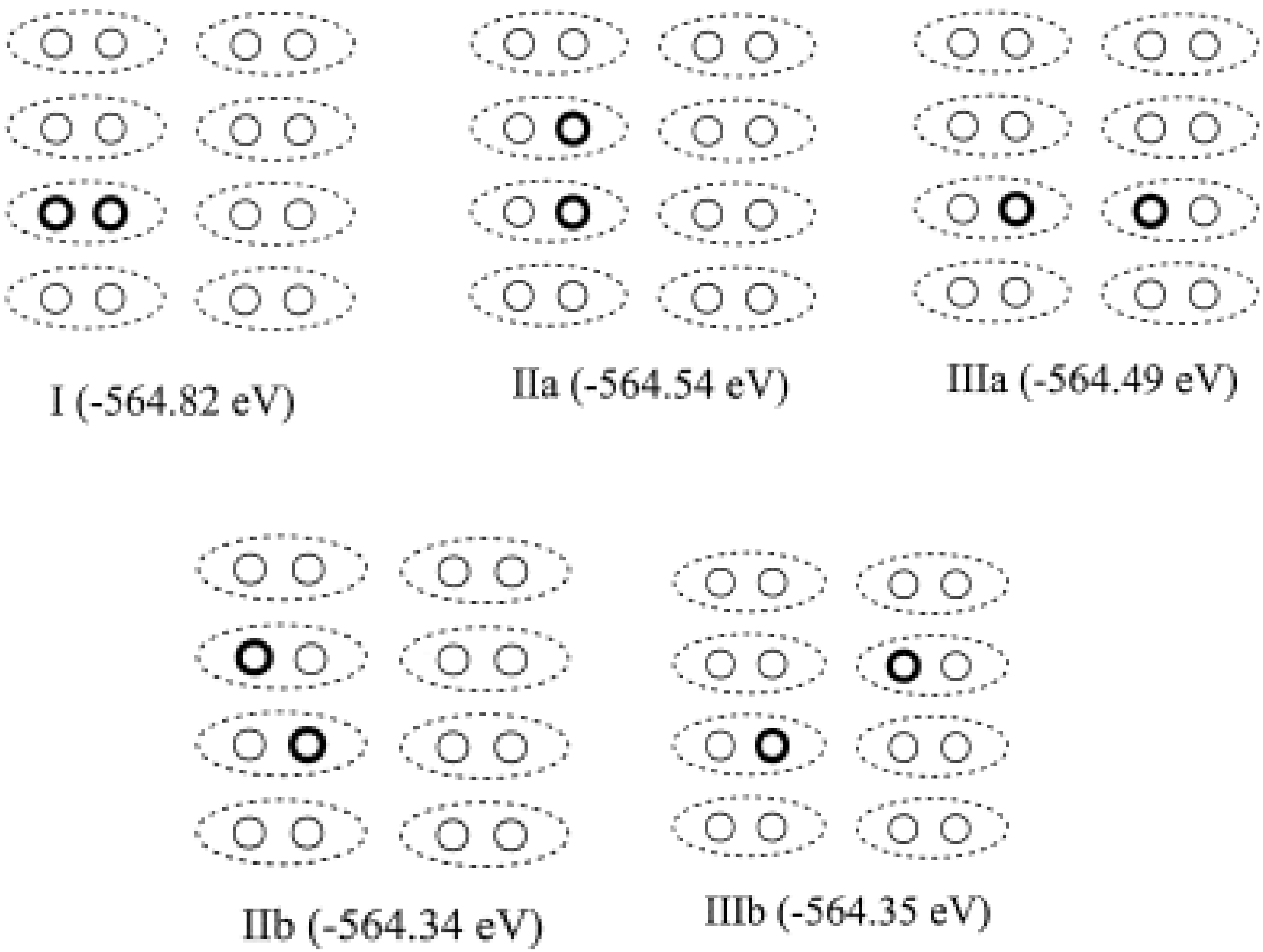
Dissociative?

Halogen gas: F_2 and Cl_2, Surf. Sci. 515 (2002) 287

Simulation of diatomic adsorption

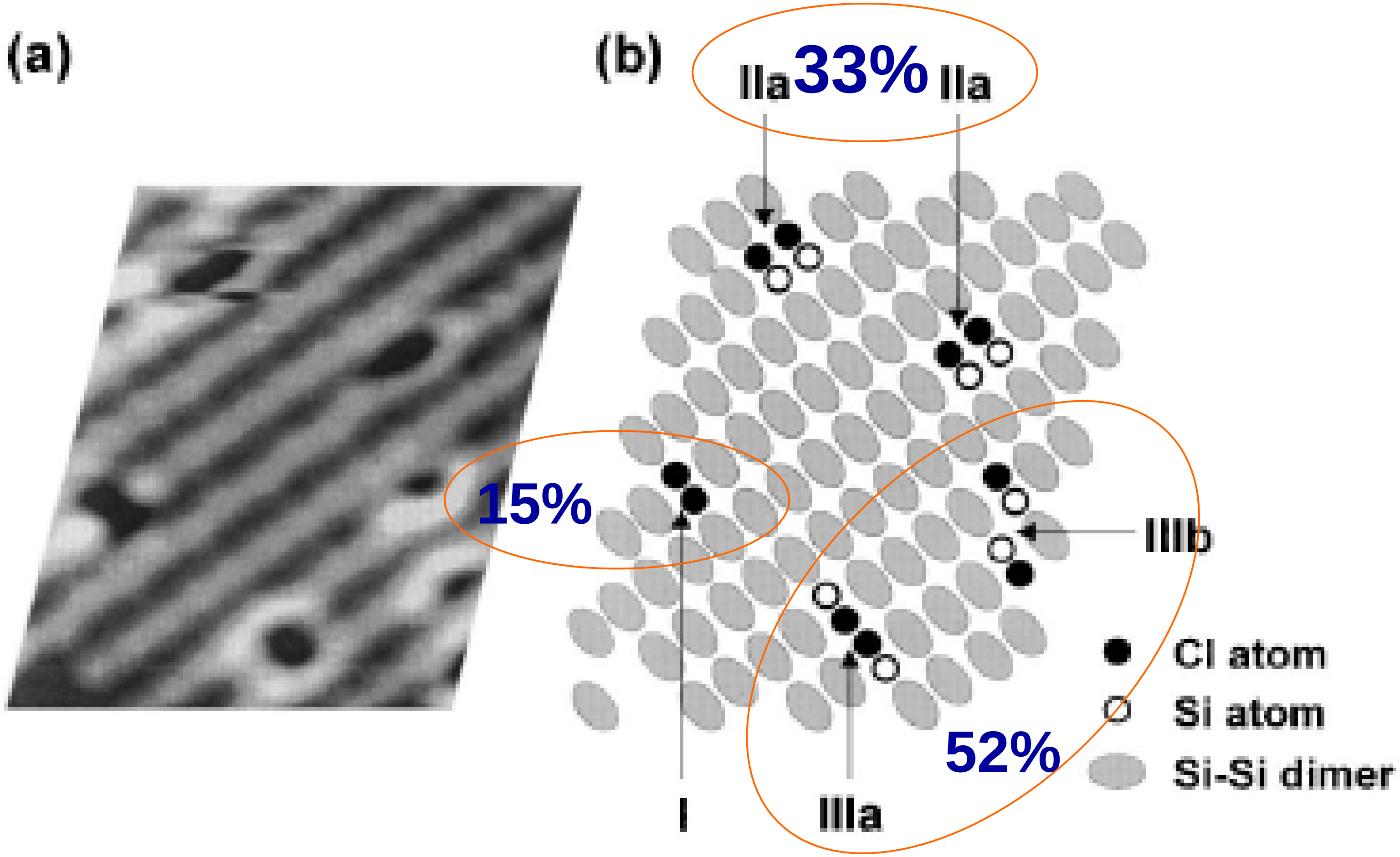


Total energy calculation



Liu, etc

STM measurement



Yates, etc

How to distinguish different adsorption mechanisms?

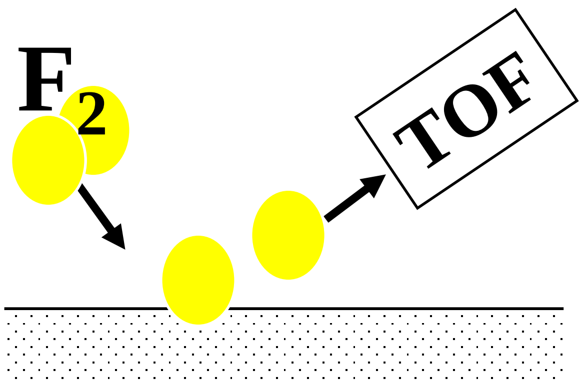
Experimental Verification of a New Mechanism for Dissociative Chemisorption: Atom Abstraction

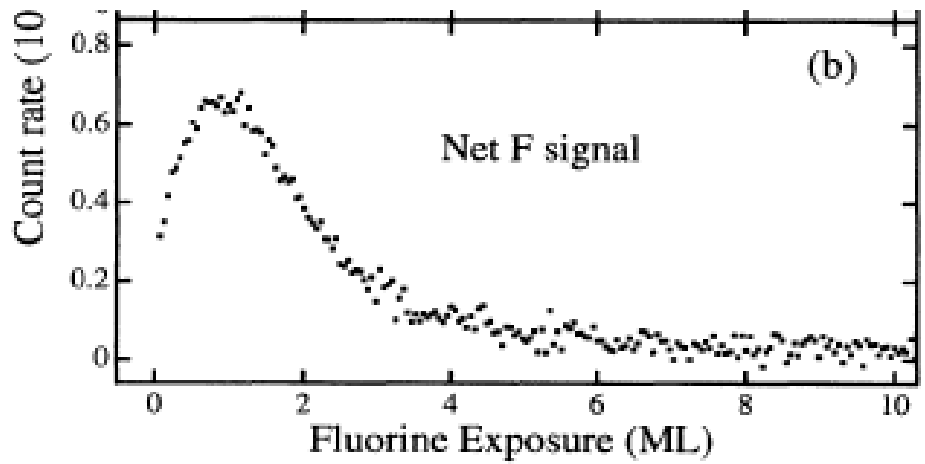
Abstractive adsorption

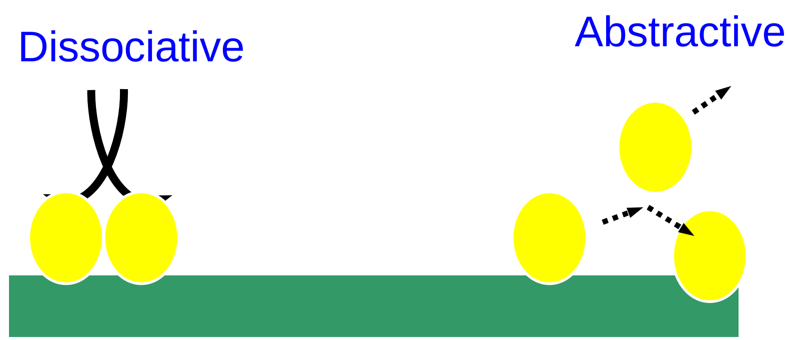
Y. L. Li, D. P. Pullman, J. J. Yang, A. A. Tsekouras, D. B. Gosalvez, K. B. Laughlin, Z. Zhang, M. T. Schulberg, D. J. Gladstone, M. McGonigal, and S. T. Ceyer

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 8 July 1994)

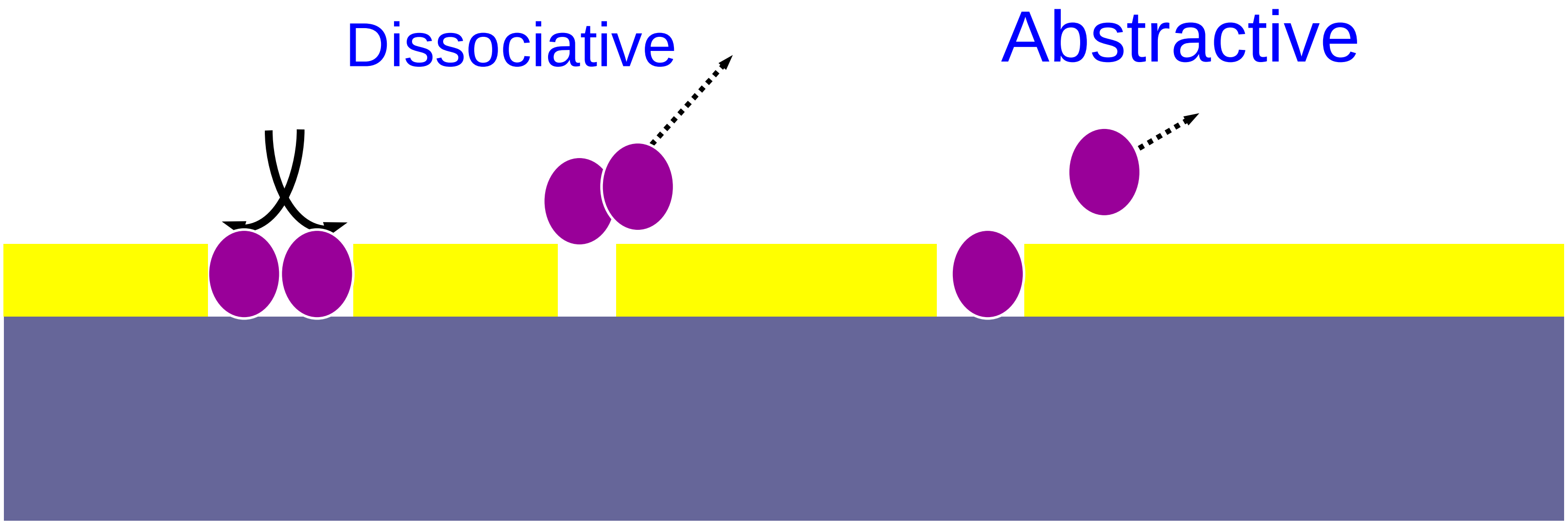




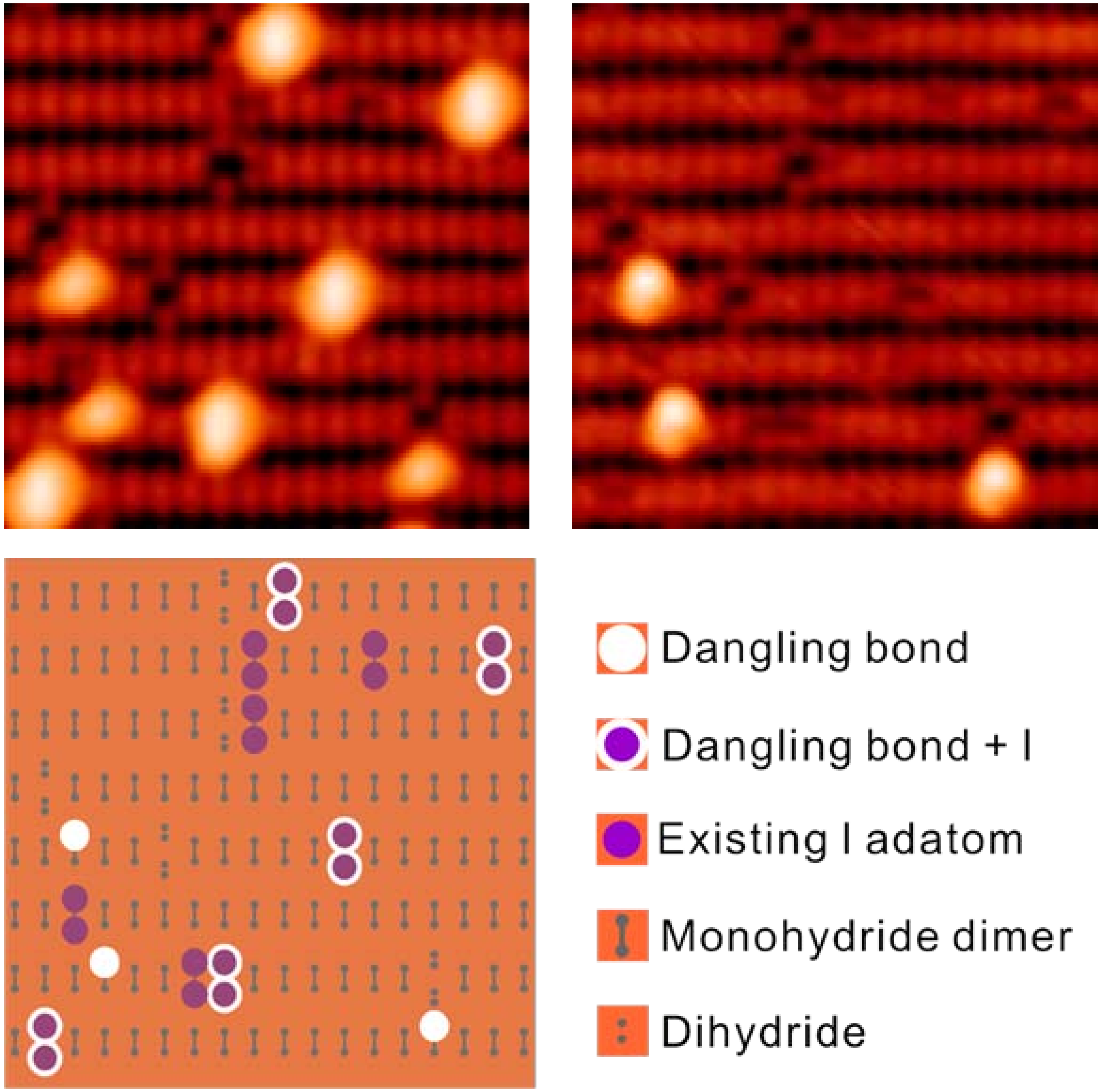


Our approach to distinguish different adsorption mechanisms

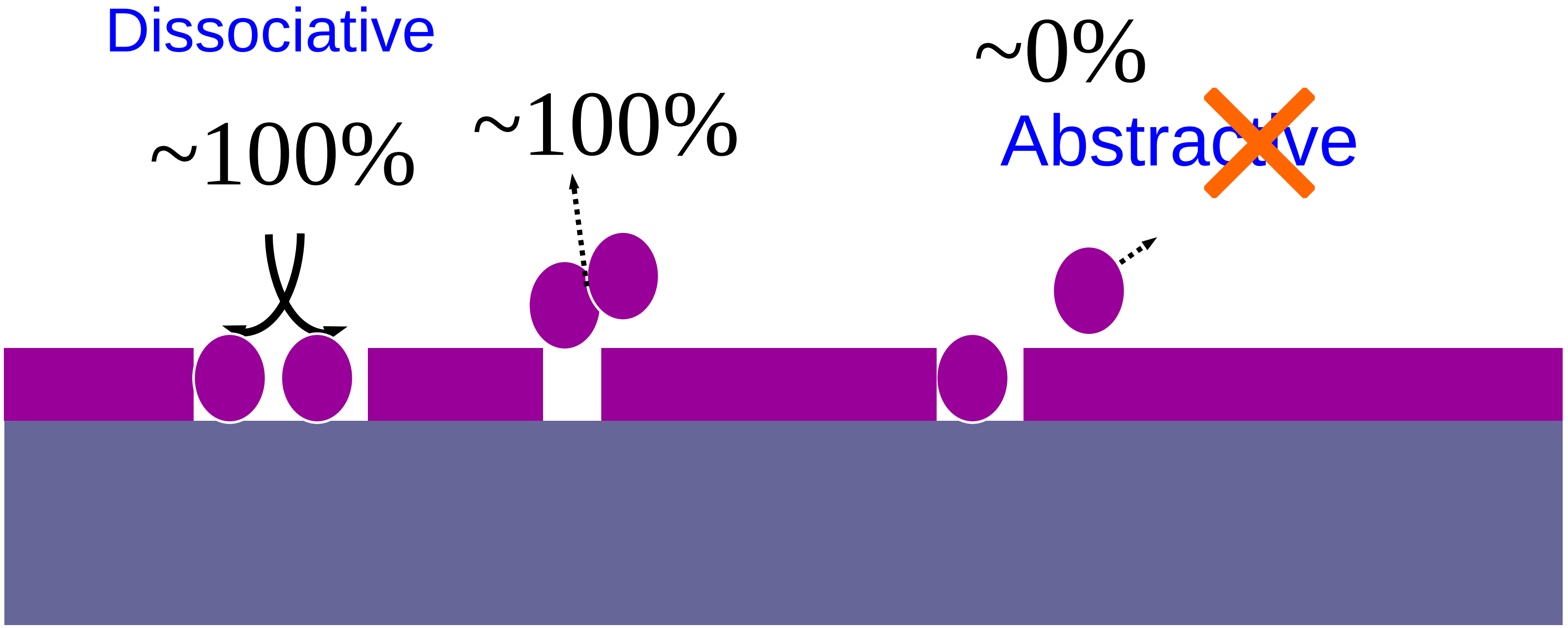
by designing the reaction sites



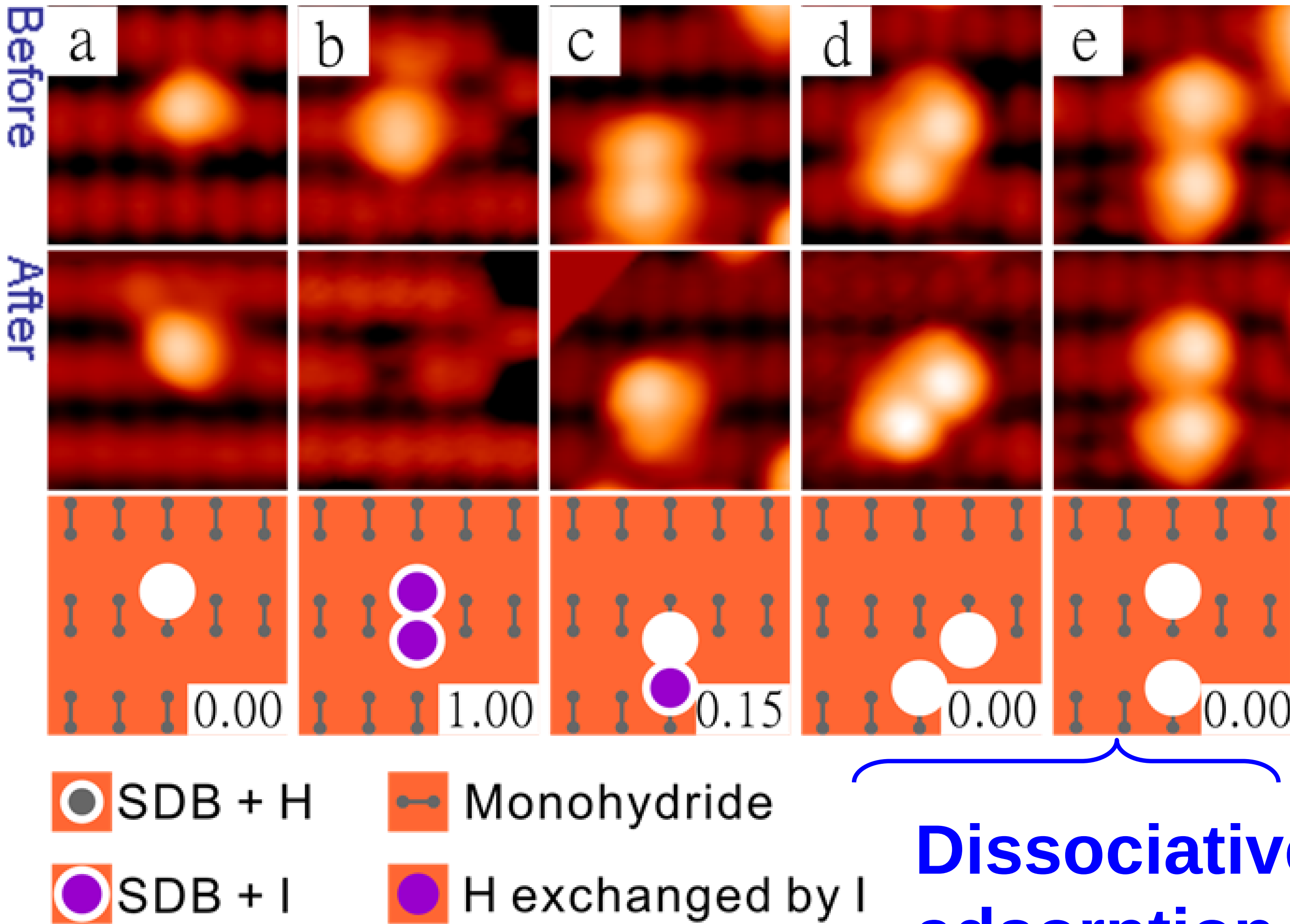
I_2 on single DB and DB pairs



How to distinguish different adsorption mechanisms?



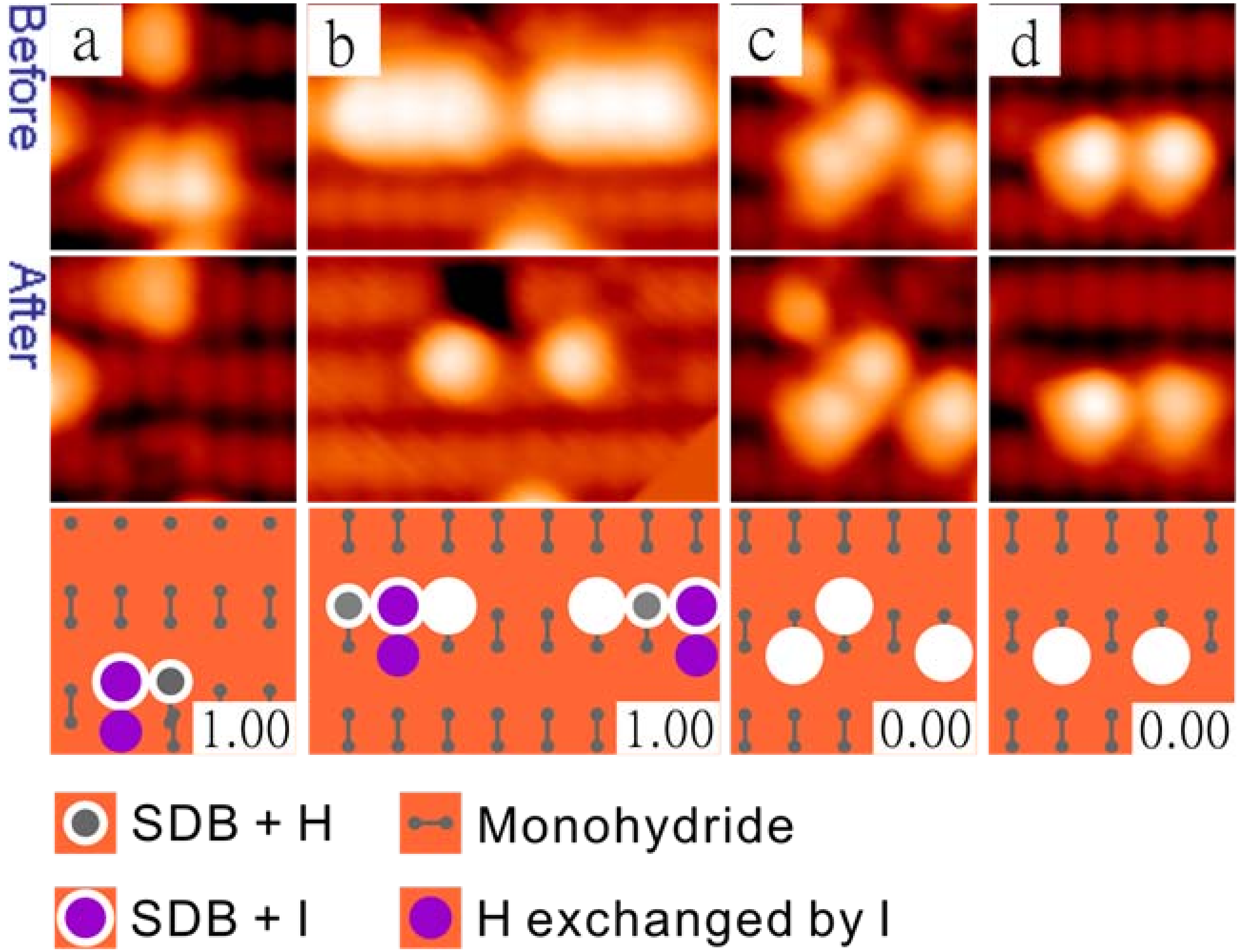
Other reaction site configuration



Dissociative adsorption needs two neighboring DBs.

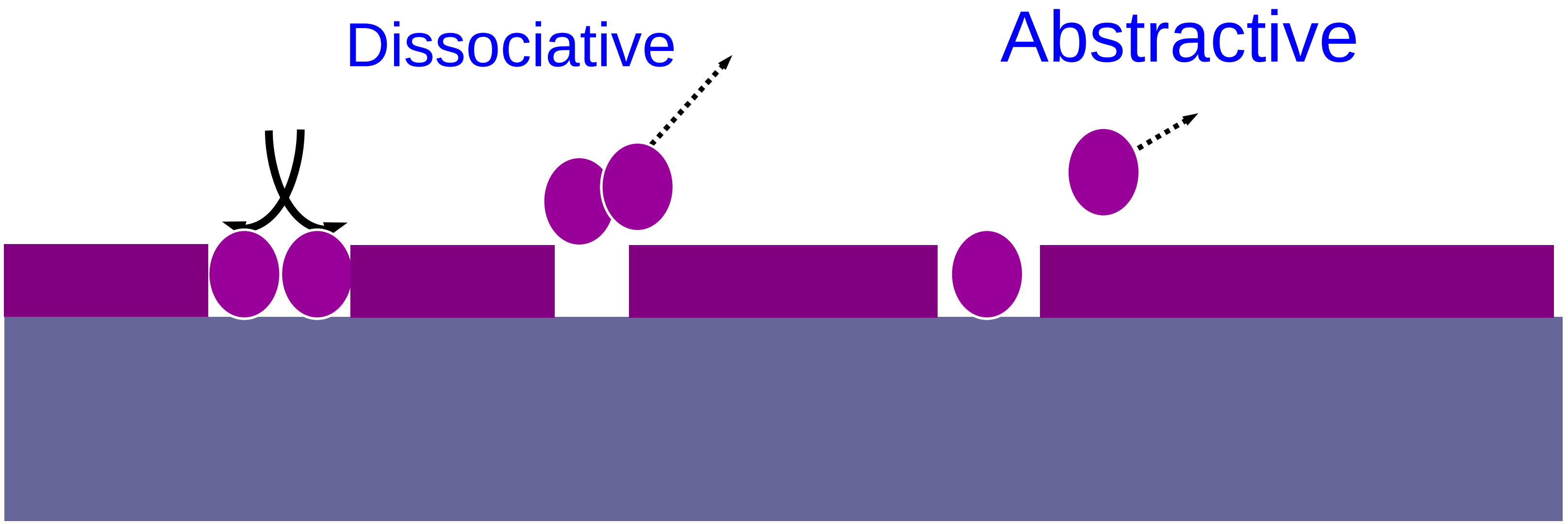
Second DB locates near perpendicular to the dimer row direction

Other reaction site configuration



Parallel to the dimer row direction

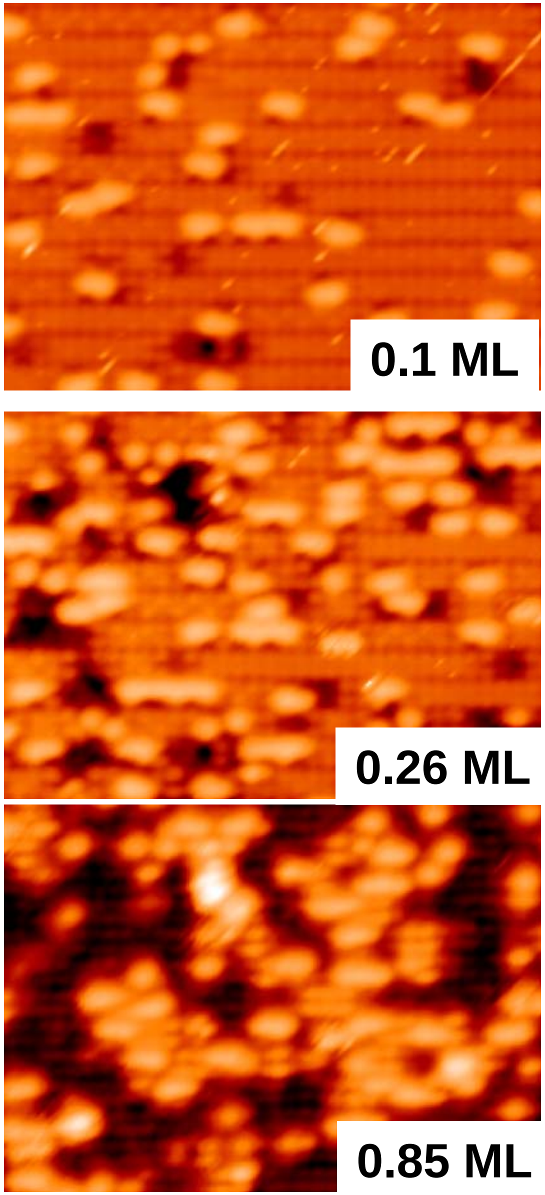
Different mask

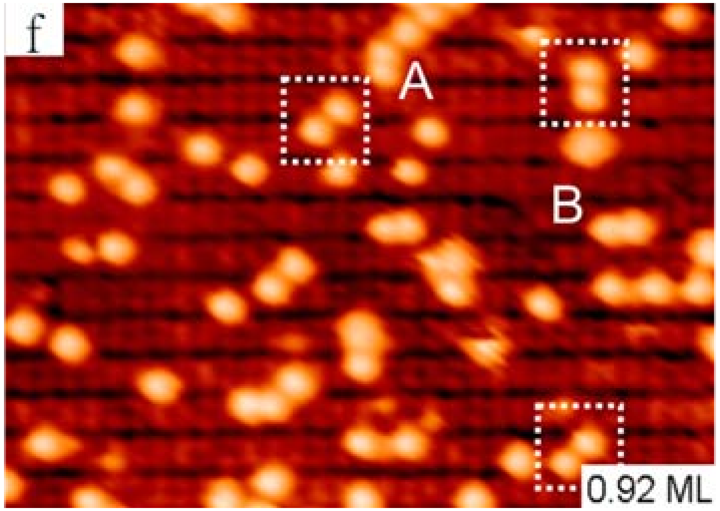


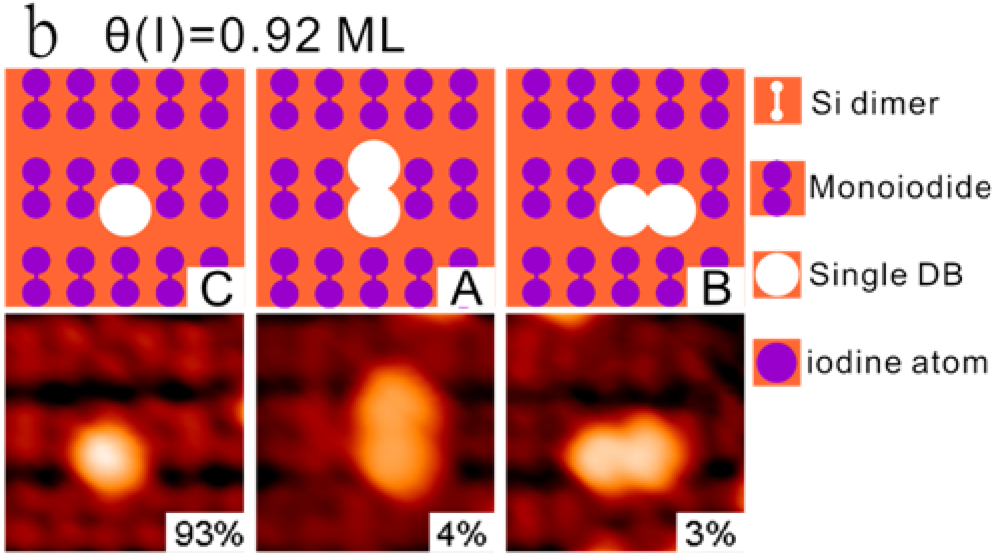
I_2 on I-terminated Si(100)

To eliminate possible complication

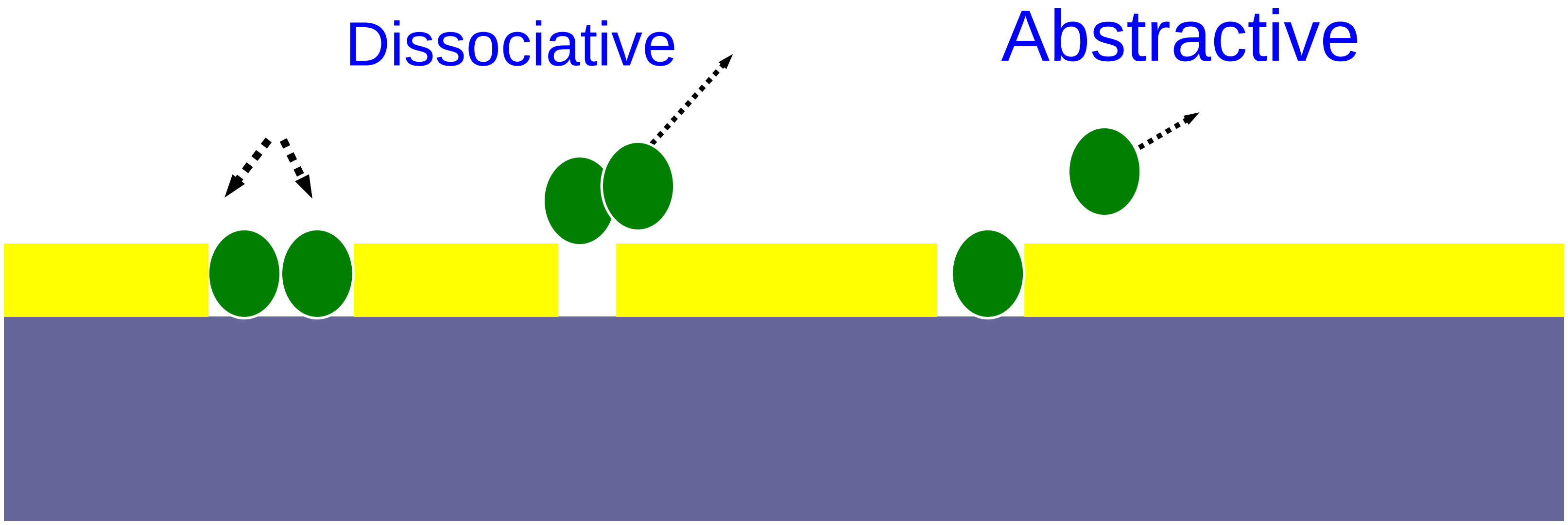
I terminated surface







Is Cl_2 adsorbed similarly?



I_2 + Si → Si-I + I   +0.86 eV

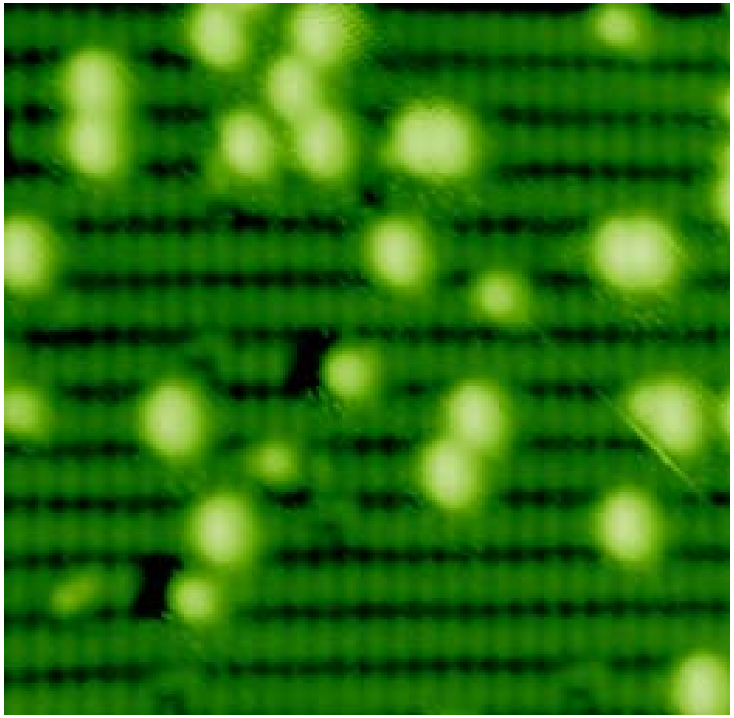
Cl_2 + Si → Si-Cl + Cl   +1.41 eV

Where does the energy go?

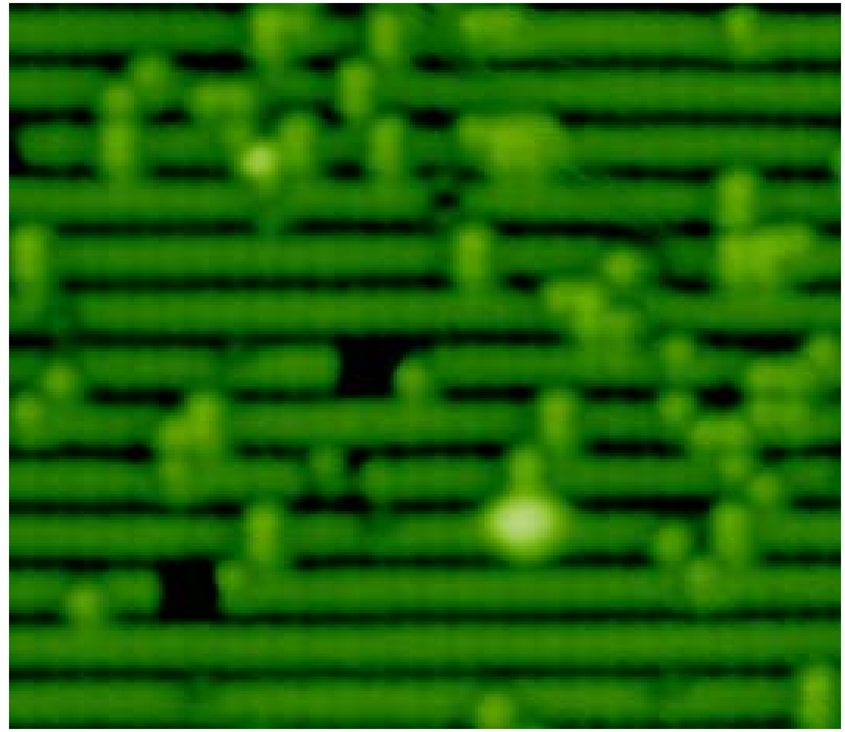
Cl_2 has different adsorption mechanism

$+Cl_2$

Before



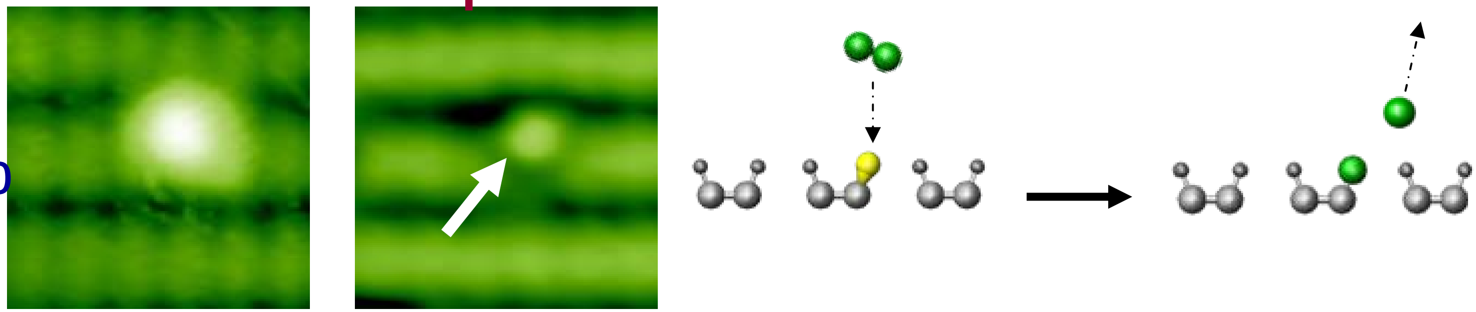
After



Cl_2 on single dangle bonds

Abstractive adsorption

55%

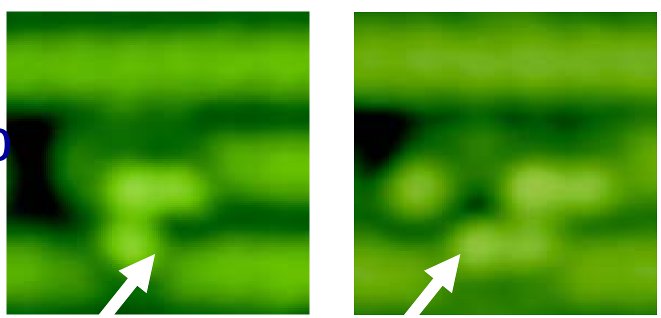


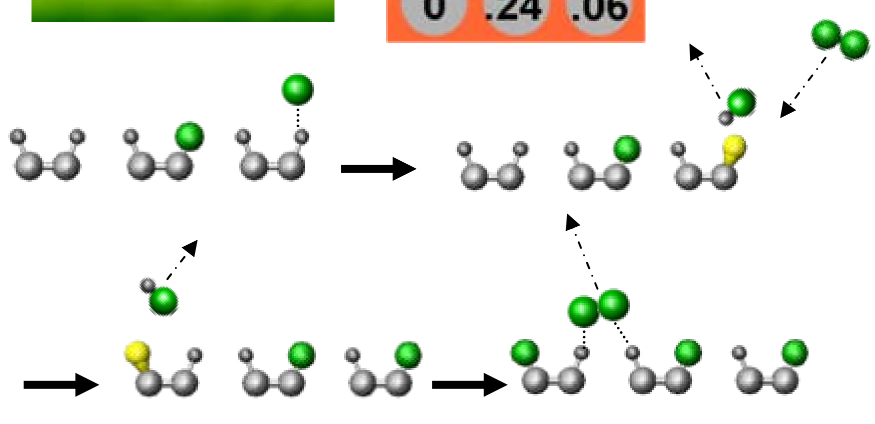
Dissociative adsorption or hot atom process

28%

Cascaded reaction

17%



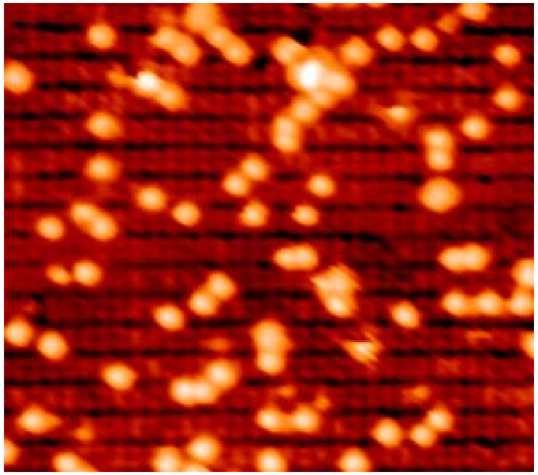


Three Cls: 5% Four Cls: 7% Five Cls: 5%

Cl_2 has different adsorption mechanism

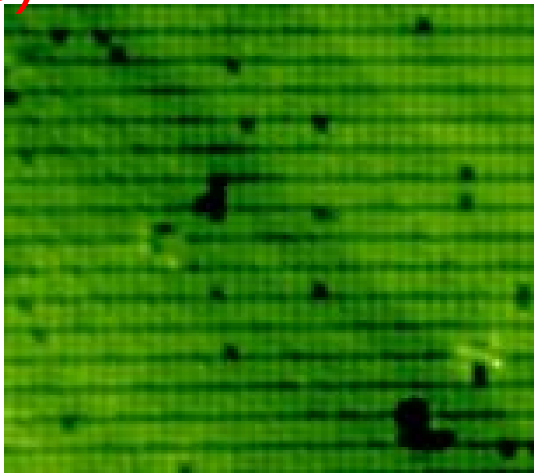
Can we saturate all active site?

I/Si(100)

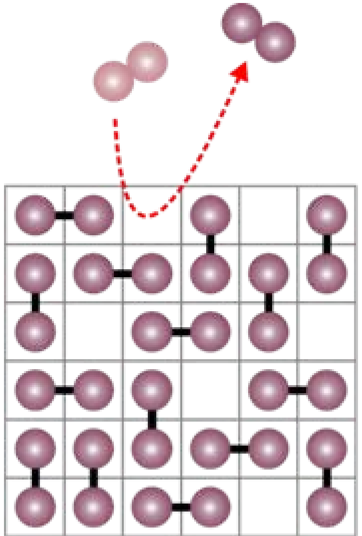


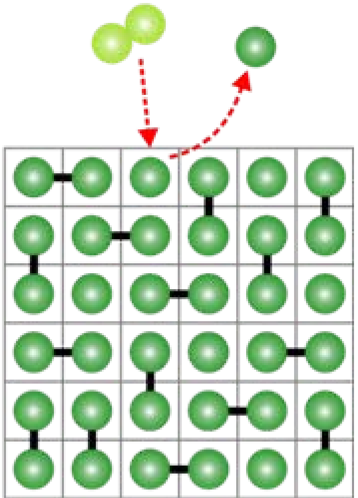
0.92 ML

Cl/Si(100)



1 ML



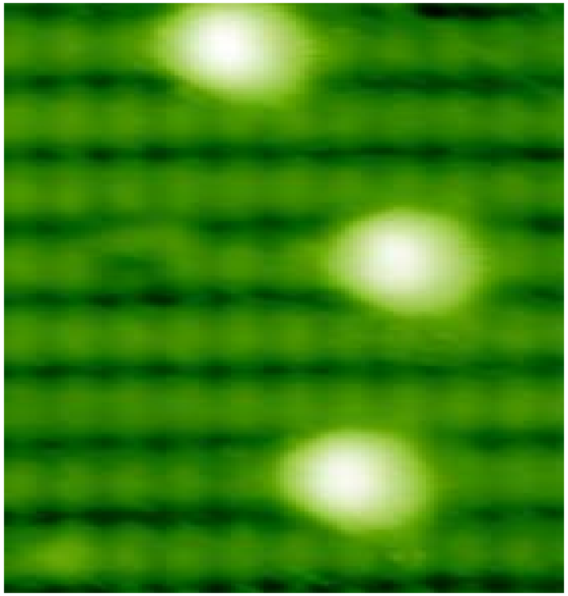


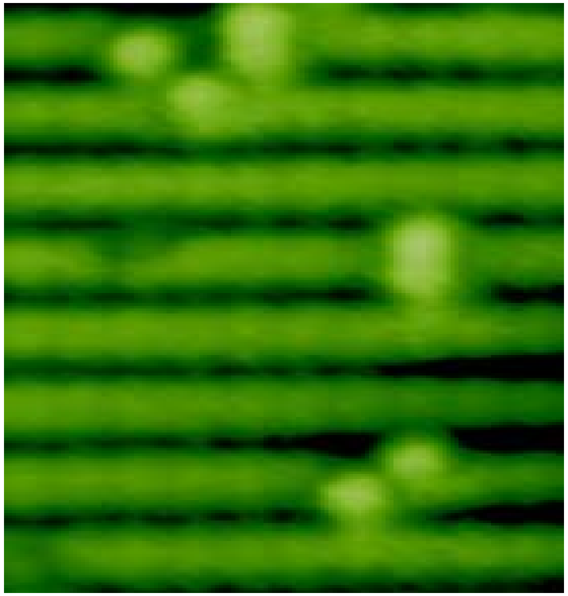
Cl_2 on DB pairs

Before

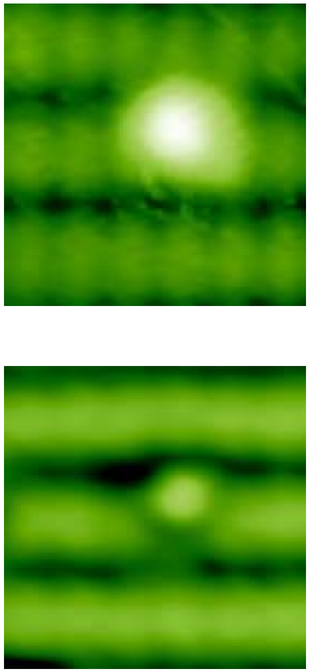
+ Cl_2

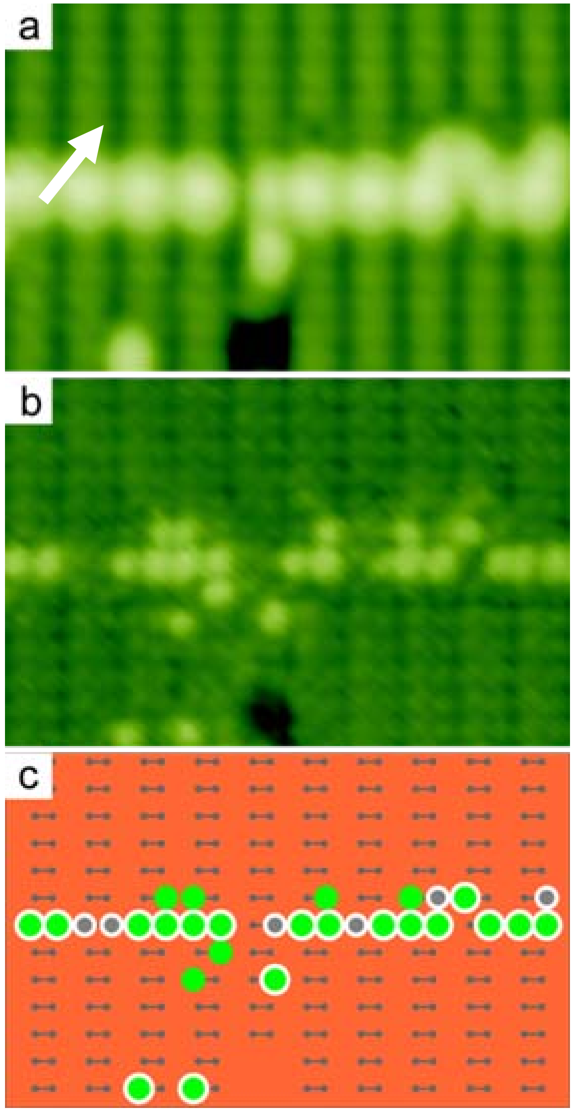
After

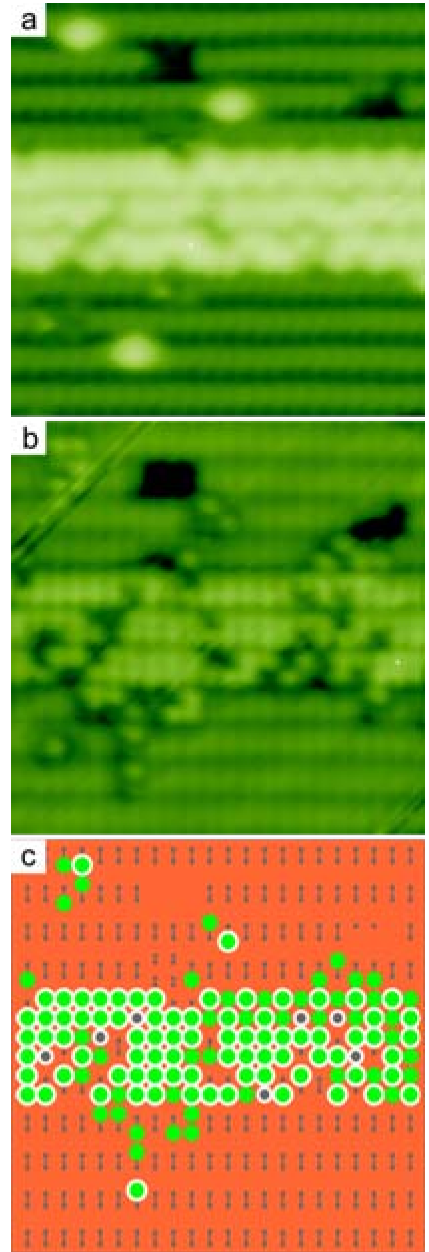


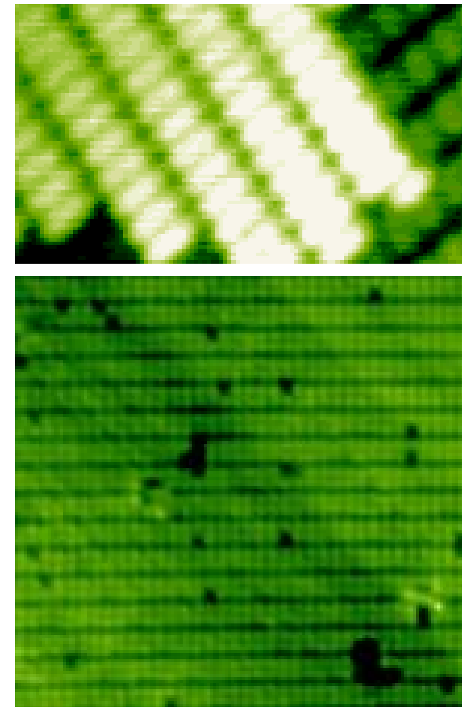


Cl_2 adsorption from 1D to 2D arranged bonds

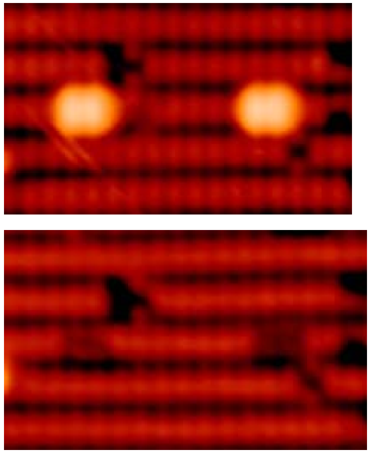








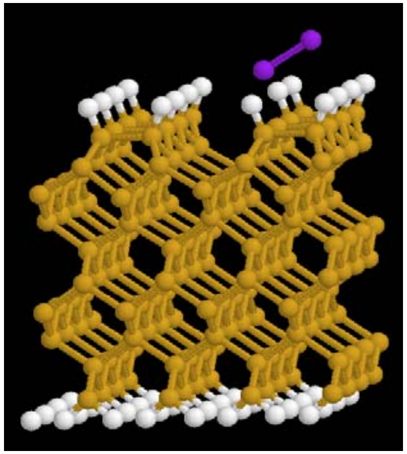
Take home message



1. **<u>Seeing and controlling</u>** a single molecular reaction is possible.

2. There is **plenty of room** in single molecule chemistry.

$$2H_2 + O_2 \rightarrow 2H_2O + \text{ENERGY}$$



3. Single molecule chemistry needs **physicists.**

Thank you for your attention.