Understanding fundamental surface science issues from atomic images

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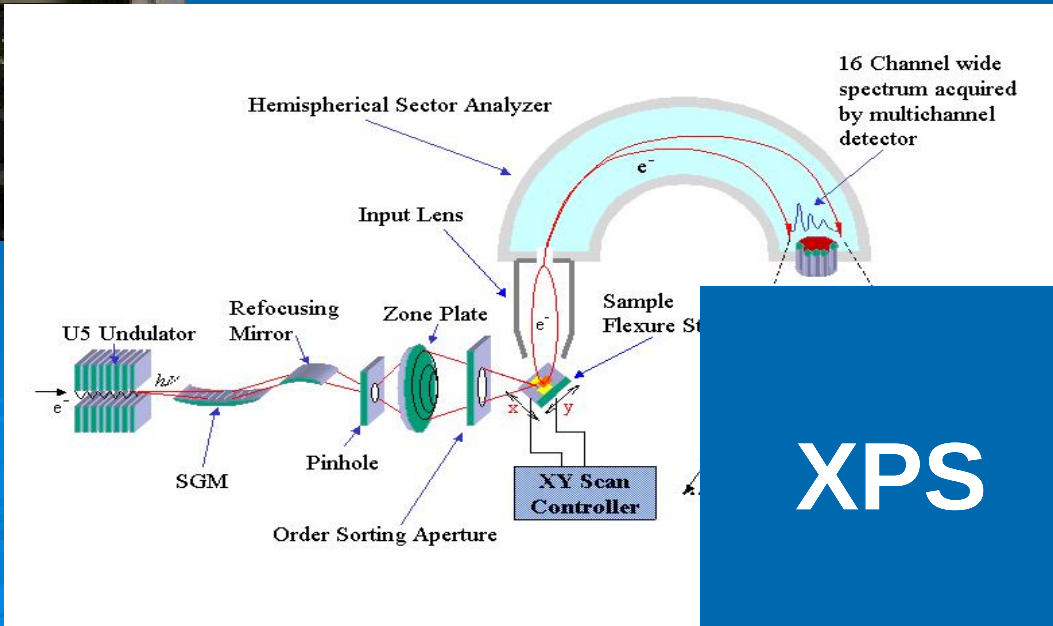
Instruments

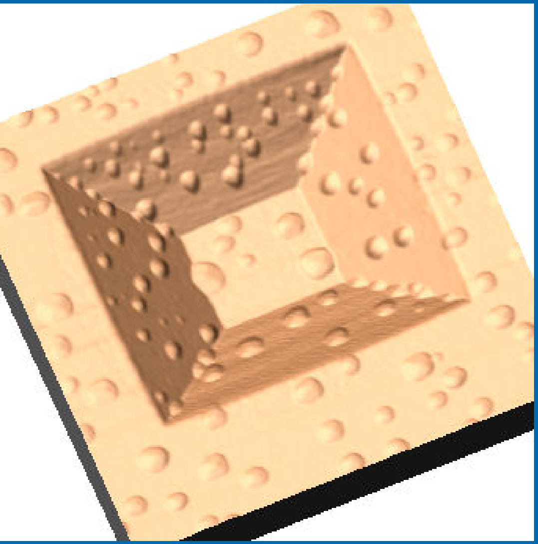
SPM



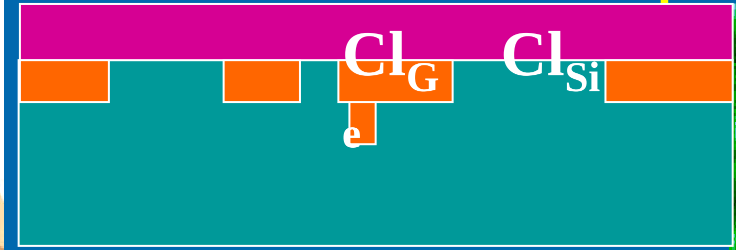
XPS

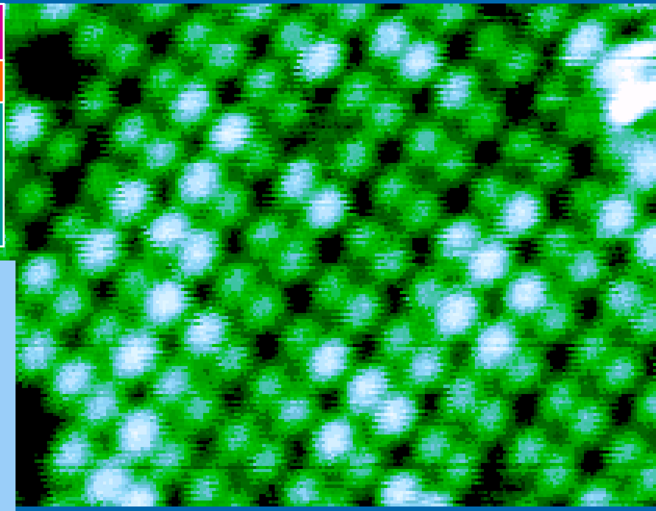
Research Topics

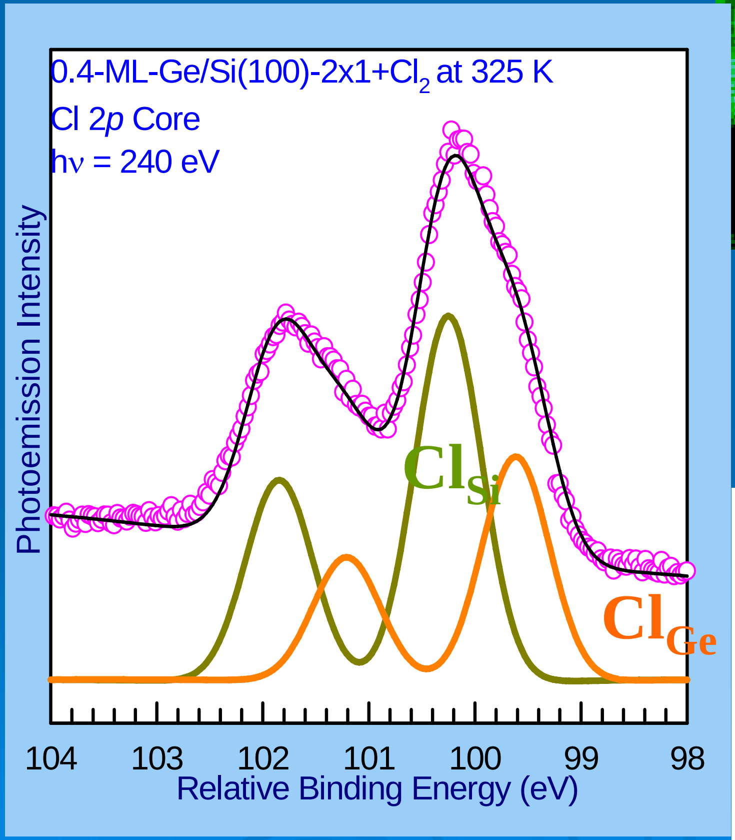
Atomic processes

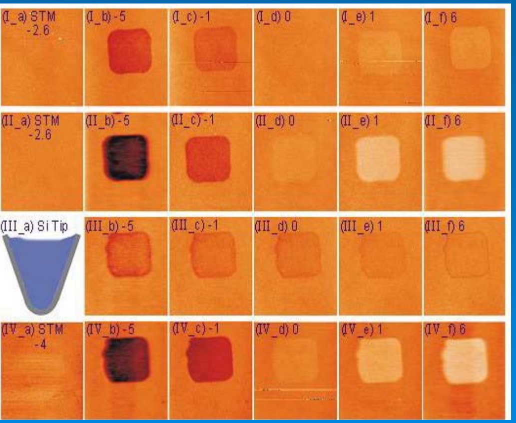


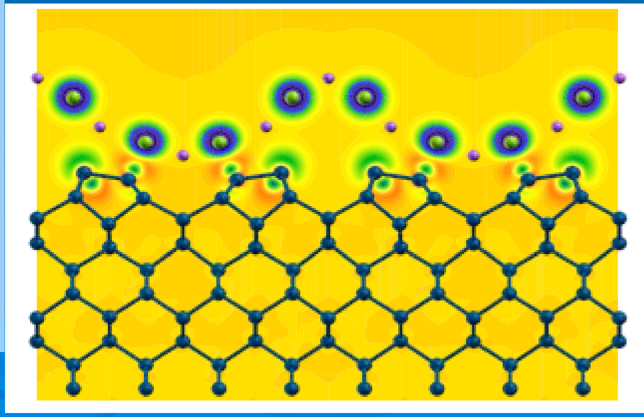
Semiconductor Growth







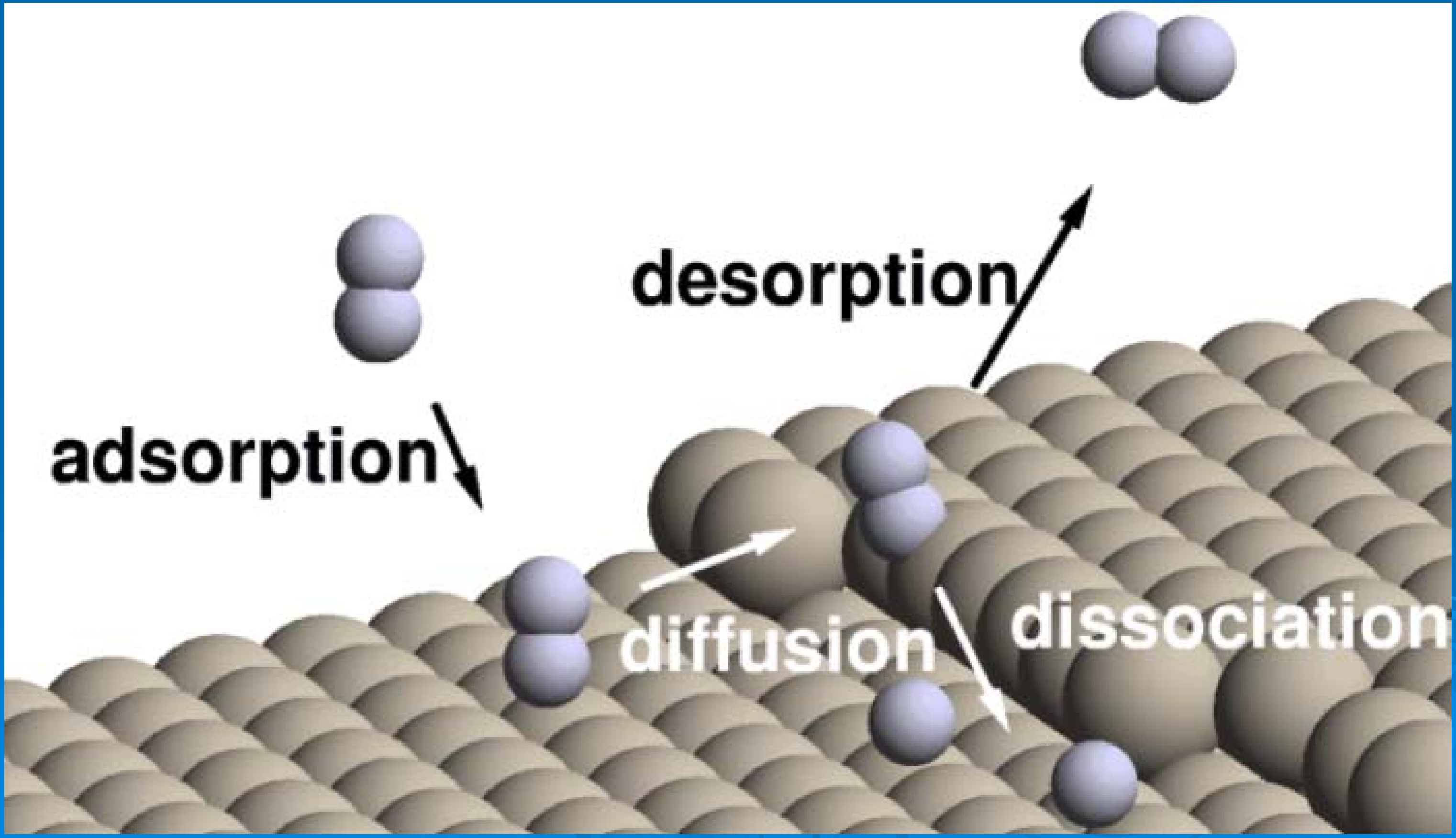




AFM physics

major goal in surface science

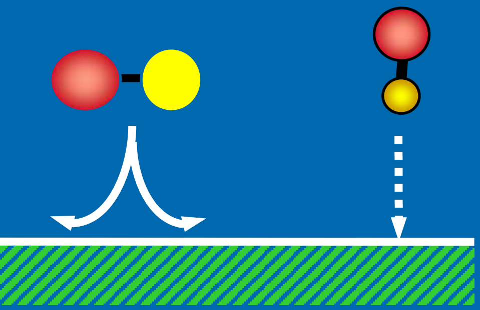
to make movies of molecules on surfaces, on a fs time scale, with 10 pm resolution.

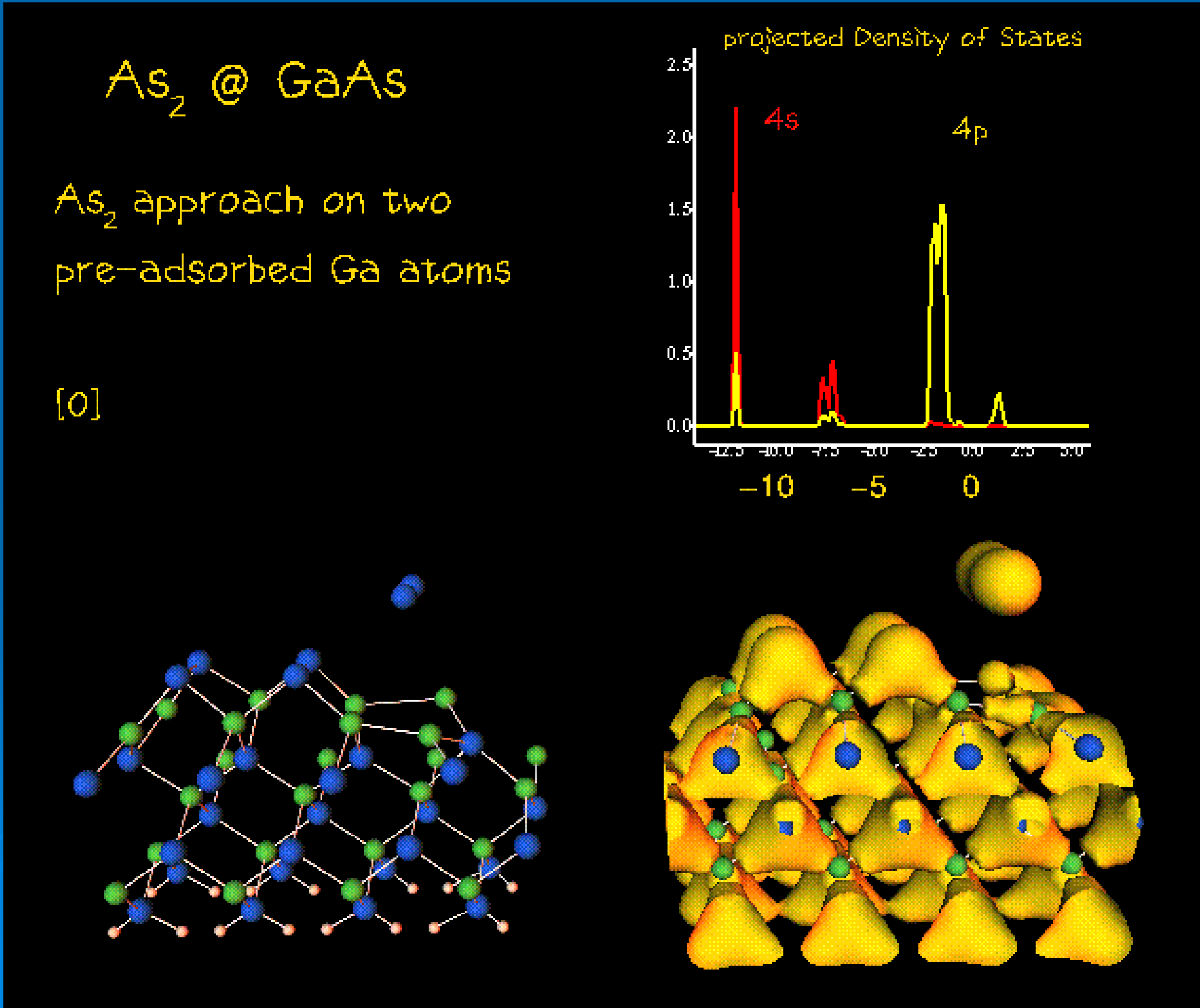


Example” As_2 Adsorption on GaAs

Dissociative

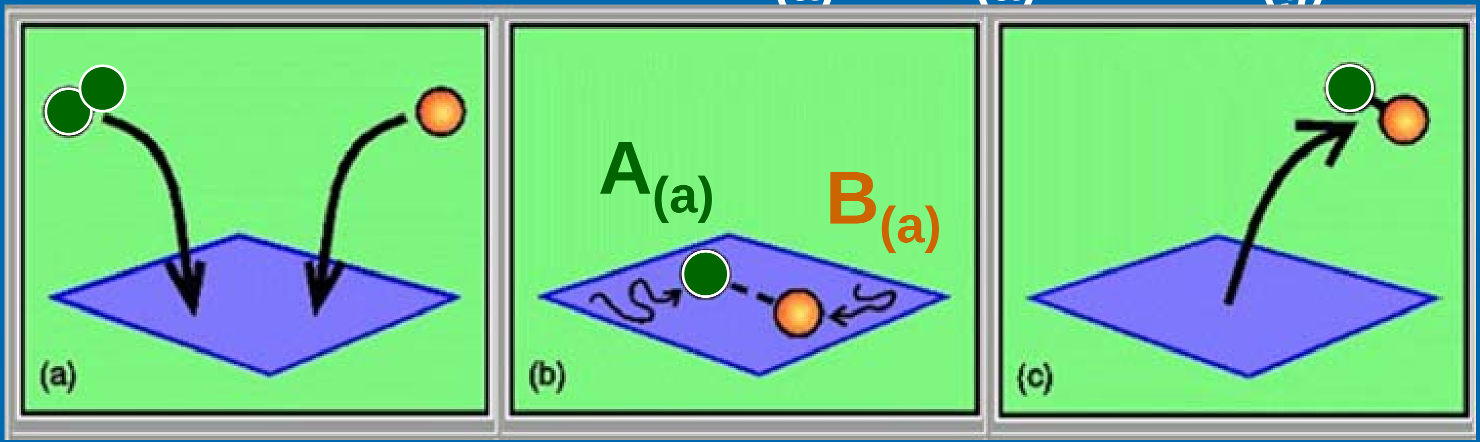
Molecular



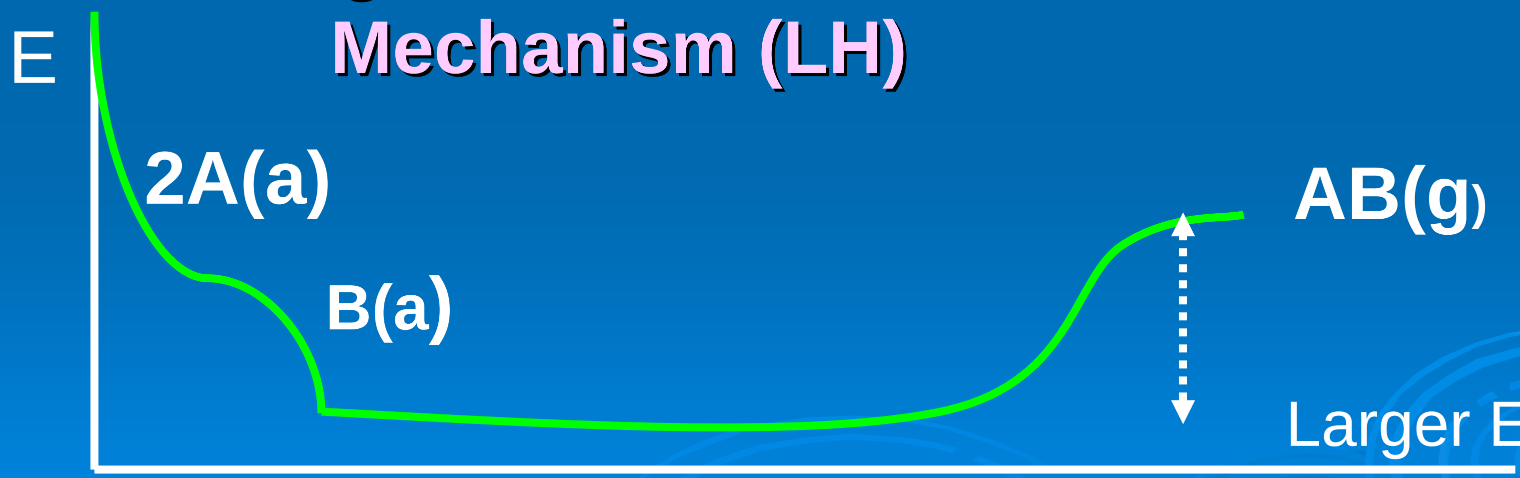


textbook surface reaction

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



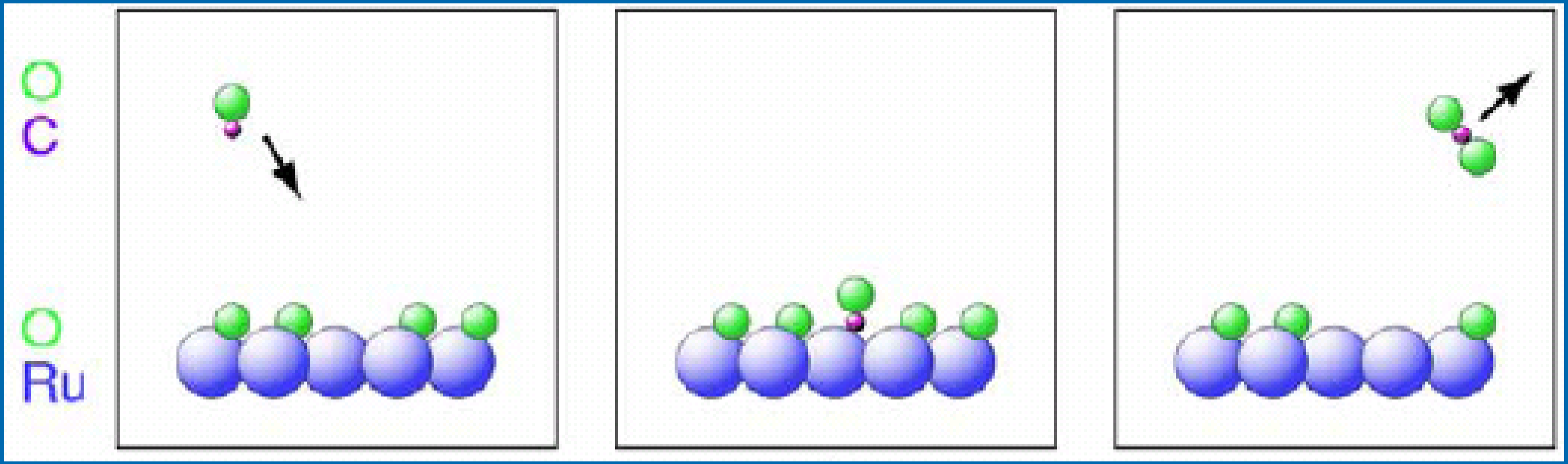
Langmuir-Hinshelwood Mechanism (LH)

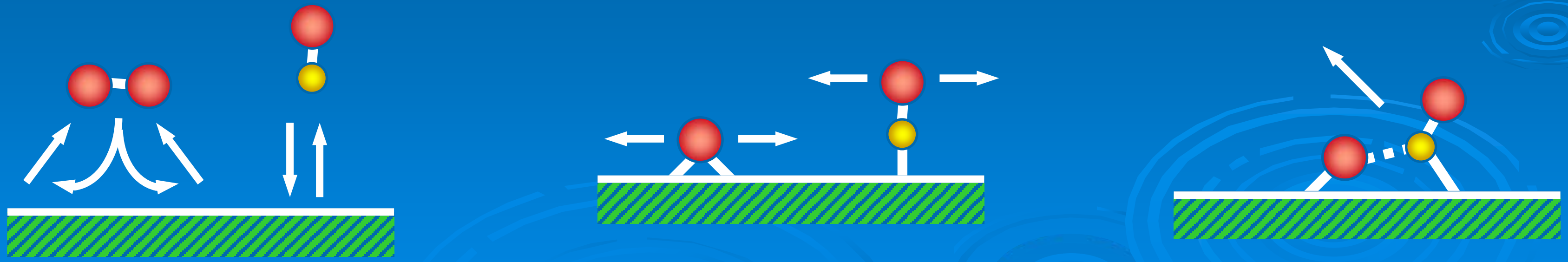


$$\text{Rate} = \nu\, e^{\frac{-E_a}{k_B T}}$$

LH example

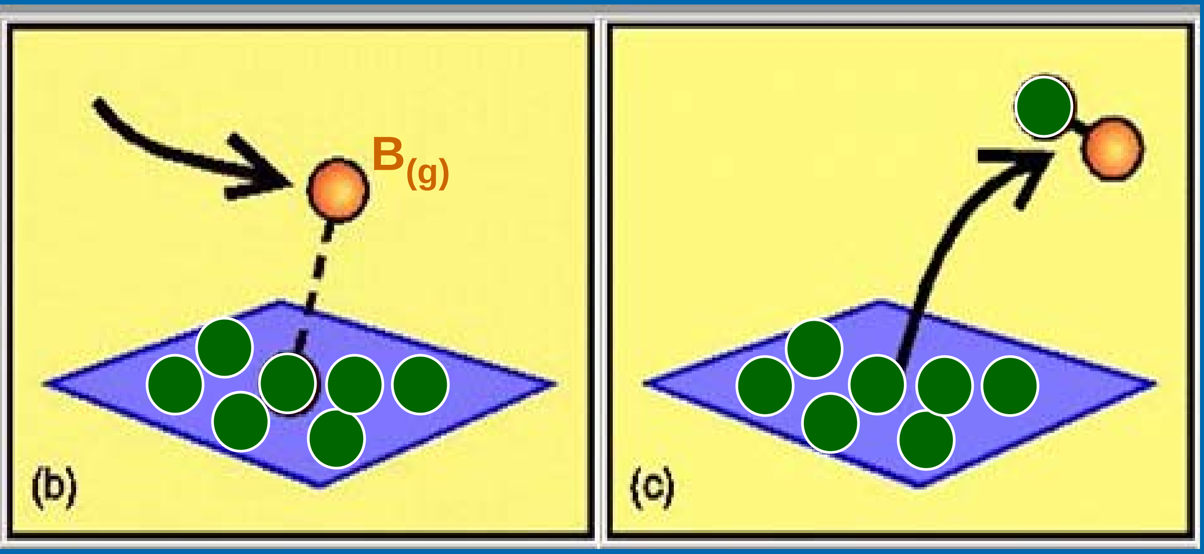
$CO + O_2 \rightarrow CO_2$

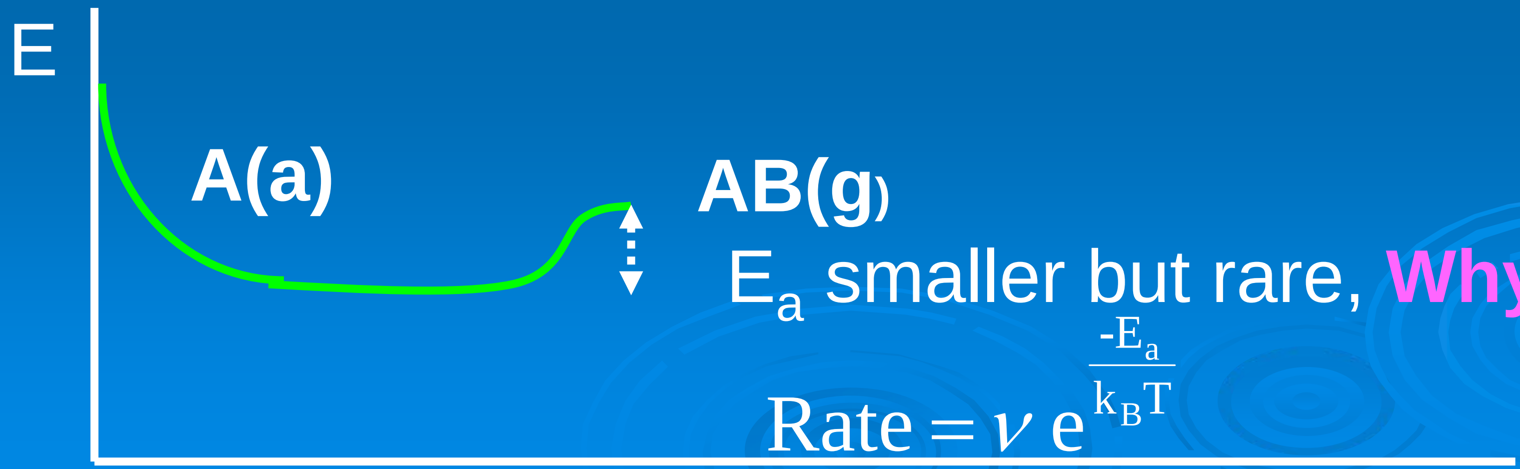




Catalytic reaction of the 2nd kind :

$A_{(g)} + B_{(a)} \rightarrow AB_{(g)}$ **Eley-Rideal Mechanism (ER)**



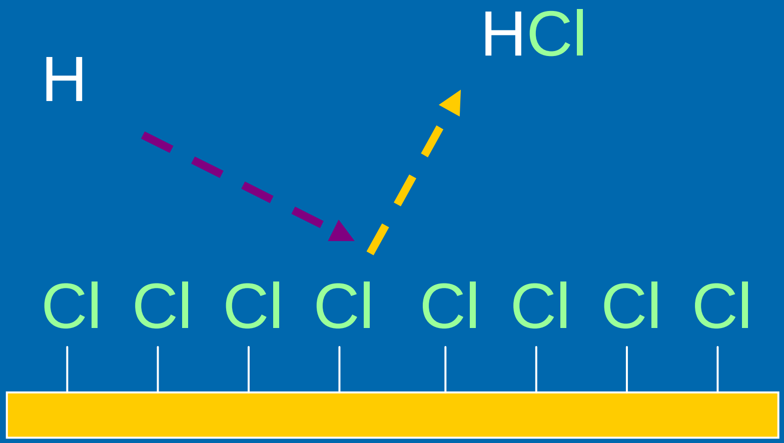


E_a smaller but rare, **Why?**

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

Cl extraction by H on Au(111)

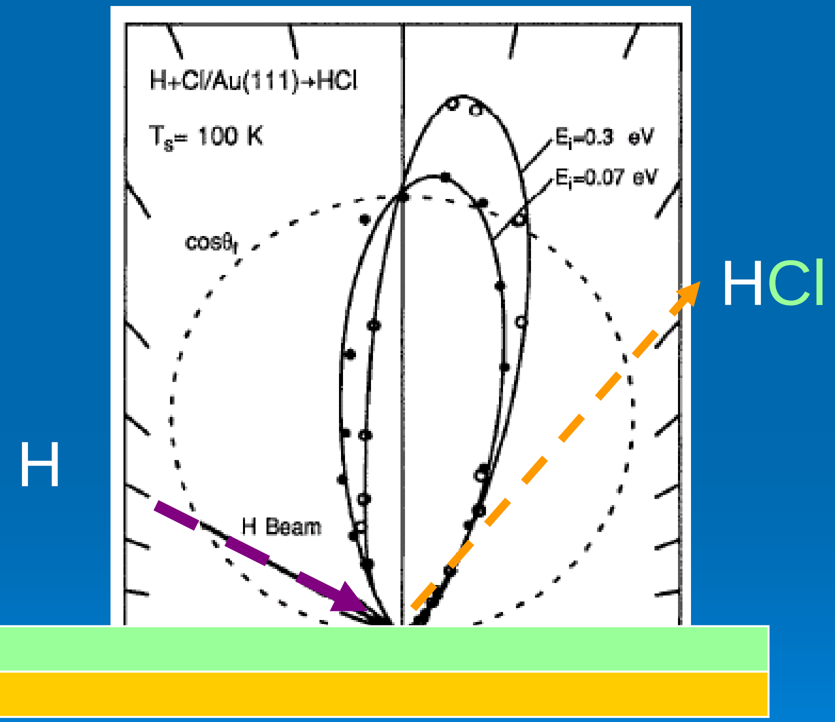
$$H_{(g)} + Cl_{(a)} \rightarrow HCl_{(g)}$$

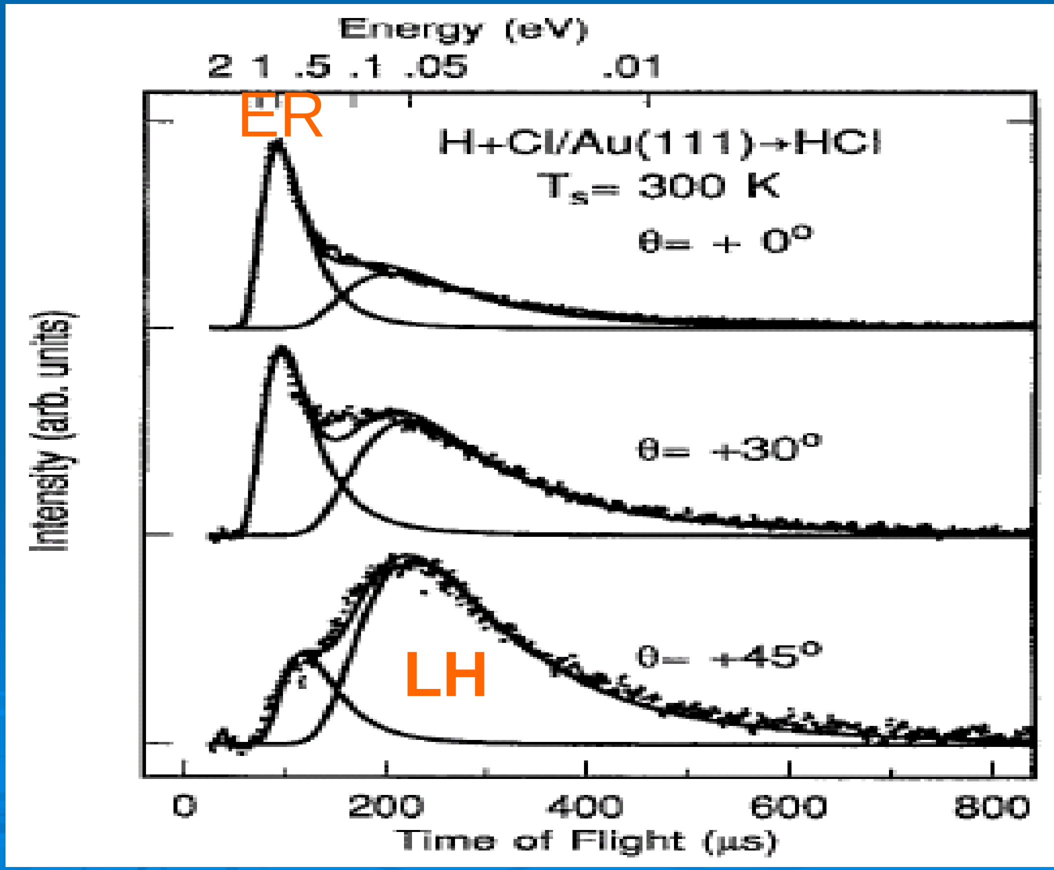


How to tell if this reaction is ER or not ER?

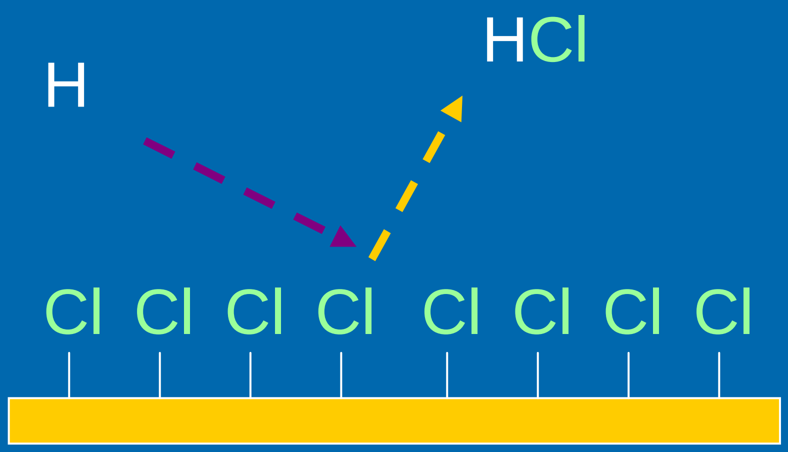
Rettner's approach:

Probing the gas product





Our approach: examine the surface



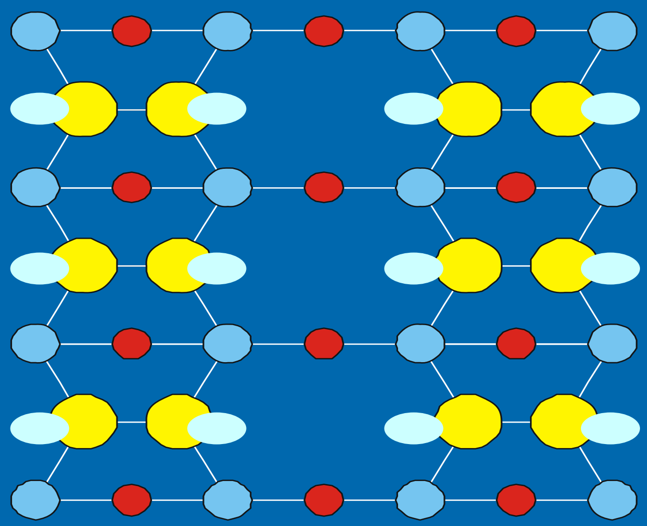
Are reaction sites random or not random?

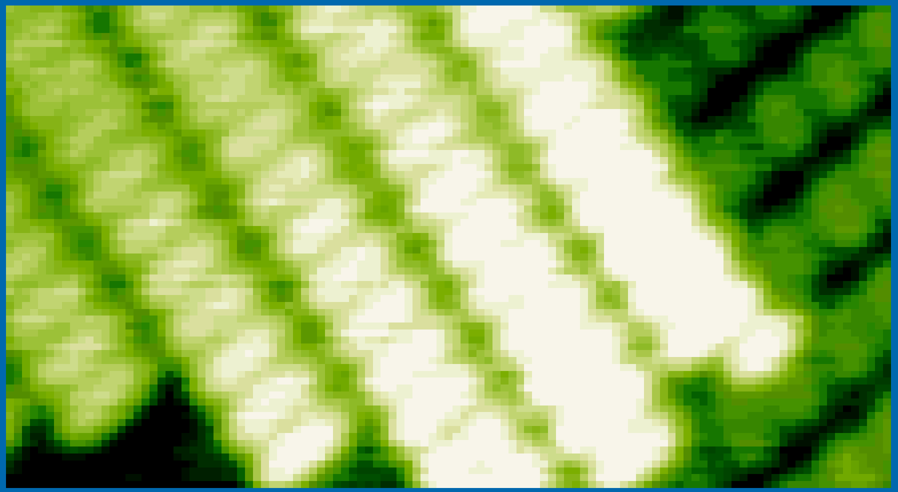
Raindrops on the windshield

ER or not ER ?

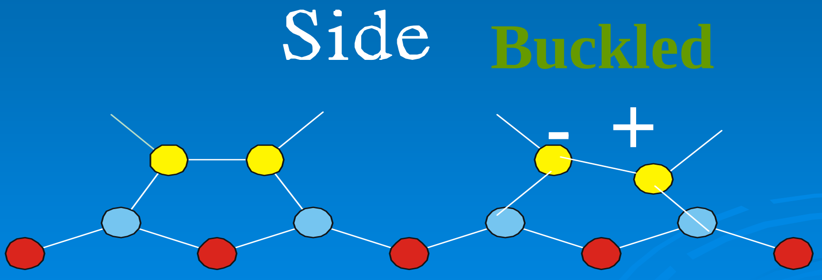
Atomic structure of Si(100)-2×1

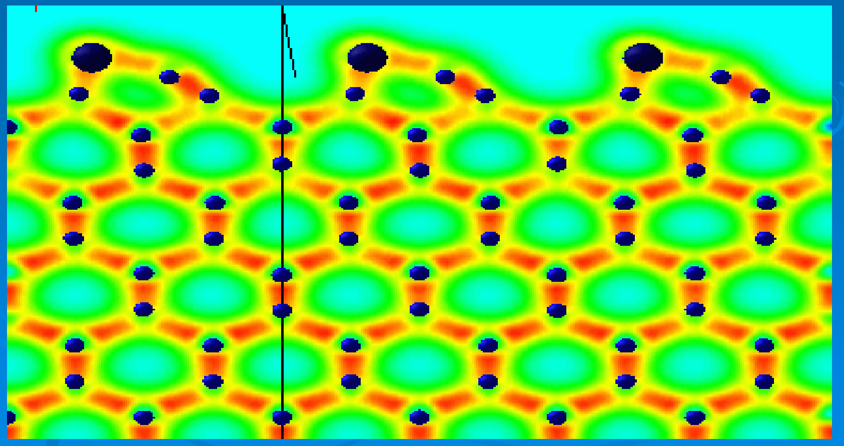
Top



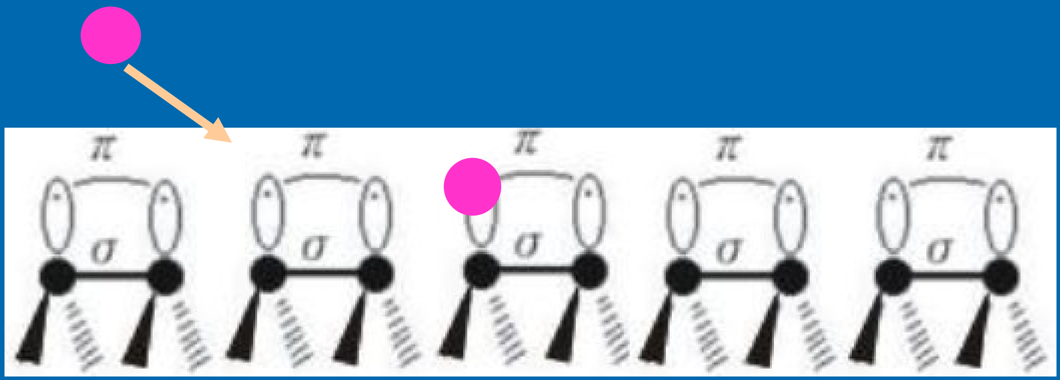


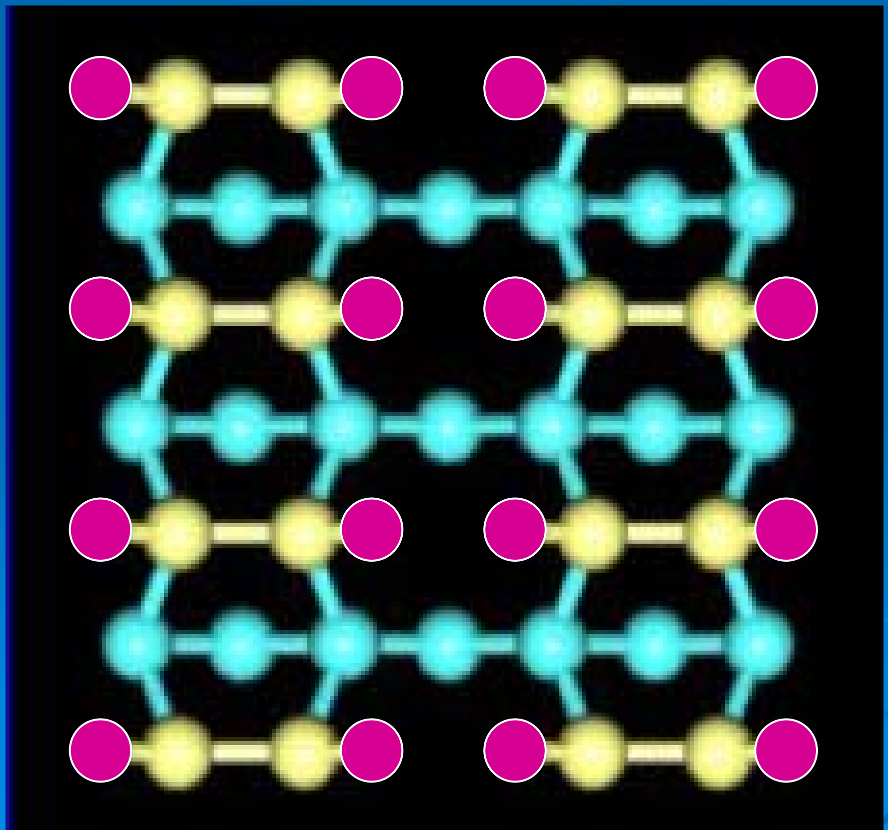
Side

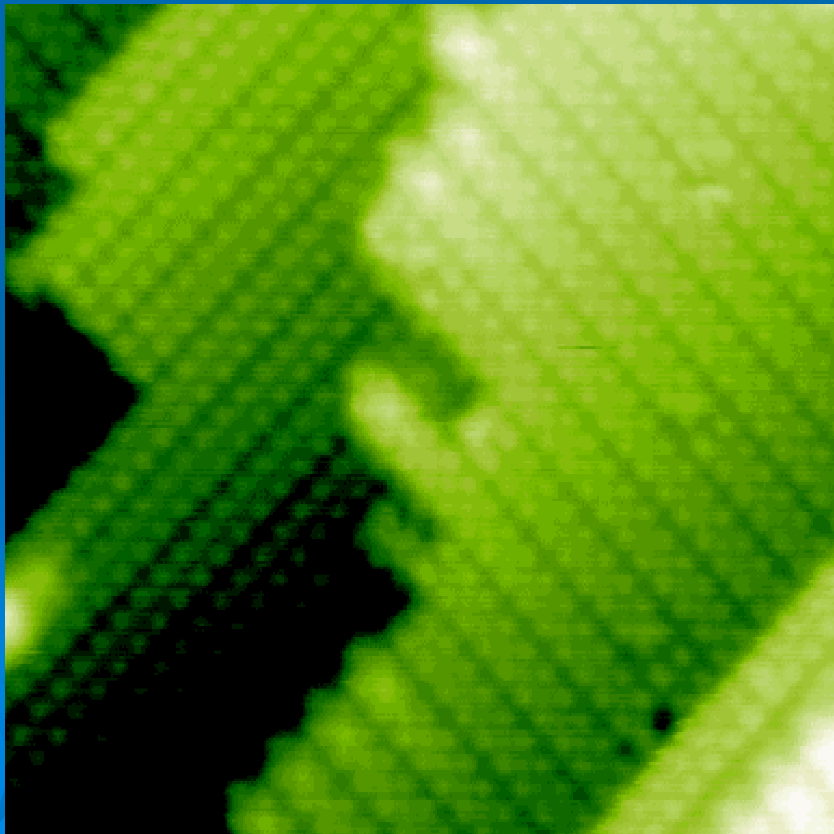




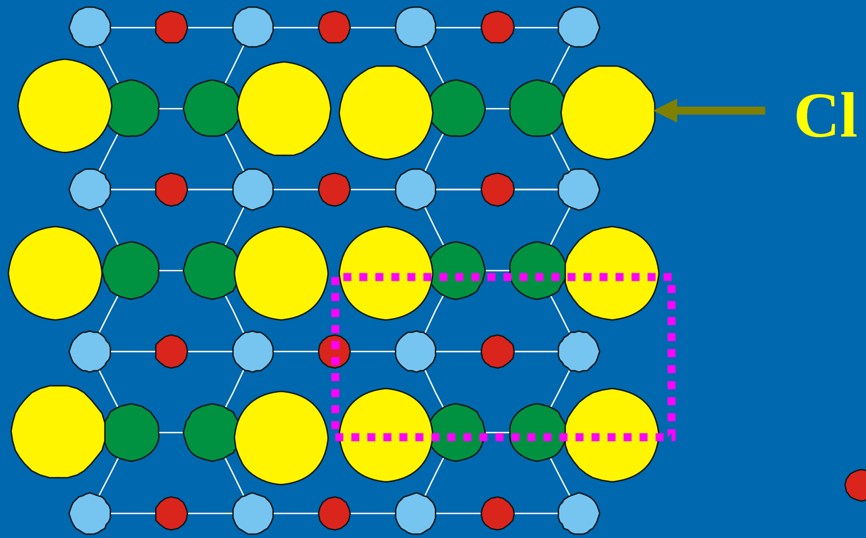
Atomic Hydrogen adsorption on Si(100)



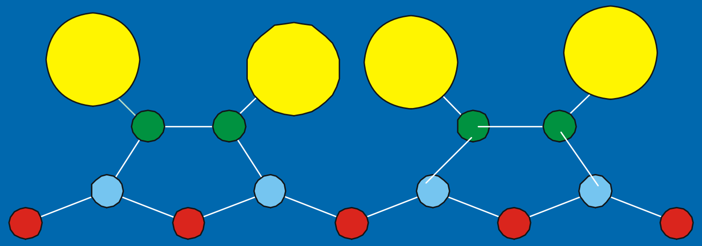


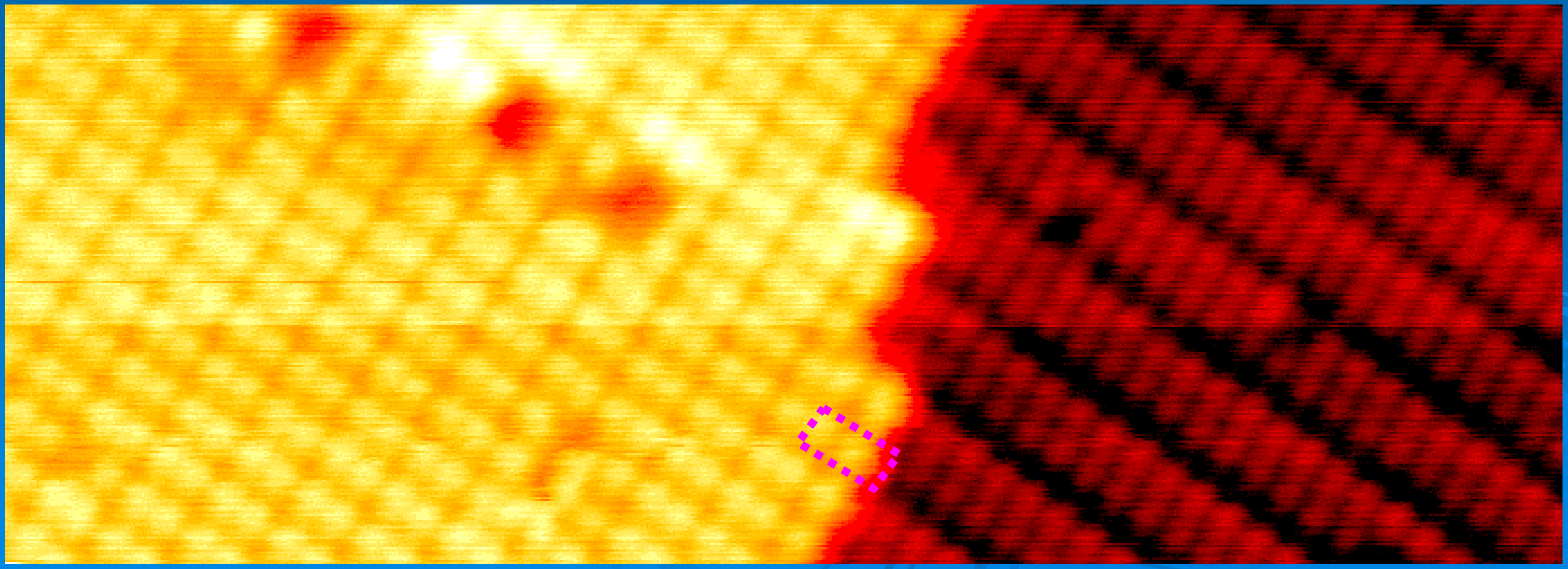


Cl on Si(100)



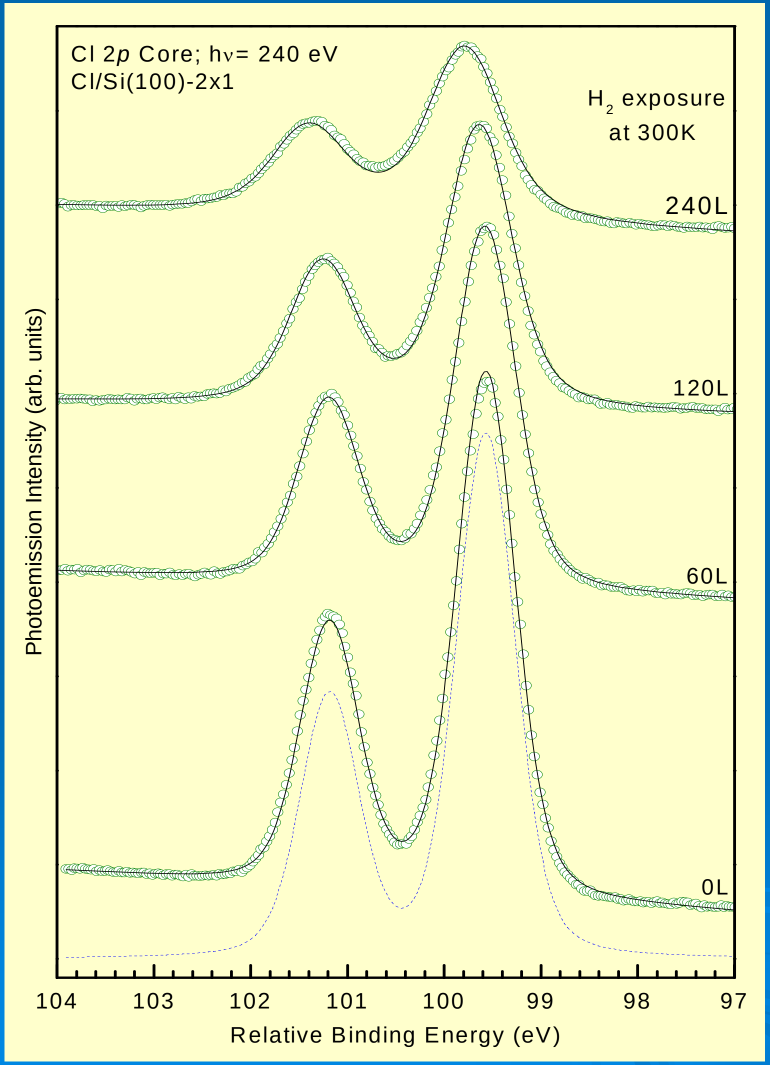
Side view

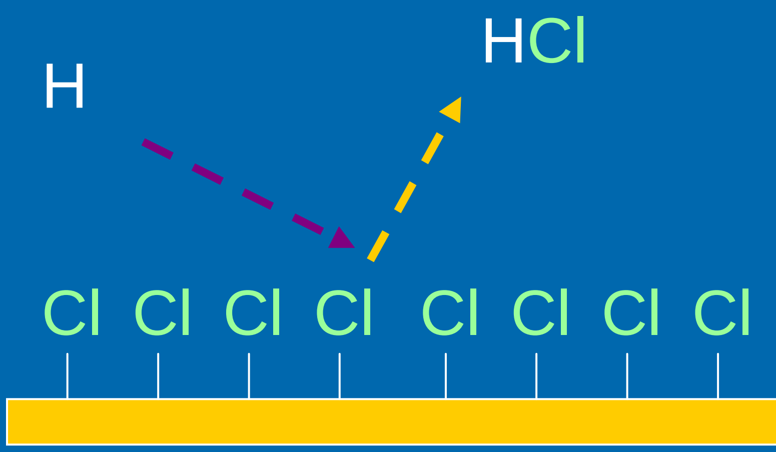




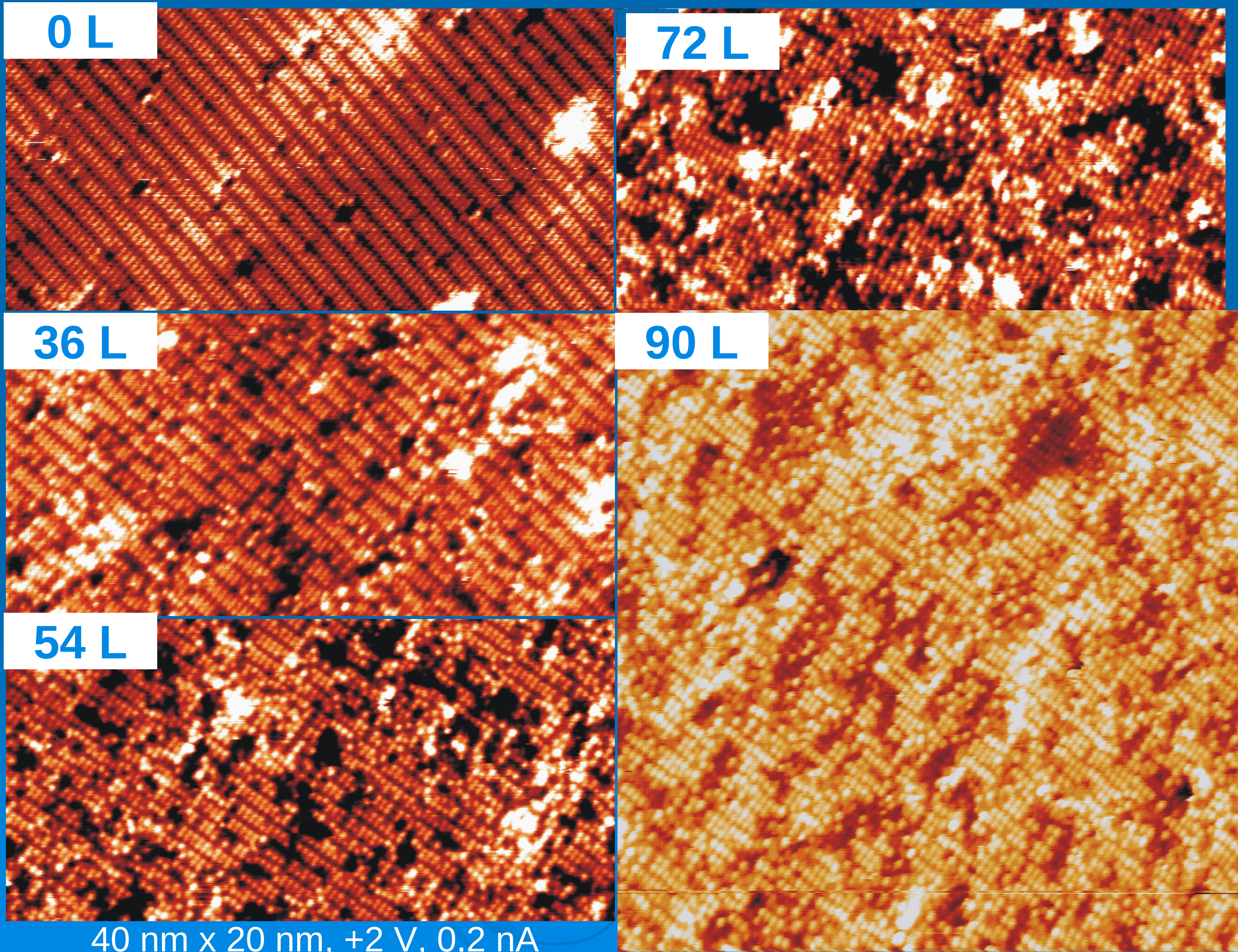
Cl extraction by H on Si(100)-2x1

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





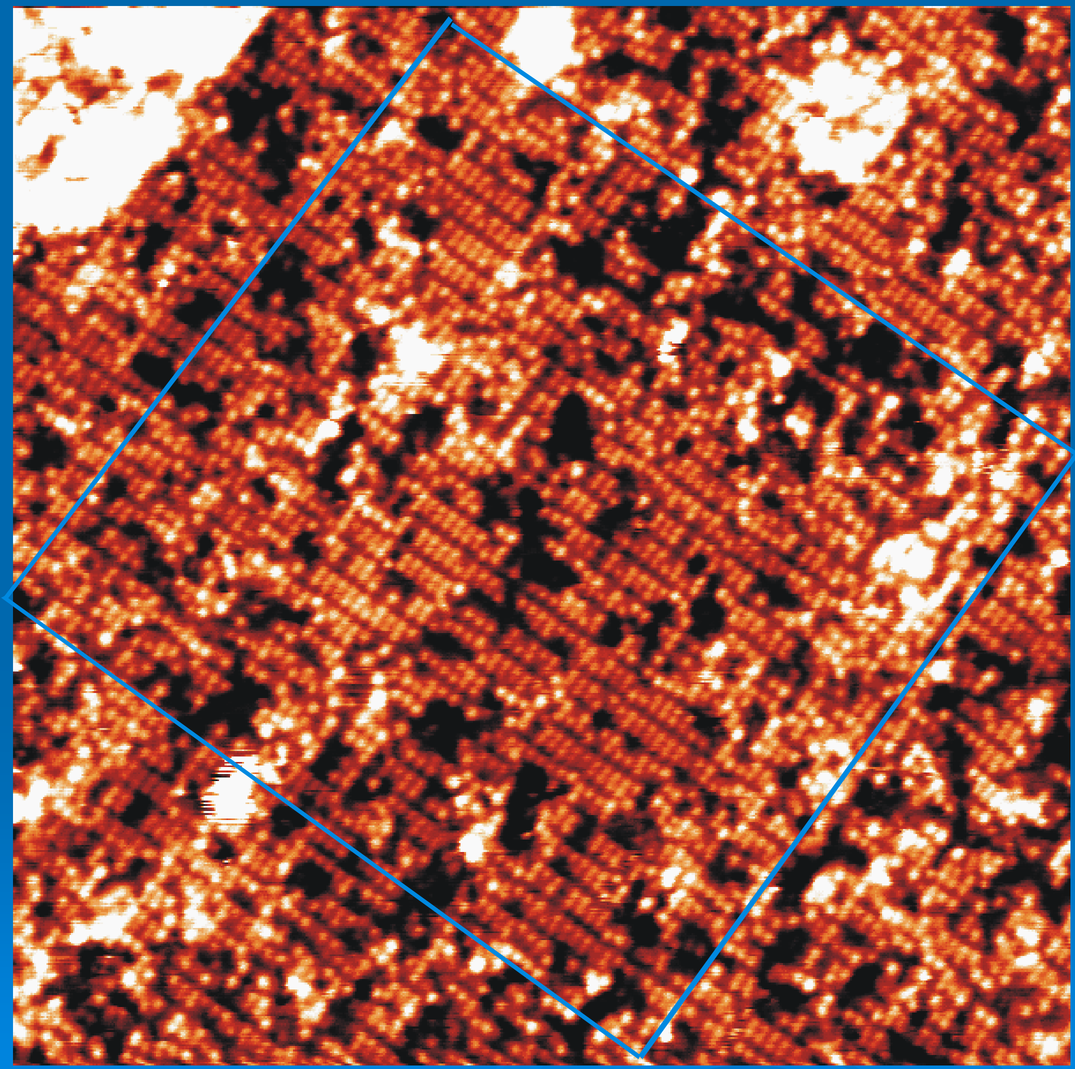
H bombardment on Cl/Si(100)-2x1



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

Analysis is not trivial

54 L H-atom dosage



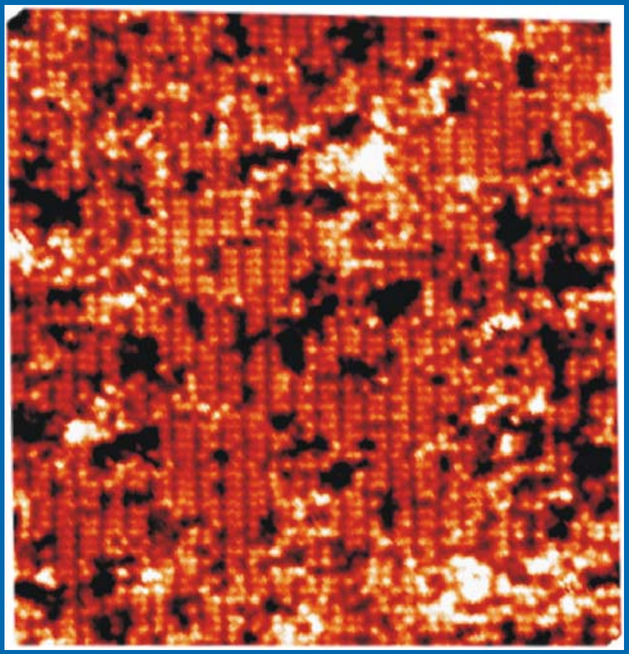
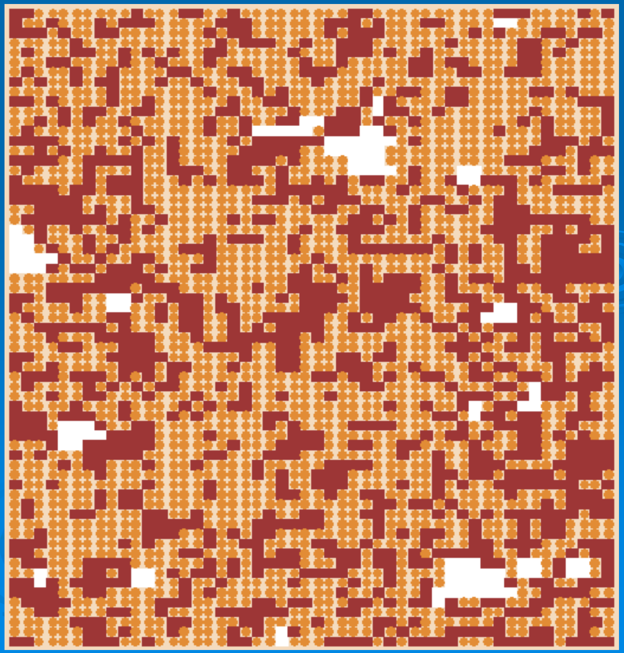
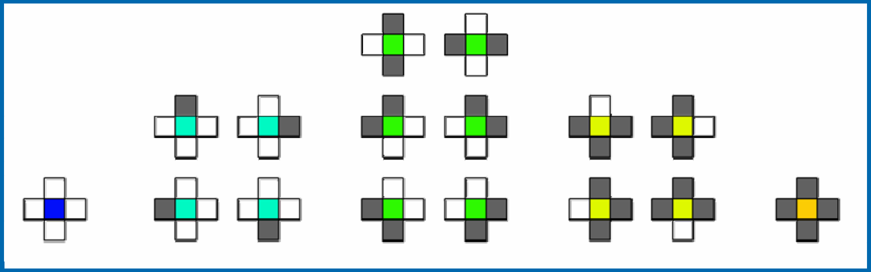
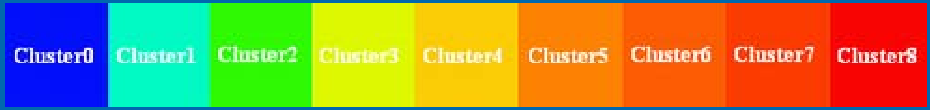


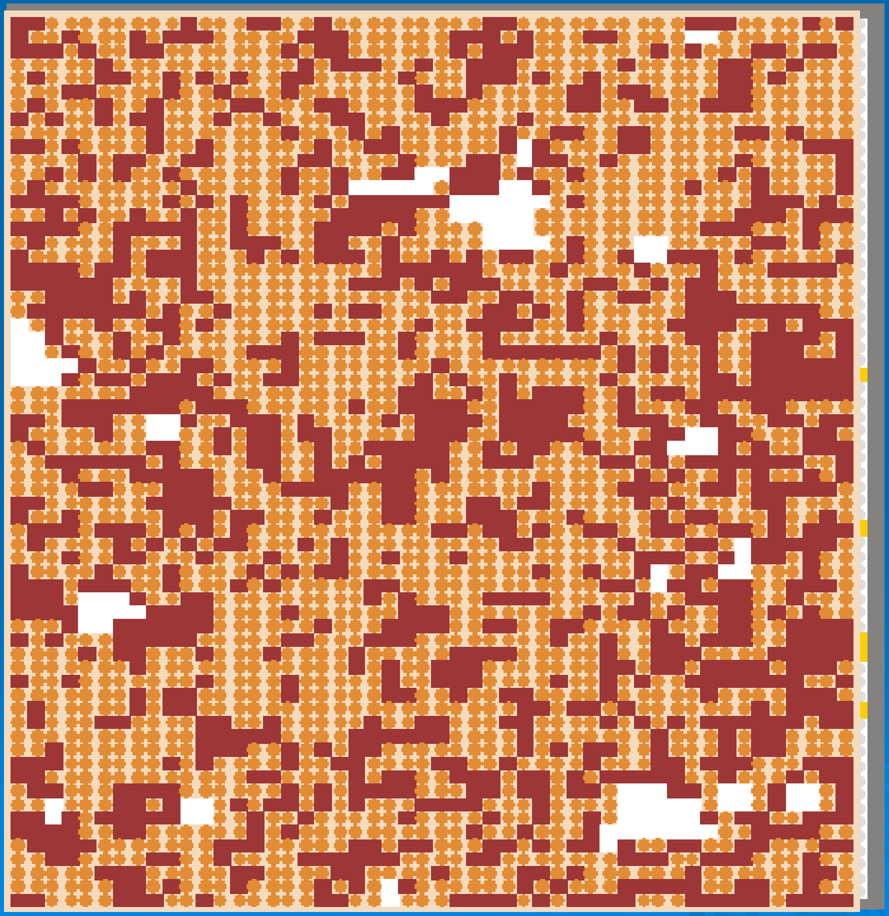
image digitization

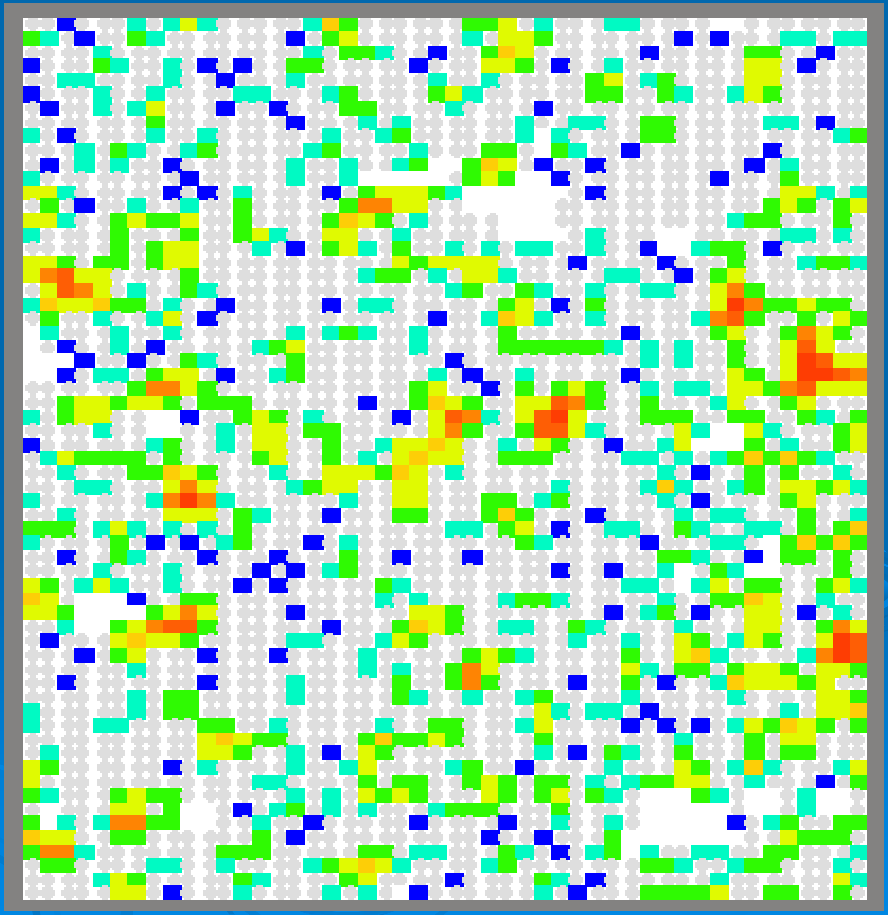


Classify Reaction Sites





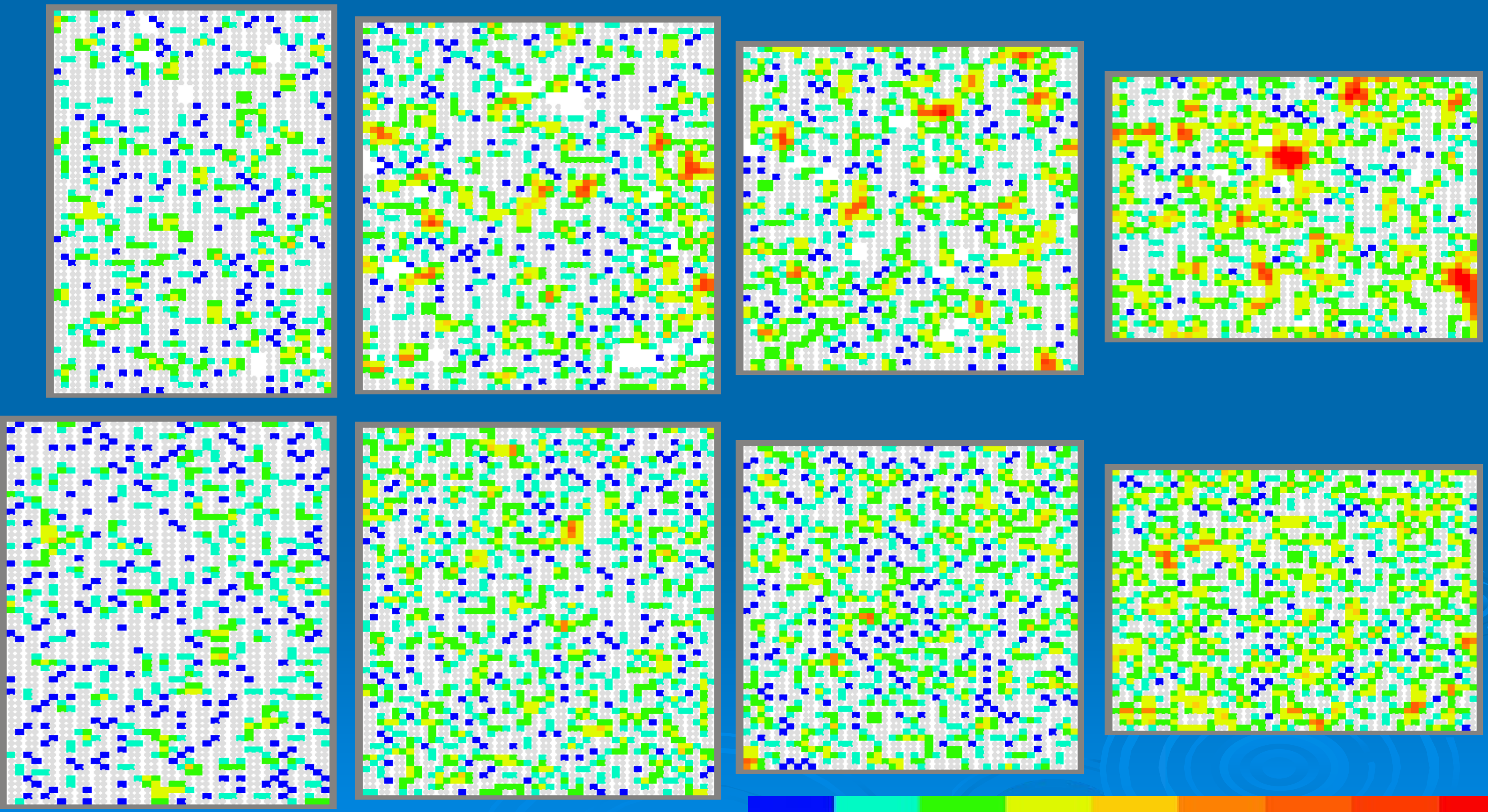




Comparison

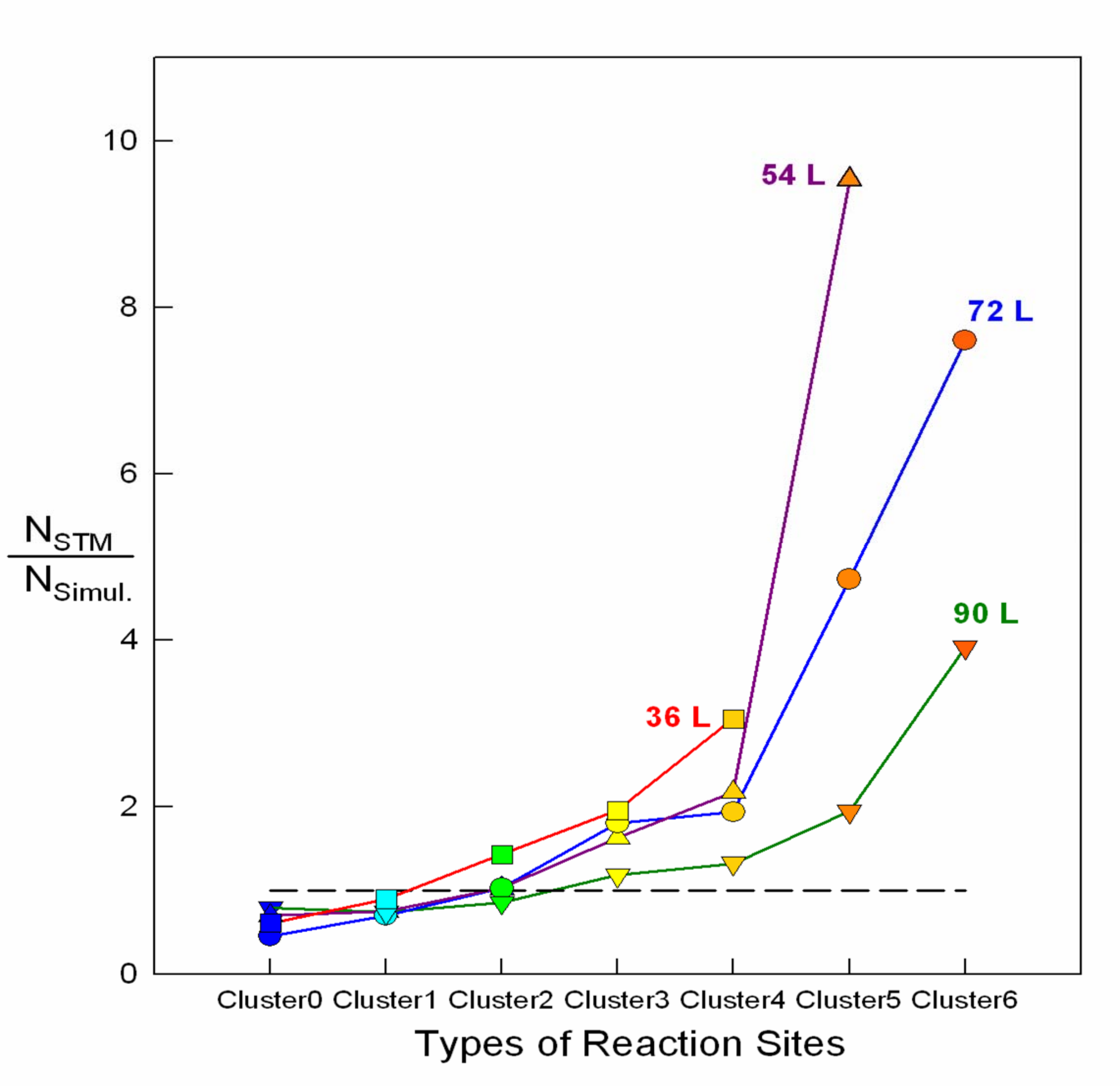
STM Data Analysis

36 L | 54 L | 72 L | 90 L



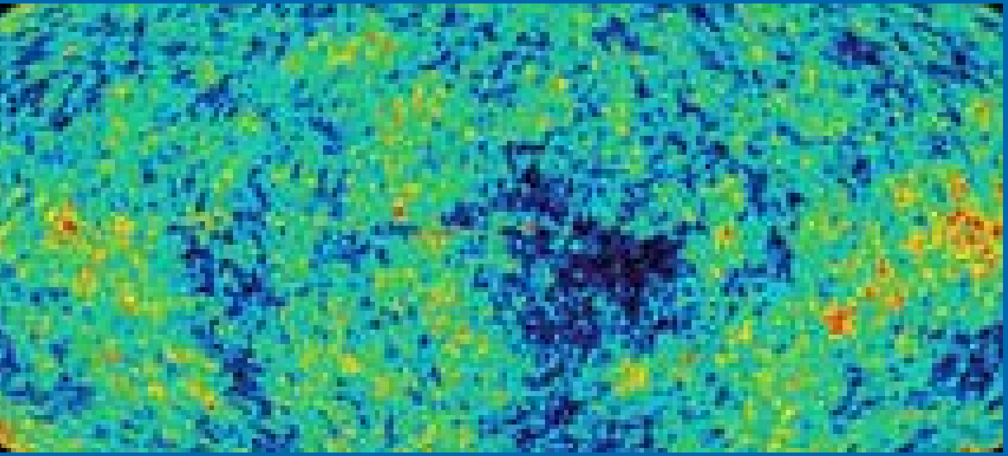
Random Simulation

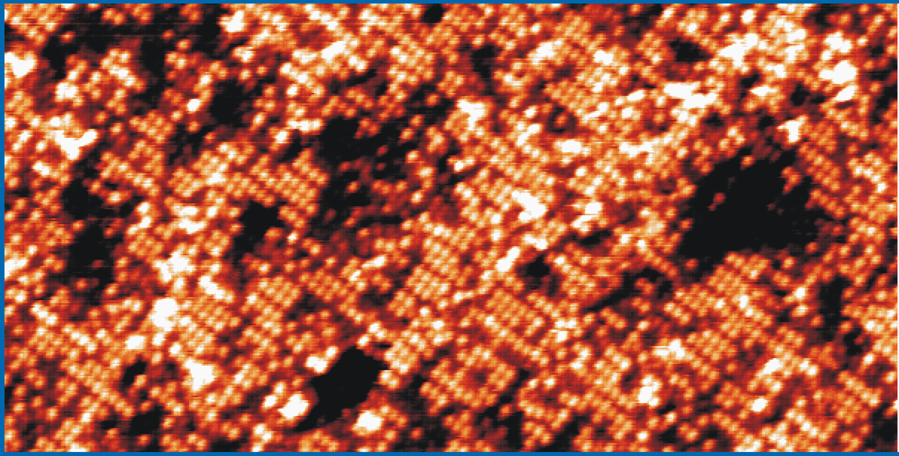
Comparison



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.

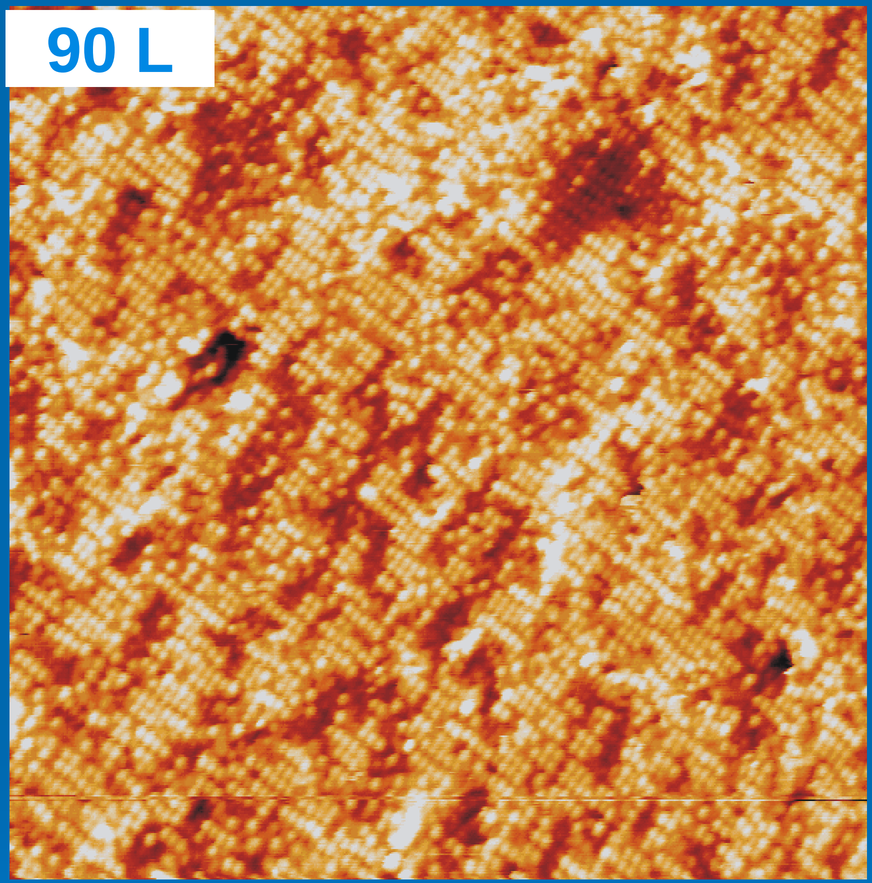


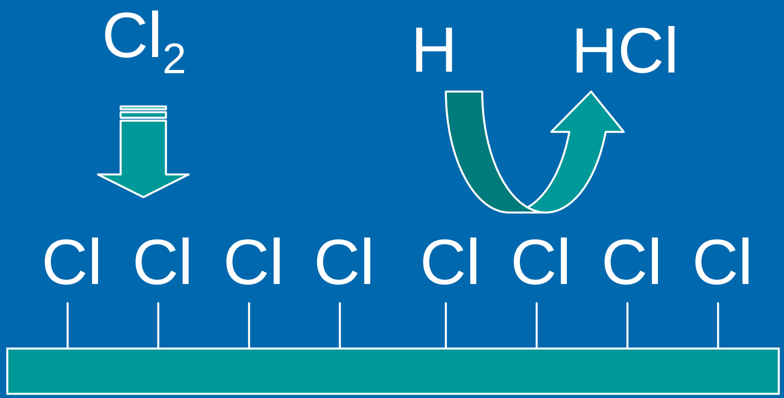


Time scale: 10^{18} : 10^{-12}

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

Summary



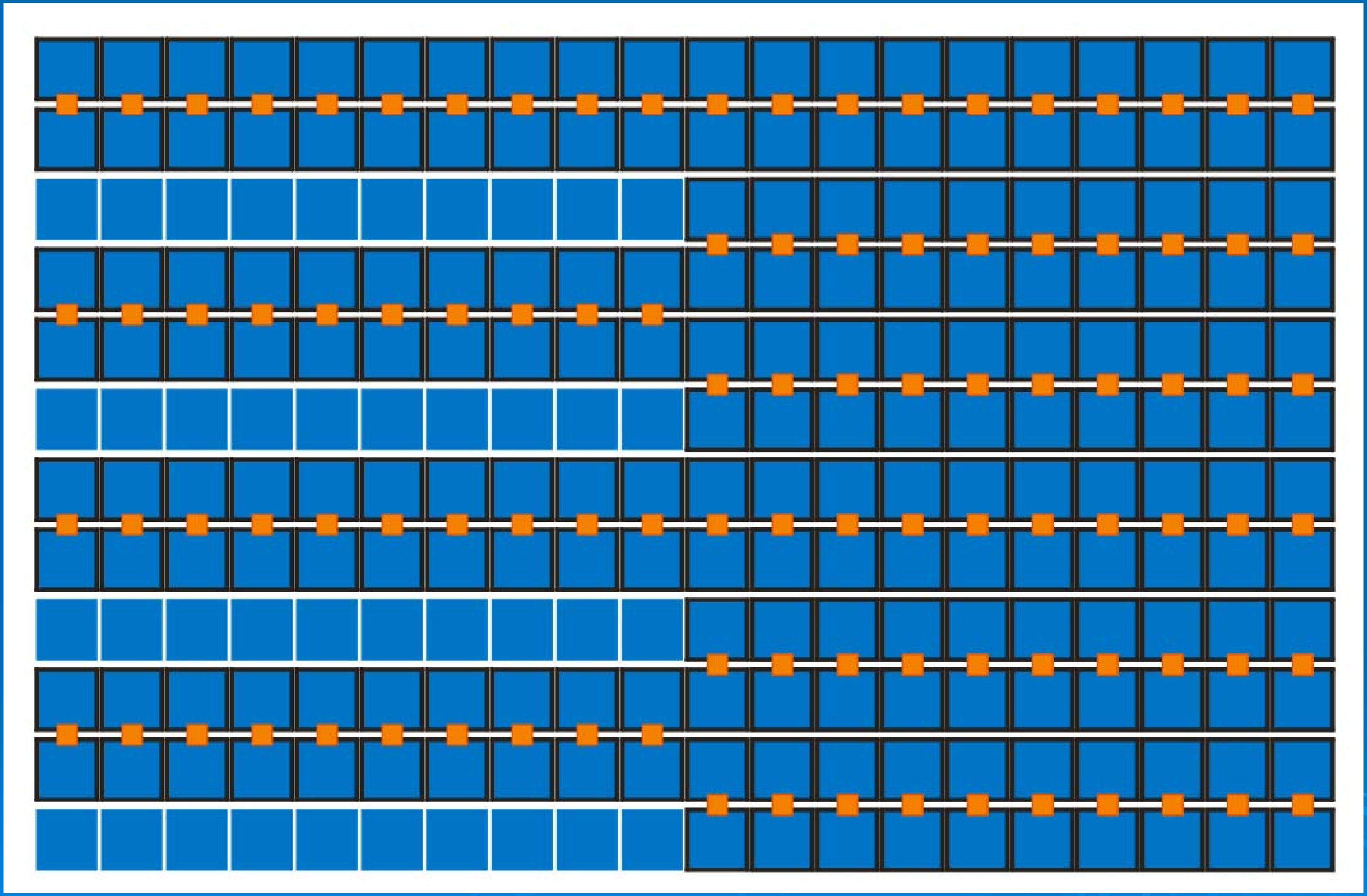


ER or not ER ?

- Hot atom mechanism plays an important role.

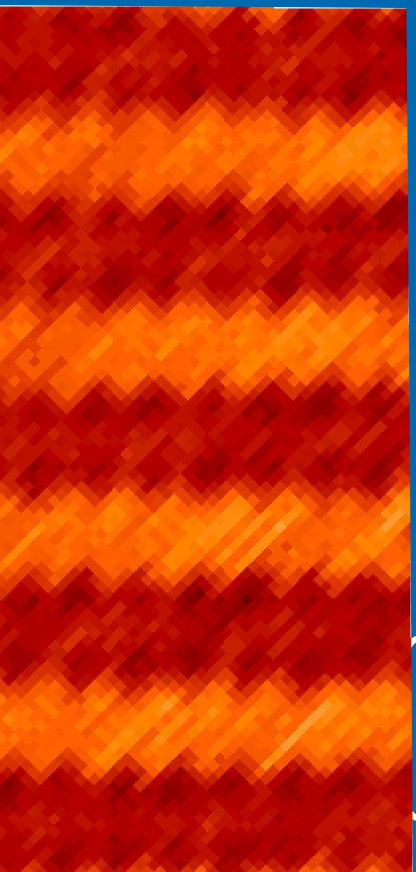
- STM might not be perfect for this kind of study, still very useful.

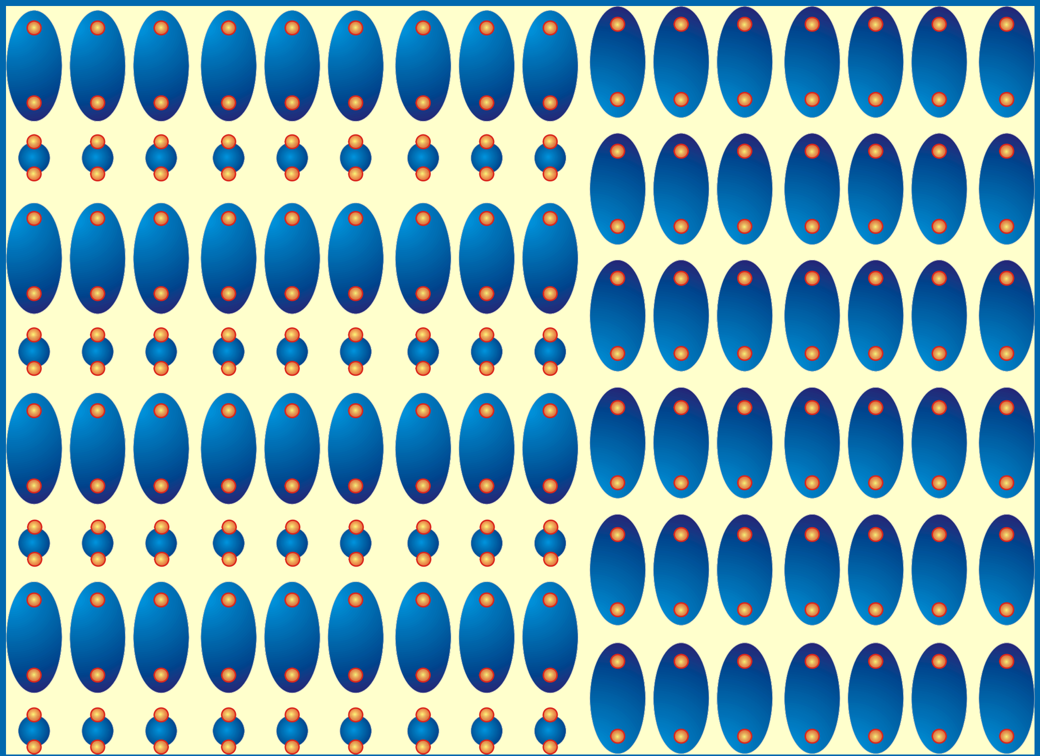
How 2D structure Phase Transition occurs



3x1 2x1

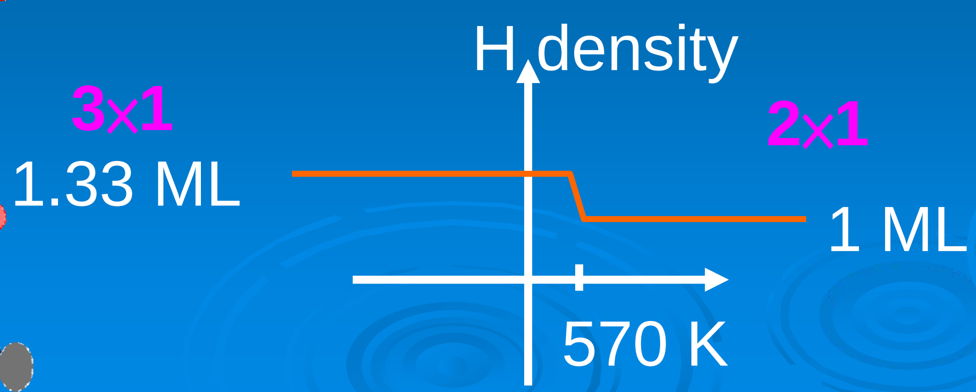
2x1→3x1 transition ≡ H reduction process

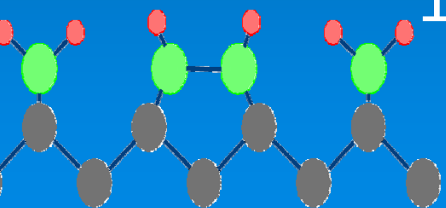


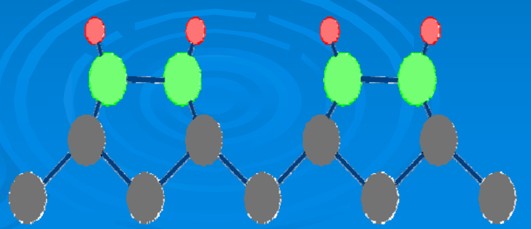


} 2x1

1 ML

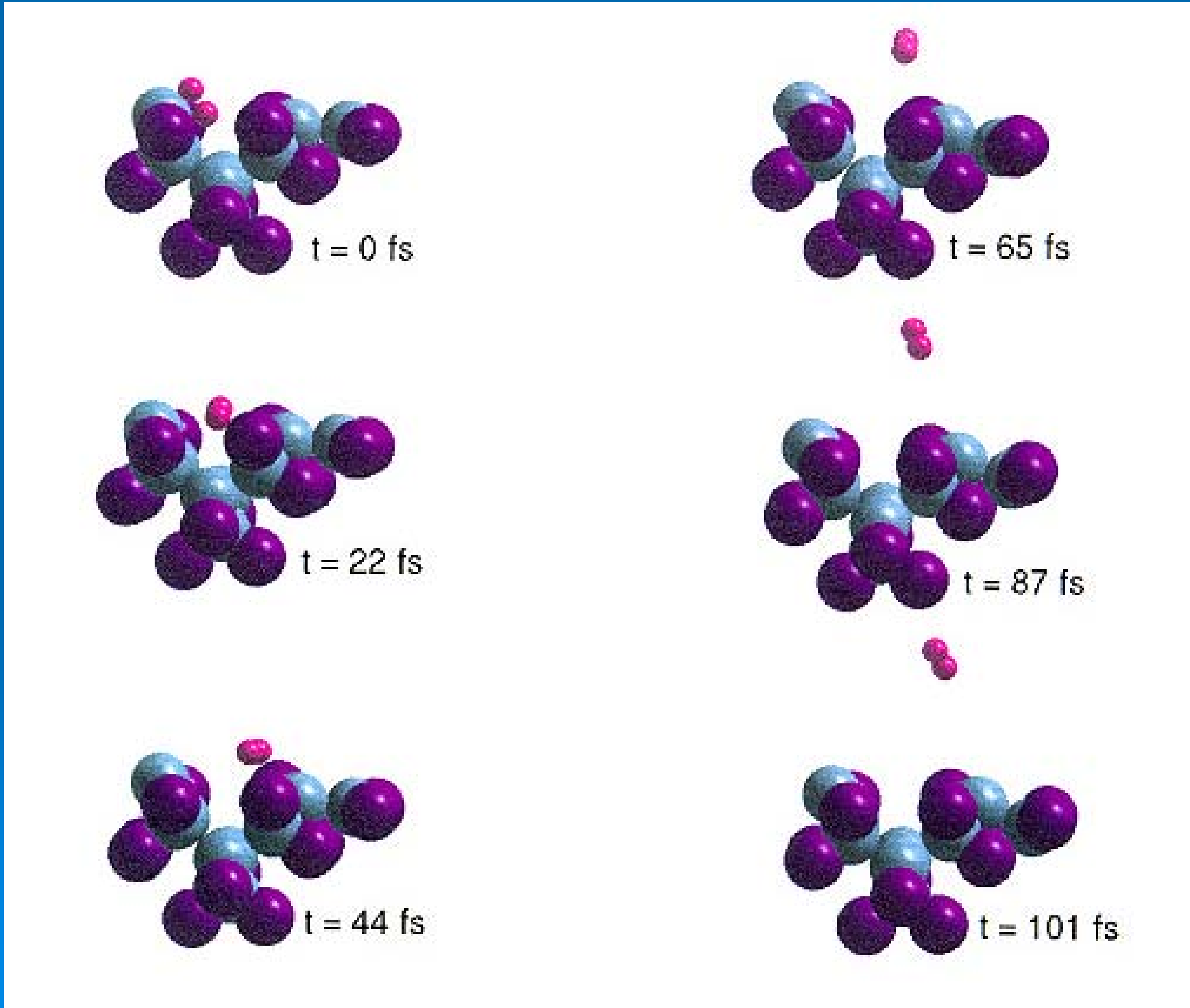






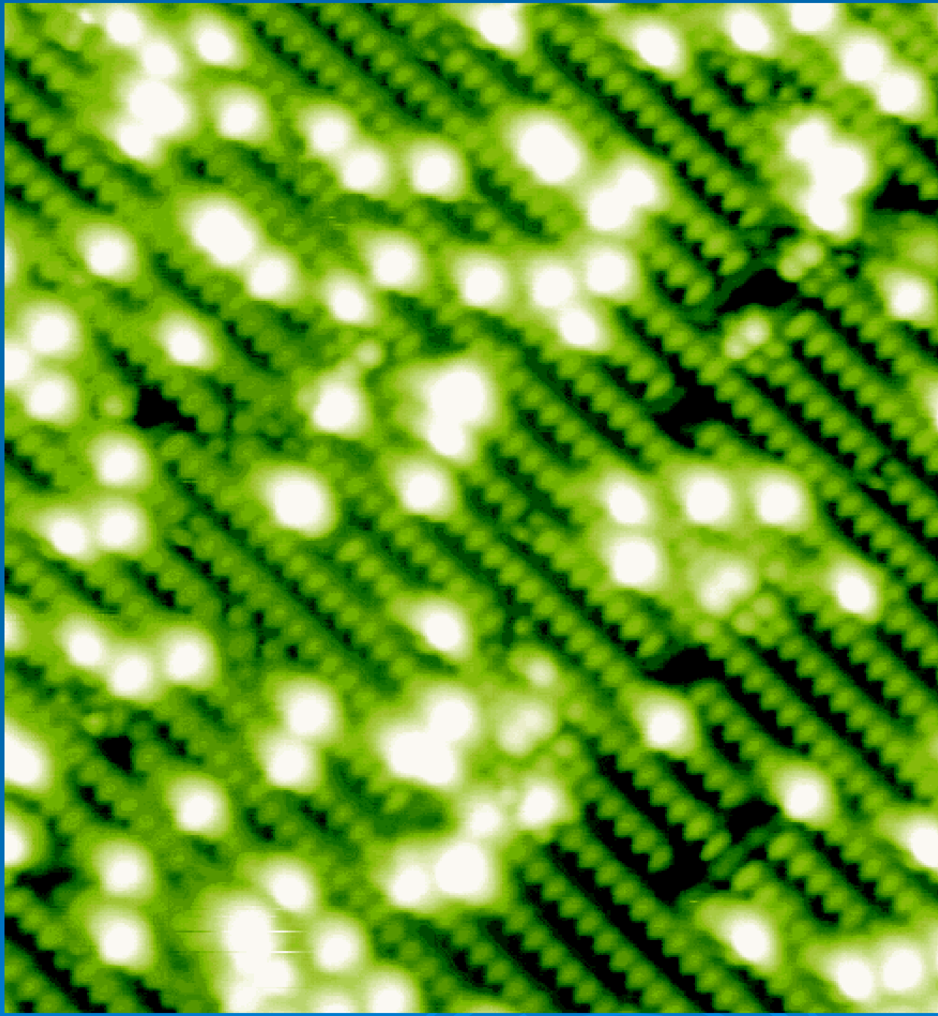
Hydrogen desorption from Si (100)

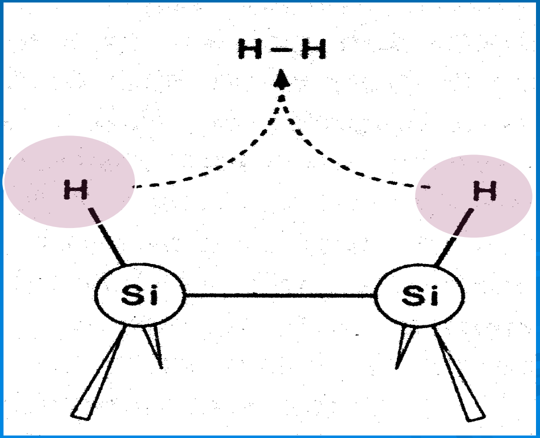
via *Ab Initio* Molecular Dynamics <u>Emily A. Carter</u>



H_2 thermal desorption from Si_2H_2

725 K
for 1 min

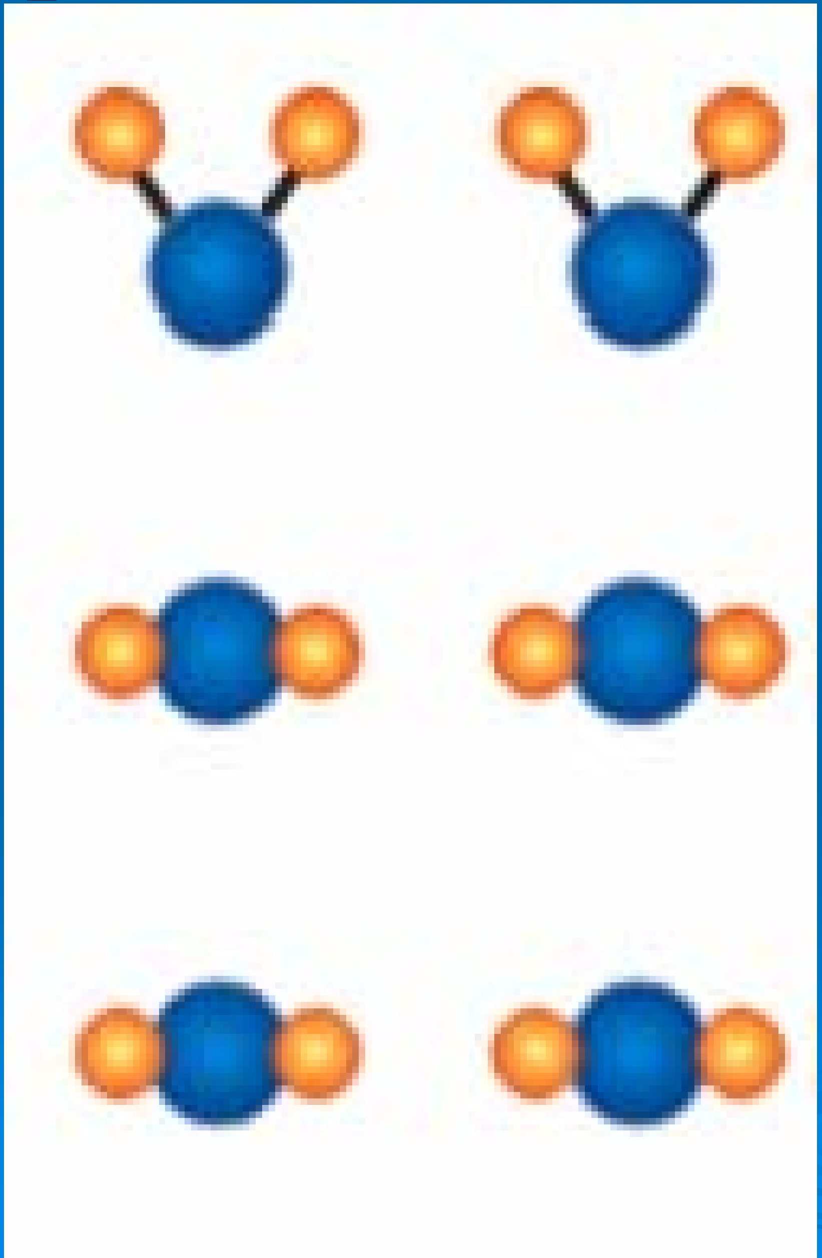




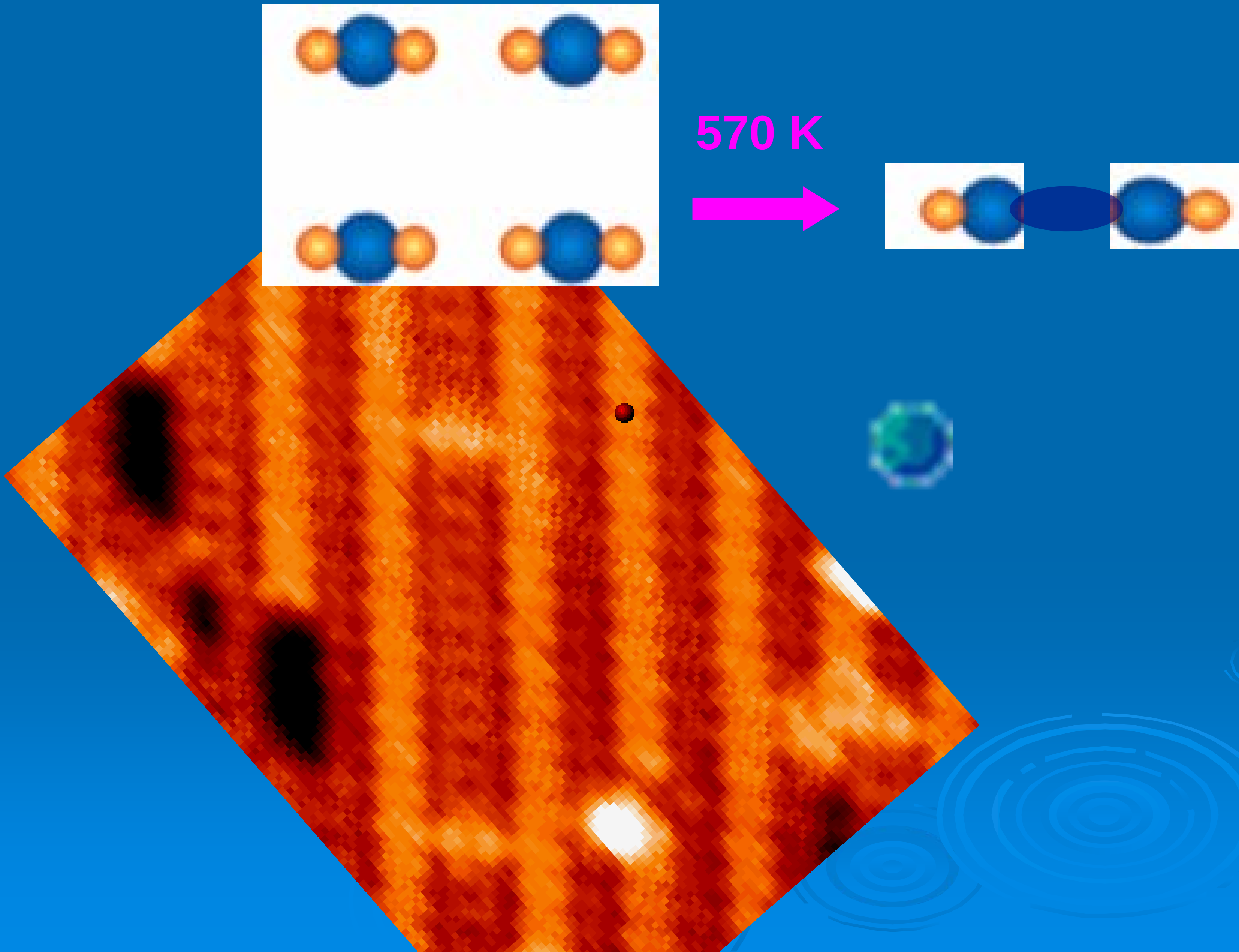
H_2 desorption from SiH_2 570 K

Side view

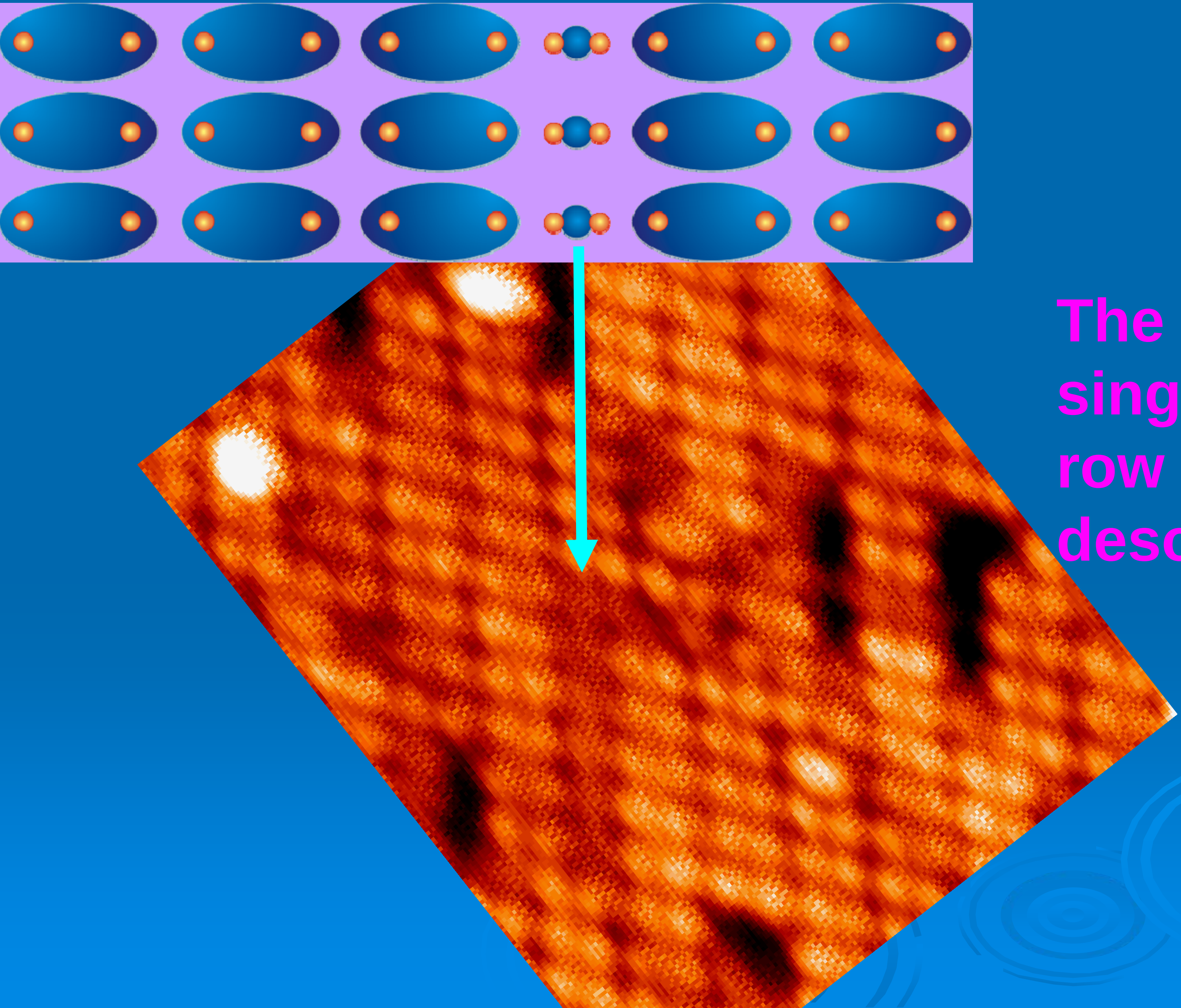
Top view



H_2 desorption from SiH_2

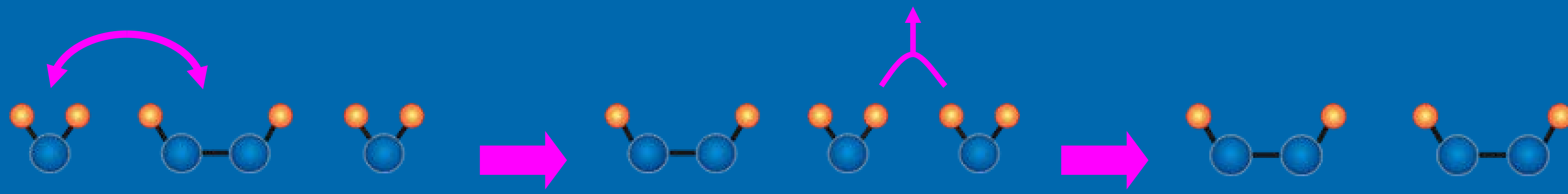


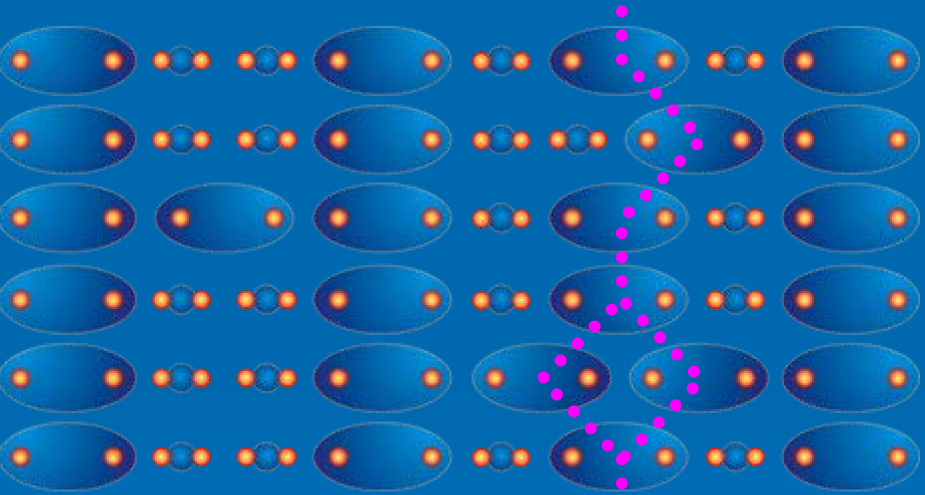
H_2 desorption from SiH_2

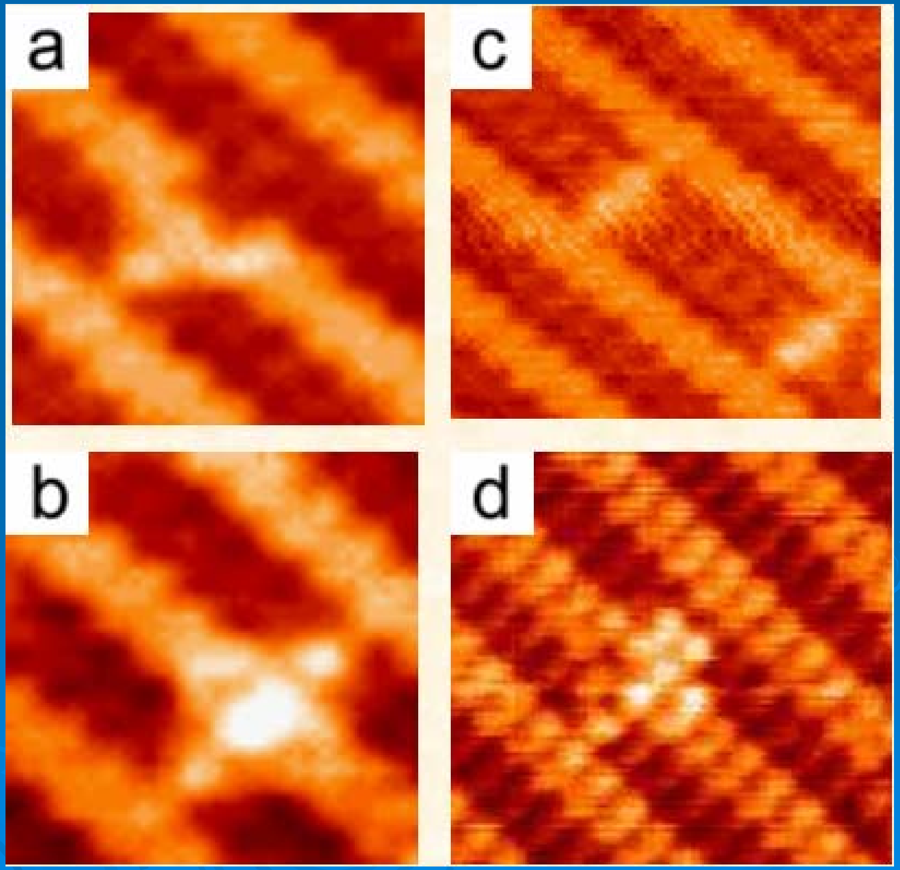


The trapped single dihydride row does not desorb H_2

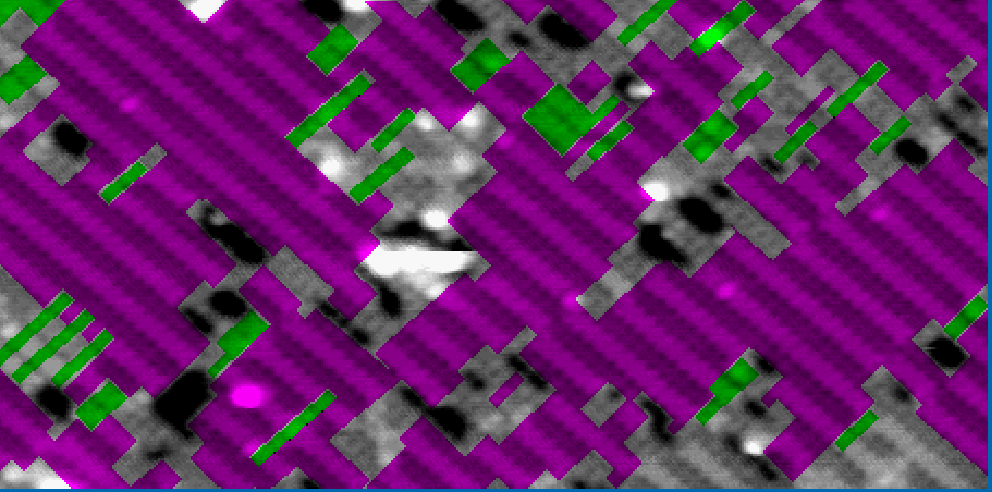
H_2 thermal desorption from dihydrides





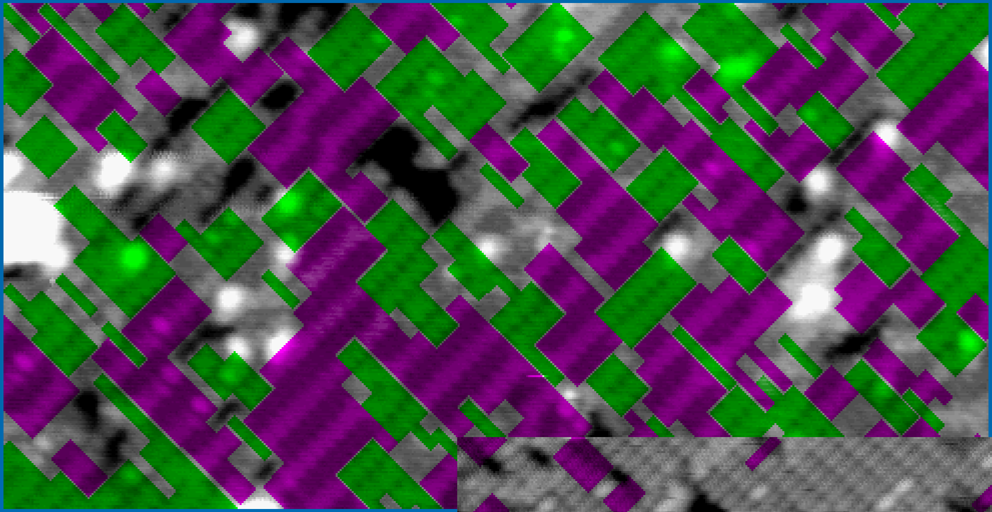


30 min at 570 K

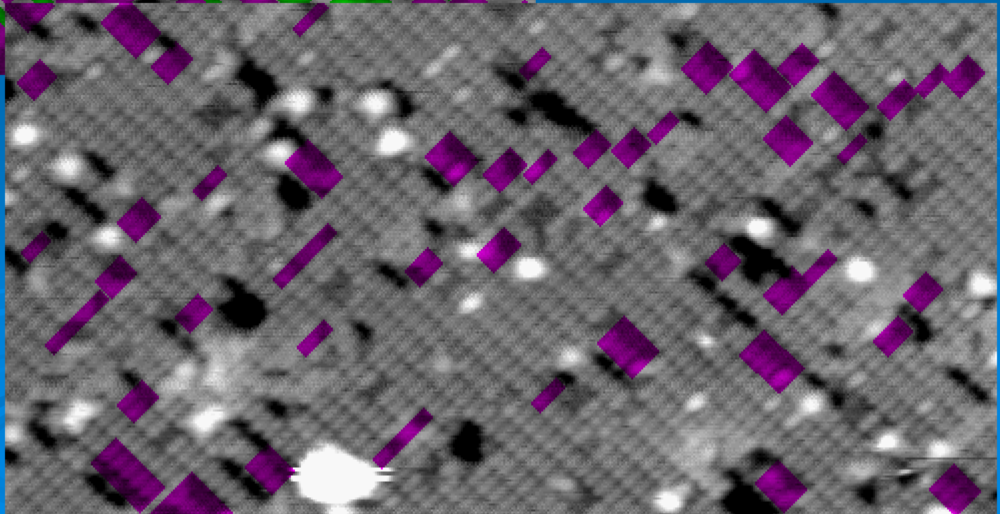


0.5 hrs

4.5 hrs



33 hrs

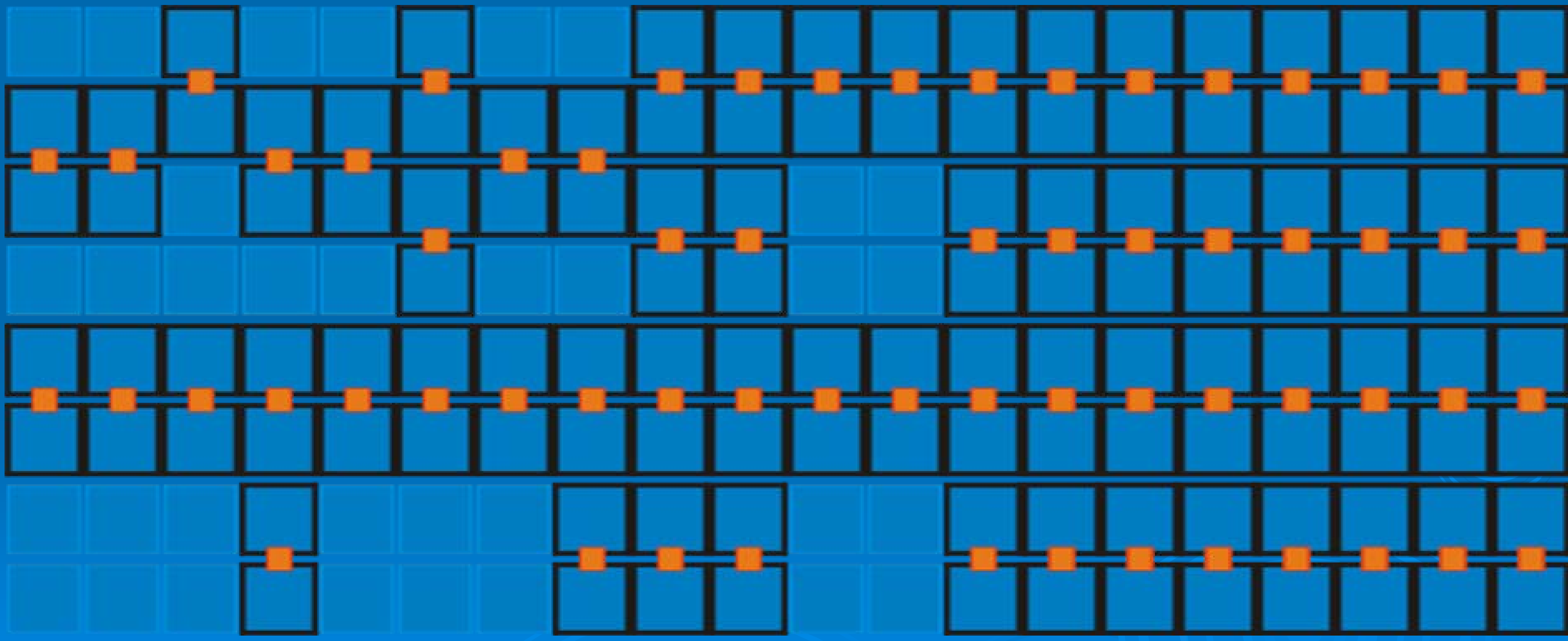


The answer

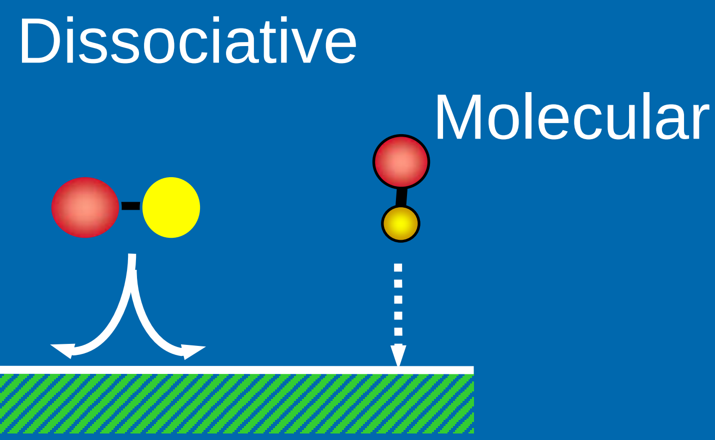
Two step processes

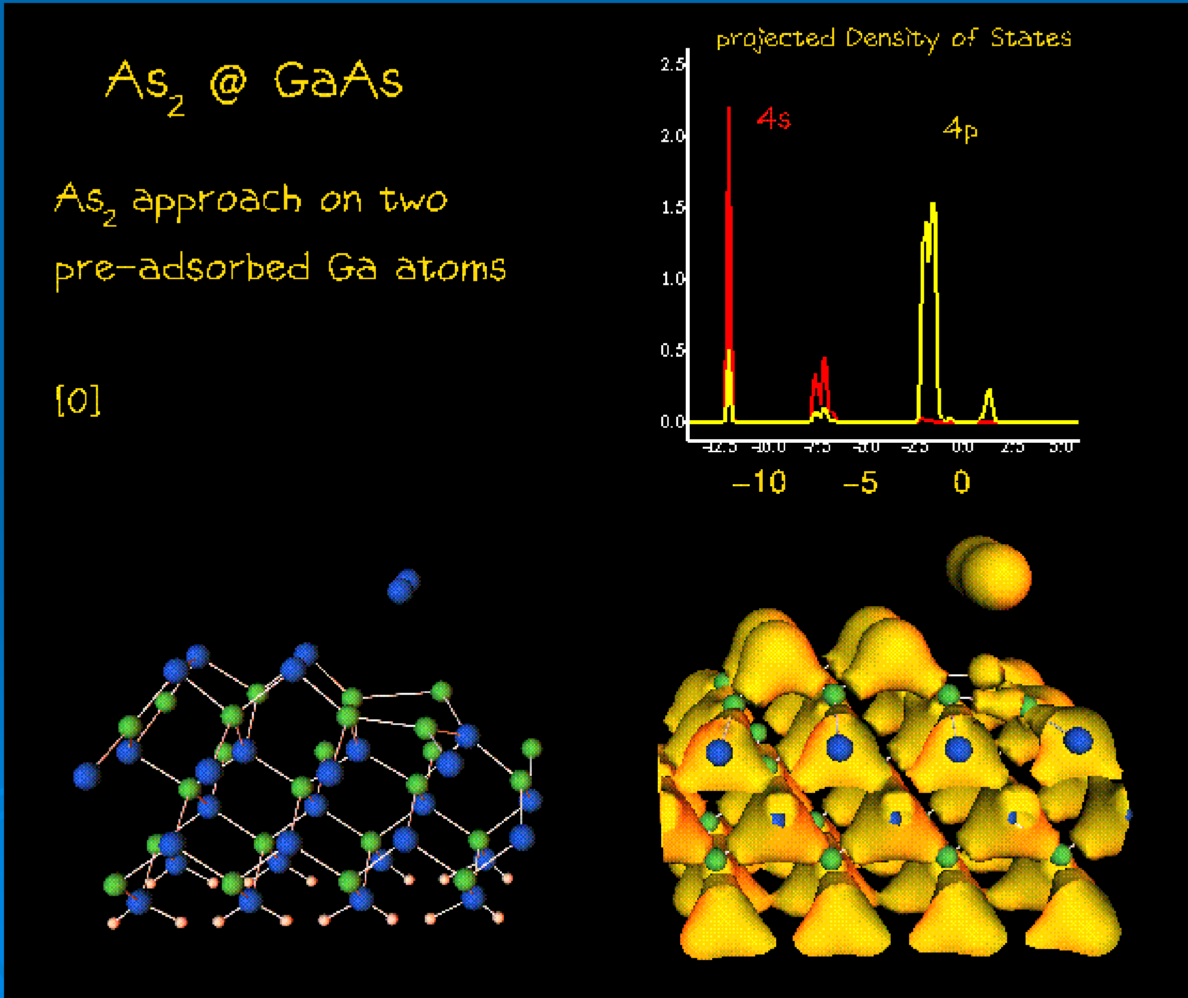
Step 1 Step 2

Switch **Desorb** **Grow**



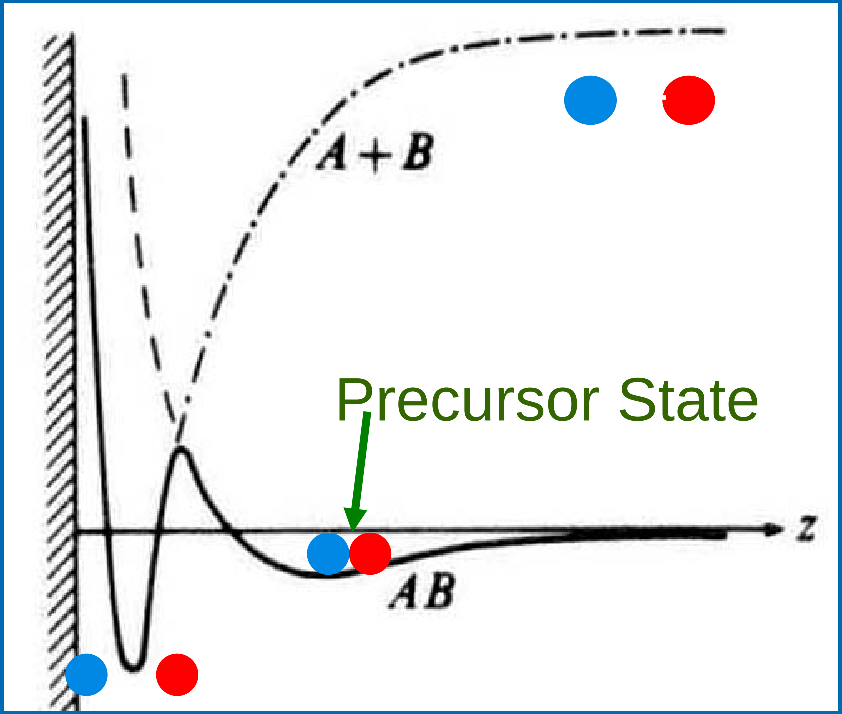
Adsorption of diatomic molecules

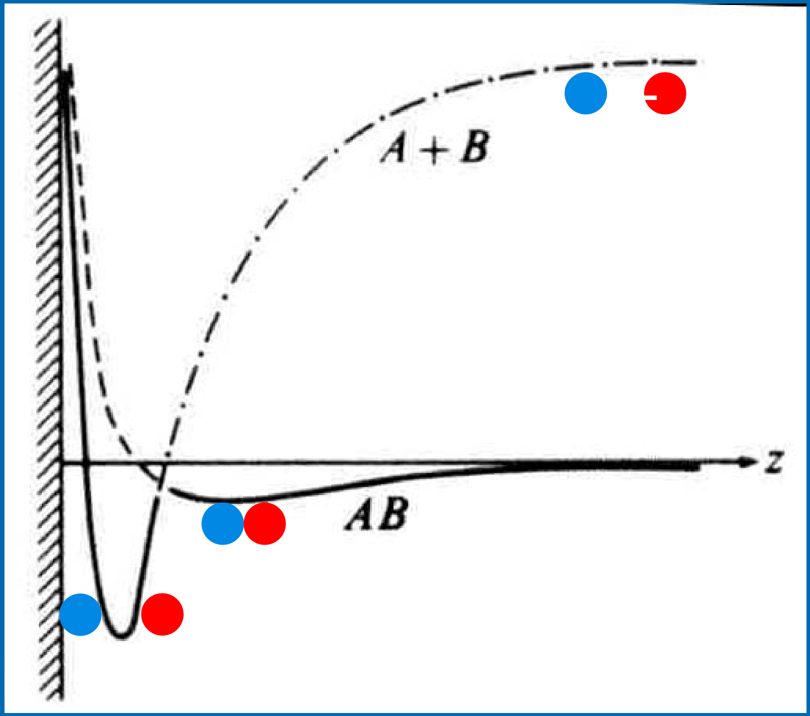




Adsorption Energy Diagrams:

Activated vs. nonactivated



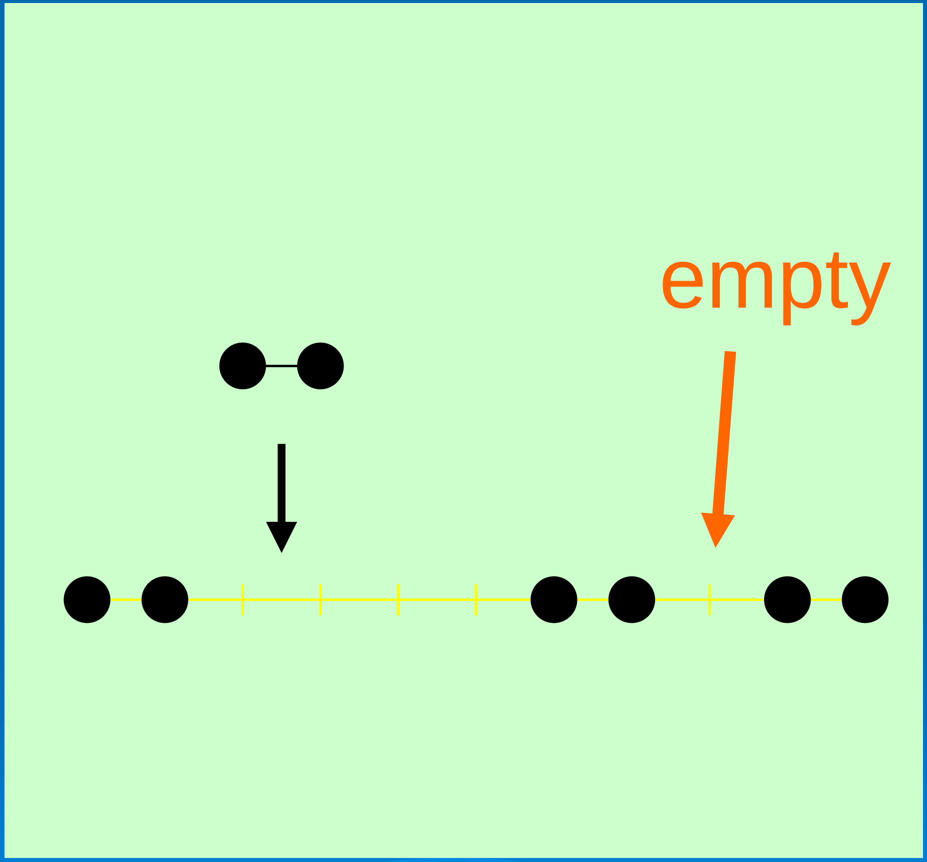


Questions:

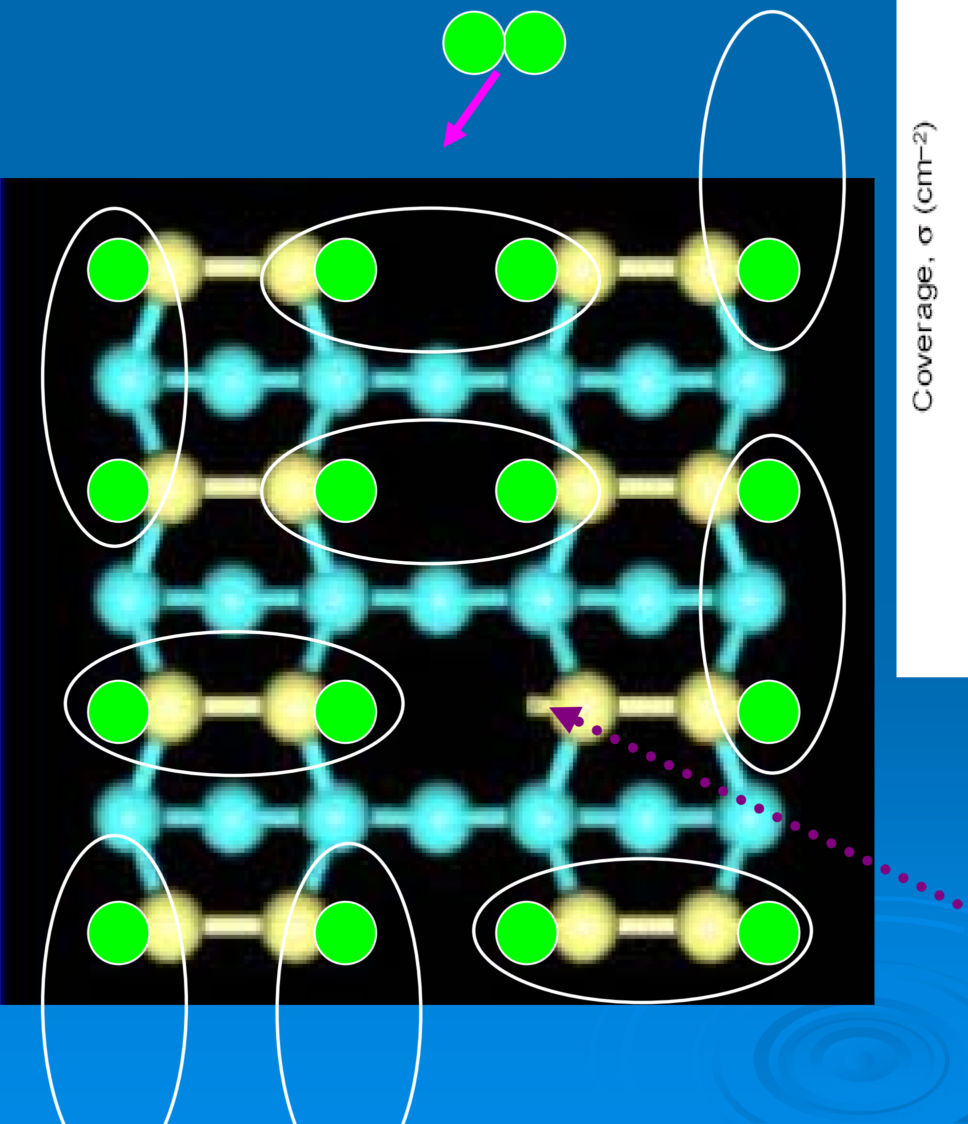
can we predict if adsorption of AB is activated or nonactivated?

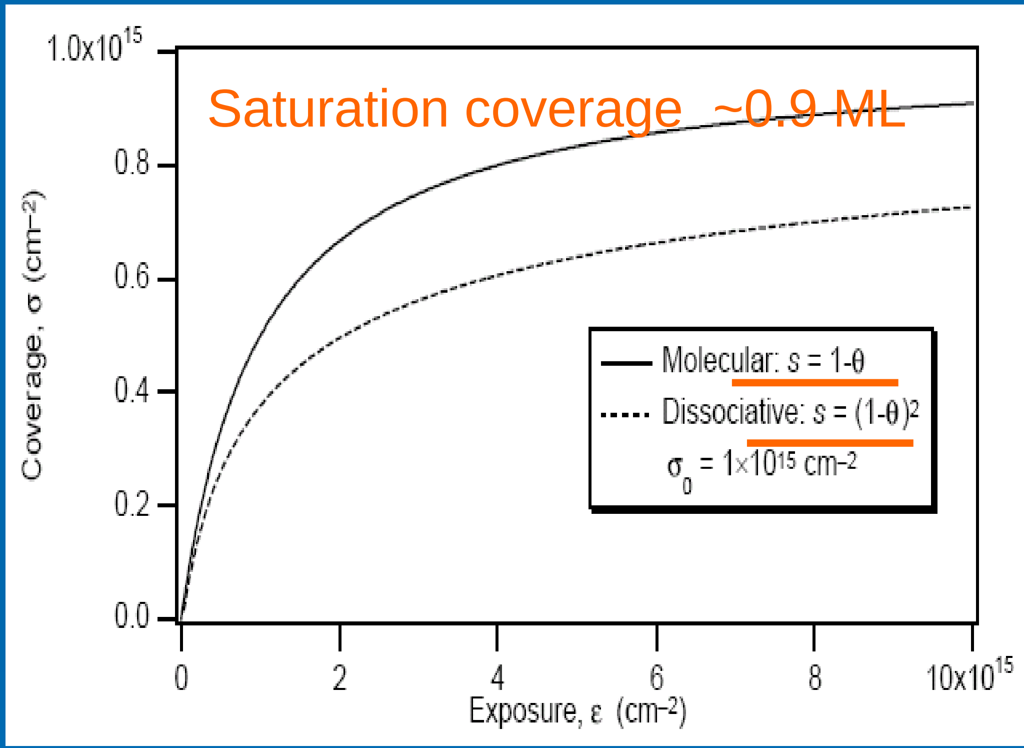
Activation energy same for adsorption and desorption?

Random Sequential Adsorption



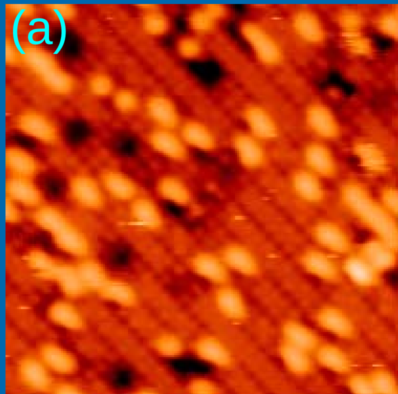
Immobile diatomic Dissociative Adsorption on a square surface



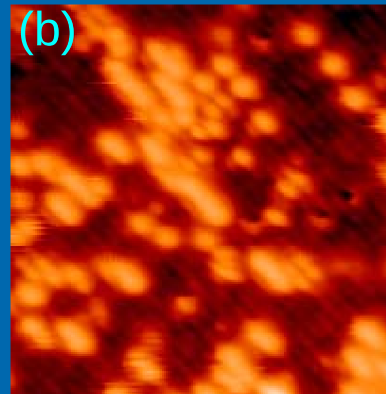


Vette *et al*, JCP 1974

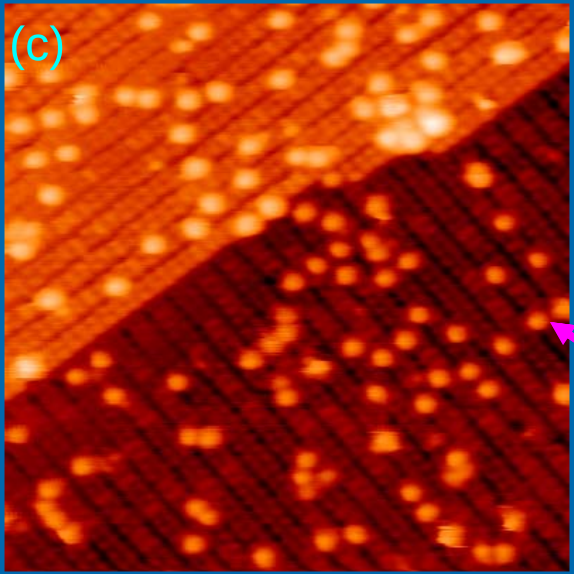
I_2 adsorption on Si(100)



0.06 L V_s=1.82 V

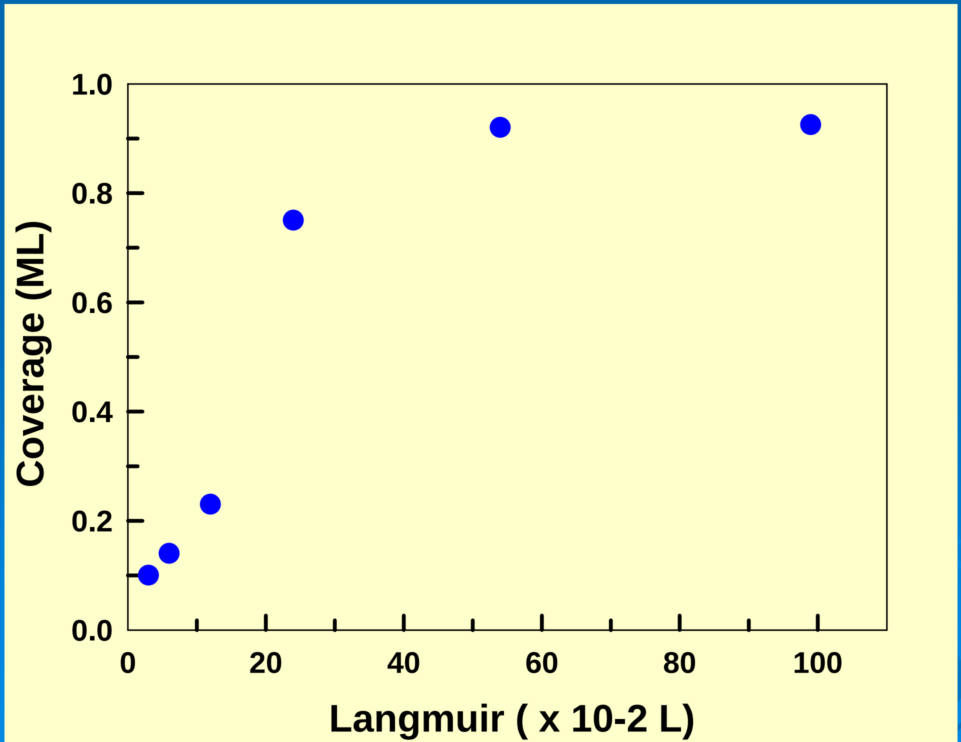


V_s=1.82 V
0.24 L

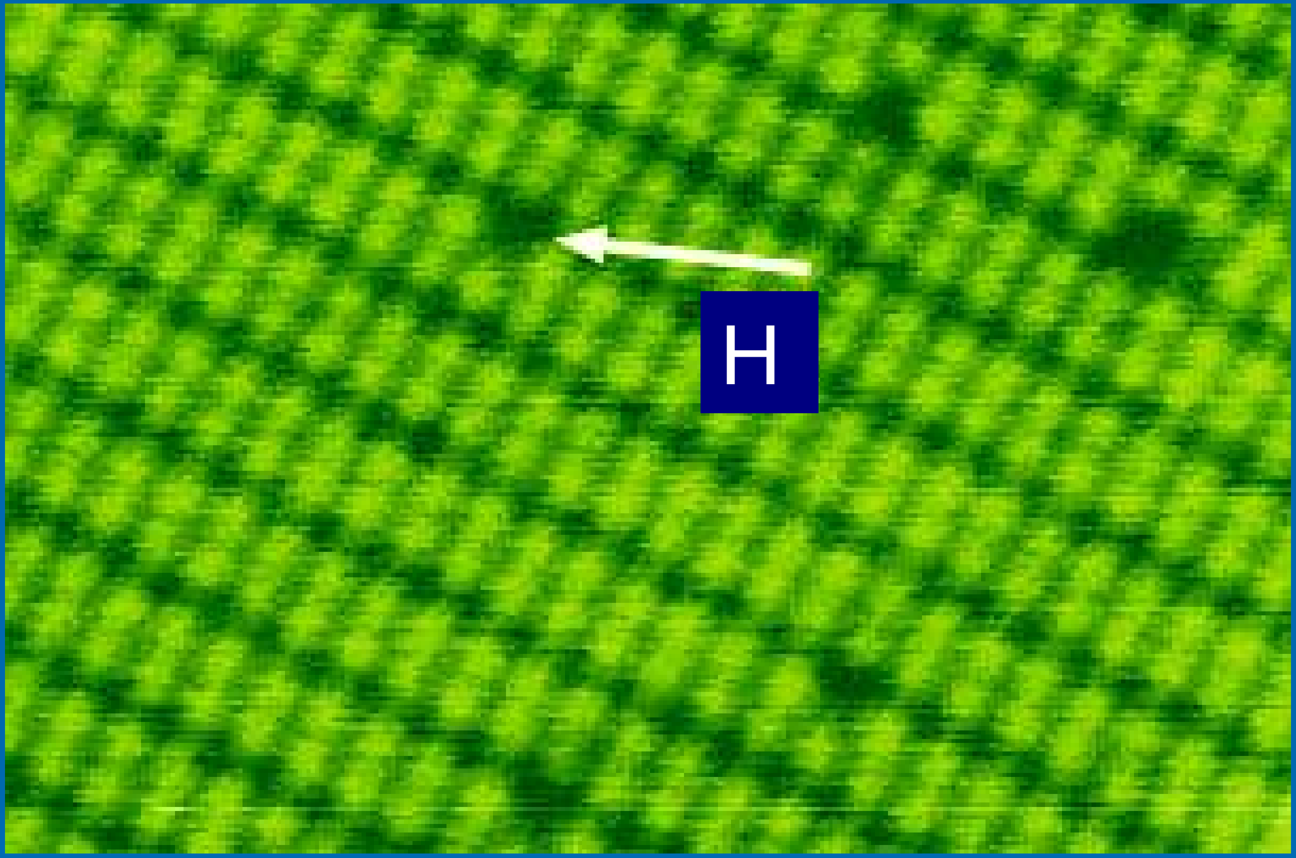


V_s=-2.3 V, dosing= 1.14 L

I / Si(100)-2x1 1.14 L



Cl saturated Si(100)-2×1 surface



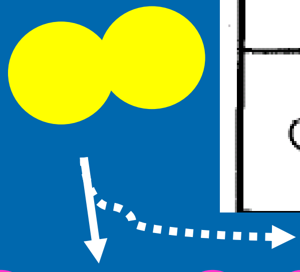
Saturation coverage >0.97 ML

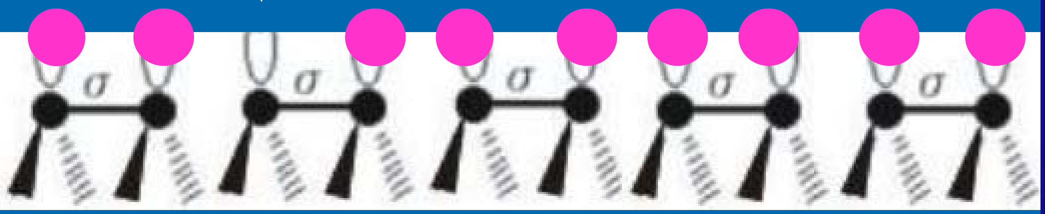
⇒ **Usual models for Immobile diatomic dissociative not correct**

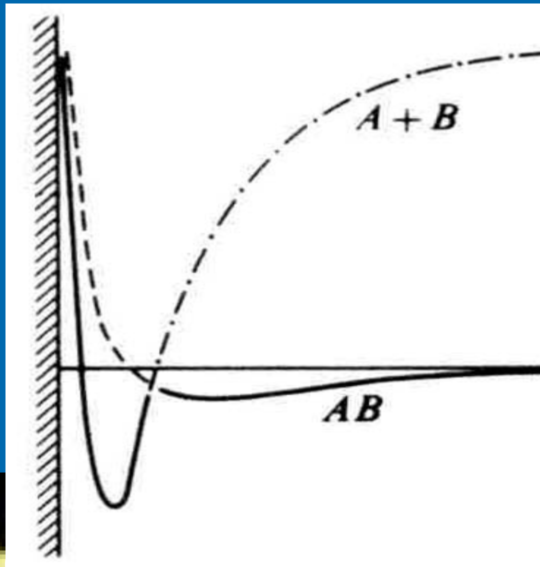
To be adsorbed or not to be

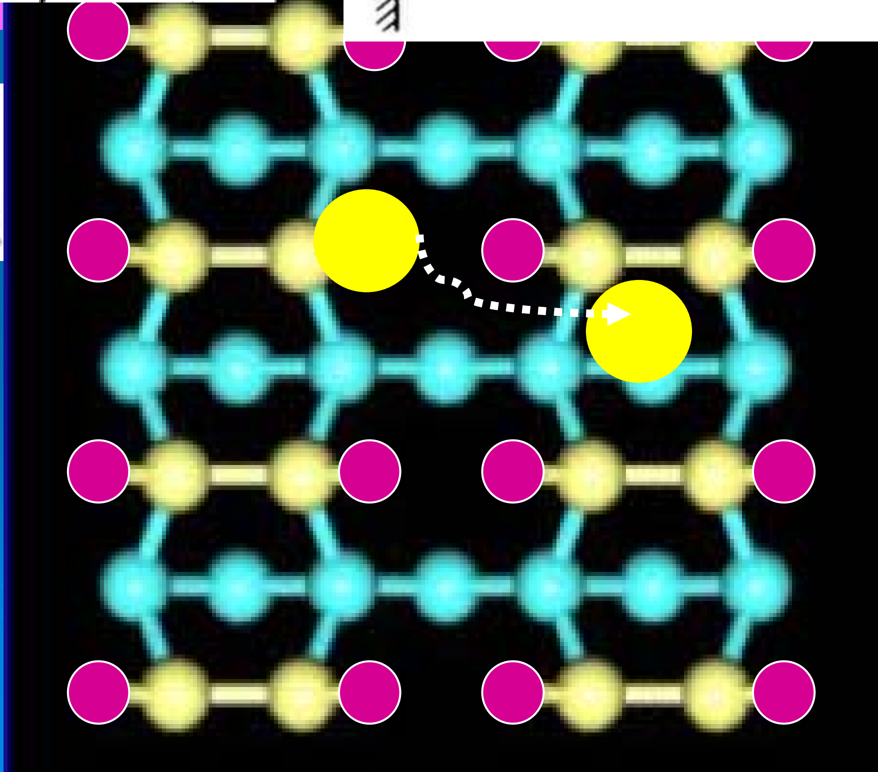
on a single dangling bond

	O_2	O–O: 1.207	5.12
	H_2	H–H: 0.741	4.48
	Cl_2	Cl–Cl: 1.986	2.48
	HF	H–F: 0.917	5.87
	HCl	H–Cl: 1.274	4.43
	HBr	H–Br: 1.414	3.76





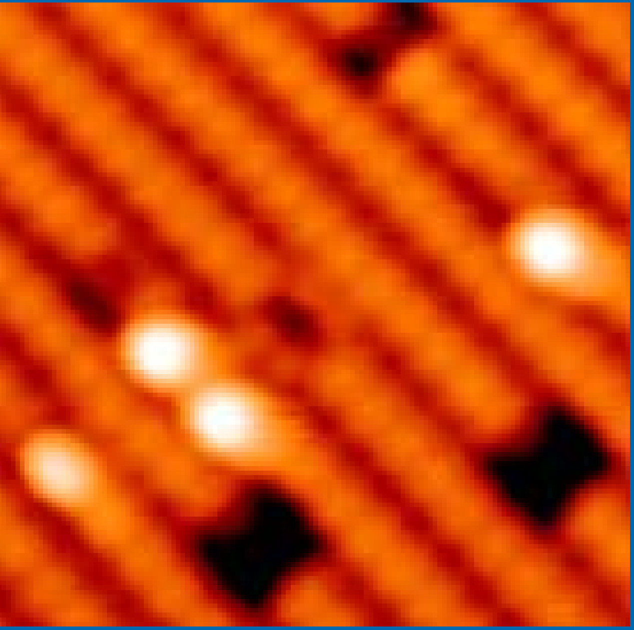


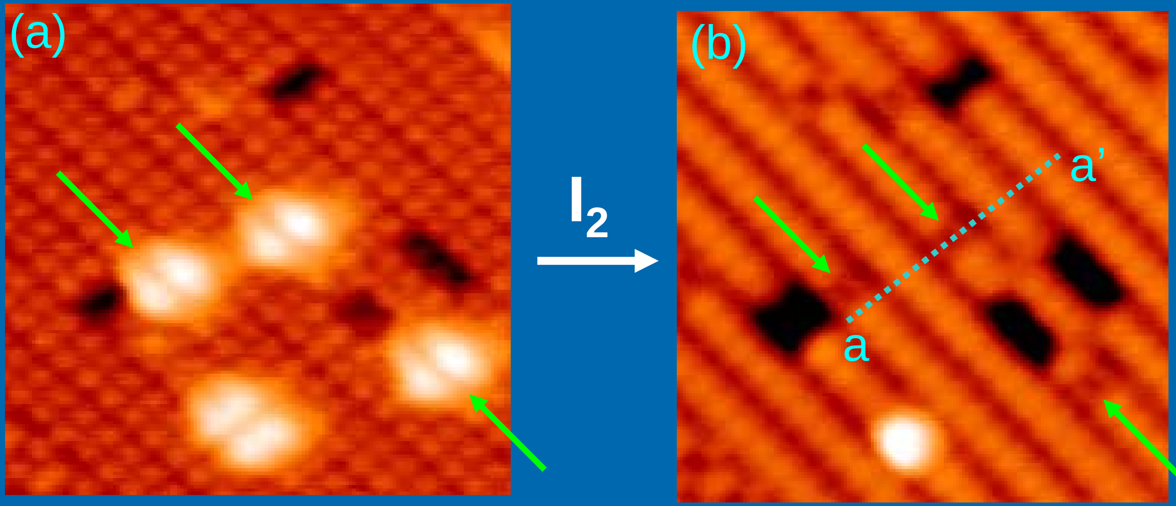


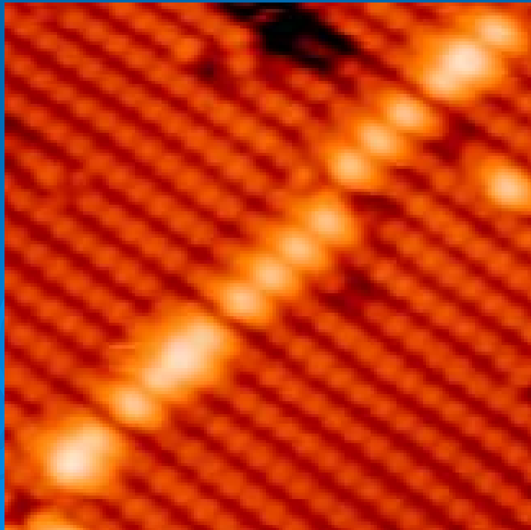
3.91-4.18 eV for Si-Cl
2.48 eV for Cl-Cl

3.26 eV for Si-H
4.48 eV for H-H

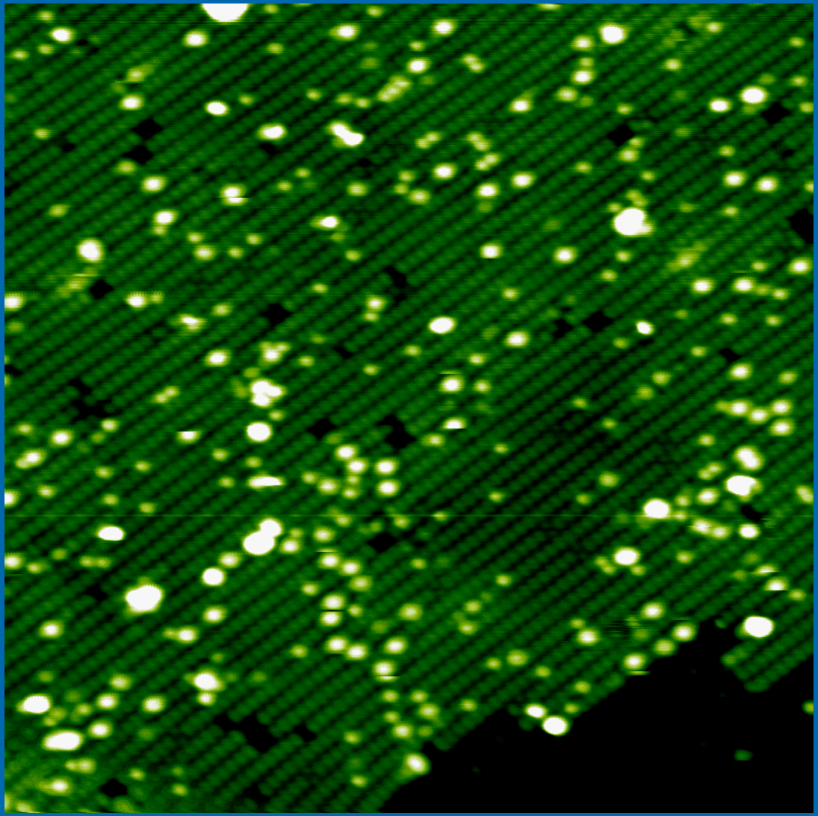
I_2 adsorption on isolated single dangling bonds and dangling bond chains

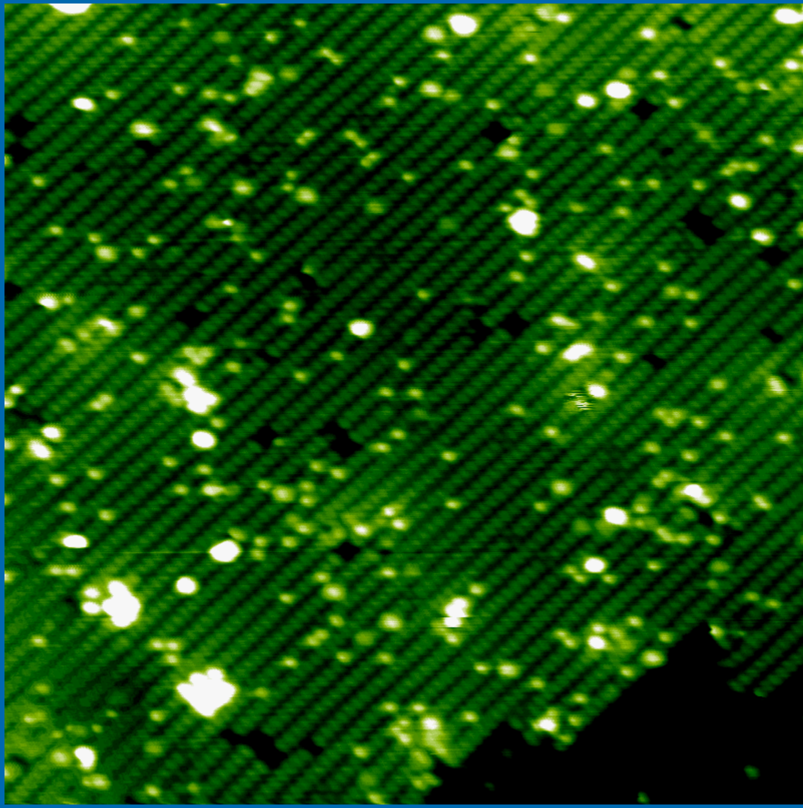






Unsaturated H/Si(100) surface





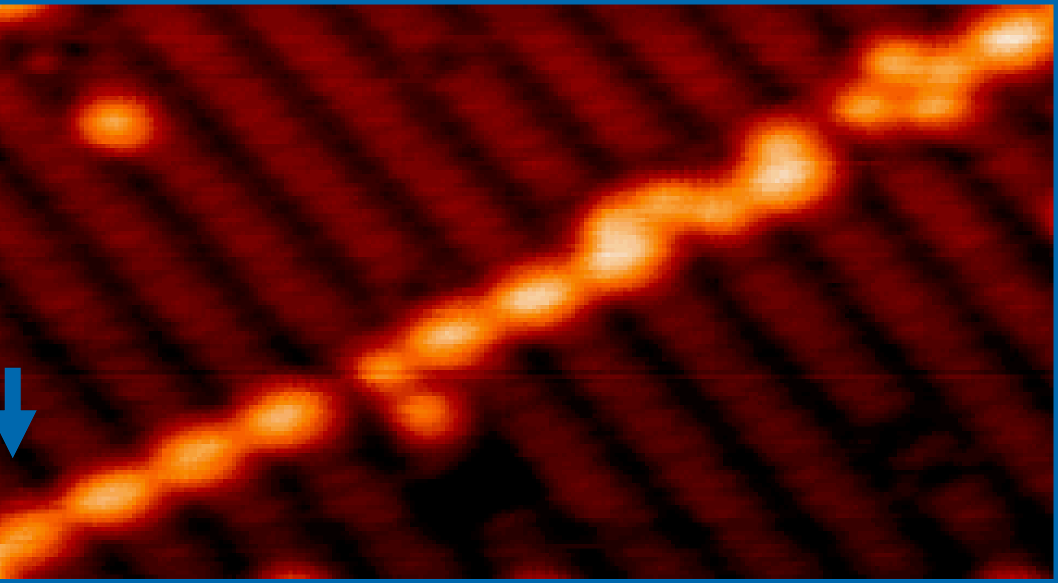
-2.2 V

-2.2 V

	個數
Single DB ⟶ Cl	171
Single DB ⟶ H	26
H ⟶ Cl	19
同 row 和不 row 置換	9
Total DB	197
Single DB 變成氯的機率	180/197＝91%

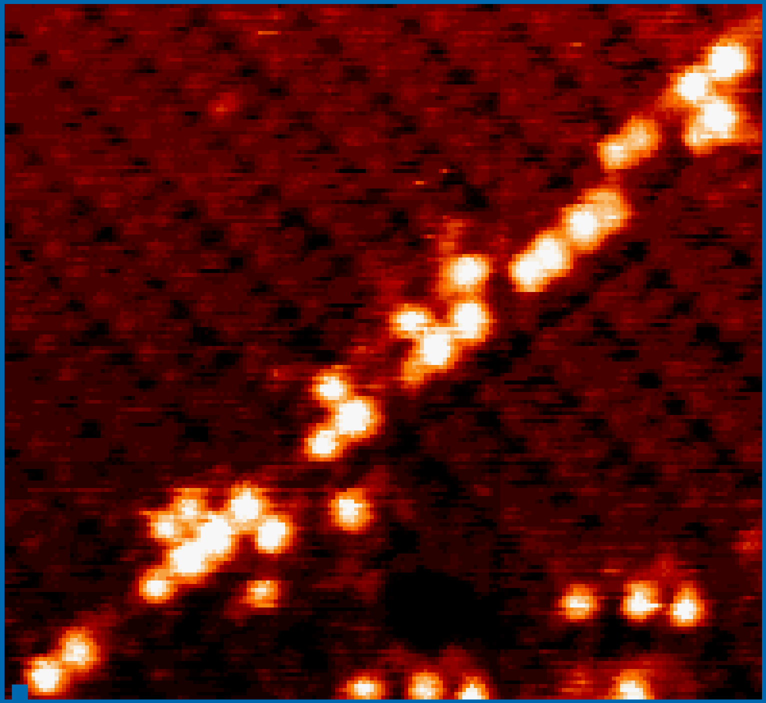
Adsorption on a paired DB wire

DB wire by STM tip desorption

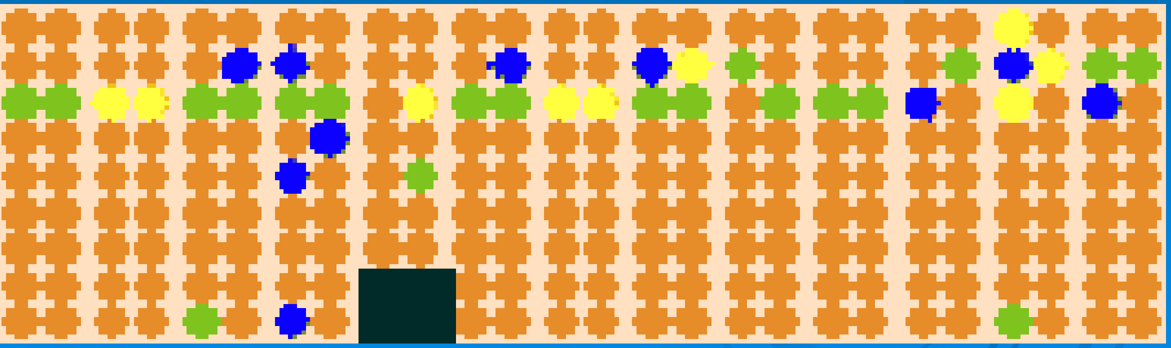


Vs = -1.82V

After Cl_2 exposure



Vs = +1.82V



Paired DB 9

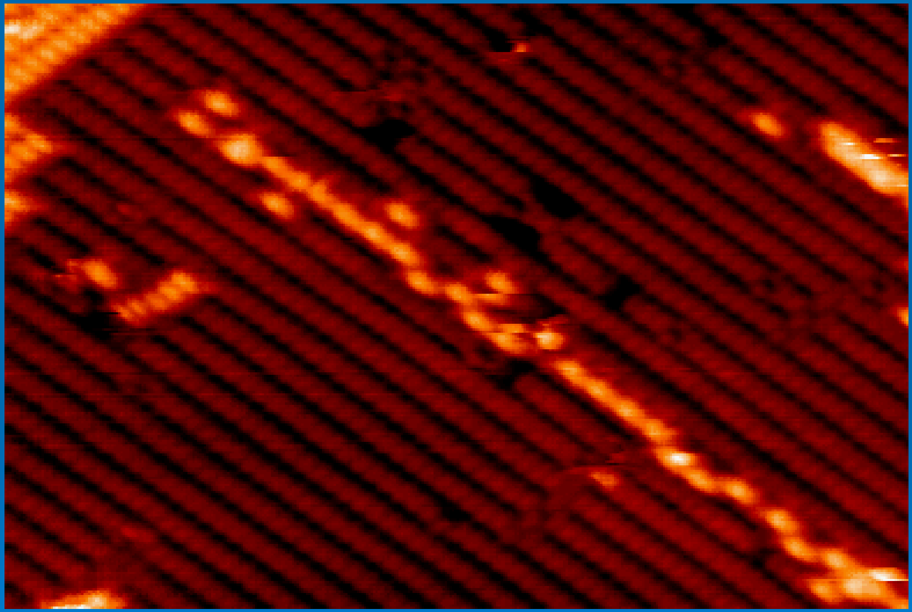
Paired Cl 7

→ 77%

Adsorption on a single DB wire

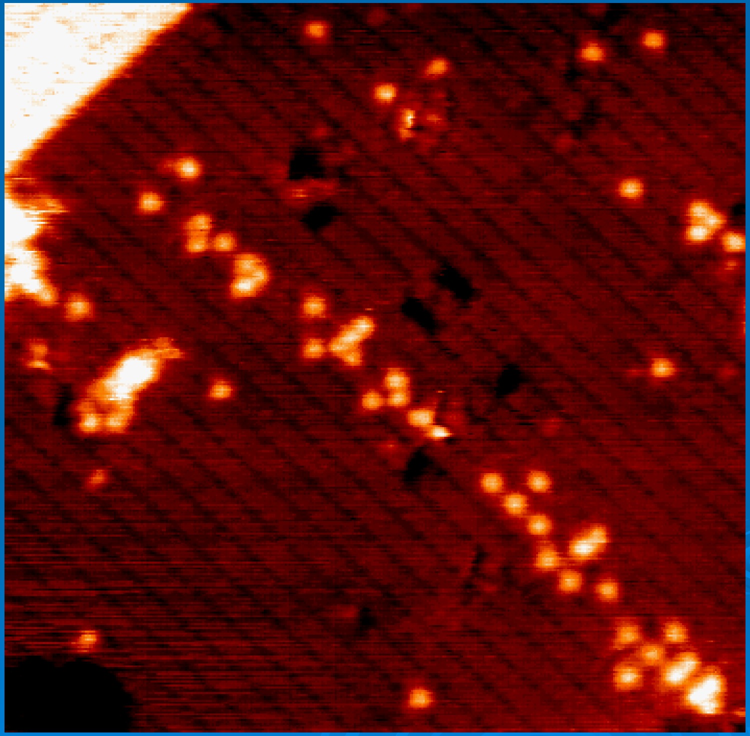
Tip desorption：II

DB wire by STM tip desorption



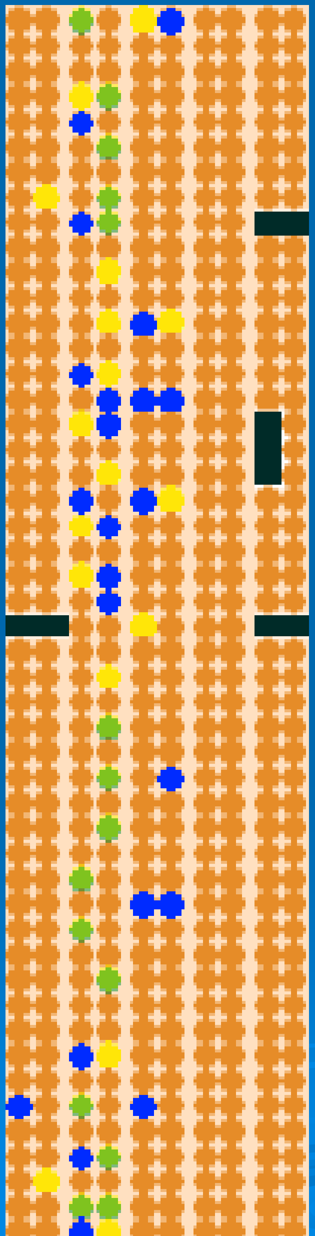
Us = -1.82V

After Cl_2 exposure



Us = +2V

Tip desorption：II



綠 DB → Cl

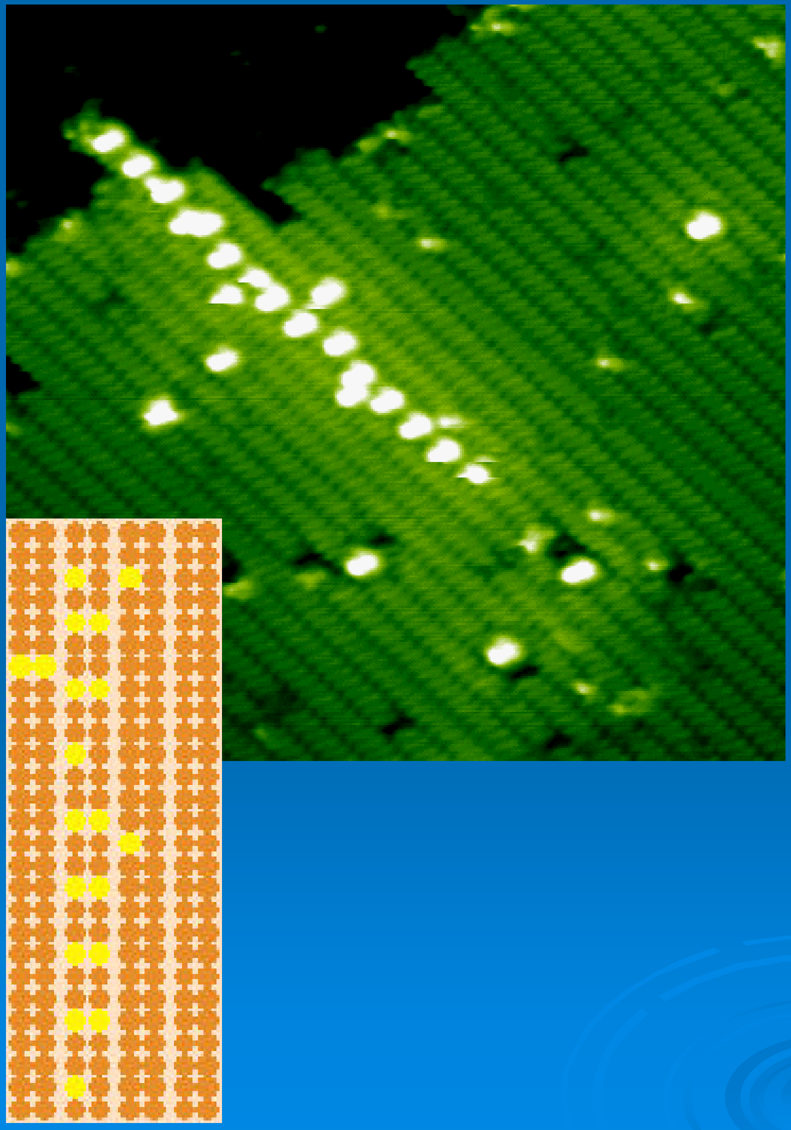
藍 H → Cl

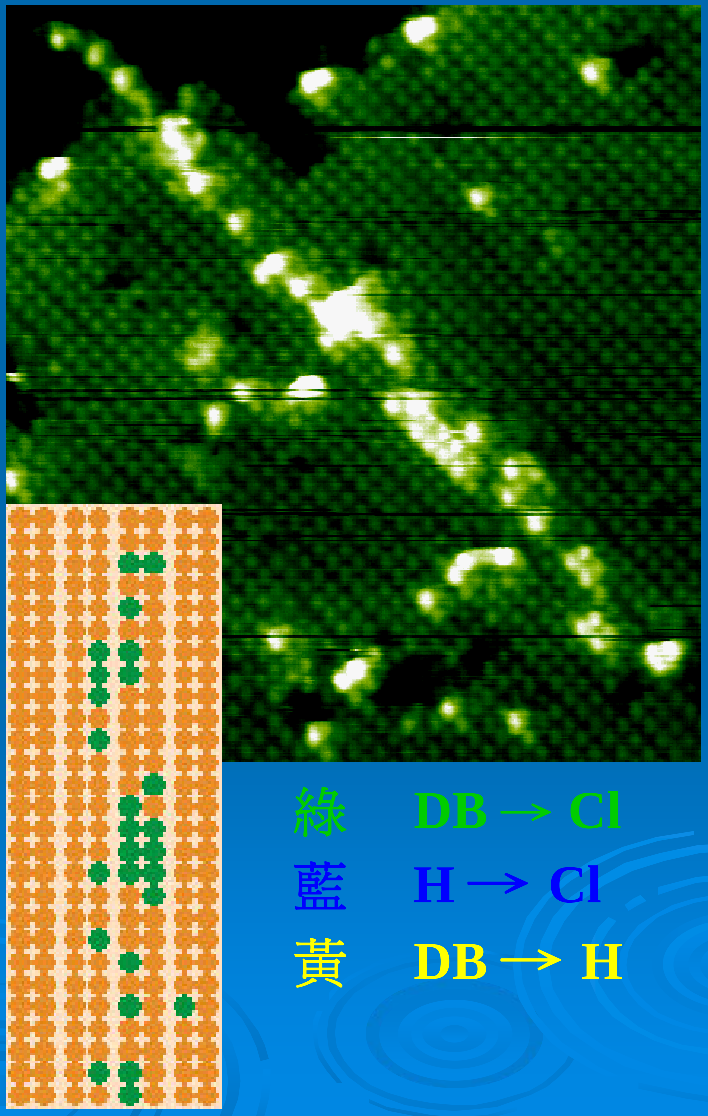
黃 DB → H

- Single DB → Cl 19
- Single DB → H 20
- H → Cl 31

Adsorption on isolated paired DBs

Tip desorption：Ⅲ

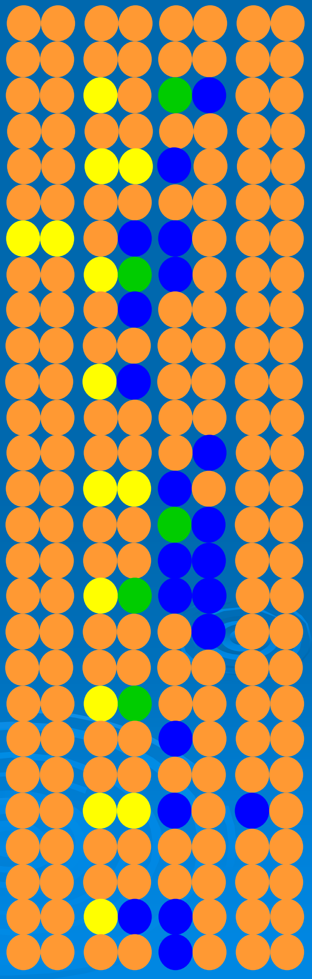




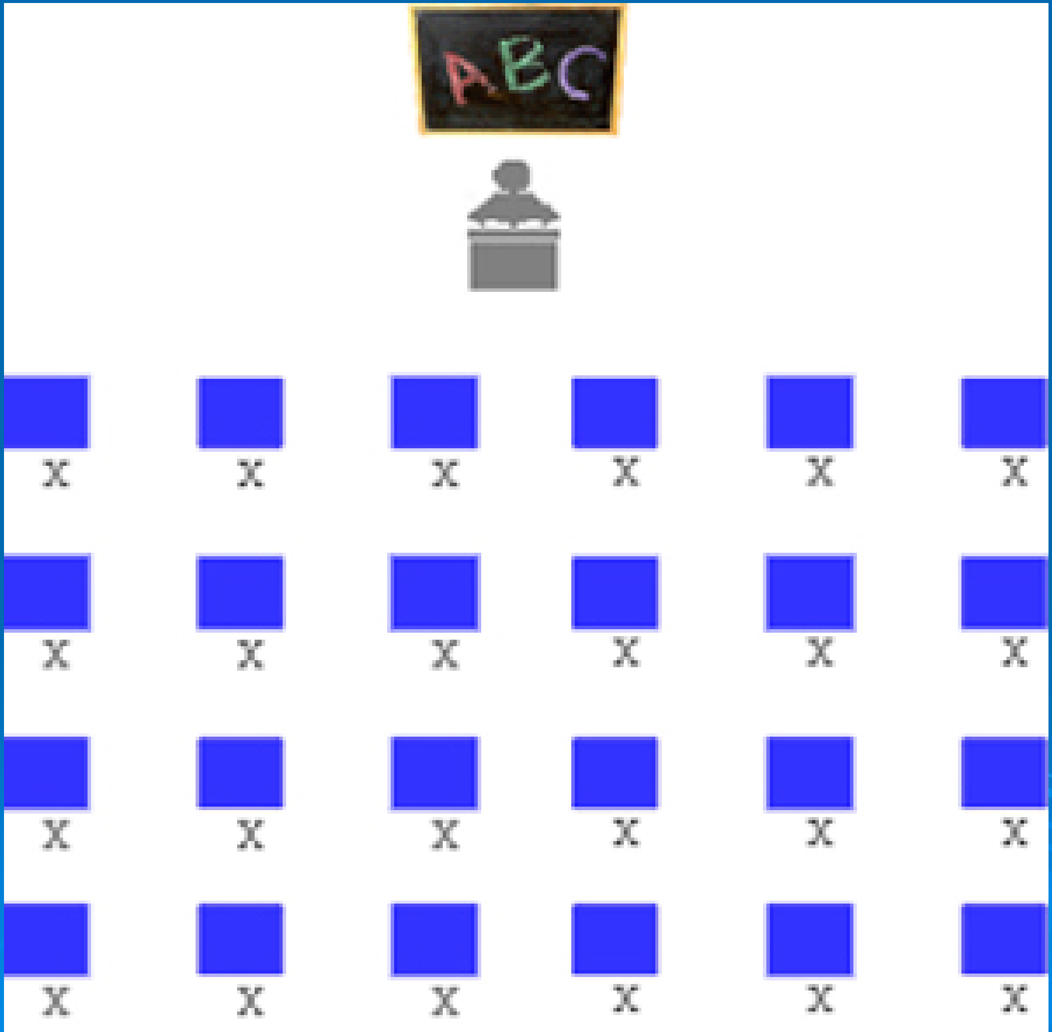
綠 DB → Cl

藍 H → Cl

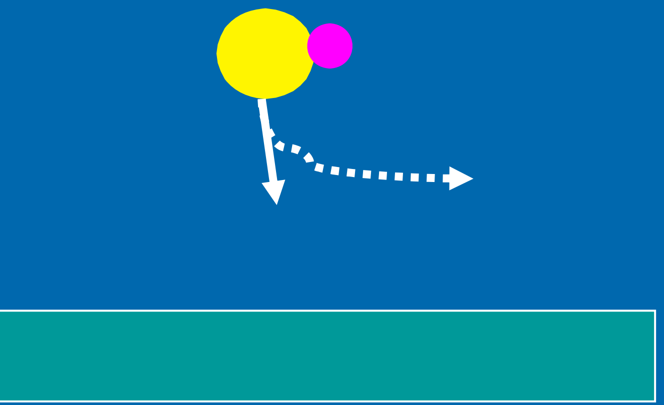
黃 DB → H



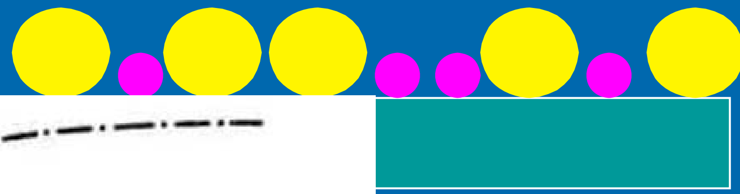
Order structure as a result of random adsorption?



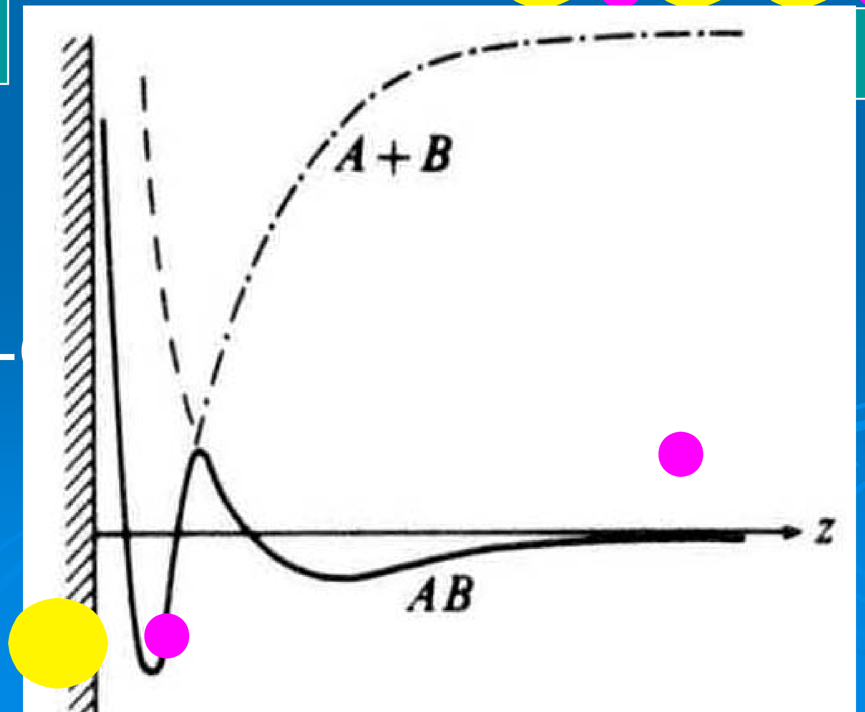
HCl + Si(100)-2×1



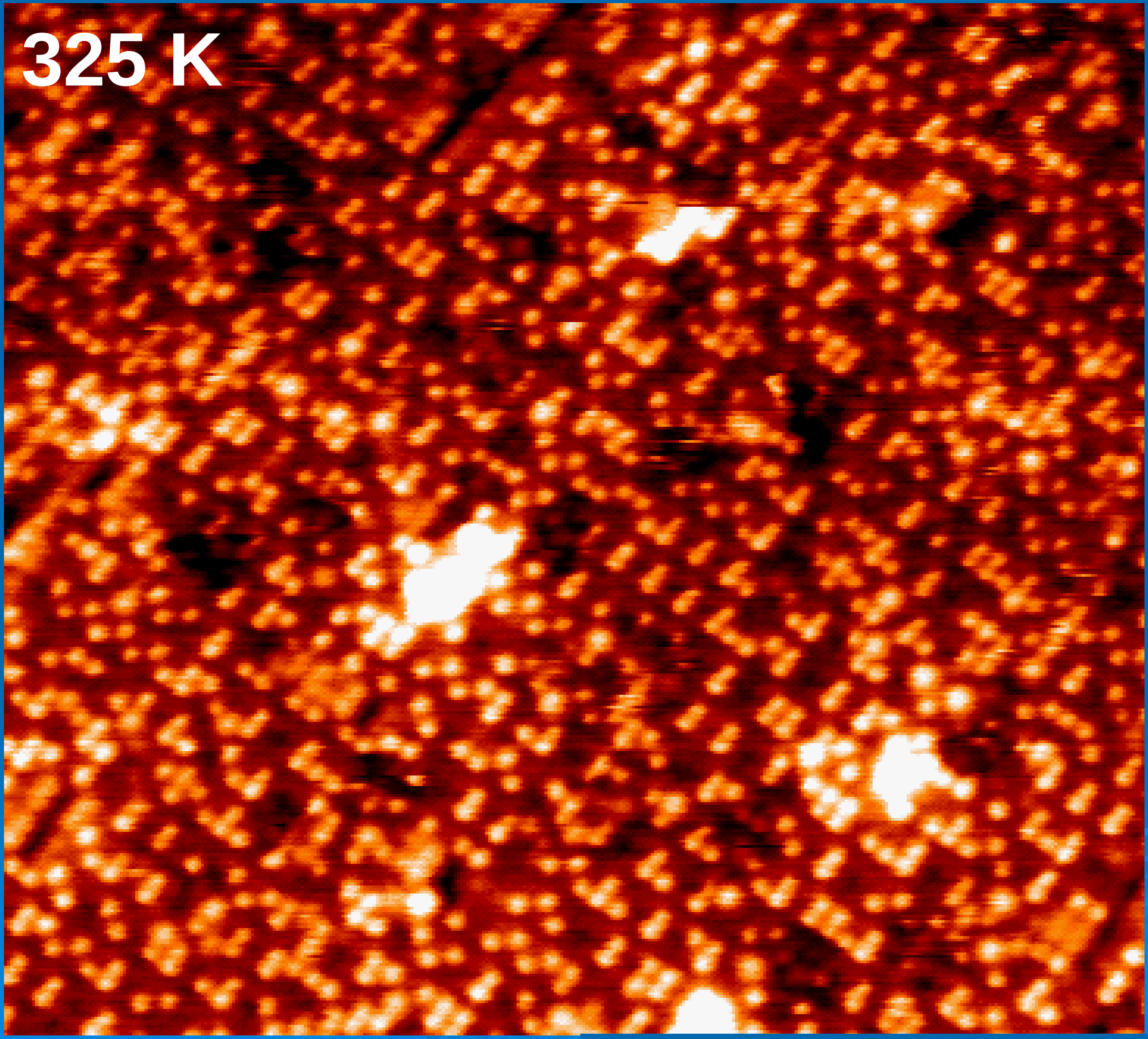
Random adsorption?



4.43 eV for H-Cl
3.91-4.18 eV for Si-
3.26 eV for Si-H

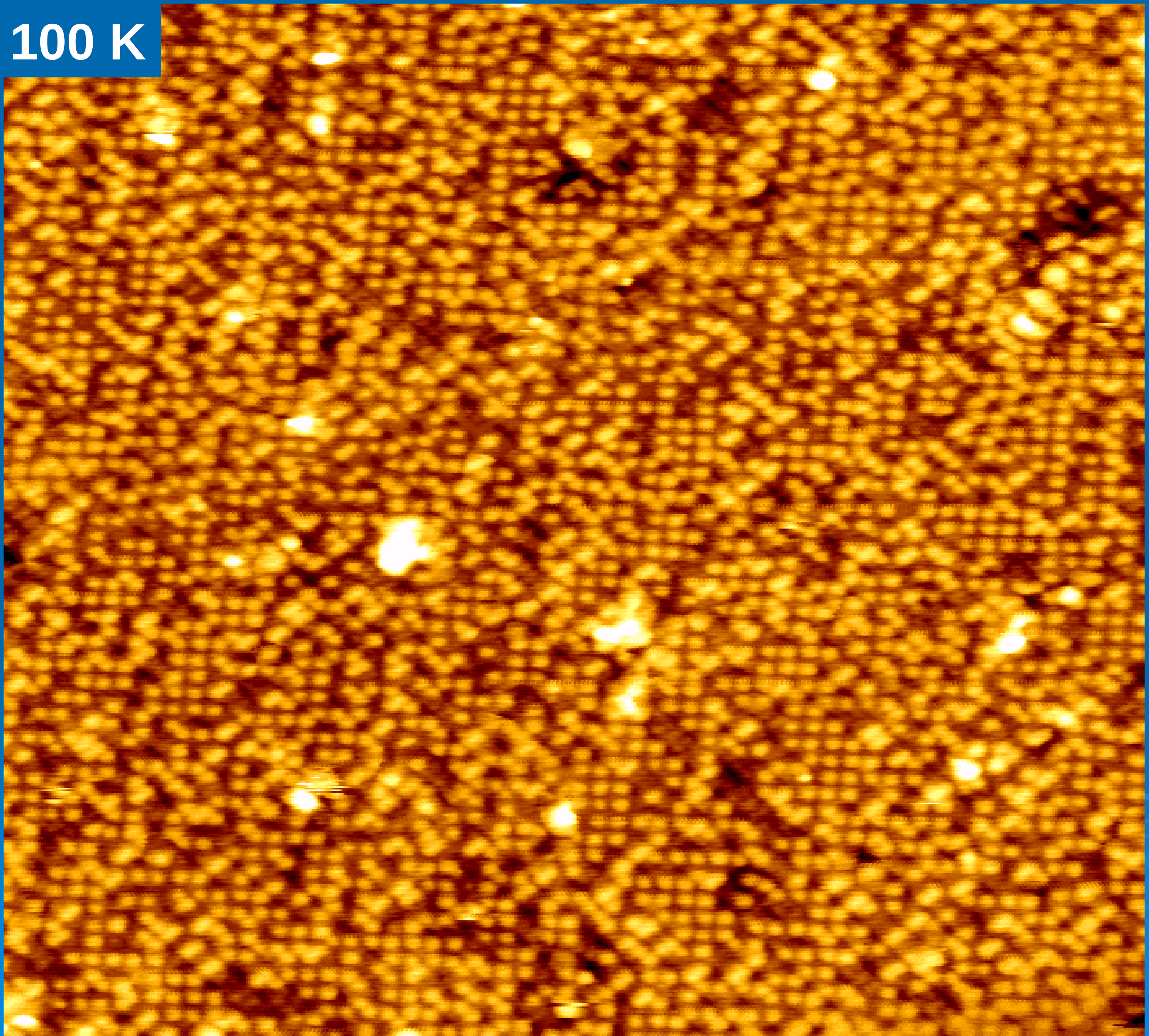


Adsorption of HCl on Si(100)-2×1

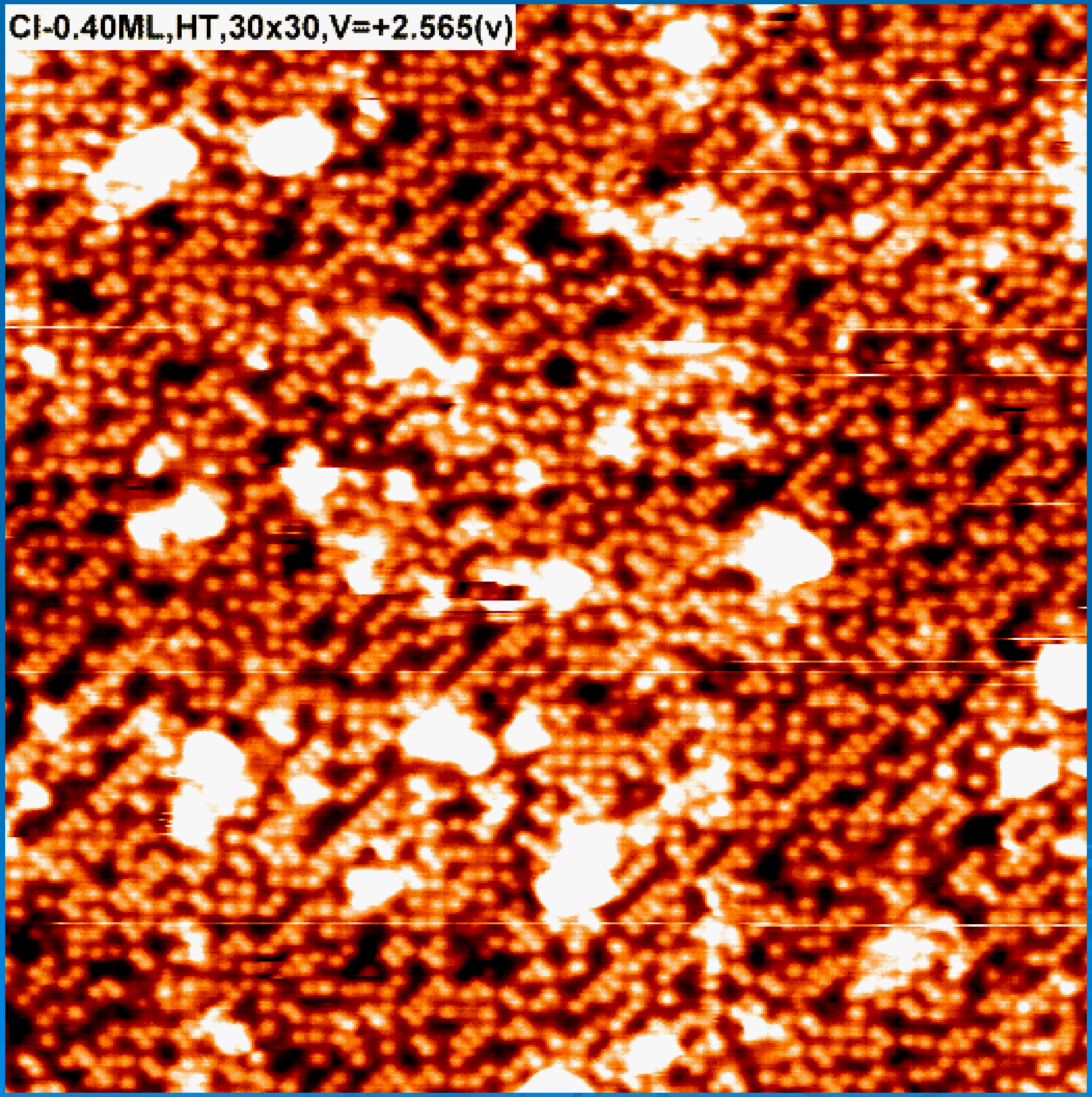


, V=+2.28 V, θ_{bright} = 0.45 ML

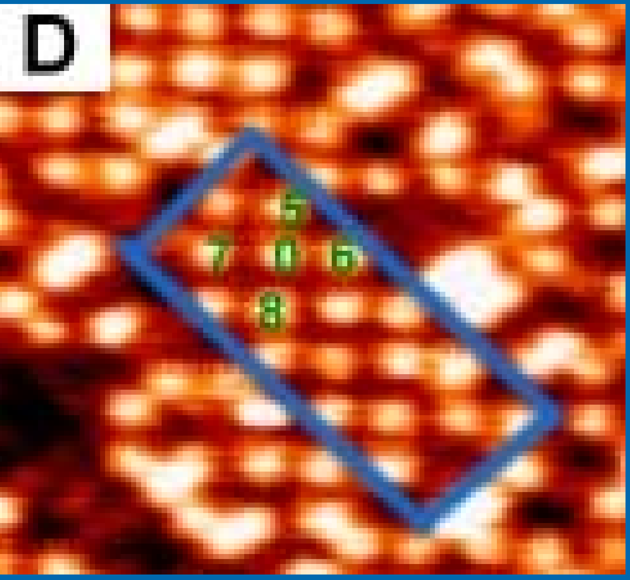
HCl + Si(100)-2x1



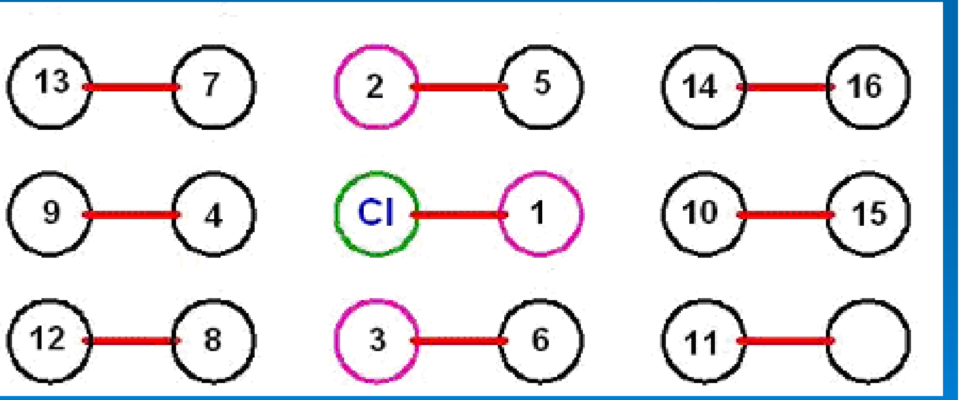
HCl + Si(100)-2×1 at 450K (HT)

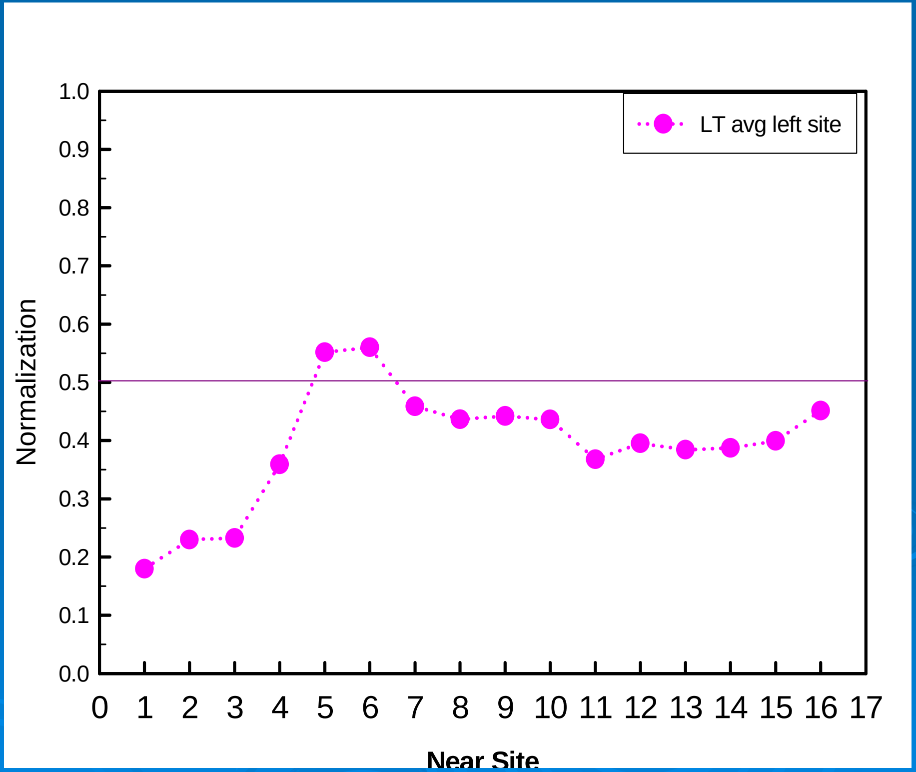


Site correlation analysis

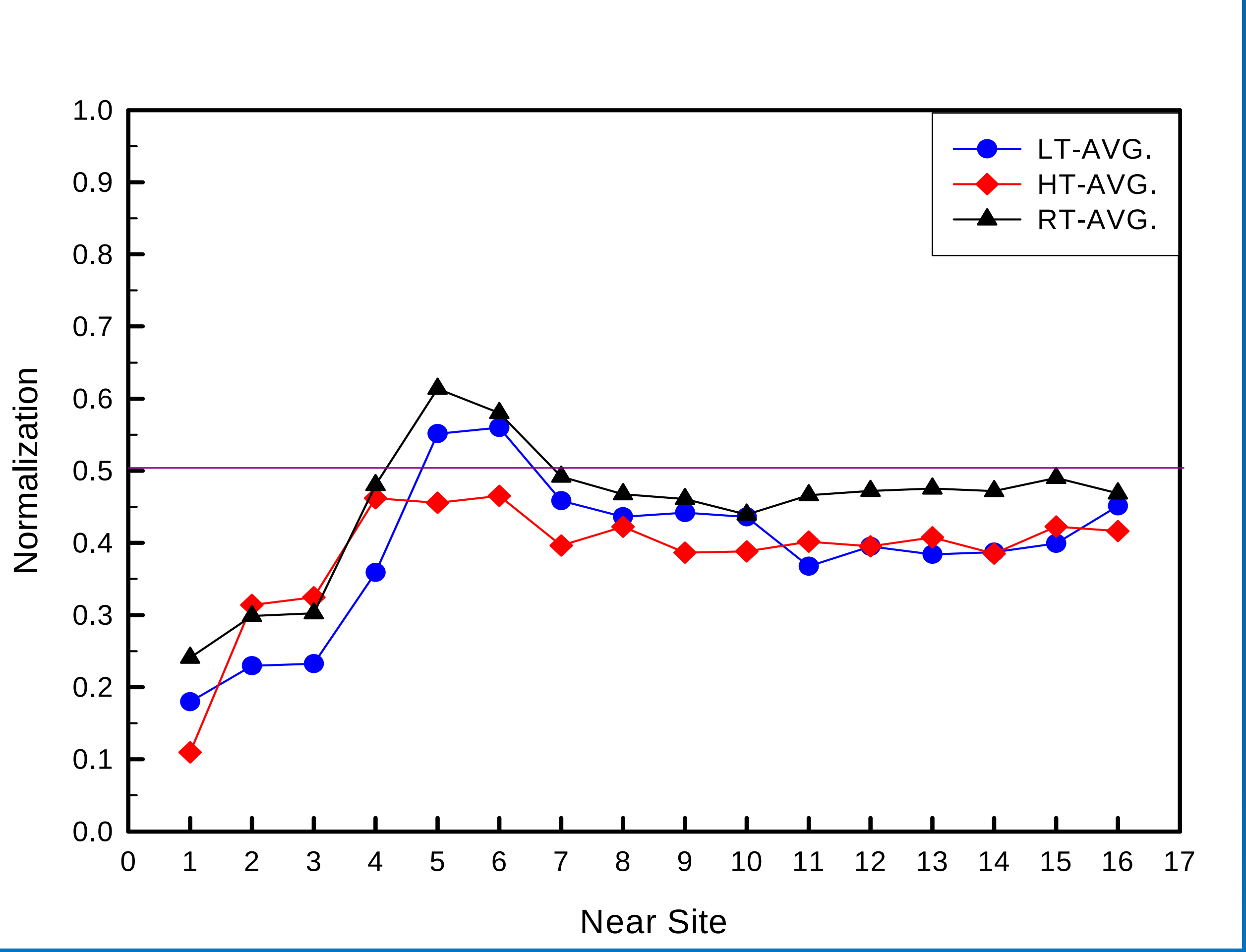


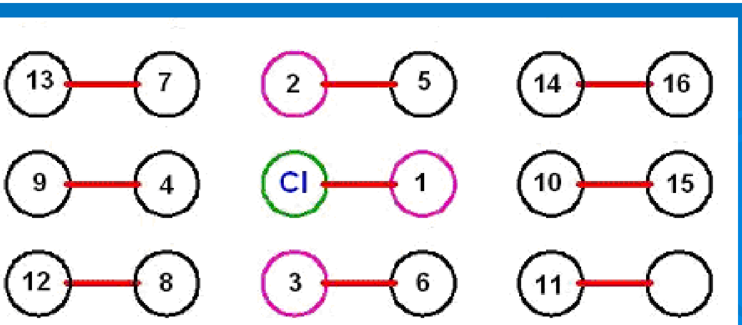
$$g(j) = N^{-1} \sum_{i=1}^{N} \frac{n_i(j)}{M(j)}$$





Result of Correlation analysis





Issues: How neighbors effect “random” adsorption?

Direct adatom-adatom swap diffusion of H on the Cl/Si(100)-2x1 Surface

Basic 2D diffusion mechanism in textbook

Phys. Rev. Lett. 57, 2287 - 2290 (1986)

From the very beginning of diffusion studies it has been assumed, and today is universally accepted,[1] that atomic diffusion in semidonductors is mediated by defects (vacancies or interstitials, depending on the material). In Si, all recent theoretical studies[2,3] of diffusion have been limited to the defect mechanisms and, in spite of years of effort, no clear agreement on the nature of diffusion has emerged and many experimental observations remain unexplained.

(d) Never observed before?

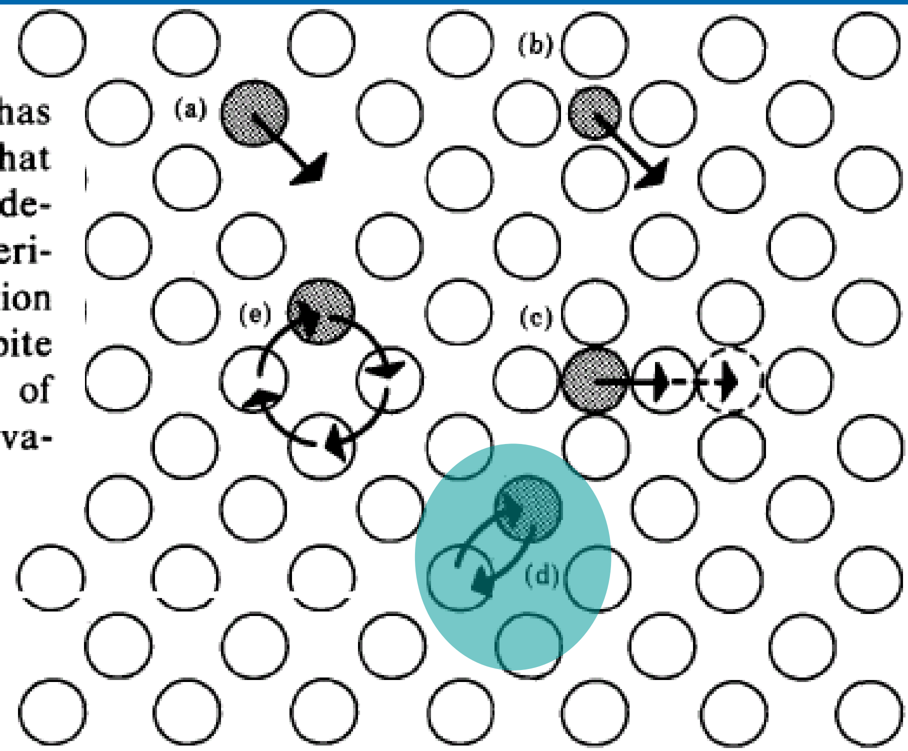
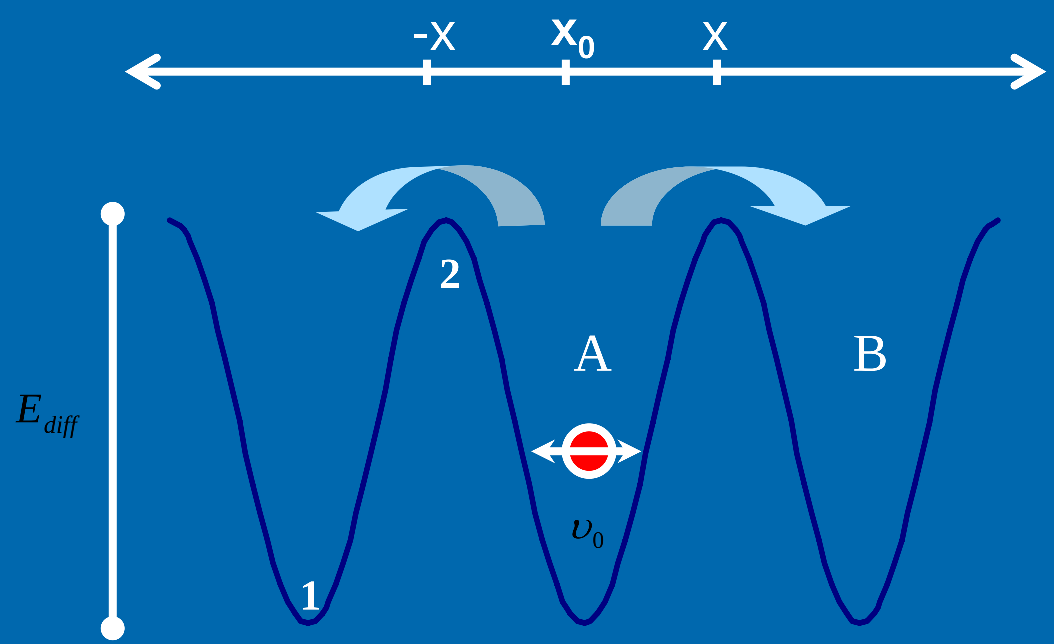


FIGURE 3.1 Sketch of atomic diffusion mechanisms in a two-dimensional square lattice. (a) An atom diffuses by jumping into a neighboring vacant lattice site. (b) A interstitial goes to a neighboring interstitial site. (c) An interstitial pushes an atom from its lattice site to an interstitial site. (d) Two neighboring atoms swap position directly. (e) Ring rotation of four atoms.

Hopping via atom-vacancy exchange



Arrhenius relation :

$$R_{A\rightarrow B} = P \times e^{-\frac{E_a}{kT}}$$

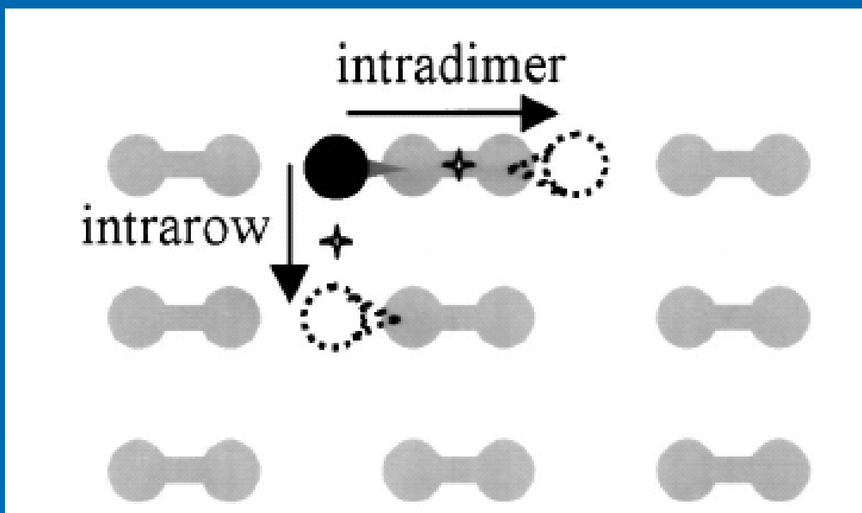
R $\Rightarrow$ hopping rate

P $\Rightarrow$ frequency prefactor

E $\Rightarrow$ activation energy (or "diffusion barrier") for the event that causes the system to move from A to B.

H-vacancy exchange diffusion

on the Si(001)



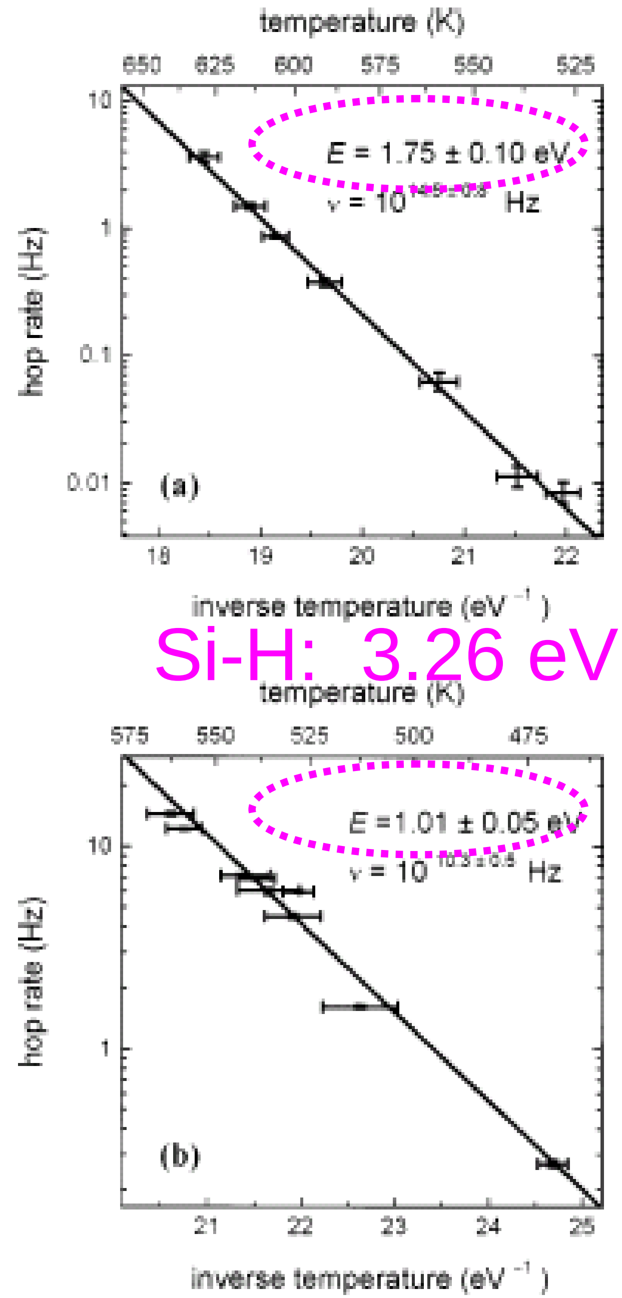


FIG. 4. Arrhenius plots for (a) intrarow and (b) intradimer H diffusion. The solid lines are weighted fits. From the slopes of these lines, we find the activation energies, E, and from the intercepts we find the attempt frequencies, ν.

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Observed 2D diffusion

3: Small clusters exchange positior vacant sites: The diffusion of Ge dim the Ge(001) surface

VOLUME 84, PHYSICAL REVIEW LETT

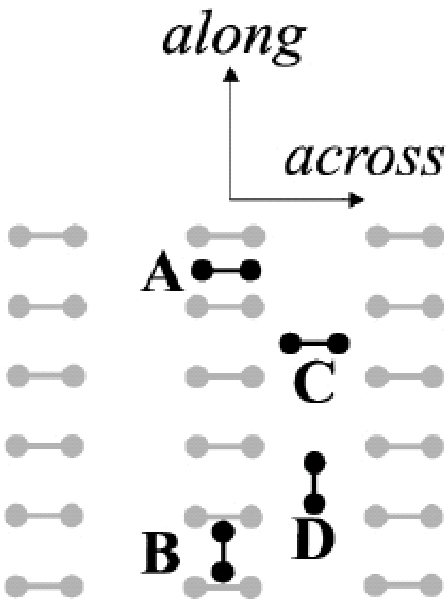


FIG. 1. Schematic diagram of the configurations of adsorbed Ge dimers on Ge(001). Gray dumbbells repre substrate dimers and black dumbbells represent the a dimers.

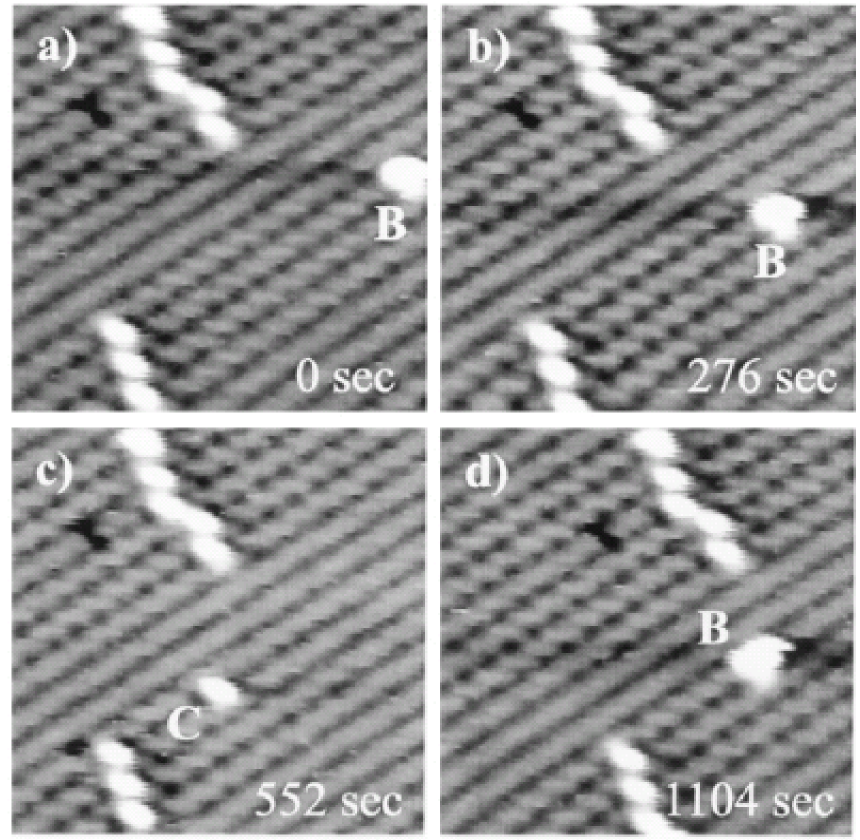
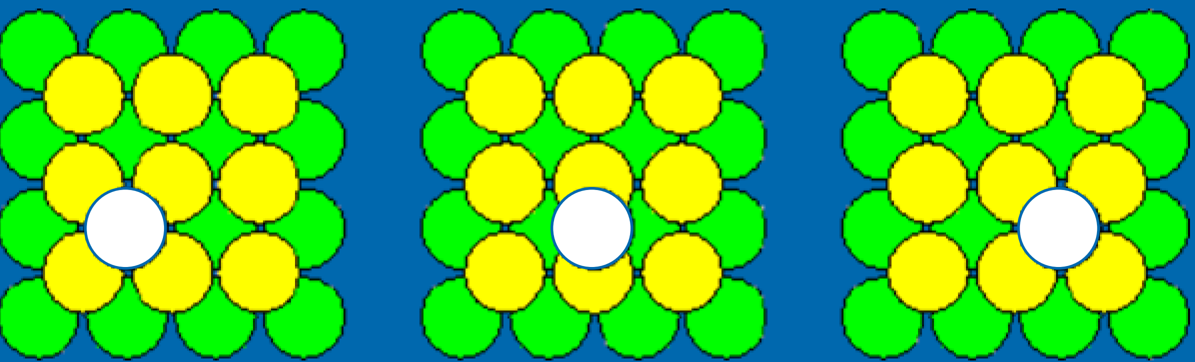


FIG. 2. Successive empty-state scans of the same area (100 Å × 100 Å) of a Ge(001) surface after the deposition of ~1% of a monolayer Ge. The time elapsed is depicted in the images. (a),(b) Diffusion of an on-top dimer (B) along a substrate dimer row. (b),(c) The on-top dimer (B) jumps to a trough position (C). (c),(d) The trough dimer (C) jumps to an on-top position of an adjacent substrate row (B) (sample bias +1.6 V and tunneling current 0.7 nA)

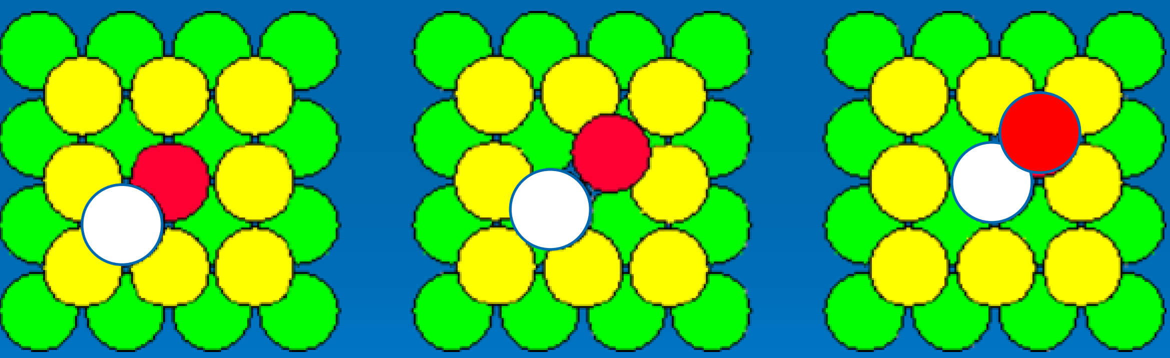
Self Diffusion at metal surfaces: surprises…

B.D. Yu and M. Scheffler, Phys. Rev. B 56, R15569 (1997)



Hopping mechanism

Ag(100) Δ*E* = 0.45 eV
Au(100) Δ*E* = 0.83 eV



Exchange mechanism

Ag(100) Δ*E* = 0.73 eV
Au(100) Δ*E* = 0.65 eV

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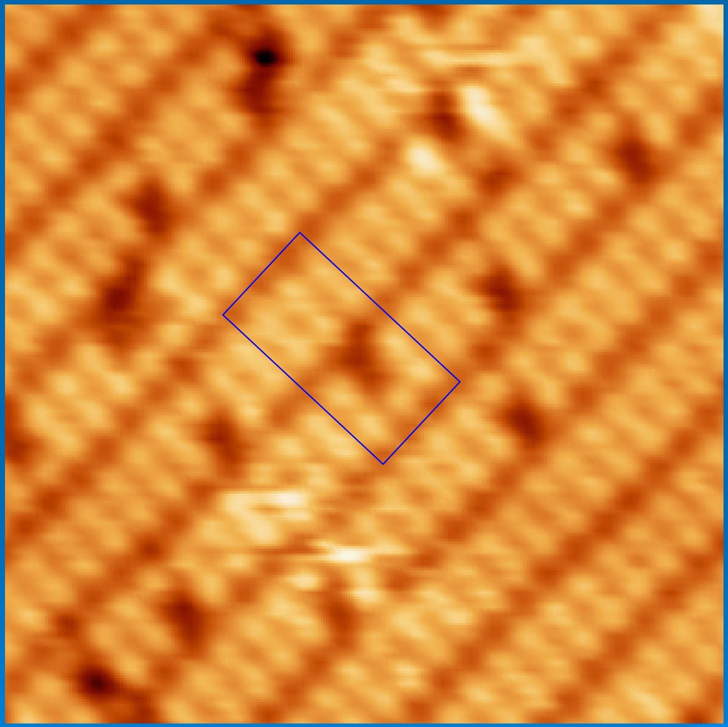
Surface Self-Diffusion on Pt(001) by an Atomic Exchange Mechanism

G. L. Kellogg and Peter J. Feibelman
Sandia National Laboratories, Albuquerque, New Mexico 87185
(Received 29 March 1990)

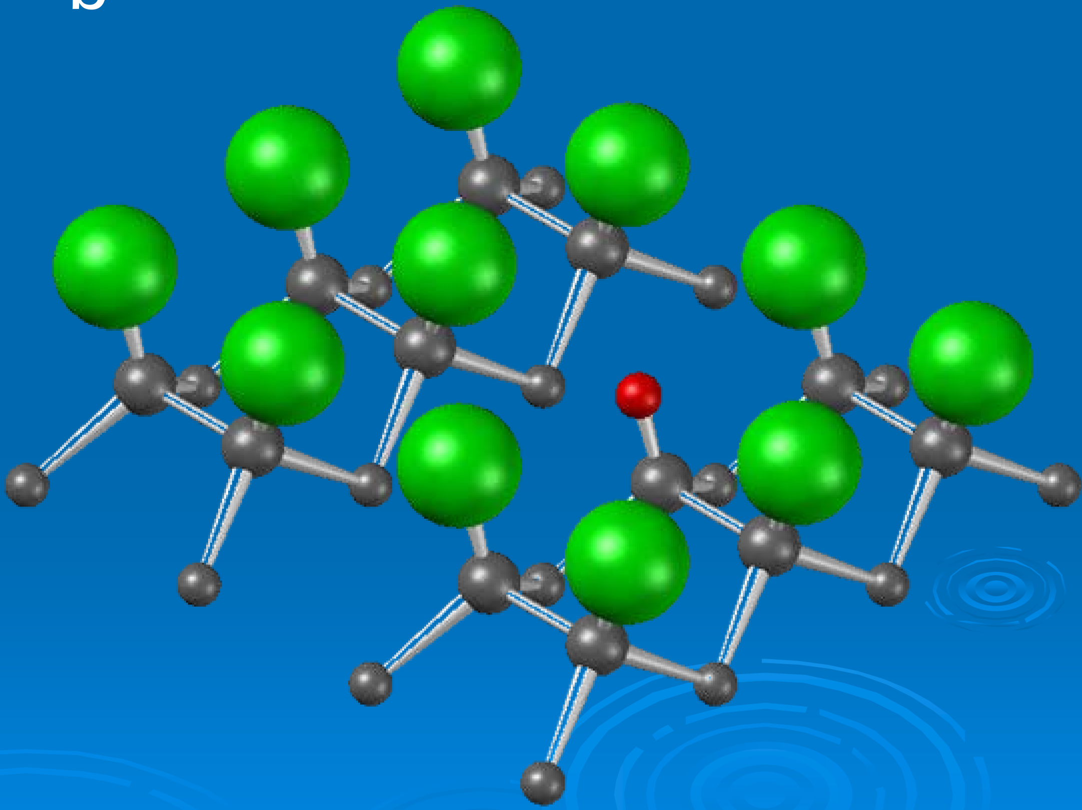
E_a=0.47 eV
so small !!

Atomic Model

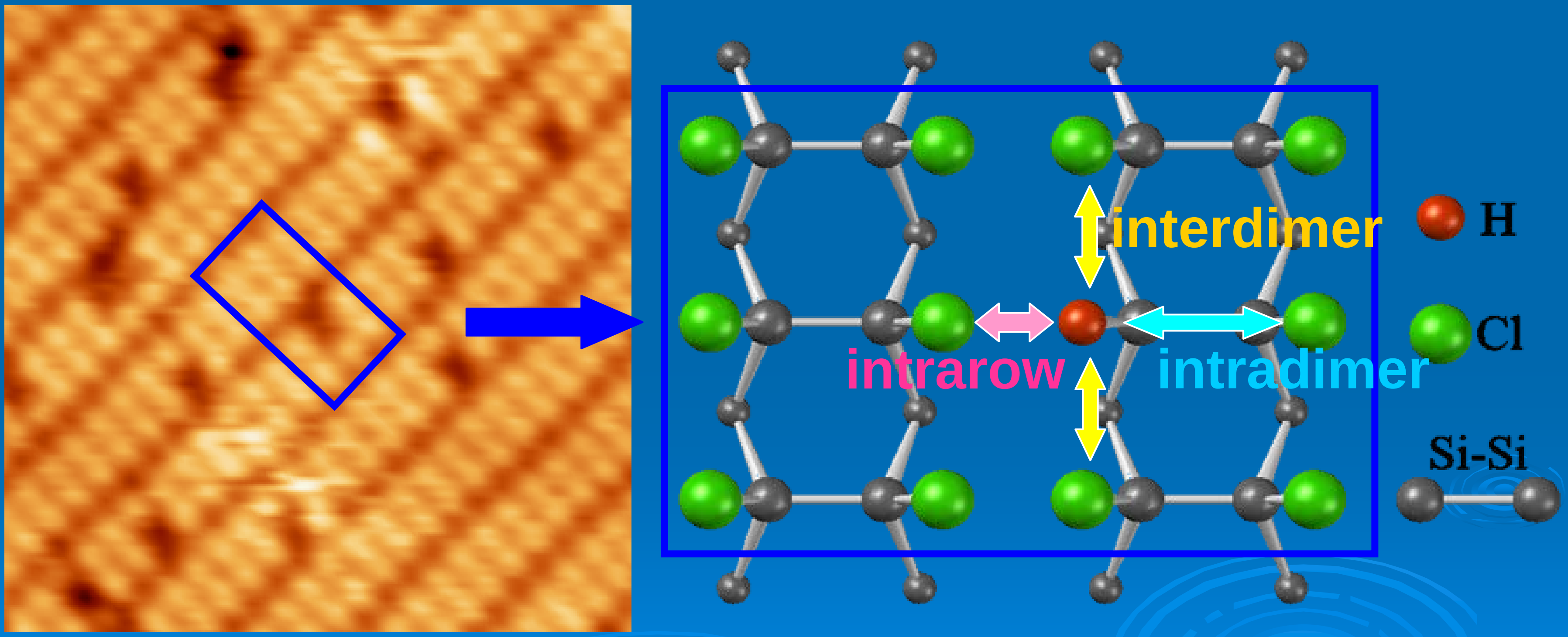
a



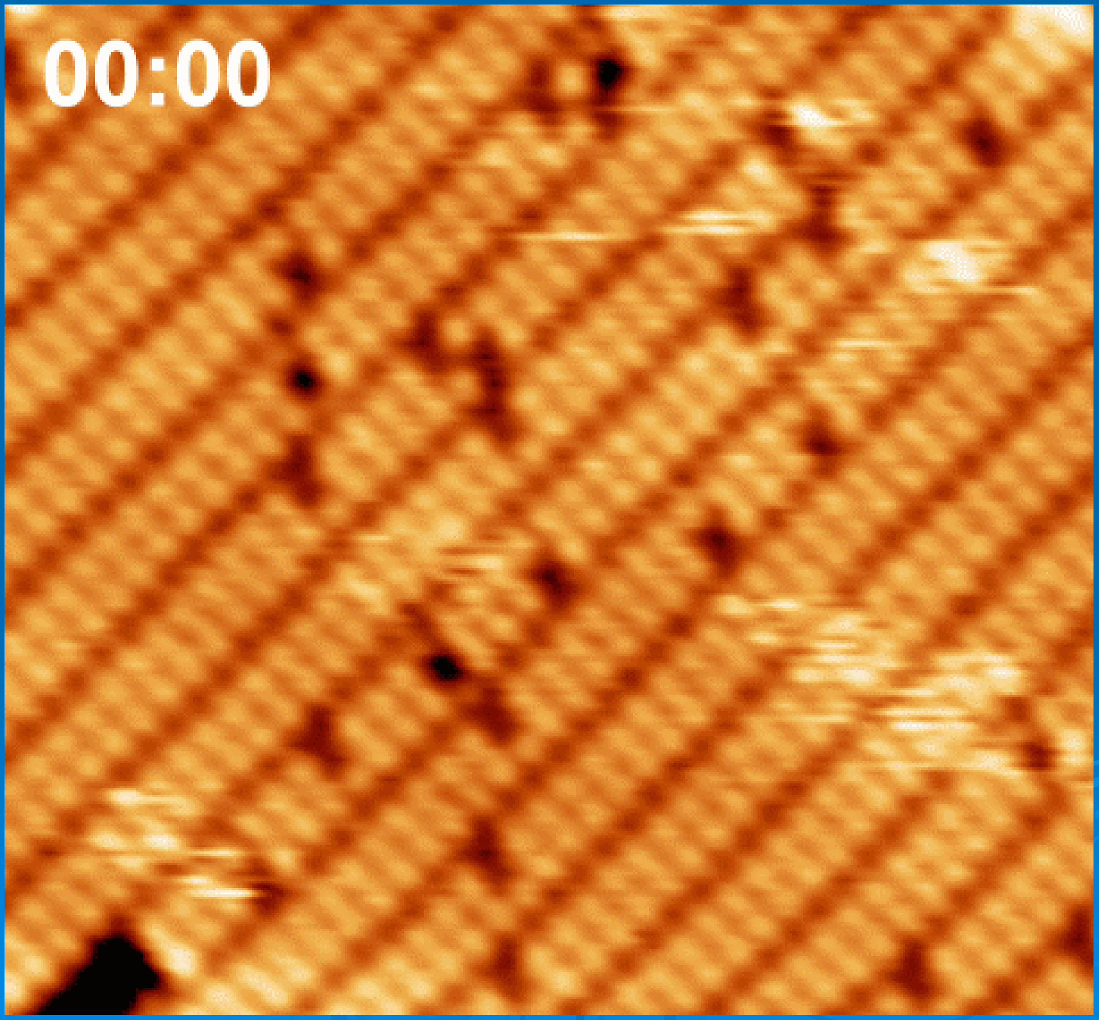
b



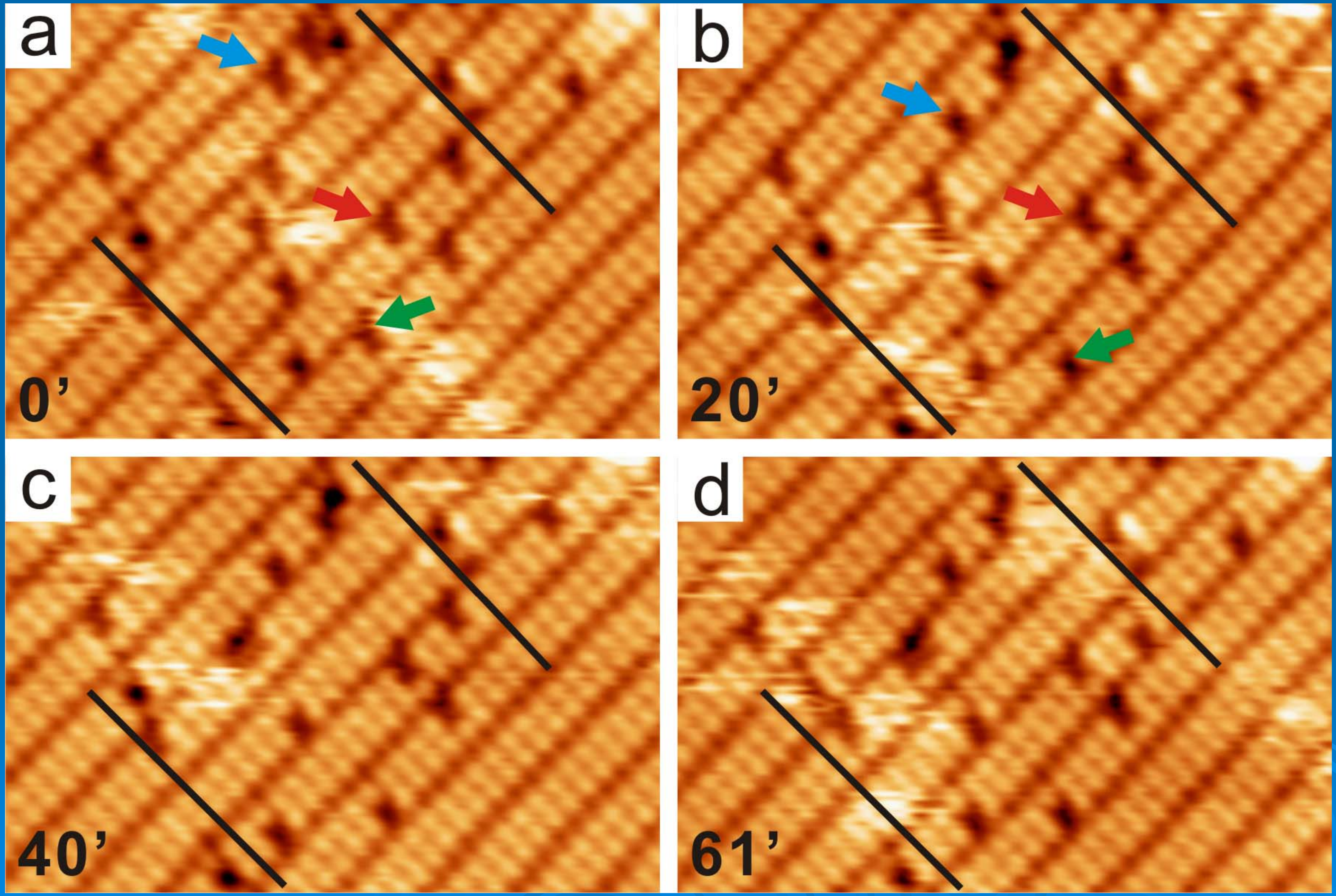
Three Pathways for H/Cl Exchange



STM Movies for H-site diffusion on the Cl/Si (100)-2x1 surface at 560K

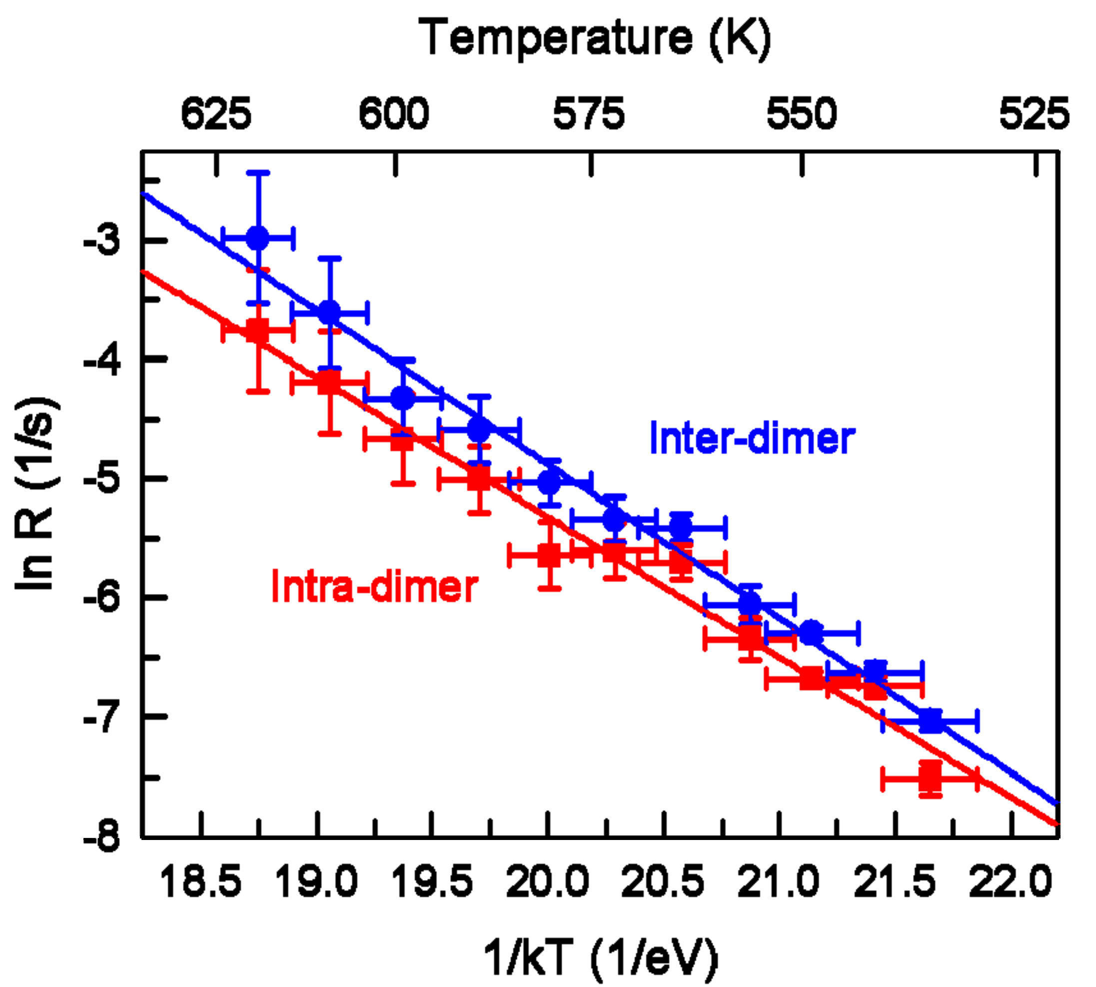


4 consecutive STM images (20 s/frame)



at 560K (V_{sample}= -2.2 V, Setpoint= 0.23 nA, 5Å x 8Å) H-coverage 0.02ML

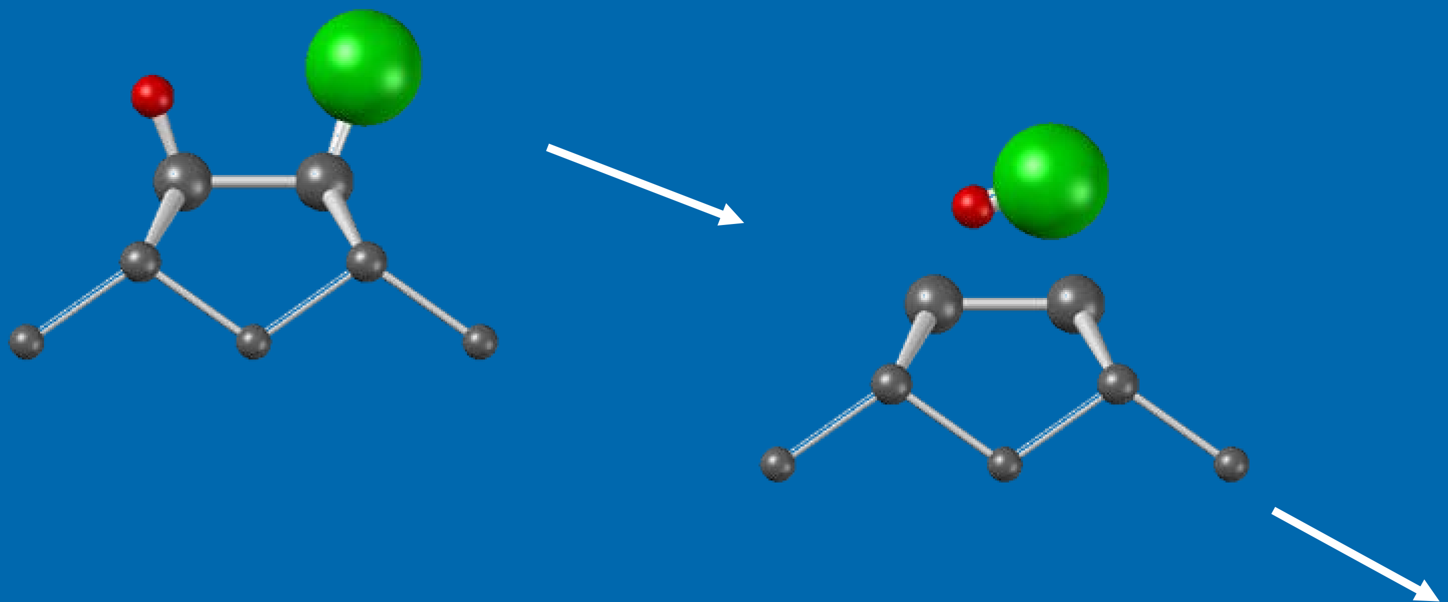
Arrhenius plot of H/Cl exchange

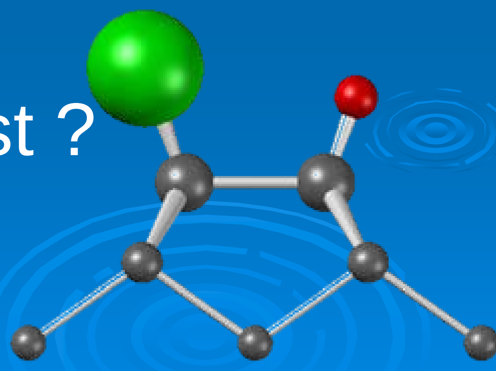


E_a(inter - dimer) = 1.29 eV P(inter - dimer) = 1.31 x 10^9 s^{-1}

E_a(intra - dimer) = 1.17 eV P(intra - dimer) = 6.64 x 10^7 s^{-1}

Modeling H/Cl exchange





Issues:

1. Molecular intermediate state really exist ?
2. Role of vibration modes, phonons in diffusion?

the major goal in surface science:
to make movies of molecules on surfaces, on a fs time scale, with 10 pm resolution.

Conclusions:

1. Diatomic molecules like I_2, Cl_2, H_2, HCl are great actors and SI(100) are a good stage for illustration of fundamental issues.

2. Current experimental approach: with 10 pm resolution YES, on a fs time scale, NO.