Scanning Tunneling Microscopy Study of Adsorbate/Surface Interactions and Dynamics

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Outline

Introduction to scanning tunneling microscopy (STM)

An example of STM applications – study of H/Si(001)

Other STM applications – current research interest

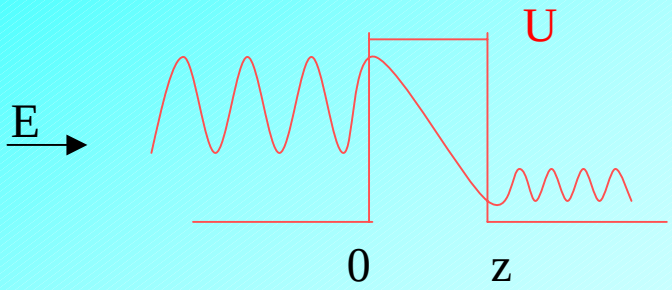
Invention of STM

G. Binnig and H. Rohrer, Helv. Phys. Acta 55, 726 (1982).

(IBM Zurich)

Noble Prize 1986 (photo by C.Chen)

One Dimensional Square Barrier – Tunneling Effect



$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial z^2}+U\Psi=E\Psi$$

$$T \sim e^{-2\kappa Z} \qquad \text{where} \qquad \kappa=\sqrt{\frac{2m(U-E)}{\hbar^2}}$$

Take U-E as the work function Φ, then the characteristic length 1/κ ~ 0.1nm

Qualitatively tunneling current extremely sensitive on barrier width

Atomic resolution: lateral ~ 0.1nm, vertical ~ 0.01nm

Quantitative Description – Modified Bardeen's method

See the tunneling process as transition between states, follows *Fermi's Golden Rule*:

$$T = \frac{2\pi}{\hbar}\left|M_{\mu\nu}\right|^2 \delta(E_\mu - E_\nu) \quad \text{where} \quad M_{\mu\nu} = -\frac{\hbar^2}{2m}\oiint_{\Sigma}(\chi_\nu^* \nabla\Psi_\mu - \Psi_\mu \nabla\chi_\nu^*)dS$$

$$I = \frac{2\pi e}{\hbar}\sum_{\mu\nu}\left\{f(E_\mu)\left[1 - f(E_\nu + eV)\right]\bullet\left|M_{\mu\nu}\right|^2 \delta(E_\mu - E_\nu)\right\}$$

In the limit of small bias voltage and low temperature :

$$I = \frac{2\pi e^2 V}{\hbar}\sum_{\mu\nu}\left\{\delta(E_\mu - E_\nu)\left|M_{\mu\nu}\right|^2\right\}$$

Assuming spherical tip and s wave function of tip:

$$\frac{dI}{dV} \propto \sum_{E_f - eV}^{E_f}\left|\Psi_\nu(r_0)\right|^2 \propto \rho_s(r_0, E_f - eV) \longrightarrow \textbf{LDOS}$$

J. Bardeen, Phys. Rev. Lett. 6, 57 (1961).

J. Tersoff and D. R. Hamann, Phys. Rev. B 31, 805 (1995).

STM Instrumentation and Operation

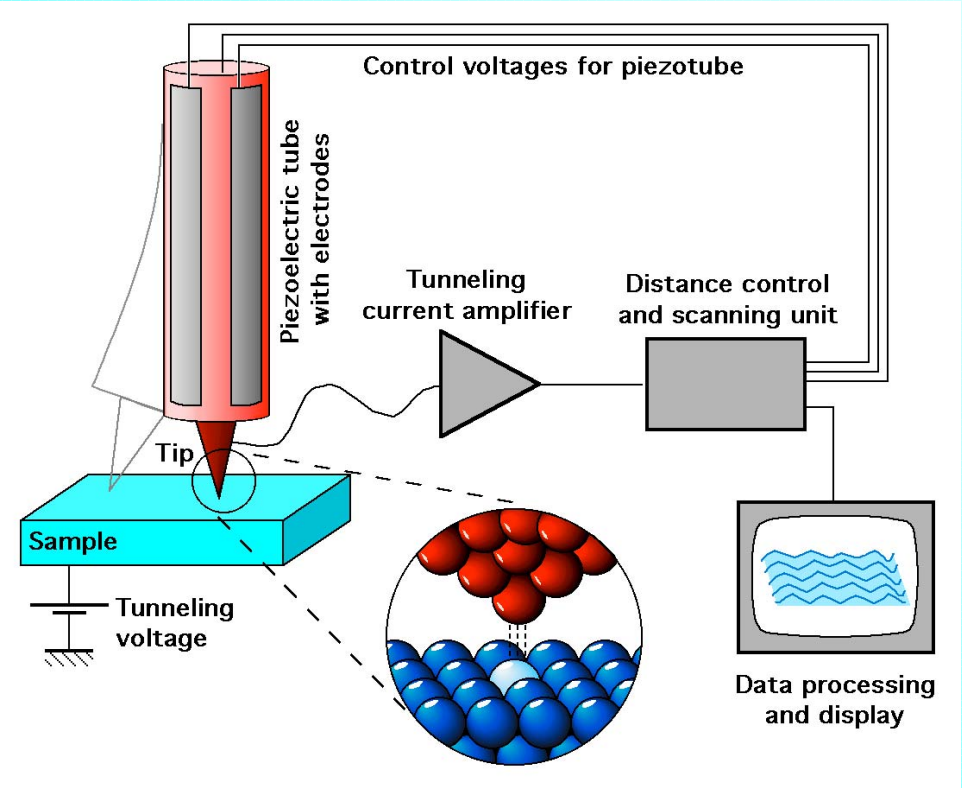
Vibration isolation: spring, air leg, Eddie current…

Current amplifier

Electrical noise reduction

Accurate positioning: piezoelectric drive ~0.1nm/V

Feedback loop



Constant current mode

STS mode

STM Applications

- **Surface structure: semiconductor, metal, layered material…**

Nucleation and growth

- **Adsorbate on surface: inorganic, organic**

- **Scanning tunneling spectroscopy: LDOS and electronic structure**

STM variations: SPSTM, STM-IETS, AFM…

Atom manipulation and surface modification

Motivations to study H/Si(001)

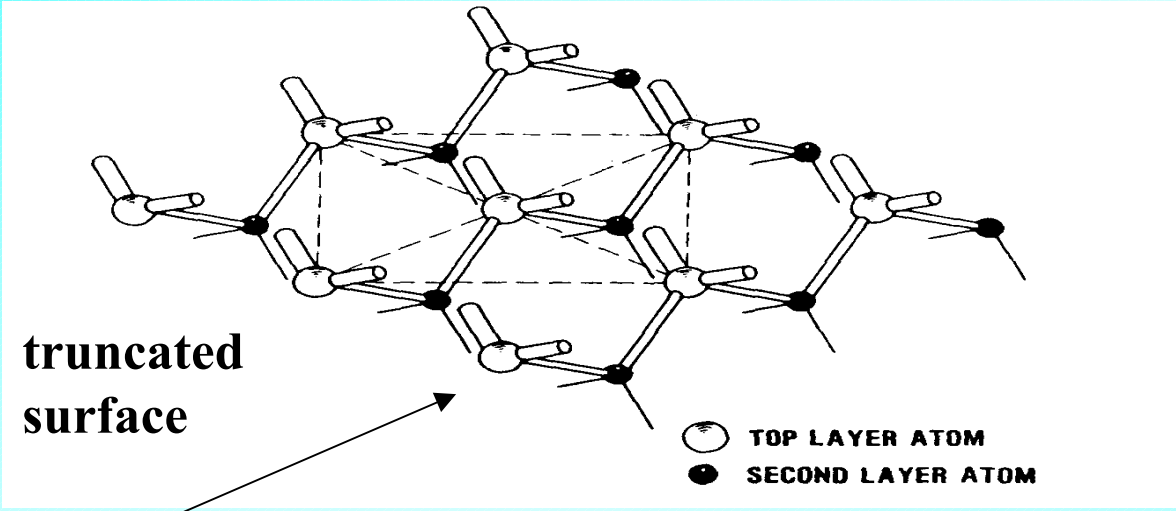
→ **H/Si(001):** **Growth of Si from SiH_4 or similar compounds**

Prototype for adsorbate/semiconductor interactions

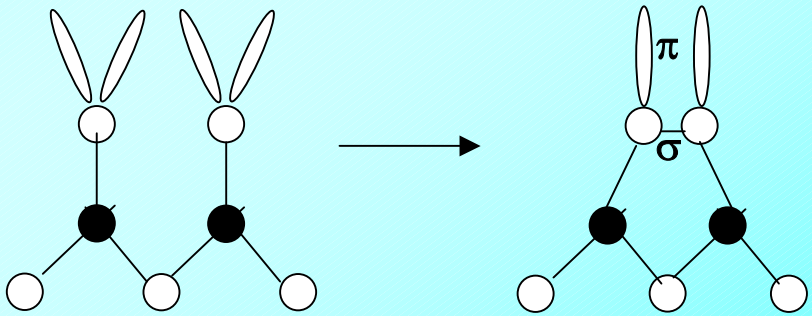
→ **STM as a powerful tool not only for structure but also for dynamics**

1. **Adsorbate-adsorbate interactions for H/Si(001)**
2. **Adsorbate-surface interaction dynamics**

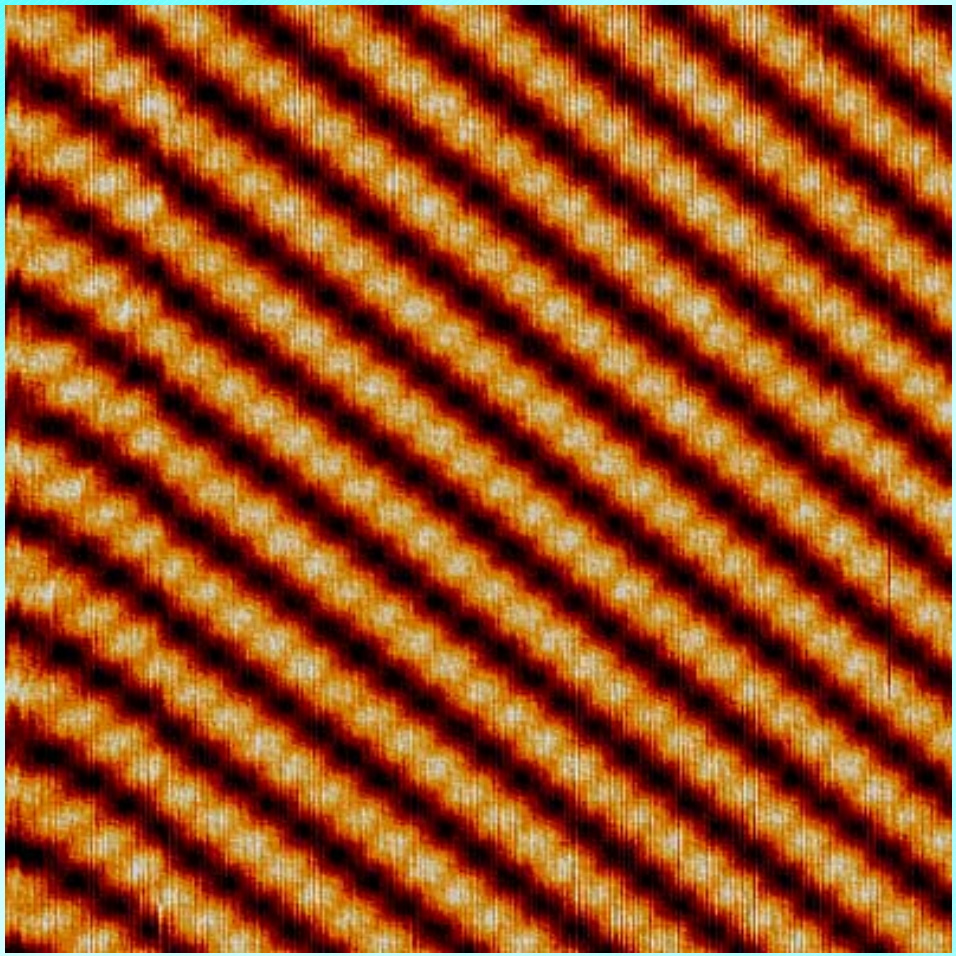
Si(001) surface reconstruction



sideview of dimer formation:



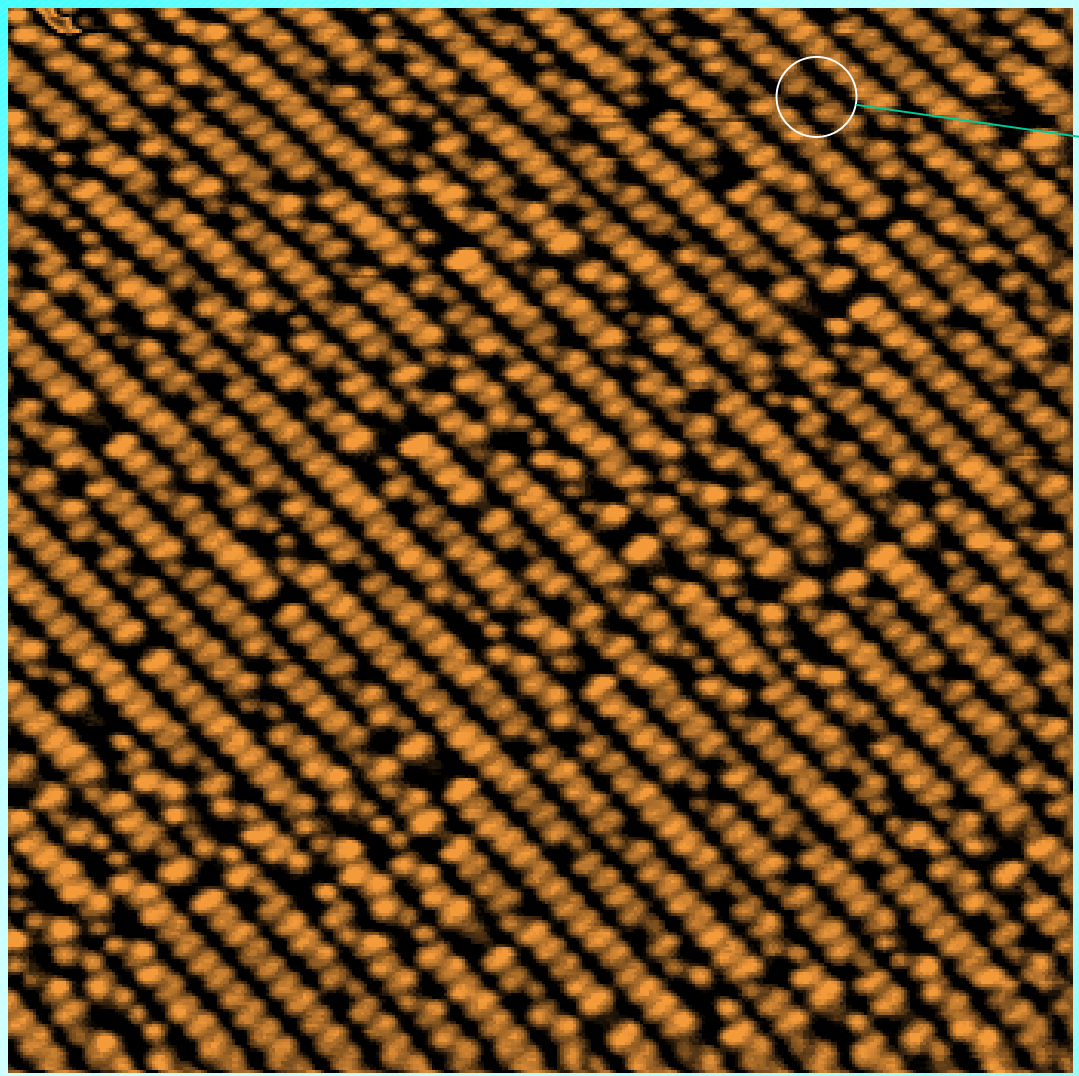
Si(001) 2×1 dimer row structure

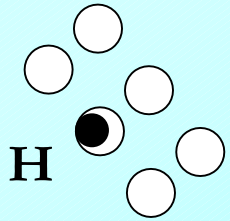


10 nm × 10 nm, -2 V, 0.6 nA

Each DB can be occupied by 1 H atom

Si(001) surface after atomic H adsorption at RT





Many singly occupied dimers

H randomly distributed

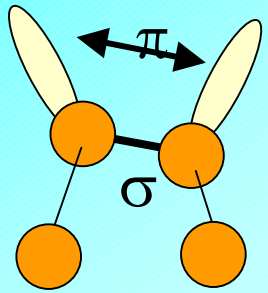
20 nm × 20 nm, -2 V, 0.7 nA

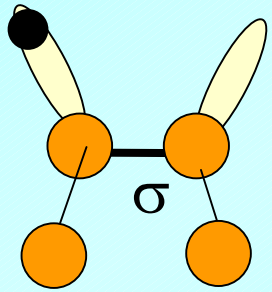
Changes in geometric and electronic structures upon adsorption of hydrogen

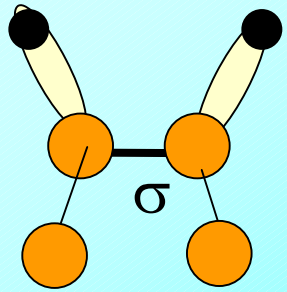
Clean dimer:
asymmetric, with π bond

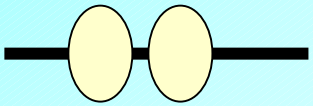
Singly-occupied dimer:
symmetric, π bond broken

Doubly-occupied dimer:
symmetric, π bond broken









π^* state

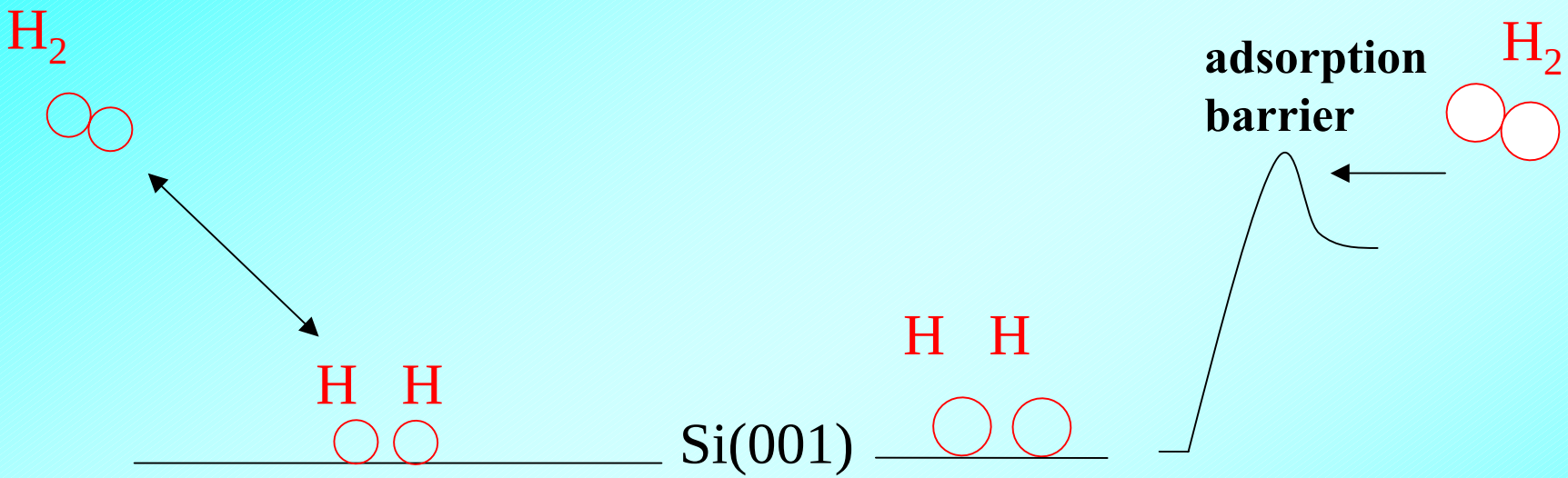
quasifree
DB states

E_F

π state

Si -H bond states

Unusual behavior of H_2 - Si(001) interaction



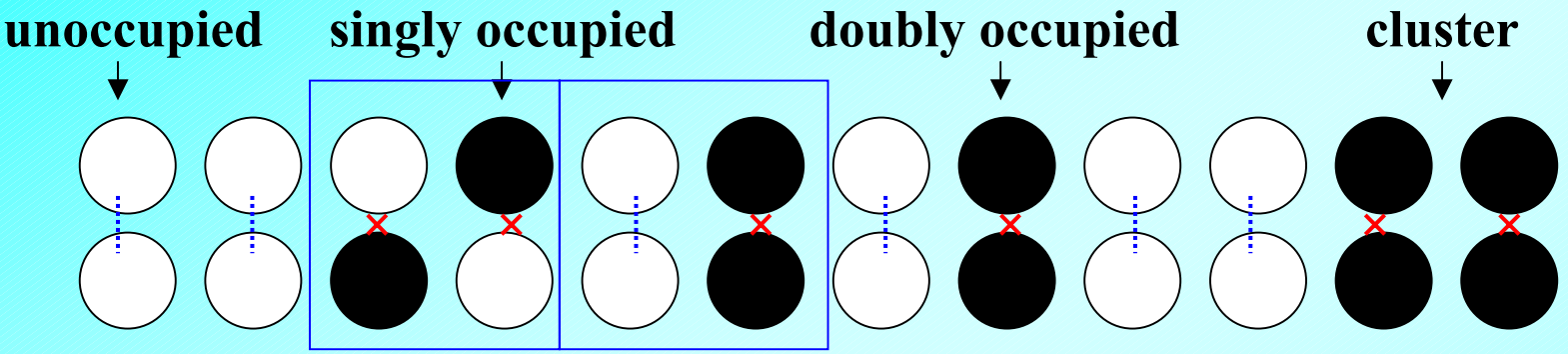
1. Strong surface temperature dependence of H_2 sticking probability

2. Near-first-order kinetics of recombinative desorption

$$R_d \equiv -d\theta/dt \approx k\theta \qquad (\text{NOT } k\theta^2) \qquad \theta \text{ — H coverage}$$

$$H + H \rightarrow H_2\,(g)\uparrow$$

Relevant surface configurations and interactions



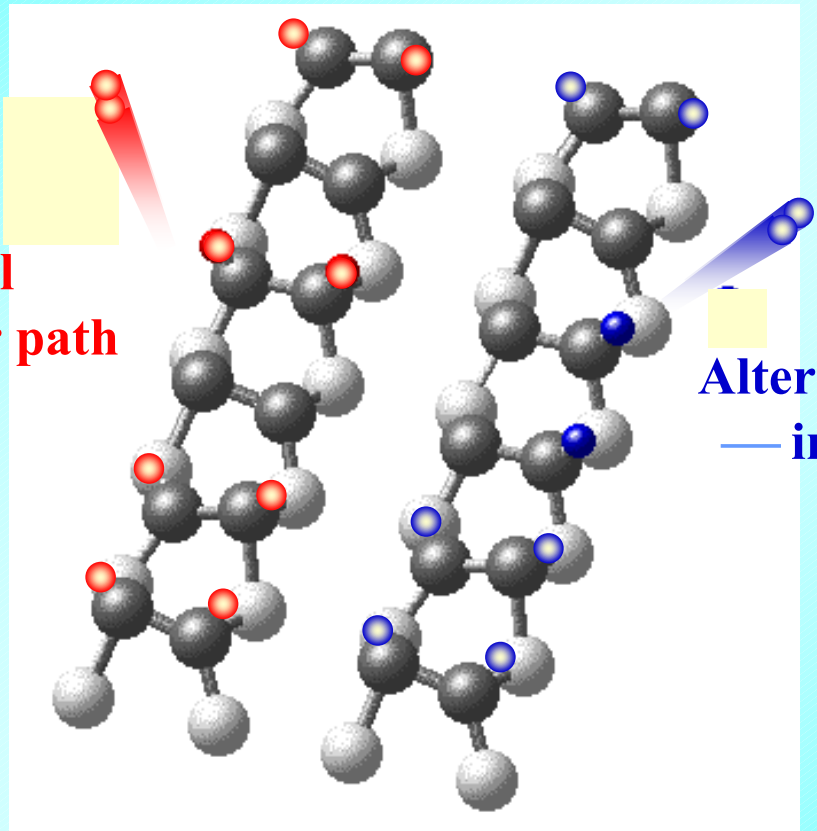
"Prepairing" mechanism can explain 1st-order kinetics naturally

Interaction strength closely related to intradimer or interdimer

- **Direct counting of different surface configurations using STM**
- **Application of statistical mechanics to infer interaction energies**

Desorption pathways in controversy

Prevalent model
— intra-dimer path



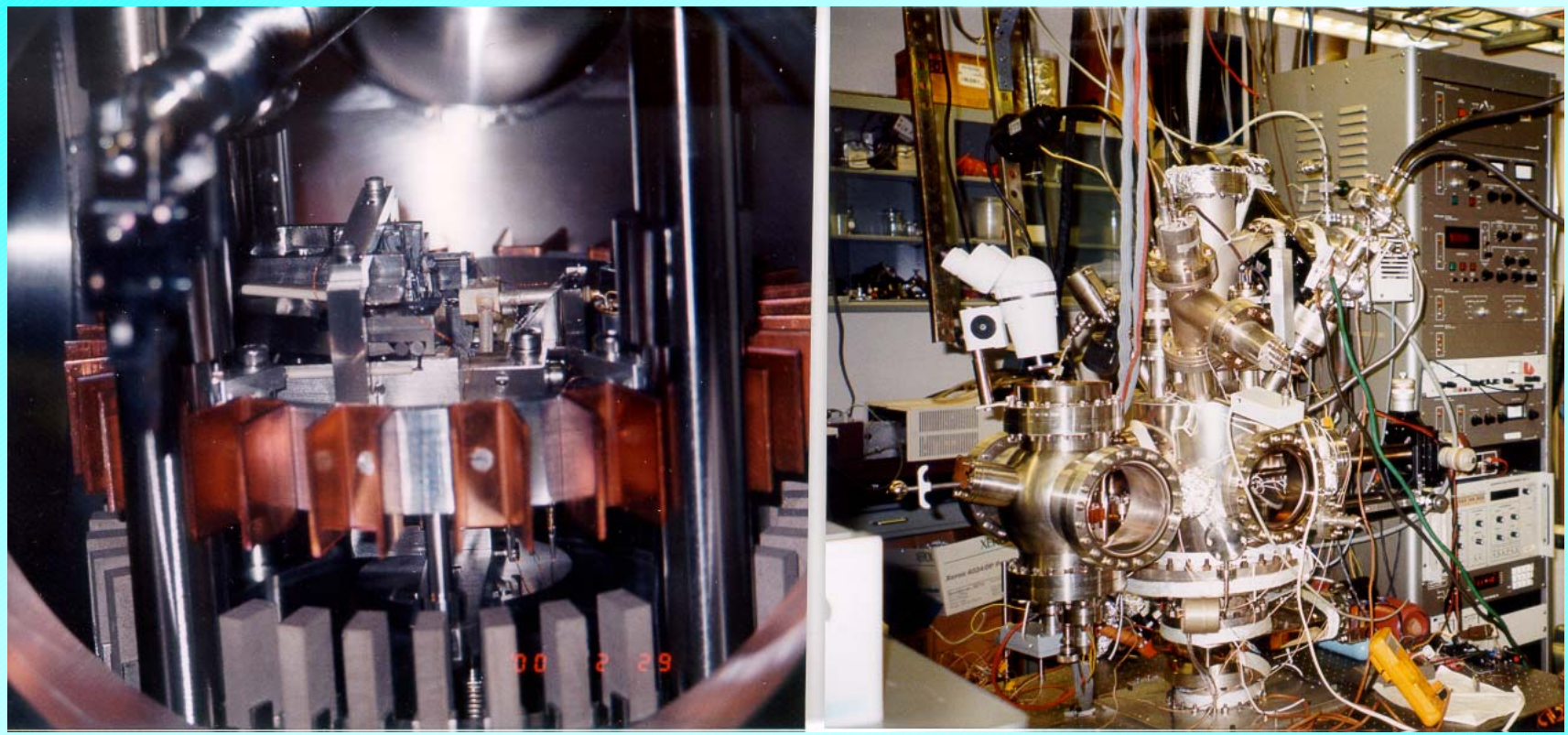
Alternative model
— inter-dimer path

Experimental

- **Apparatus:**
  - **— UHV STM, base vacuum pressure < 7×10^{-11} torr**
  - **— Tungsten tips made by electrochemical etching**
  - **— n-type silicon (10 Ω/cm), surface oriented to within 0.5°**

- **Procedure:**
  - **— Dose surface with atomic H ($0.04 \leq \theta \leq 0.65$)**
  - **— Anneal surface to reach equilibrium distribution**
  - **— STM at RT**

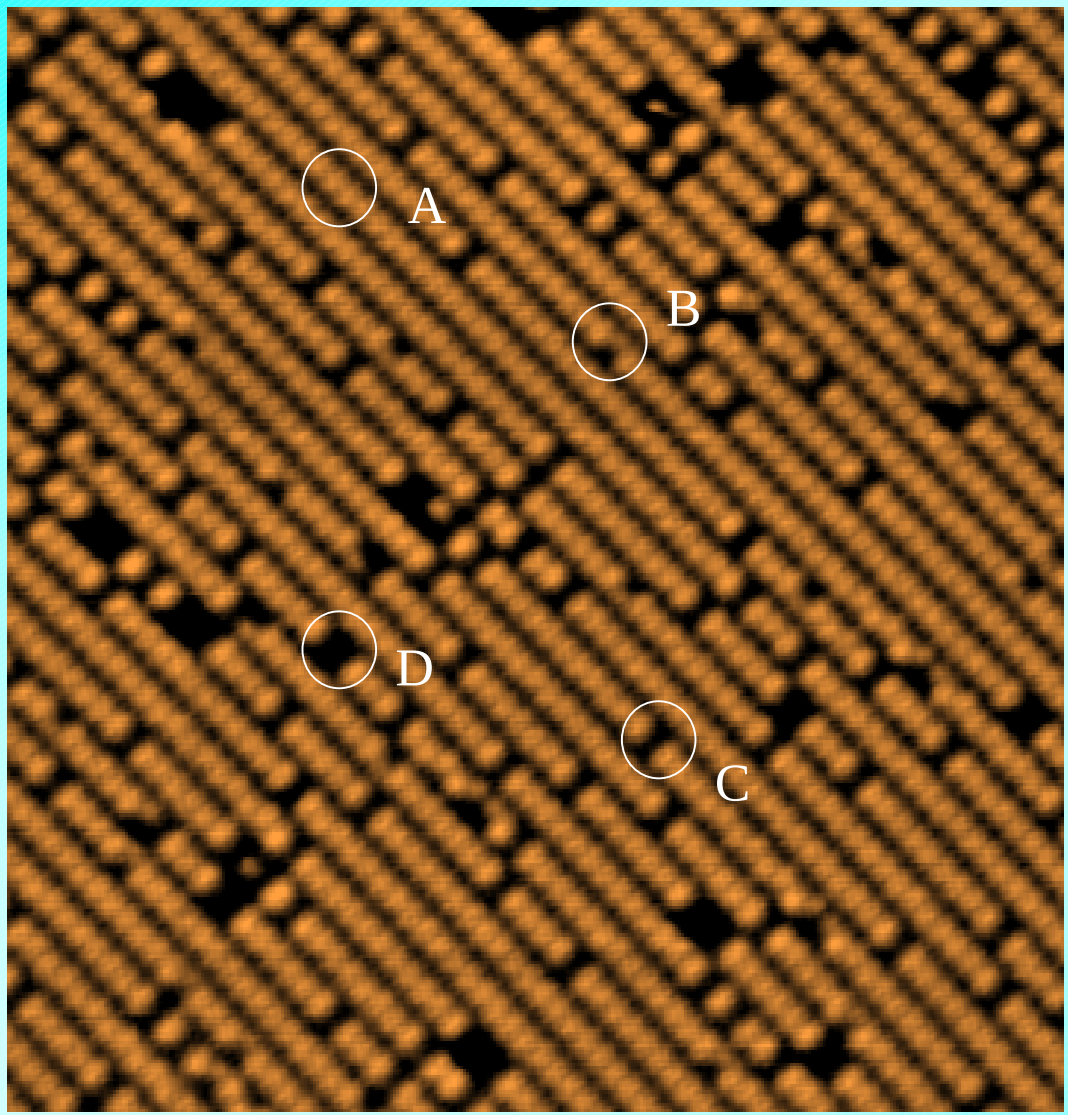
Experimental set-up

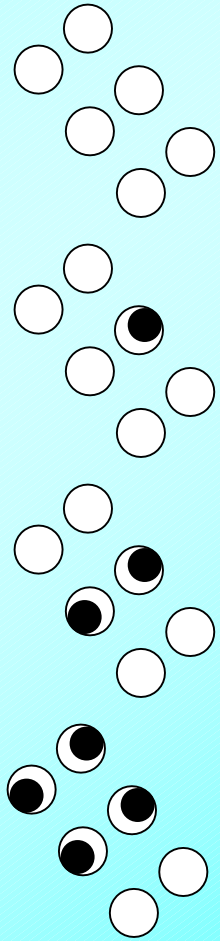


UHV with capabilities of STM, TPD, AES, optical techniques and molecular beam techniques

UHV STM, base vacuum pressure < 7×10^{-11} torr

H distribution after annealing to 640 K





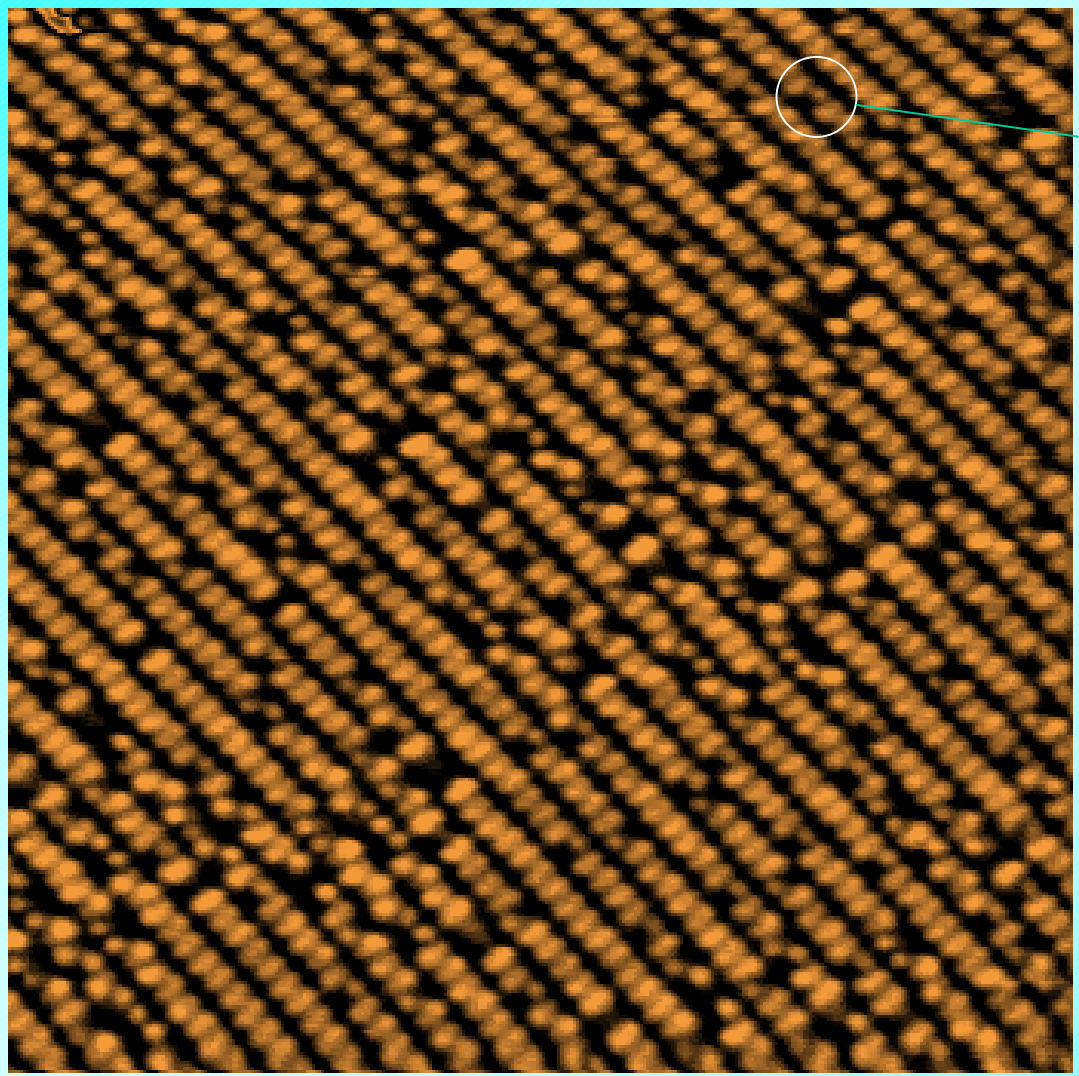
A — clean dimers

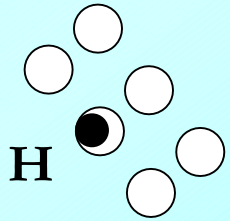
B — singly occupied

C — doubly occupied

D — cluster of doubly occupied dimers

Si(001) surface after atomic H adsorption at RT



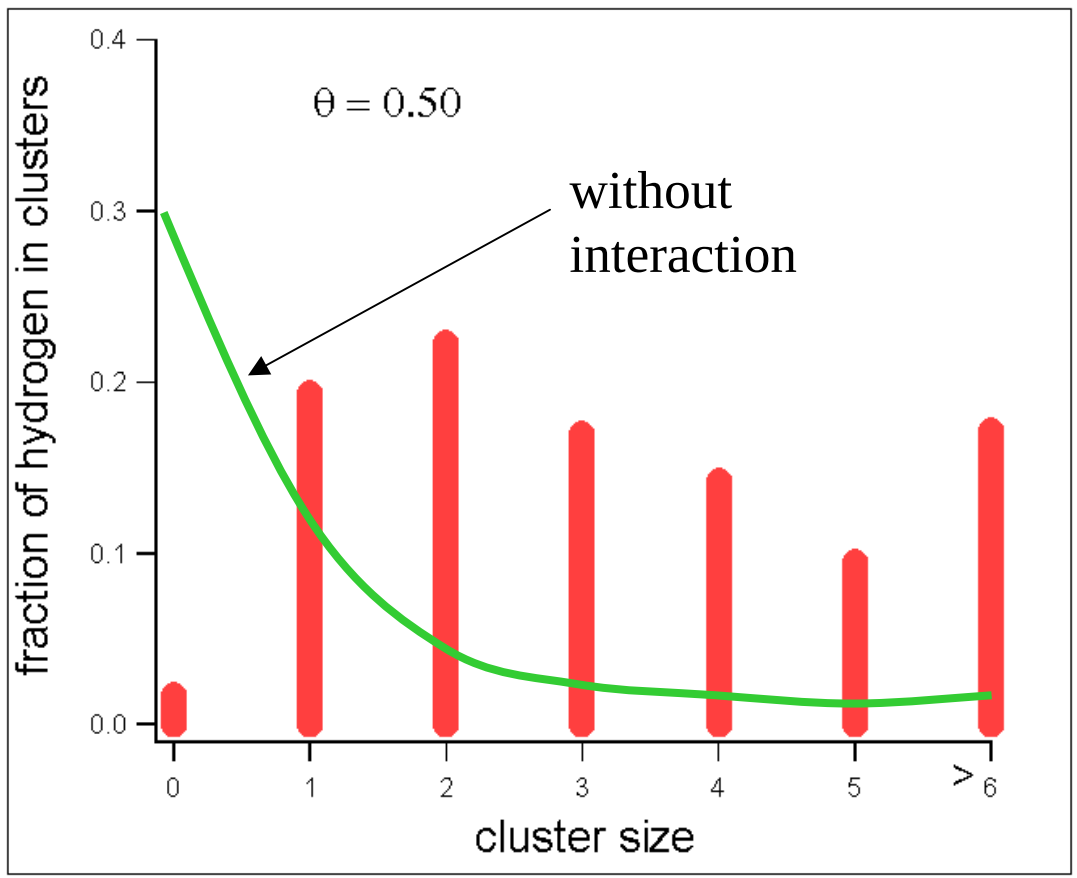


Many singly occupied dimers

H randomly distributed

20 nm × 20 nm, -2 V, 0.7 nA

Counting results of H configurations

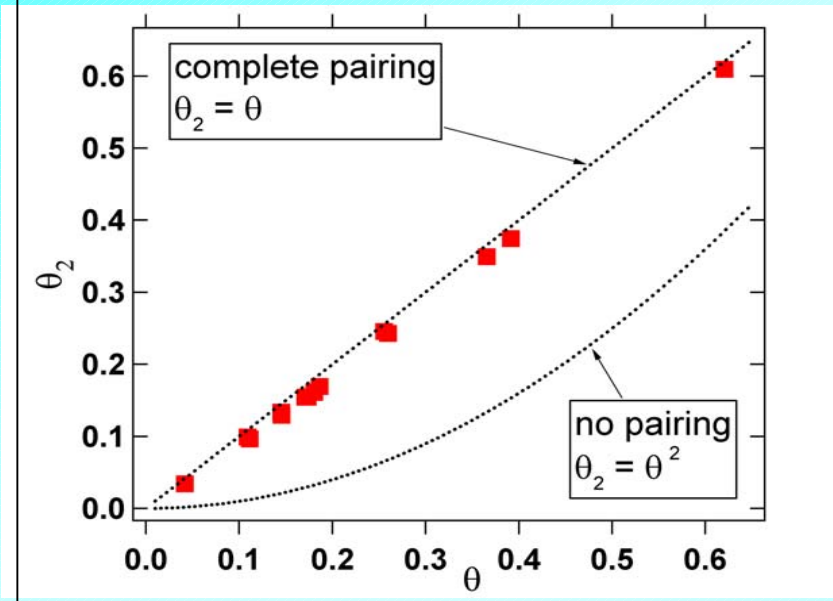


- **Most H in doubly occupied dimers**
- **Cluster size distribution is not statistical**

→ Intradimer and interdimer interactions do exist

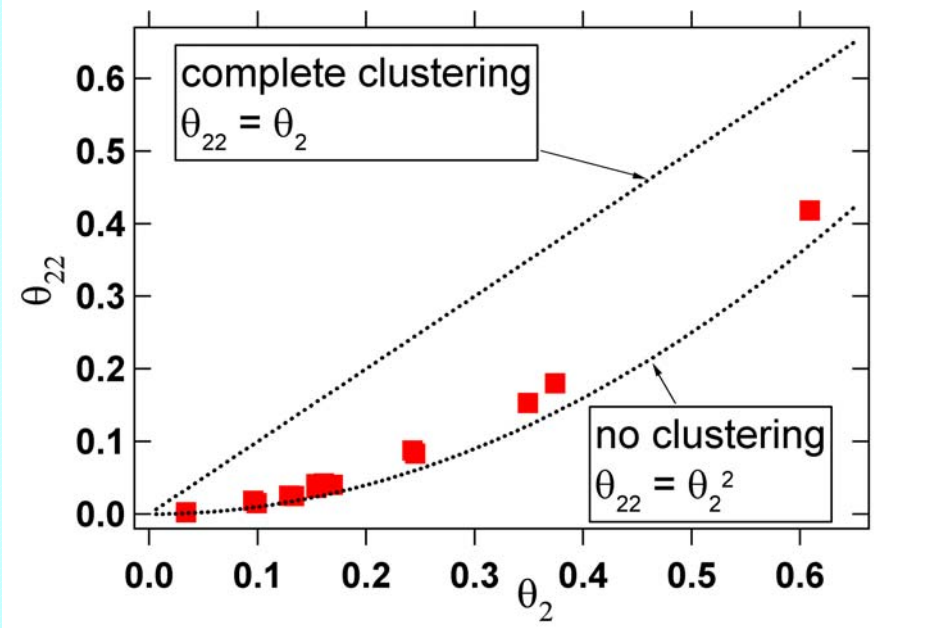
Qualitative analysis

Fraction of doubly occupied dimers



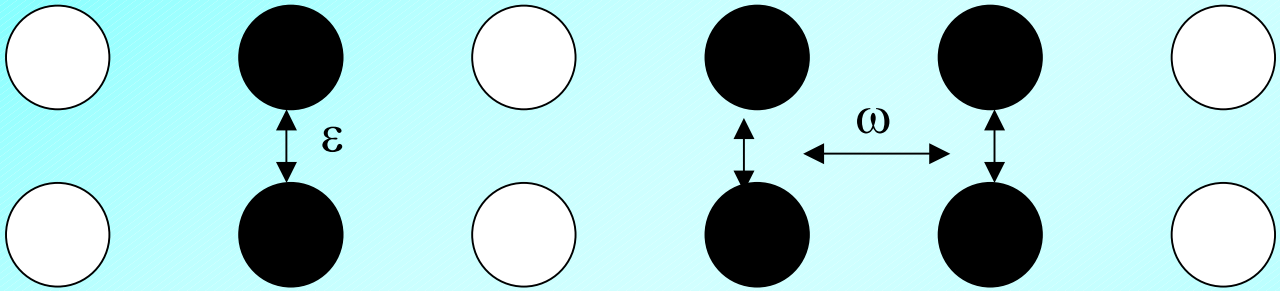
- **strong pairing**

Fraction of adjacent doubly occupied dimers



- **weak clustering**

Pairing and clustering interactions



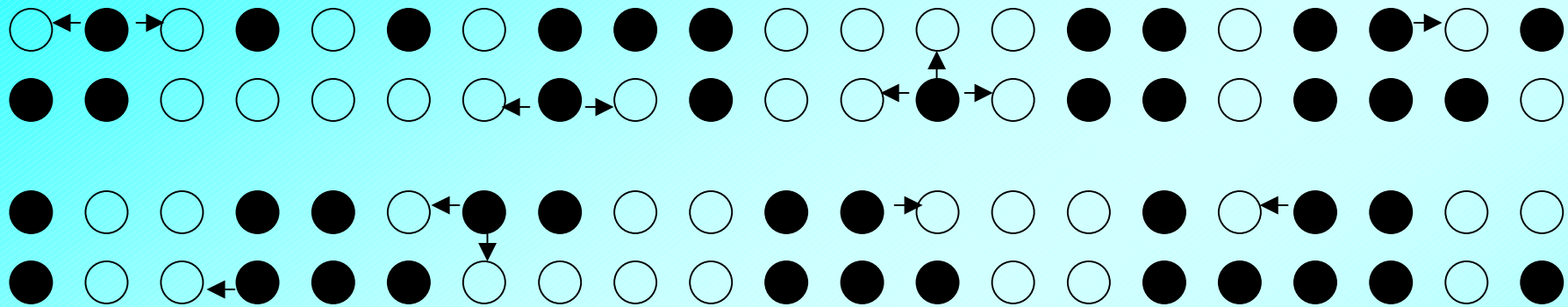
A nearest-neighbor-interaction model

Analytical fitting to θ, θ_2, θ_{22} (quasi-1D Ising Model)

Correlation function calculation

Monte Carlo simulation of cluster size distribution

Monte Carlo simulation



Monte Carlo Method:

- **Random tentative hops**
- **Hopping probability**

$p = e^{-\Delta E / kT}$ $(\Delta E \geq 0)$

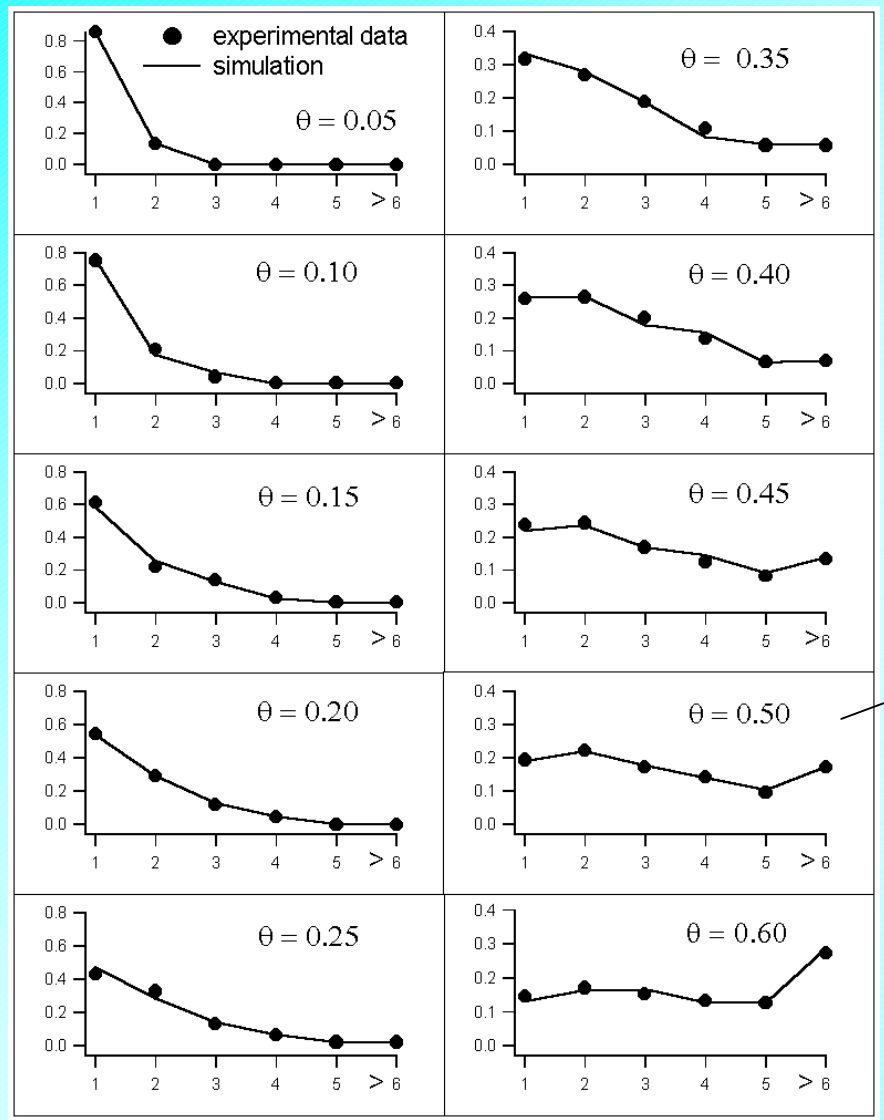
$p = 1$ $(\Delta E \leq 0)$

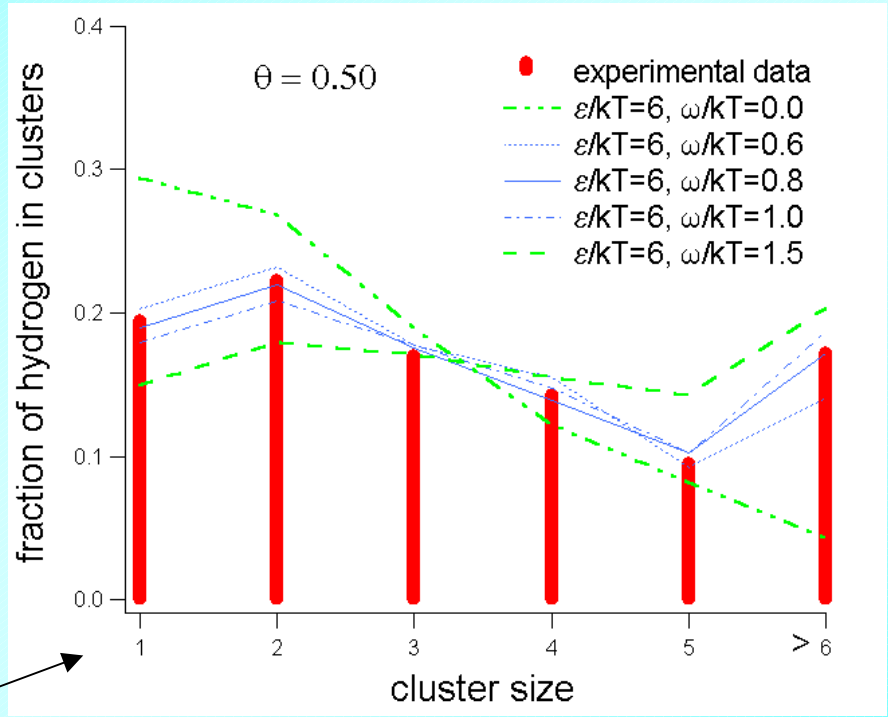
Important issues in programming :

- **Possible configurations (branches)**
- **Boundary effects**
- **Testing convergence (equilibrium)**

  ~ 10^6 tentative hops per site

Comparison of MC simulation results and experimental data





Best fit:

$\varepsilon = 0.28 \pm 0.03$ eV

$\omega = 0.04 \pm 0.01$ eV

Summary
Intradimer and interdimer interactions of H on Si(001)

Experiment and analysis

- **Direct counting of H configurations in STM images to obtain θ, θ_2, θ_{22}**
- **Most H in doubly occupied dimers. Some Clusters**
- **Analytical fitting. Correlation function. Monte Carlo simulation**

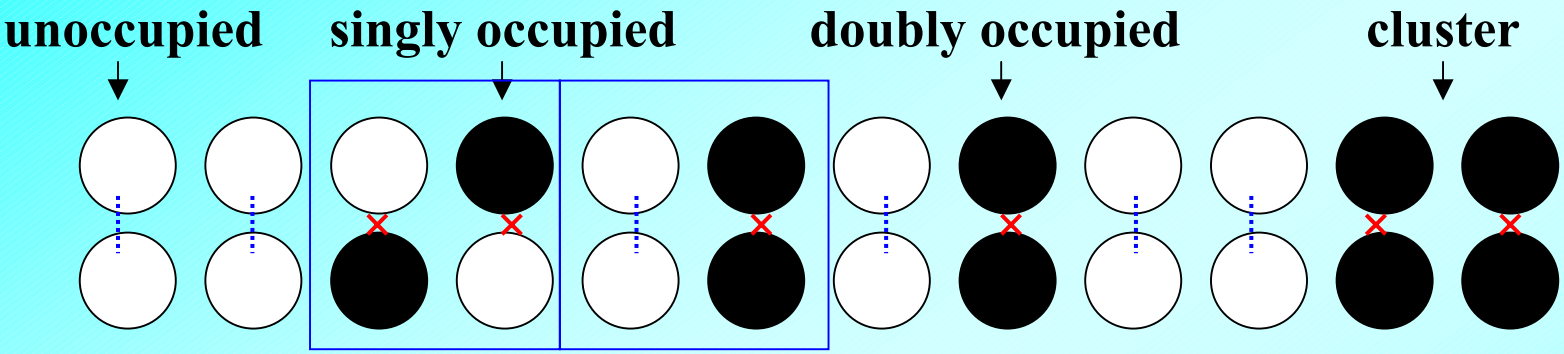
Results and implications:

- **Obtained energies in a way independent of any pathway assumptions**

  pairing ($\varepsilon = 0.28 \pm 0.03$ eV) >> clustering ($\omega = 0.04 \pm 0.01$ eV)

- **Driving force: π bonds**
- **A simple "interdimer prepairing" mechanism cannot explain the kinetics**

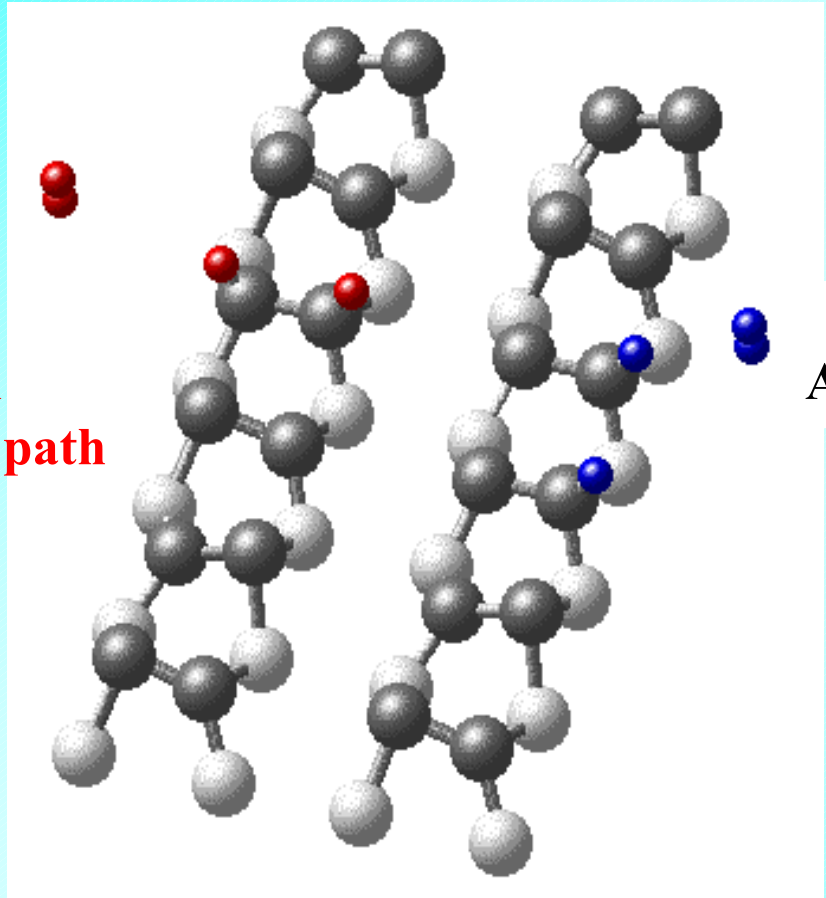
Relevant surface configurations and interactions



Driving force for pairing and clustering: recovery of π bond

Desorption/adsorption pathways in controversy

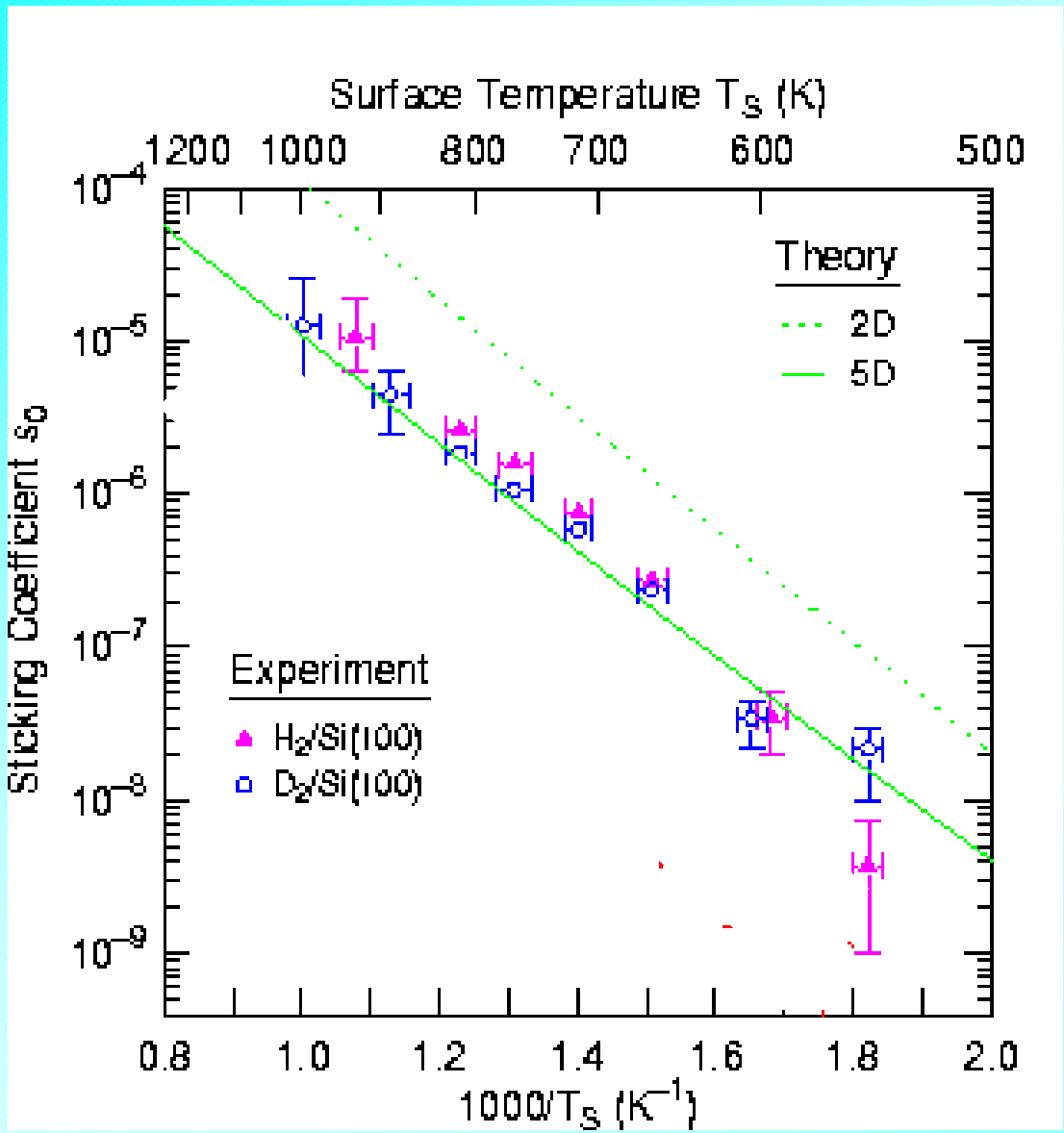
Prevalent model
— intra-dimer path



Alternative model
— inter-dimer path

Previously only theoretical calculations, no direct experimental evidence

Strong dependence of surface temperature



U. Hofer *et al.* Phys. Rev. B **54**, 5978 (1996)

At RT, extremely low:

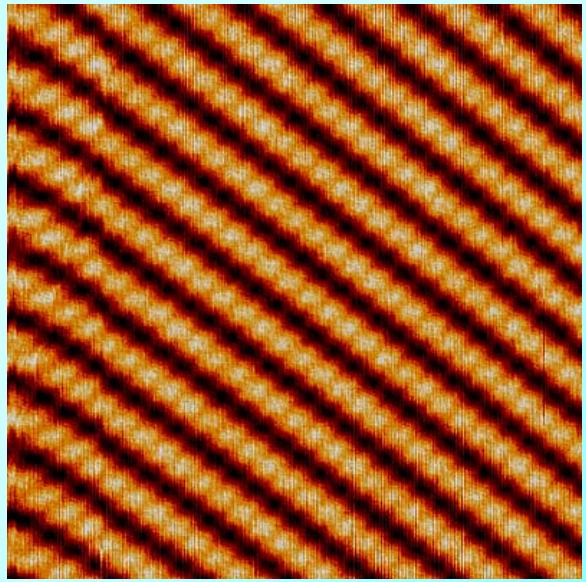
$$S_0 < 10^{-12}$$

Strong dependence on surface temperature:

$$S_0 \sim 0.1\, e^{-0.75\text{eV}/kT_s}$$

→ phonon-assisted mechanism

Experimental



- **Procedure:**

  Dosing of H_2 at the T_s ~500K

  Take STM images at RT

  AES, TPD to confirm adsorbed species

- **Special issues:**

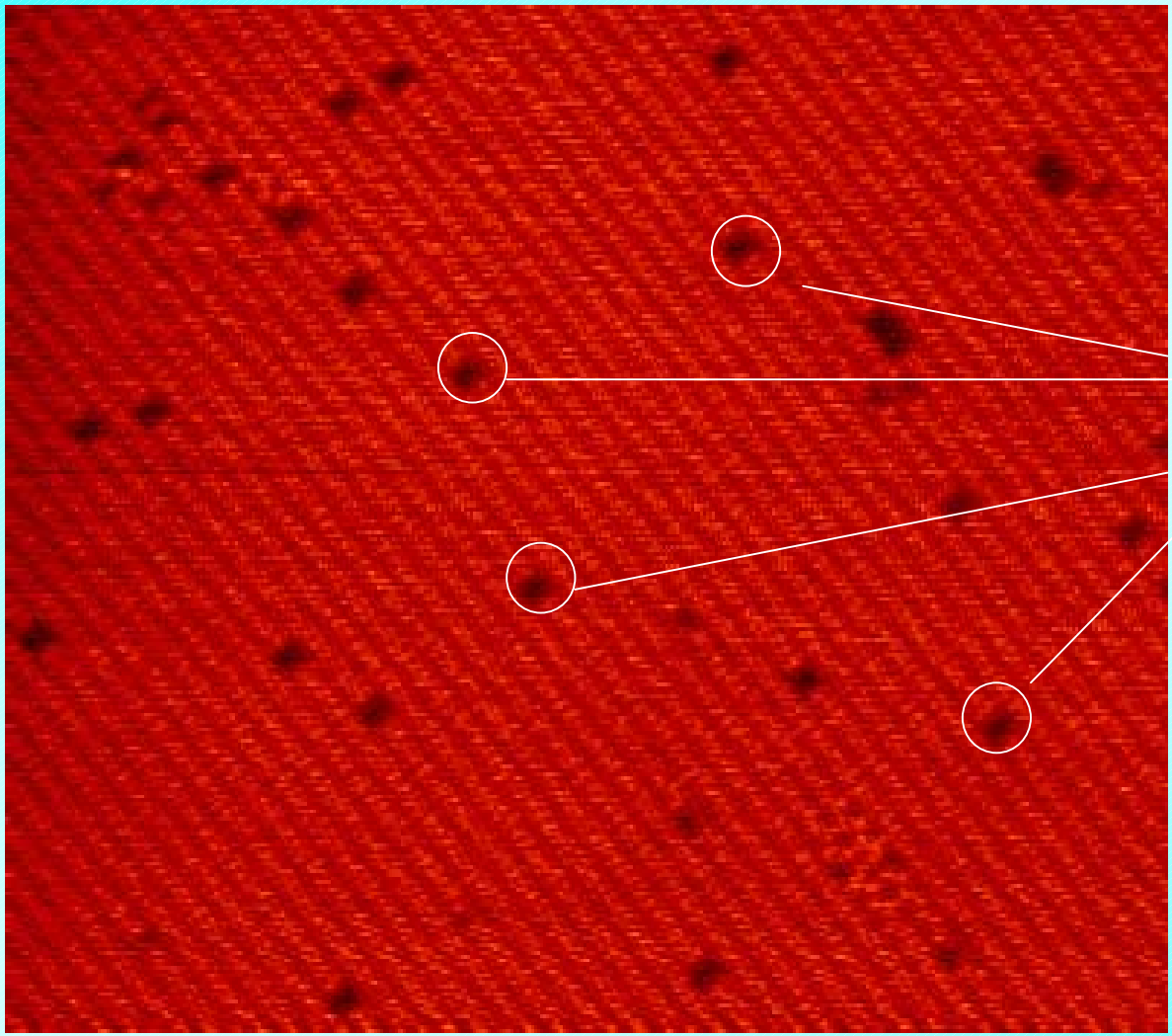
  → Impurities: clean surface (defect density <0.6%) before dosing

  → High-purity H_2 via a LN_2 cooling trap to reduce H_2O

  → All filaments turned off during and after dosing

  → T_s < 500K to avoid H diffusion

STM image of H_2 adsorption on clean Si(001) at 450K



After exposure of 10^6 Langmuir H_2 at 450K

Adsorbates in quartet configuration

Filled-state image

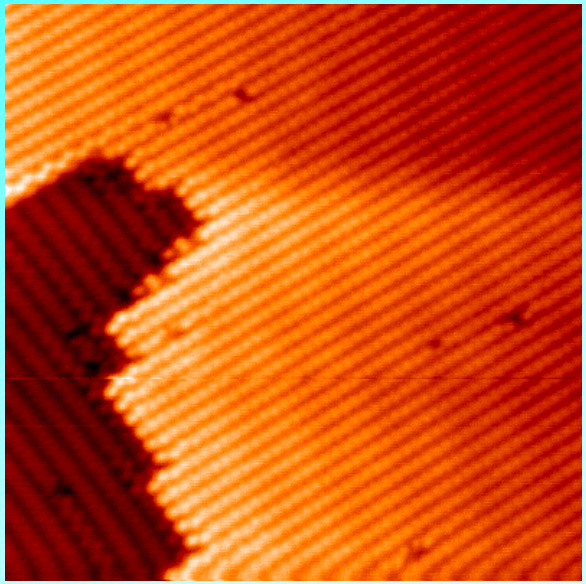
surface bias ~ -2V

current ~ 0.5nA

TPD confirmation of adsorbed species

filled-state images taken at ~ 0.5 nA, -2V sample bias

20 nm × 20 nm

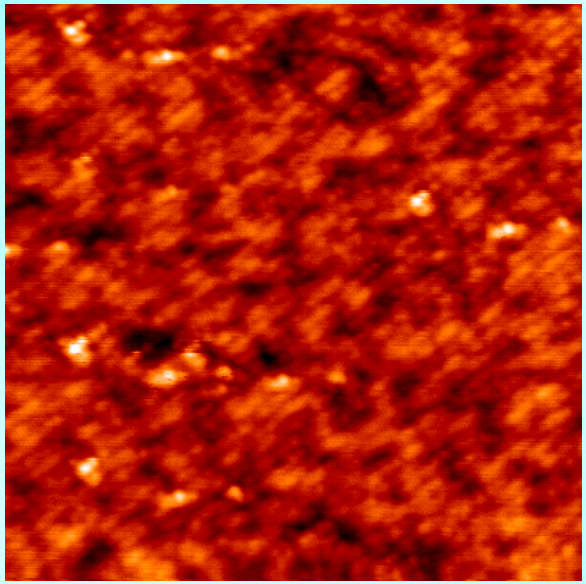


clean Si(001) before ads.

defect/contamination

~ 0.6%

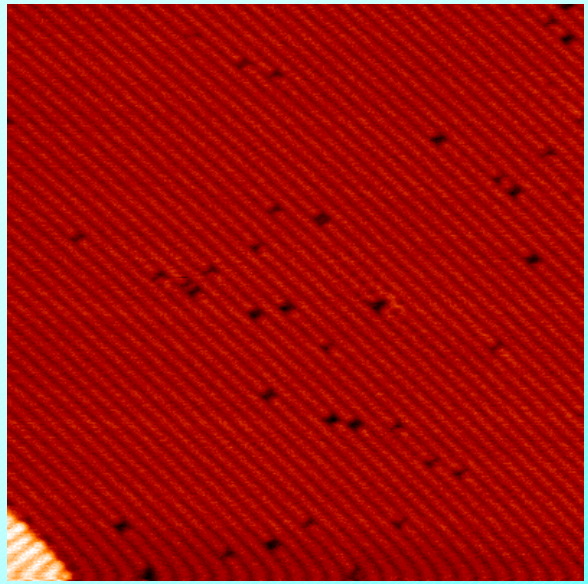
30 nm × 30 nm



ads. to ~1ML under same

dosing condition

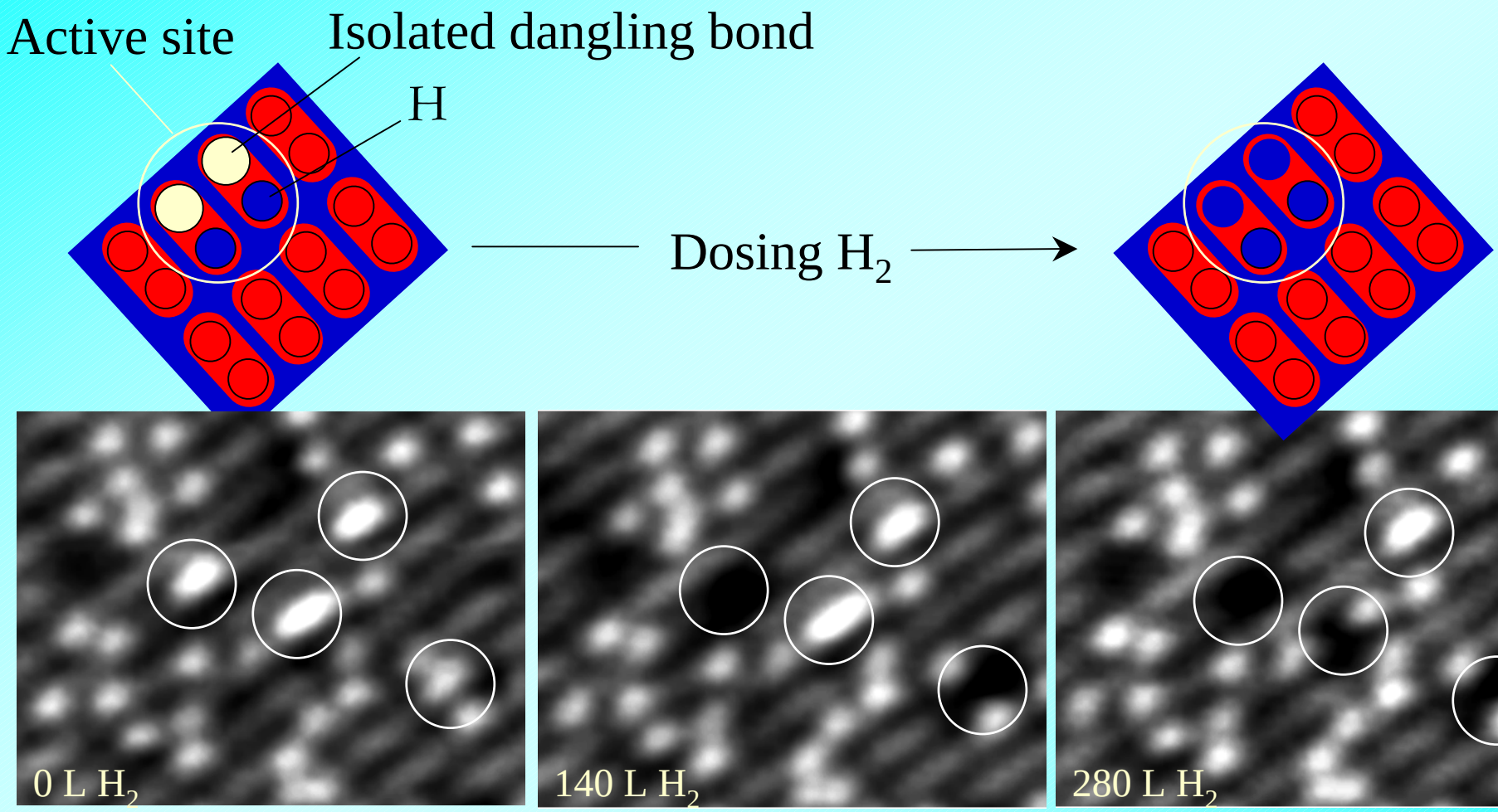
30 nm × 30 nm



after TPD to 780K

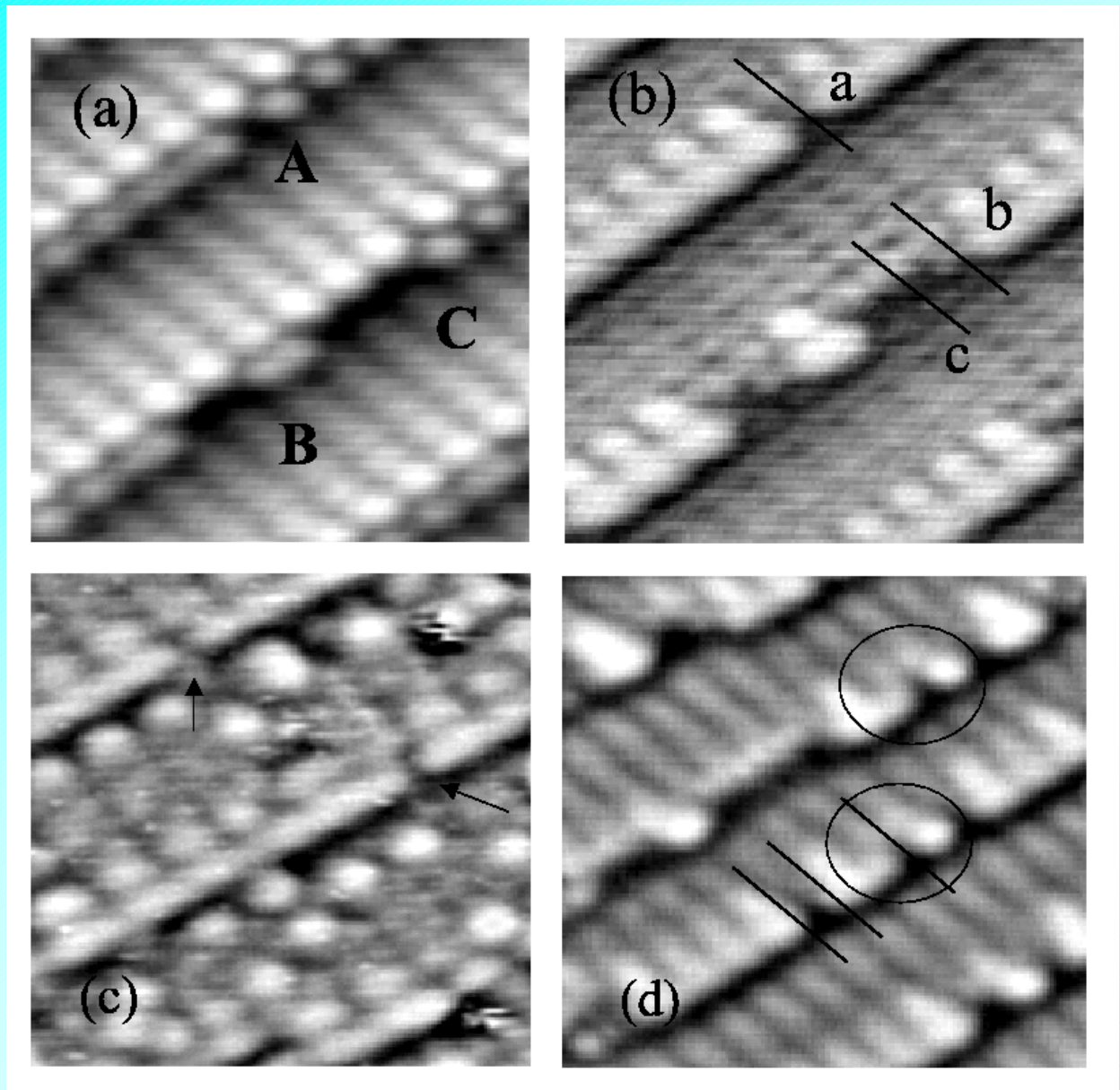
defect/contamination ~ 0.8%

Enhanced H_2 adsorption at specific sites on H/Si(001)



$S_{enh} \sim 8 \times 10^{-4} >> S_{1st}$

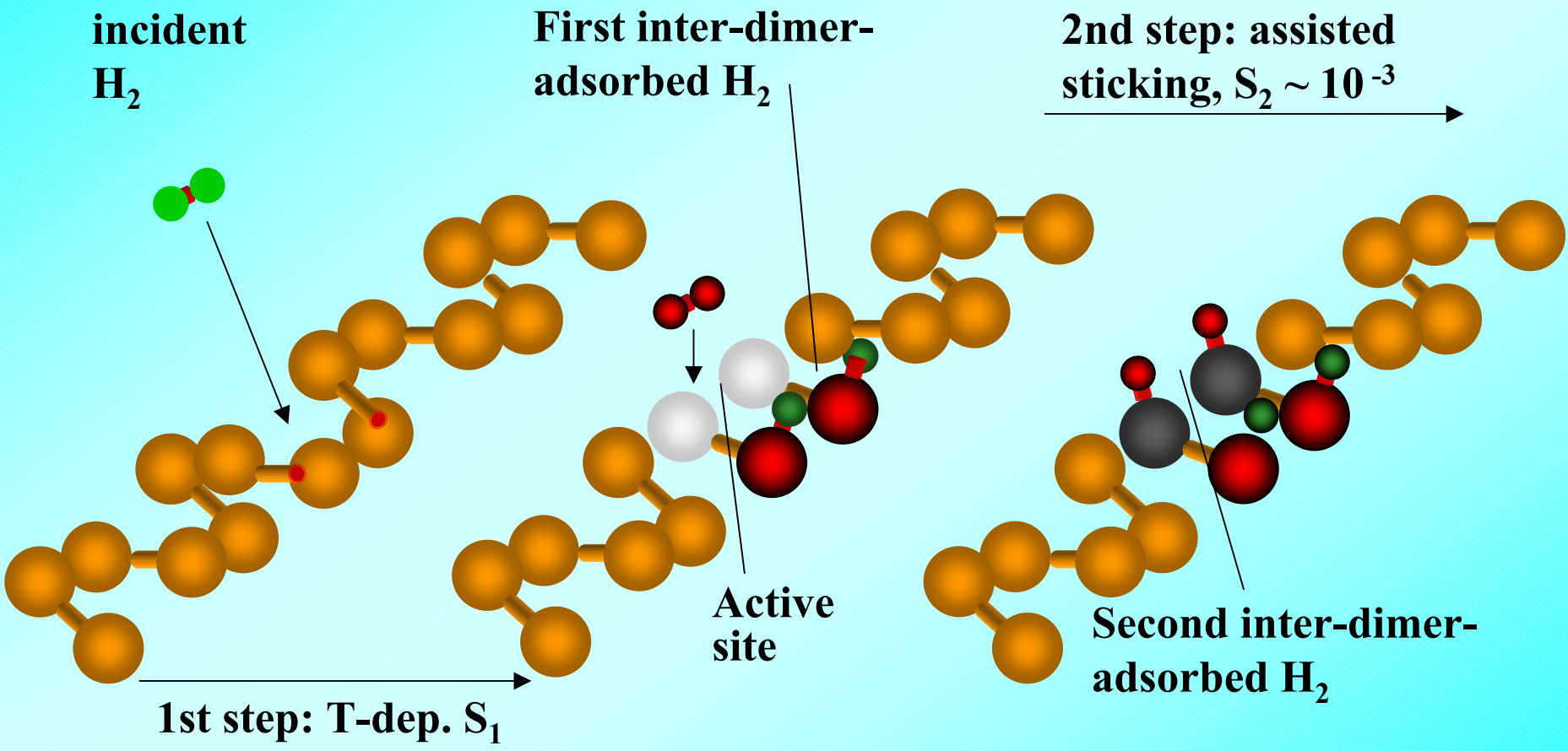
STM *images showing H_2 adsorption on D_B step sites*



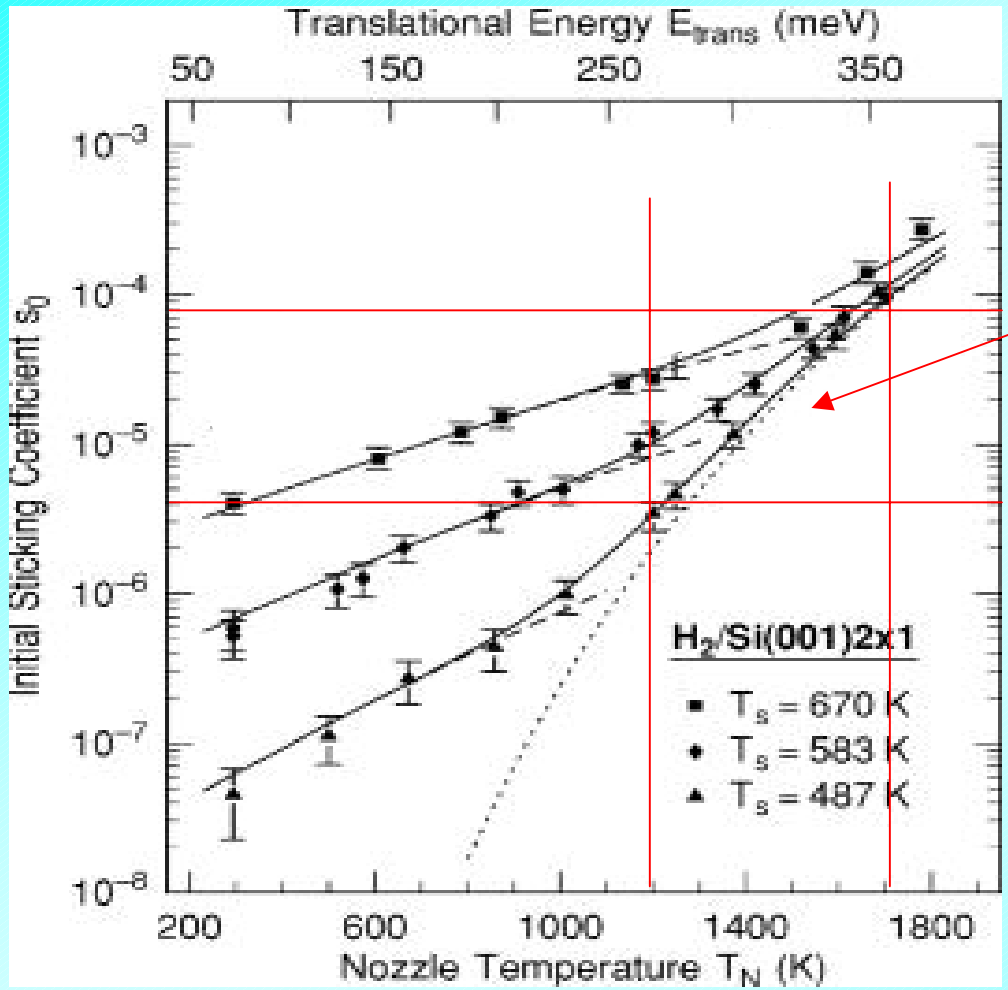
Enhanced sticking coefficient on D_B step sites over flat terrace:

$S_0 \sim 4 \times 10^{-4}$

Adsorption pathway



Considerations about nozzle temperature



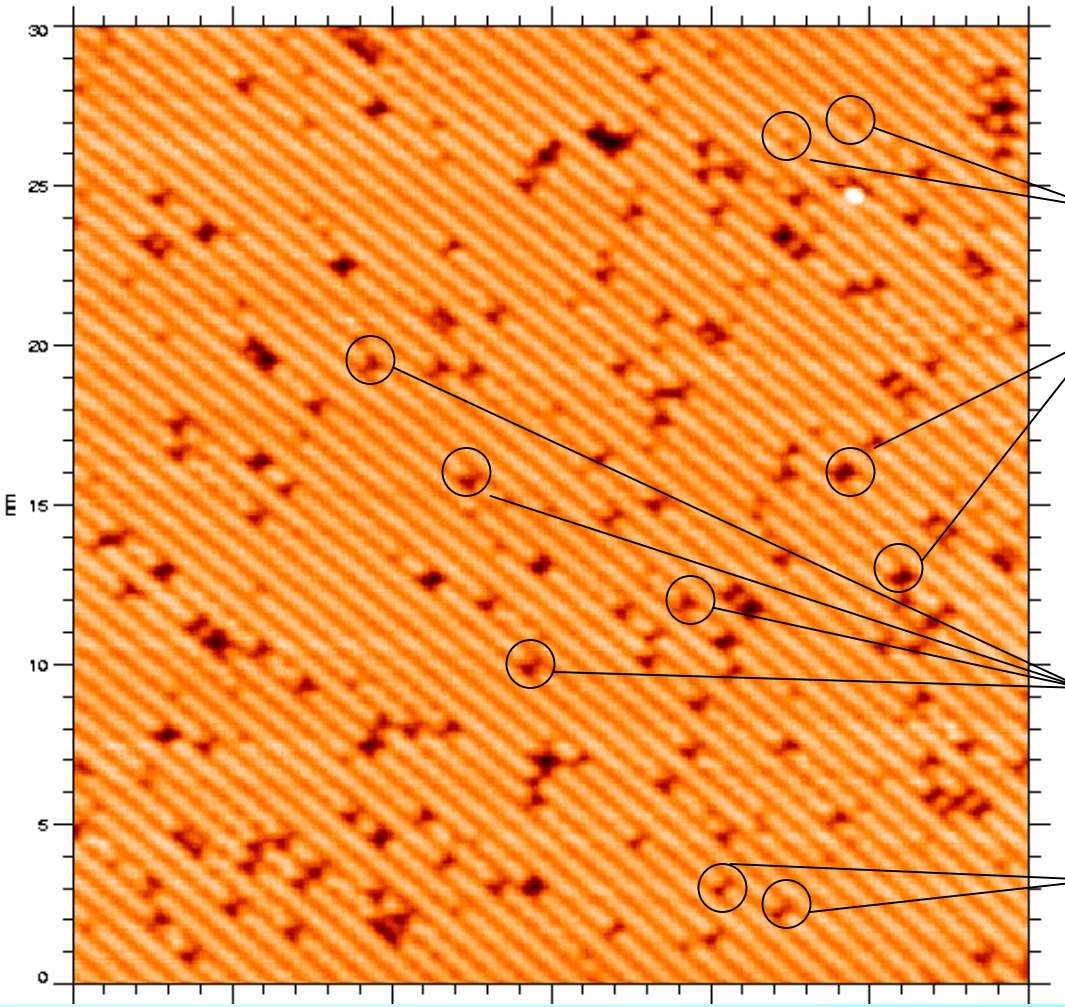
area having a chance

→ T_n < 1600K to avoid H adsorption

→ Optimal exposure so that $S_{1st} > S_{enh}\,\theta$ ($S_1 > S_2\,\theta$)

M.Duerr *et. al.*, J. Chem. Phys. 111, 10411 (1999)

Initial sticking configuration of H_2 on clean Si(001)



H_2 exposure: ~ 800 L H_2

T_s ~ 400 K, T_n ~ 1300 K

1H configuration ~ 1% of total sites

4H configuration ~ 1.5%

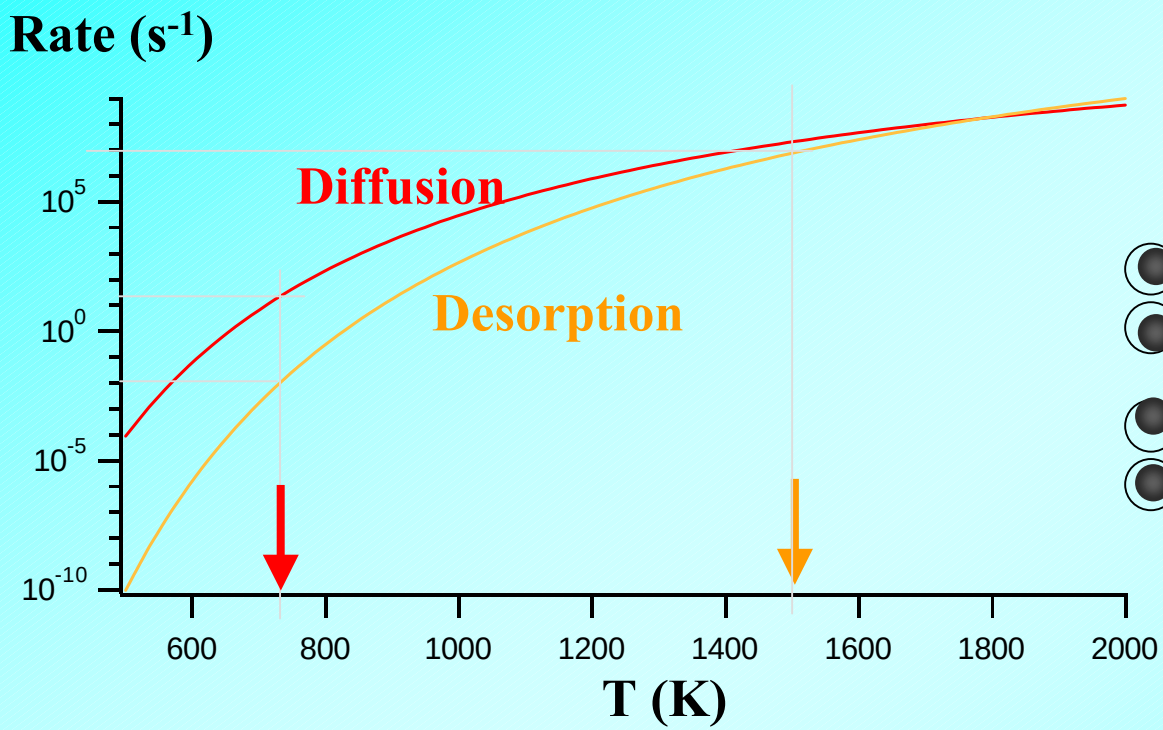
2H interdimer configuration ~ 3%

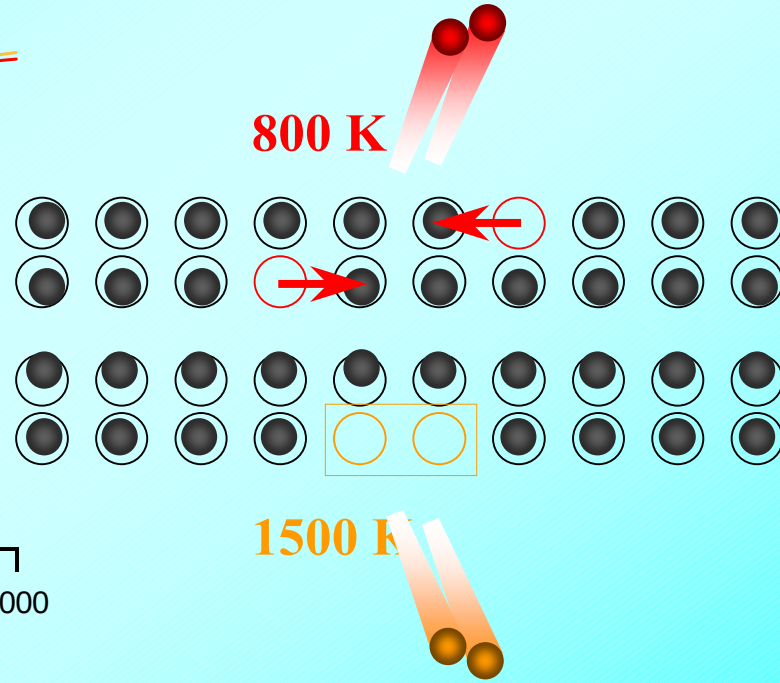
= 2.6% + 0.4% defects/contamination

2H intradimer configuration ~ 0.5%

= 0.3% + 0.2% defects/contamination

Outrunning diffusion



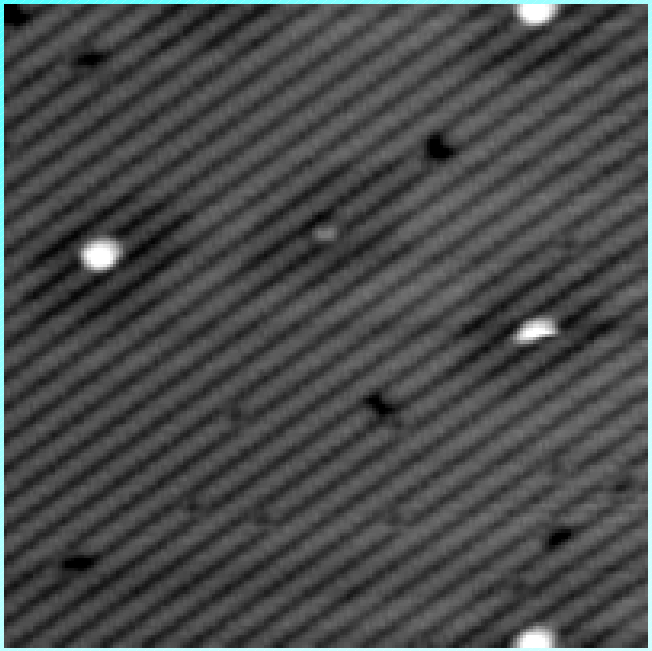


At 1500 K, desorption rate and diffusion rate comparable, ~ 10^{7} s^{-1}

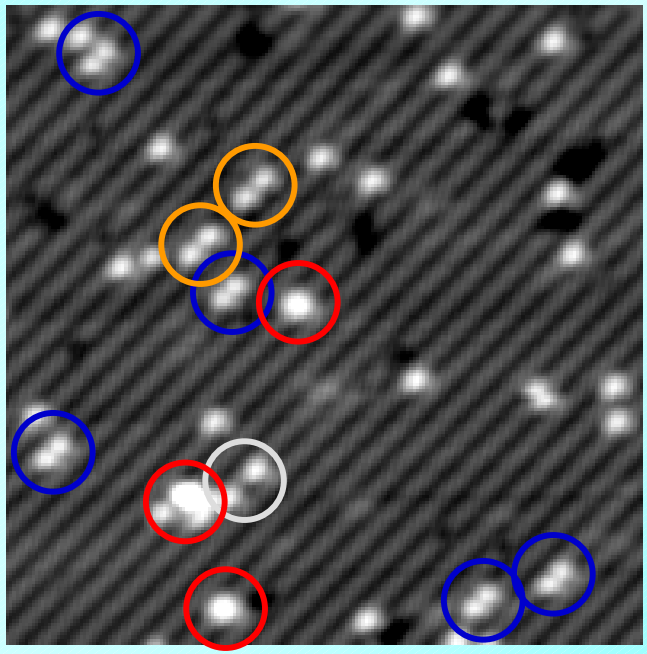
— need T flash to 1500 K for several ns — LITD to see initial desorption sites

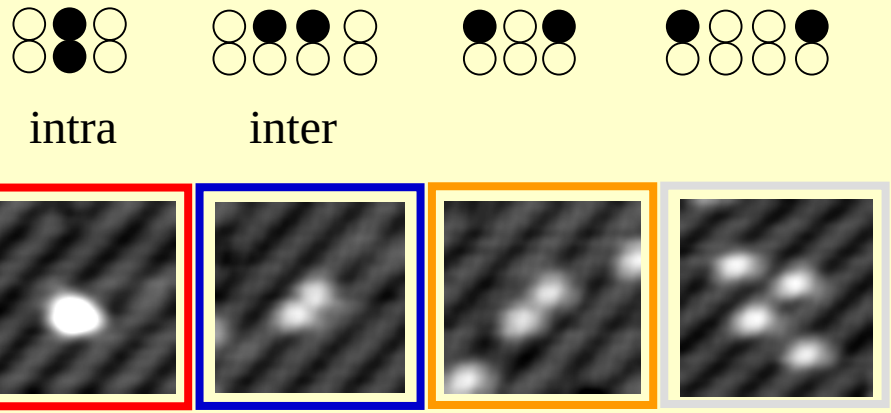
Surface before and after pulse

before

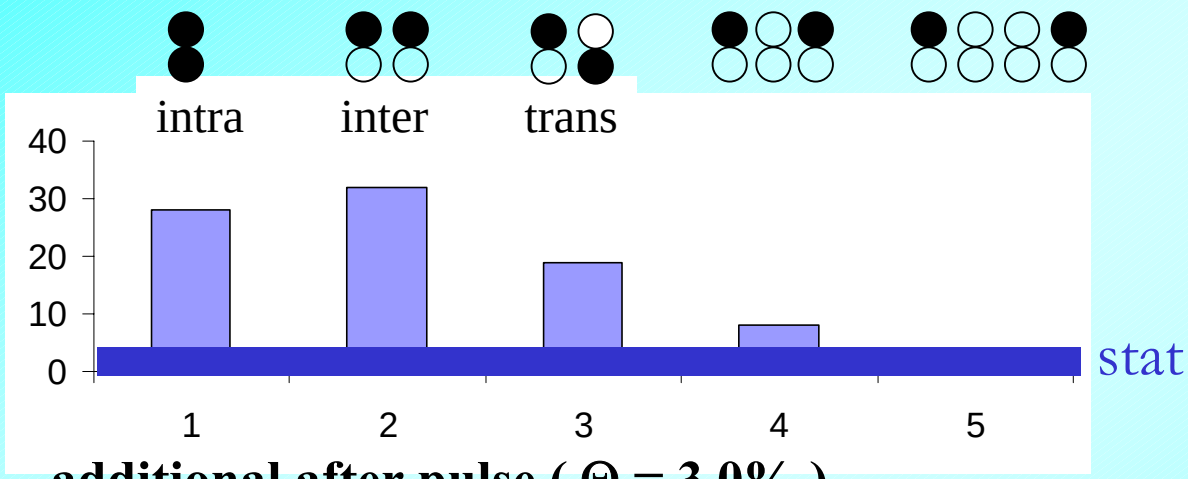


after





Direct counting and quantitative evaluation results



additional after pulse (Θ = 3.0%)

- **inter-dimer vacancy pairs more than intra-dimer pairs**
- **inter-dimer vacancy pairs 8 times higher than statistical value**

→ inter-dimer desorption pathway exsists

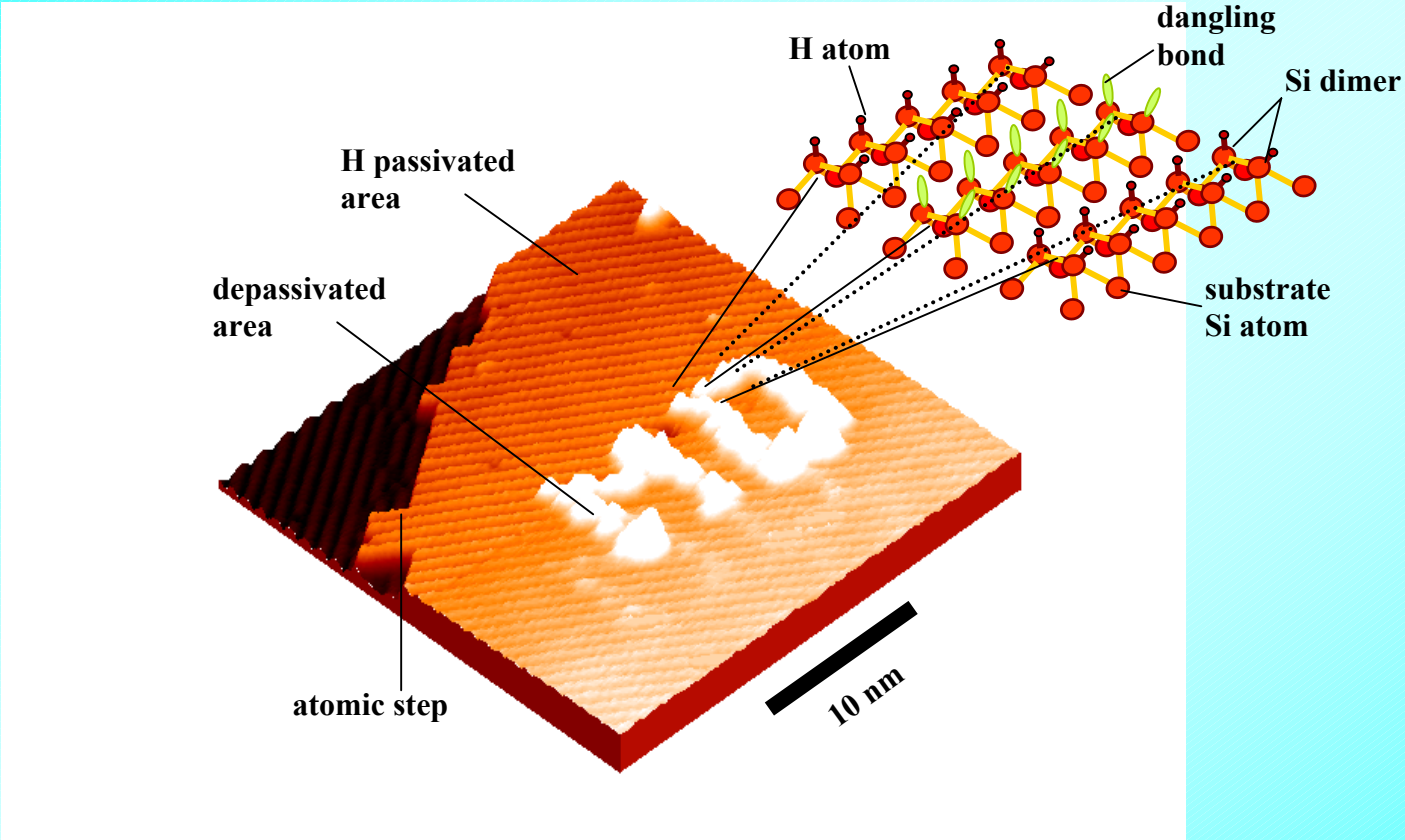
Conclusions

Dynamics of interaction between H_2 and Si(001) surface

- **Enhanced sticking probabilities up to 10 orders of magnitude higher on specific sites (STM, TPD, SHG)**
- **Interdimer pathway of H_2 adsorption preferred over intradimer pathway (STM, MB)**
- **Evidence for interdimer desorption pathway observed (STM, LITD)**

→ Studies of adsorption indicate strong coupling with surface phonons in the interdimer pathway, better explains the strong dependence on $T_{surface}$

A promising technique for nano-fabrication



Si(100)2 x 1 : H surface with STM depassivated pattern of letters “M” and “D”

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Thank you for your attention!