H atom cluster formation and recombination on the graphite (0001) surface

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University of Aarhus, Denmark

Eagle-Nebula

10-1000 K, 100-10.000 atoms/cm^3

Cloud composition

Atoms:

H, He, O, C, N, Ne, Si, Mg, S, Fe ...

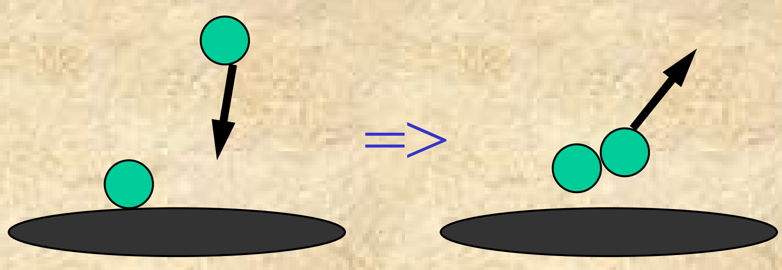
~130 Molecules:

H_2, CO, H_2O, CO_2, O_2, NH_3, CH_3OH ...

Sugars: glycolaldehyde (CH_2OHCHO)

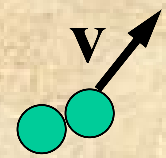
Dust grains

Energy branching in H_2 formation ?

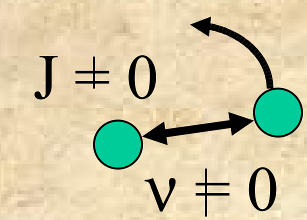


$E_{released} \sim 4.5$ eV

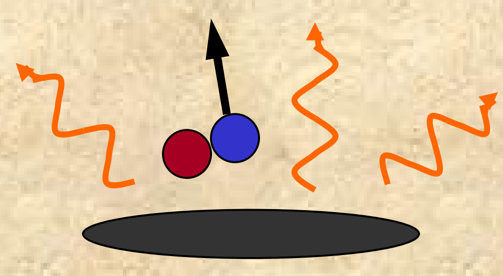
Into:



Kinetic energy ?

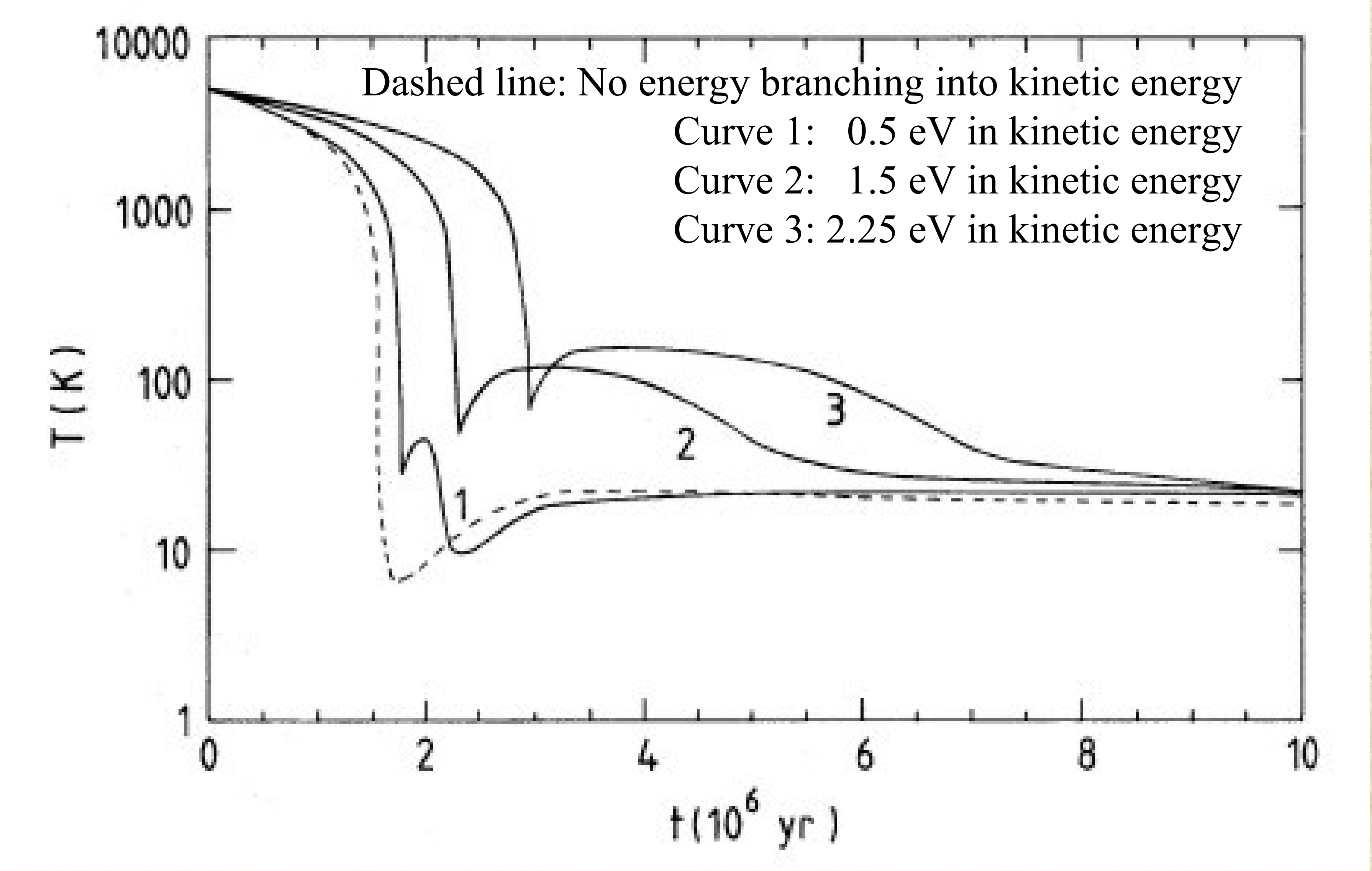


Molecular excitation ?



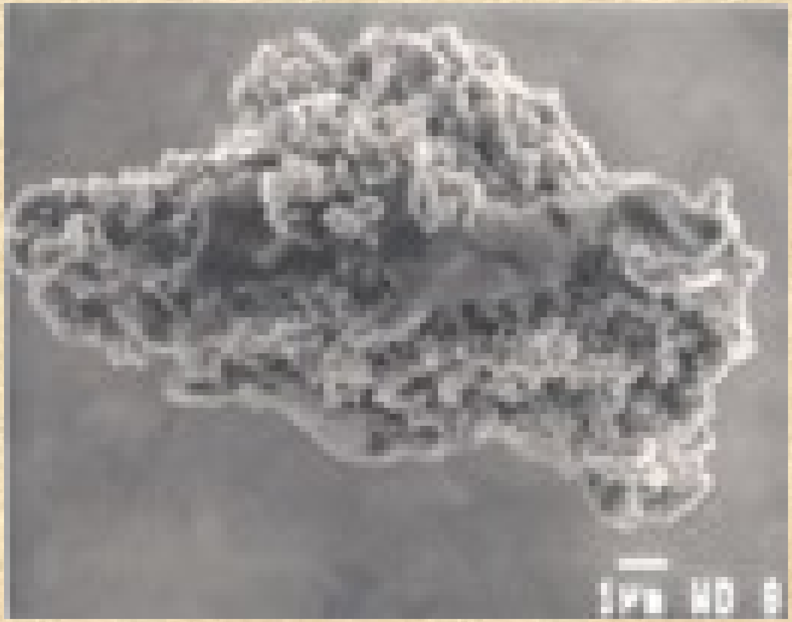
Grain heating ?

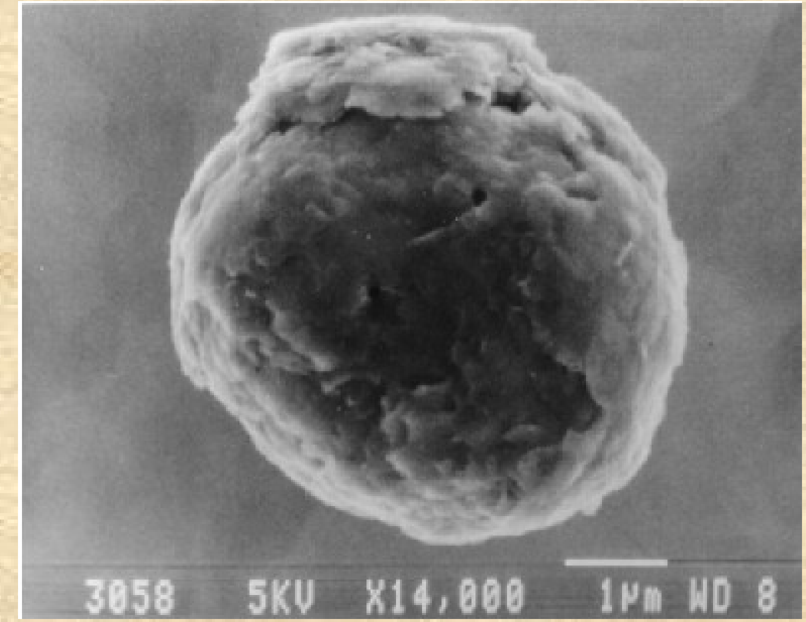
Energy release in H_2 formation and the thermal evolution of interstellar clouds



Flower & des Forêts, MNRAS 247, 500 (1990)

Dust grains





Carbonaceous grains: Graphite, Amorphous Carbon, HAC, PAH, Polymeric Carbon, Diamond

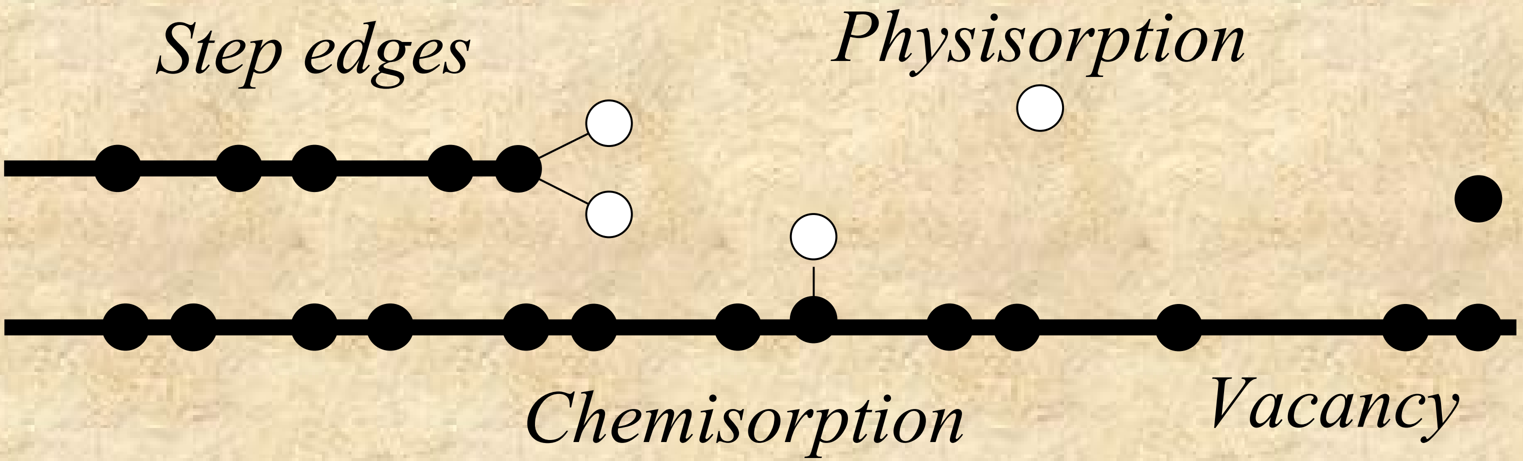
Silicates:

Olivines (Mg_2SiO_4, Fe_2Si0_4)

Ices:

H_2O, CO, CO_2, CH_3OH, CH_4, H_2CO ...

Binding sites on graphitic surfaces



Physisorption: Creighan et al, J. Chem. Phys. 124, 114701 (2006)

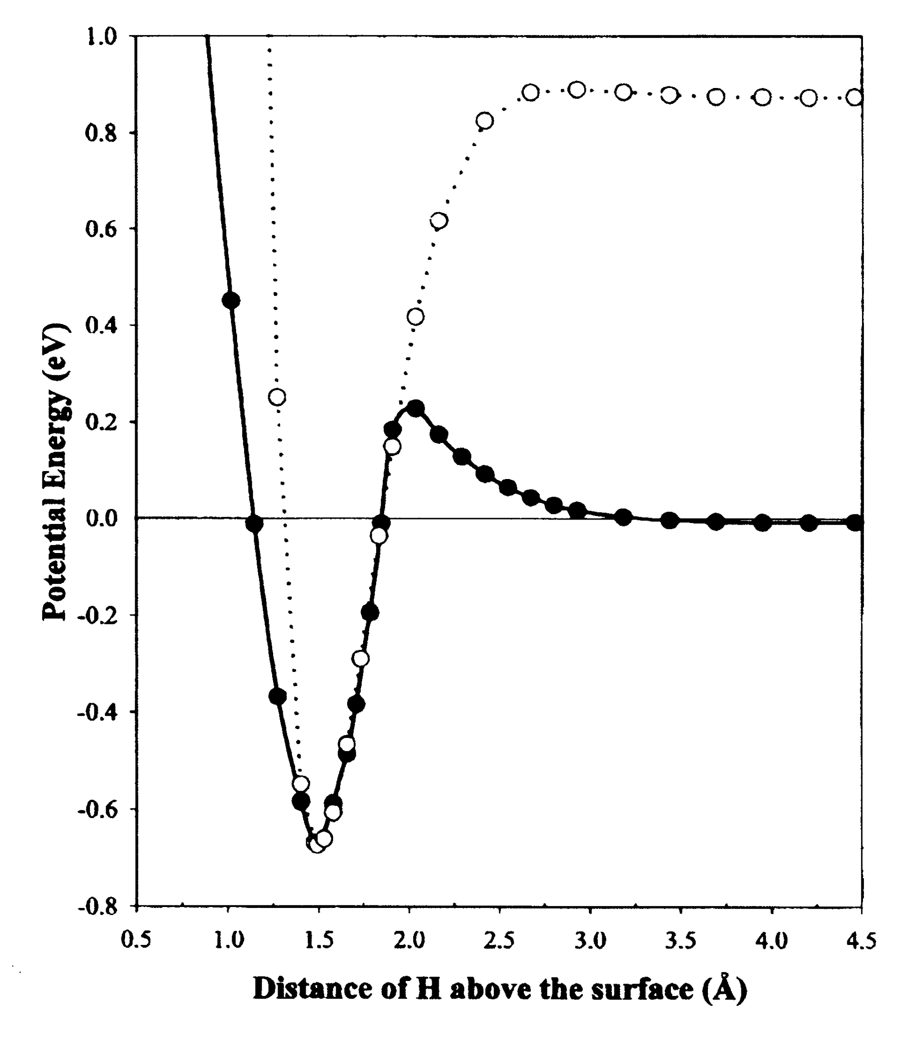
Chemisorption - basal plane: Jeloica & Sidis, Chem. Phys. Lett. 300, 157 (1999)

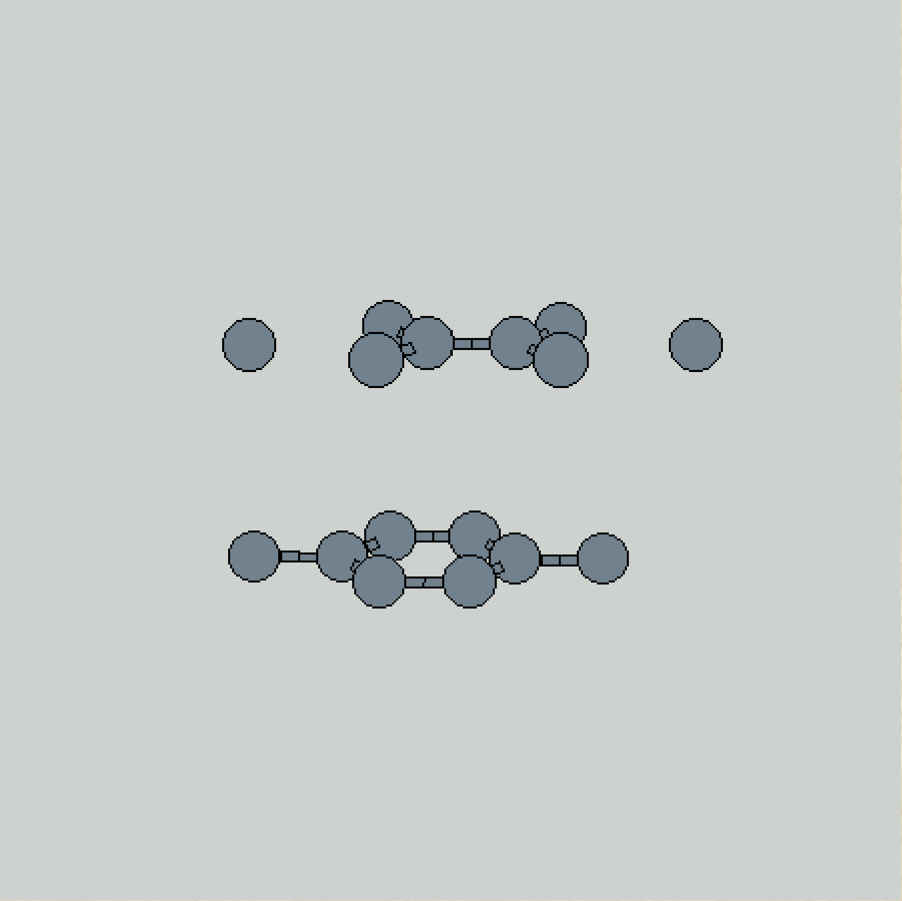
Chemisorption at defects: Sha et al, J. Am. Chem. Soc. 126, 13095 (2004)

Güttler et al, Surface Science 570, 218 (2004)

H chemisorbed on HOPG

Jeloica & Sidis, Chem. Phys. Lett. 300, 157 (1999)

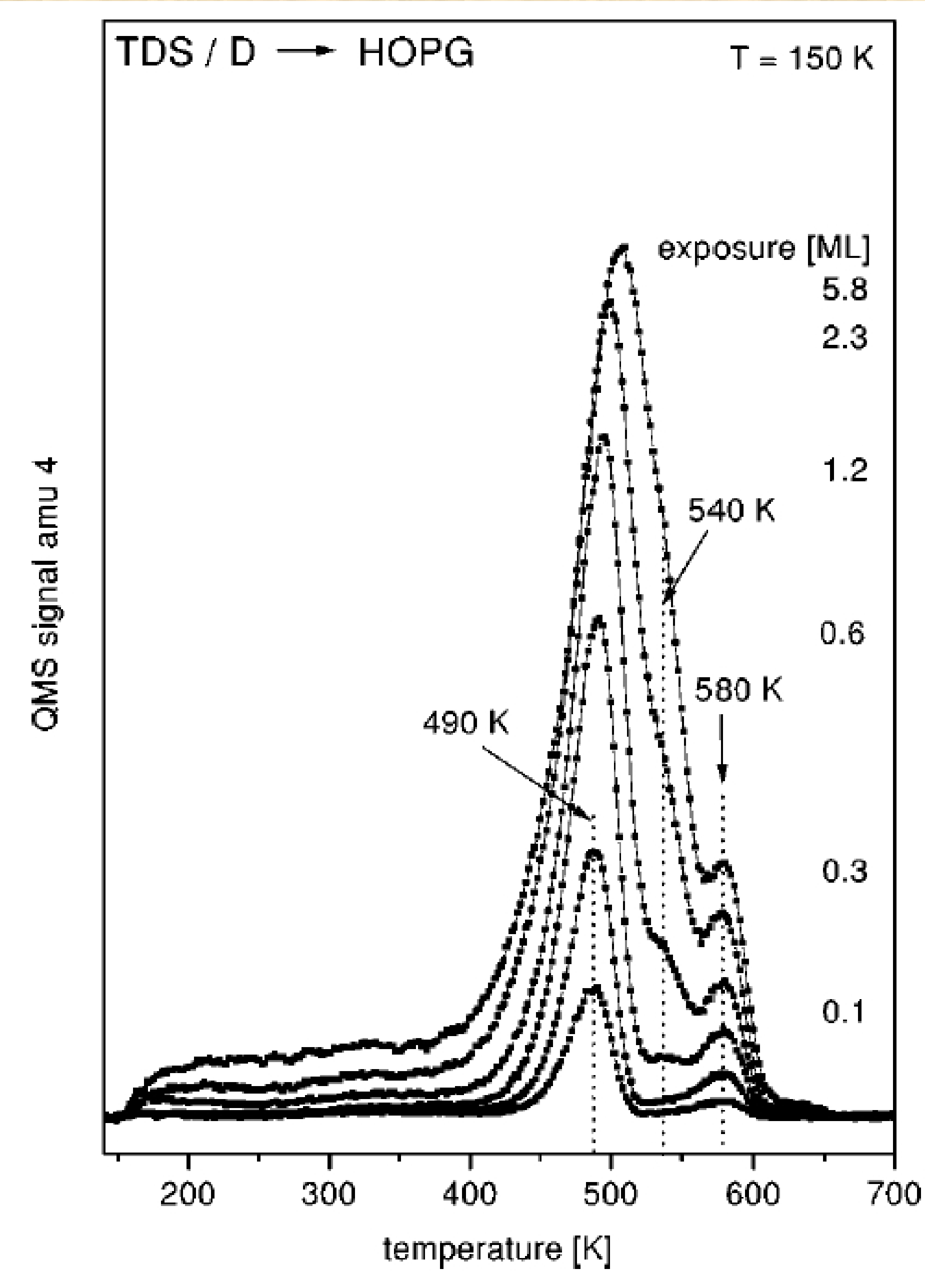




Eva Rauls

Brett Jackson et al.

H_2 formation on graphite



$$\frac{d\Theta}{dt} = -k_0\, e^{-E_B/k_B T}\, \Theta^n$$

n=1

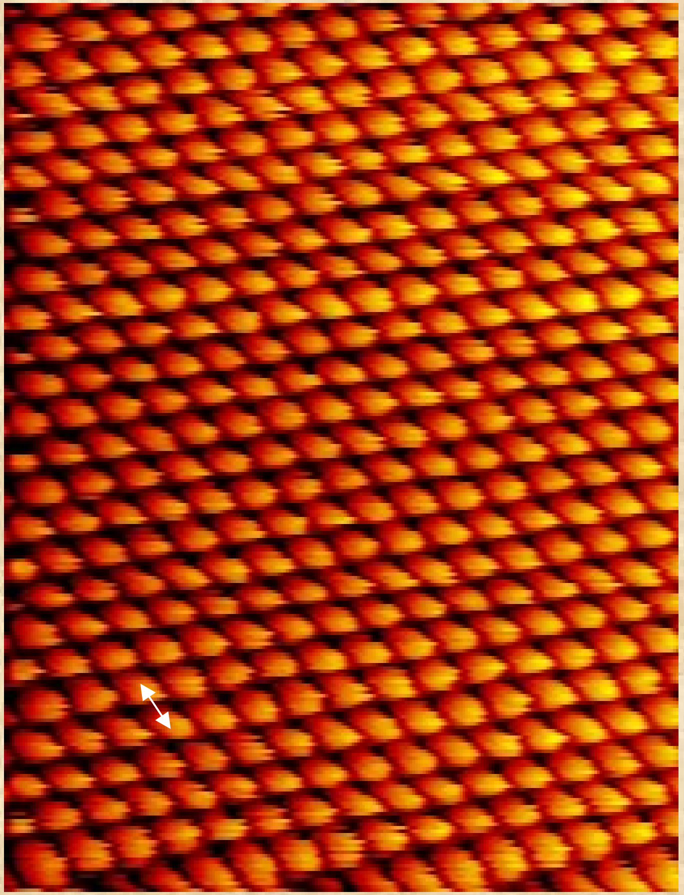
=> First order desorption

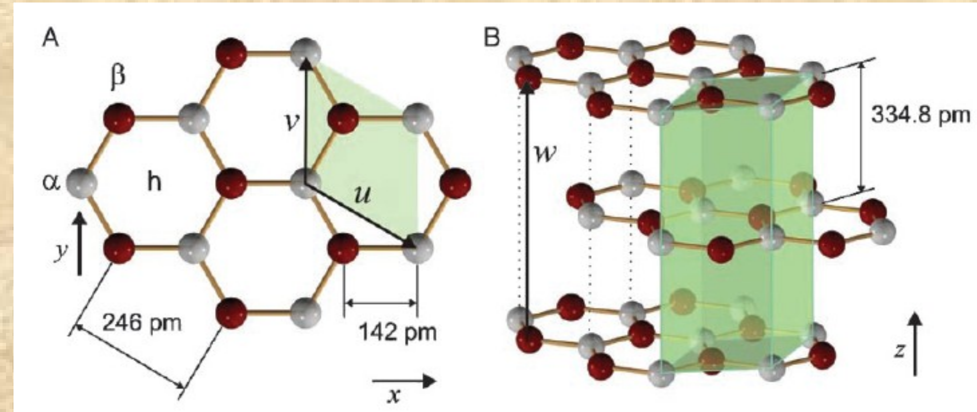
490 K => 1.4 eV

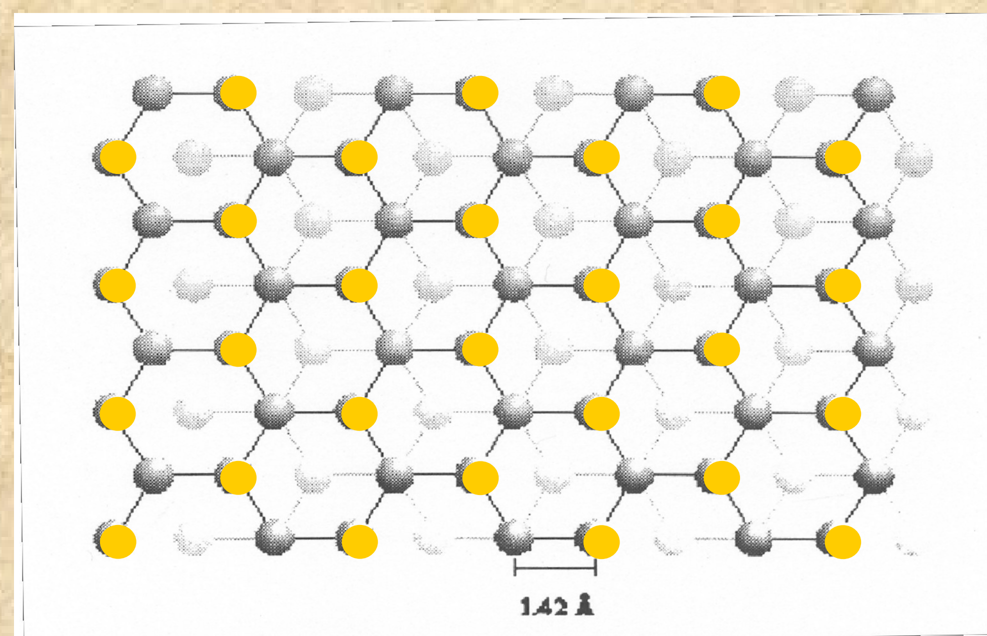
580 K => 1.6 eV

Zecho et al, J. Chem. Phys. 117, 8486 (2002)

STM on graphite

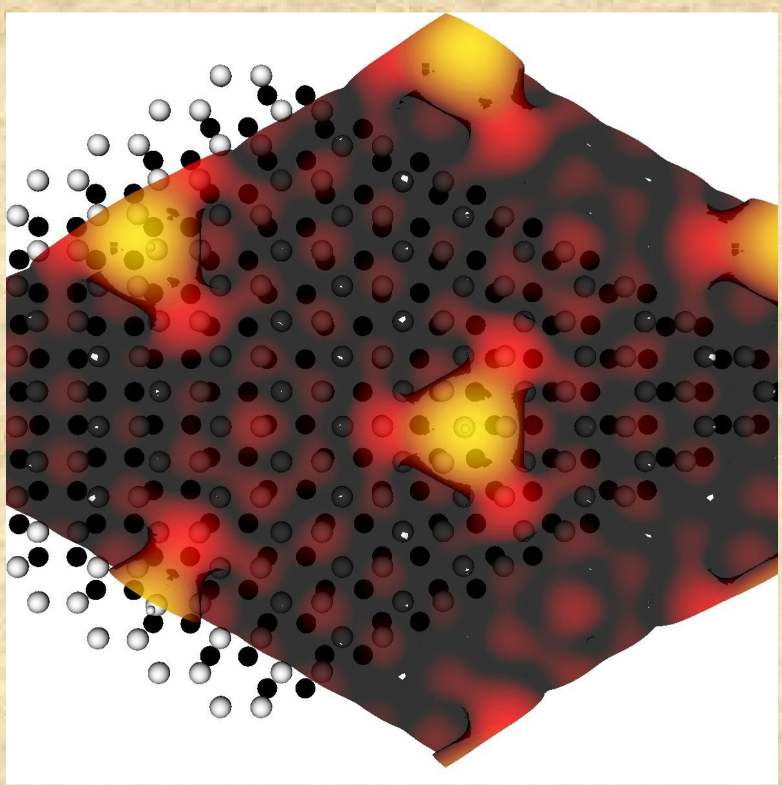




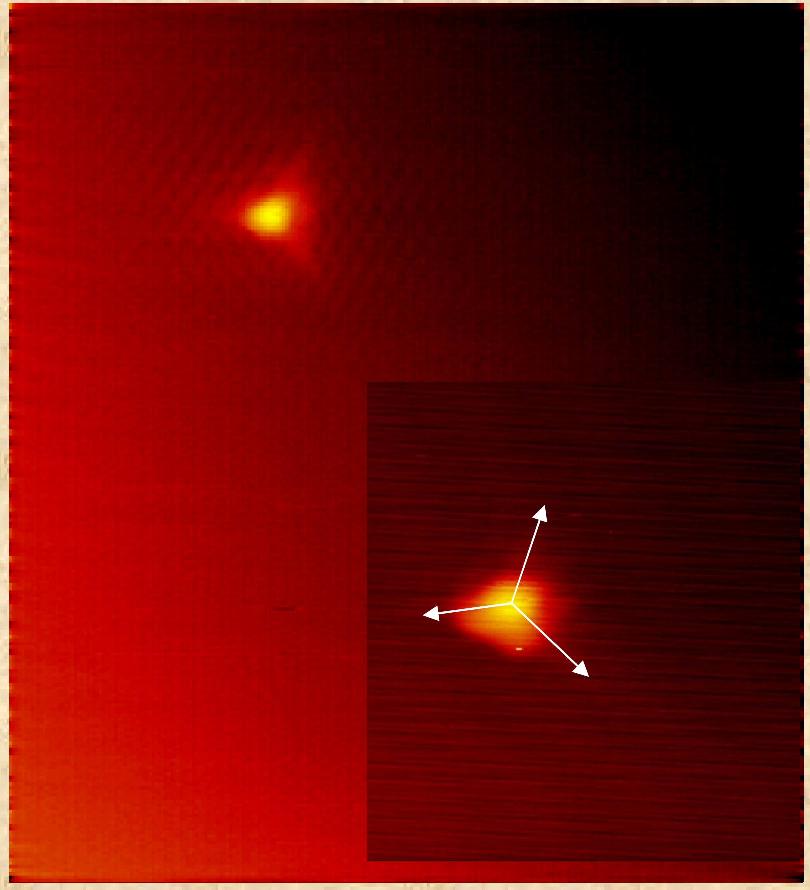


↕ 2.46 Å

Hydrogen on graphite –Monomers



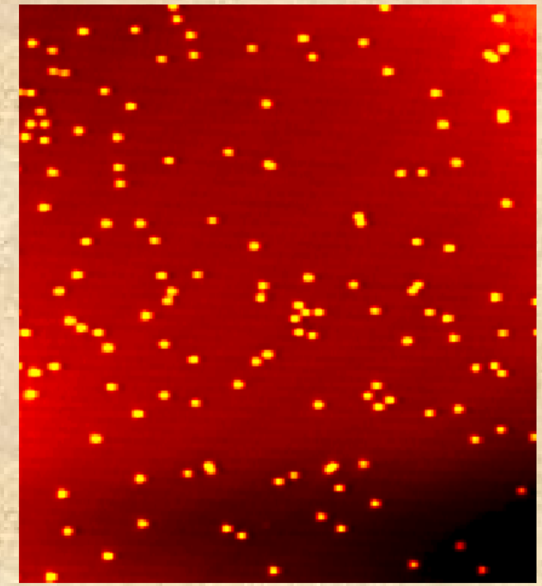
Zeljko Sljivancanin



155 x 171 Å^2 , 180 K
V_t~ -710mV, I_t~ -0.16nA

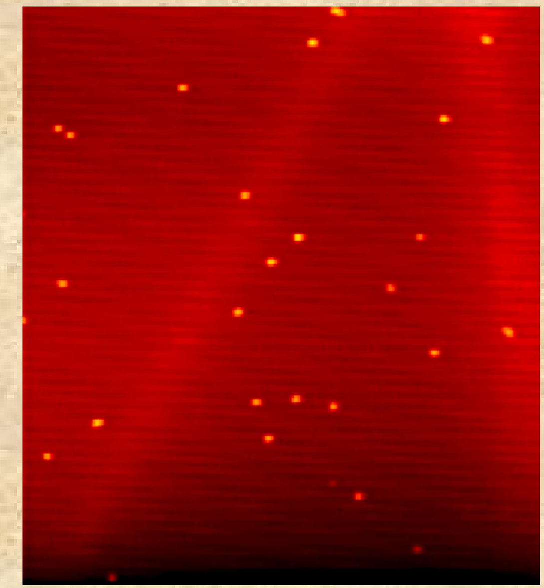
Monomer desorption

Flux:
10^{12} $cm^{-2}s^{-1}$
Θ~0.03%
STM at
~180 K



1030 x 1140 Å^2

RT → 20%



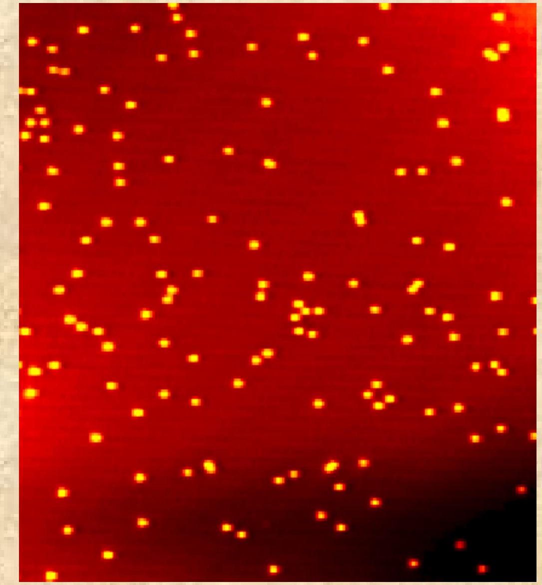
1030 x 1140 Å^2

Experiment: Upper limit: τ = 6 min.

Theory: E_b = 0.9 eV, ν = 10^{13} s^{-1} => τ = 130 s

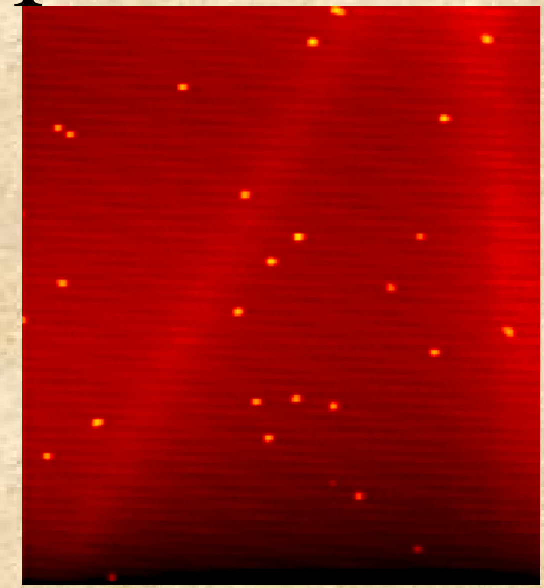
Monomer desorption

Flux:
10^{12} cm^{-2}s^{-1}
Θ~0.03%
STM at
~180 K



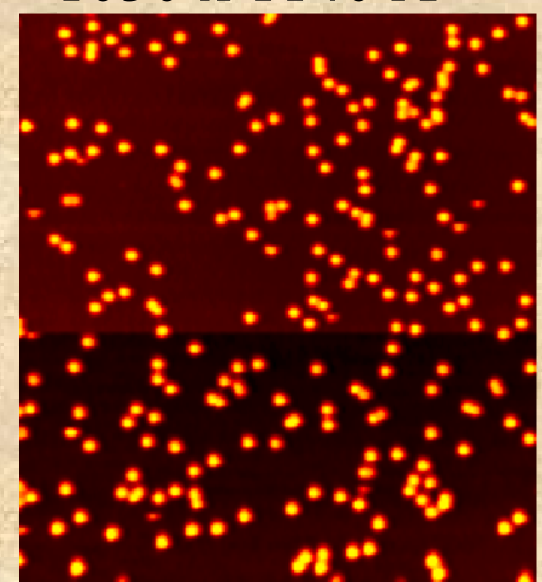
1030 x 1140 Å^2

RT → 20%



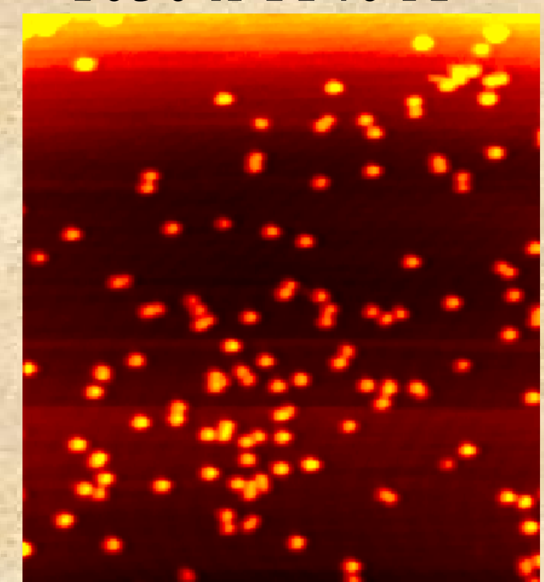
1030 x 1140 Å^2

Flux:
10^{14} cm^{-2}s^{-1}
Θ~0.2%
STM at
~170 K



1030 x 1140 Å^2

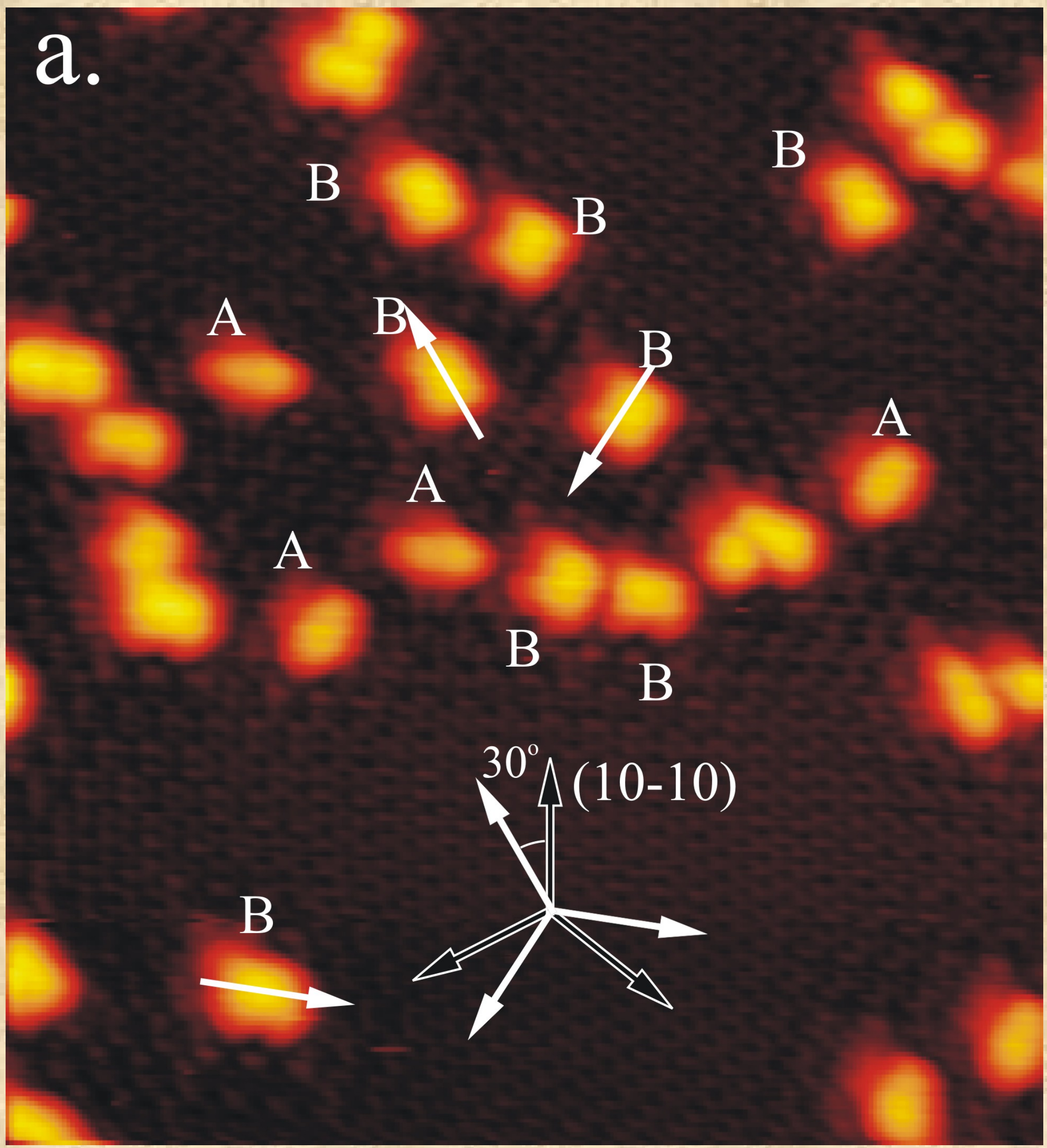
RT → 80%



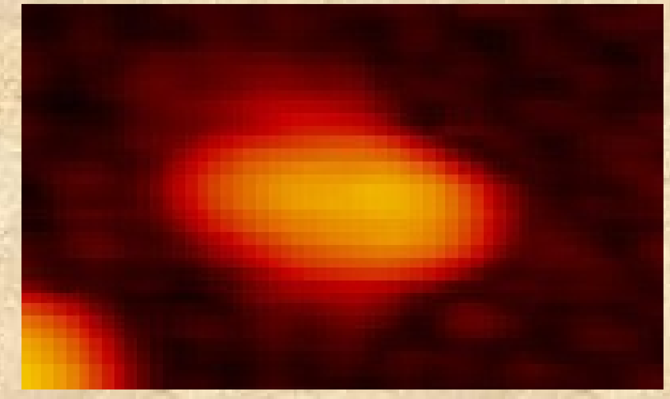
515 x 570 Å^2

H-Dimers on graphite

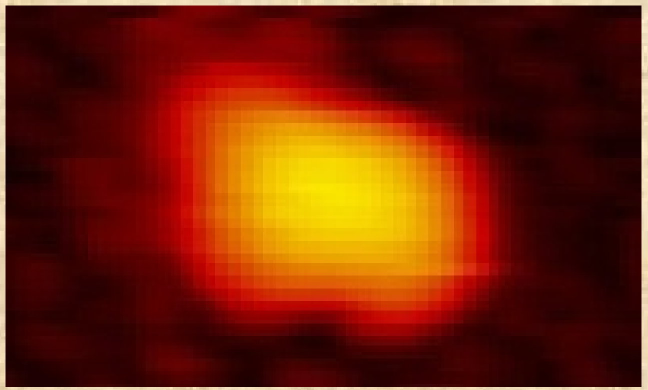
103 x 114 Å^2



Dimer A



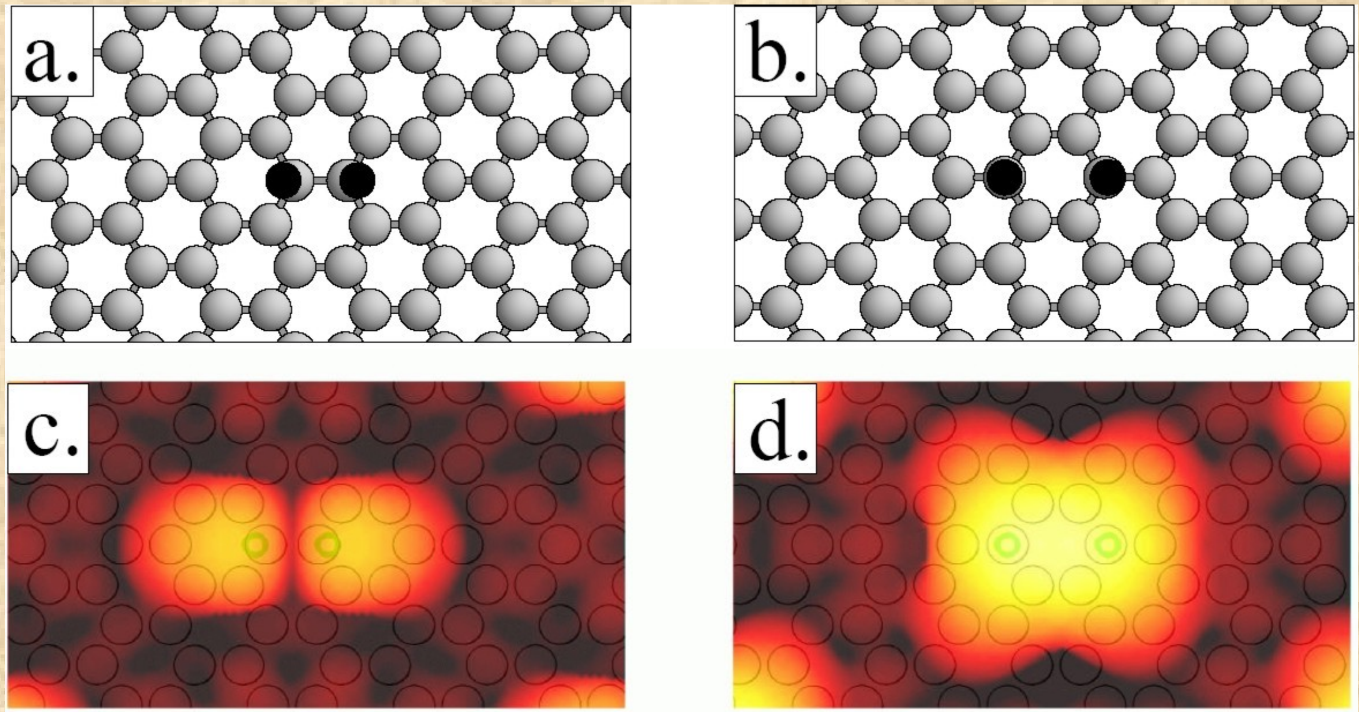
Dimer B



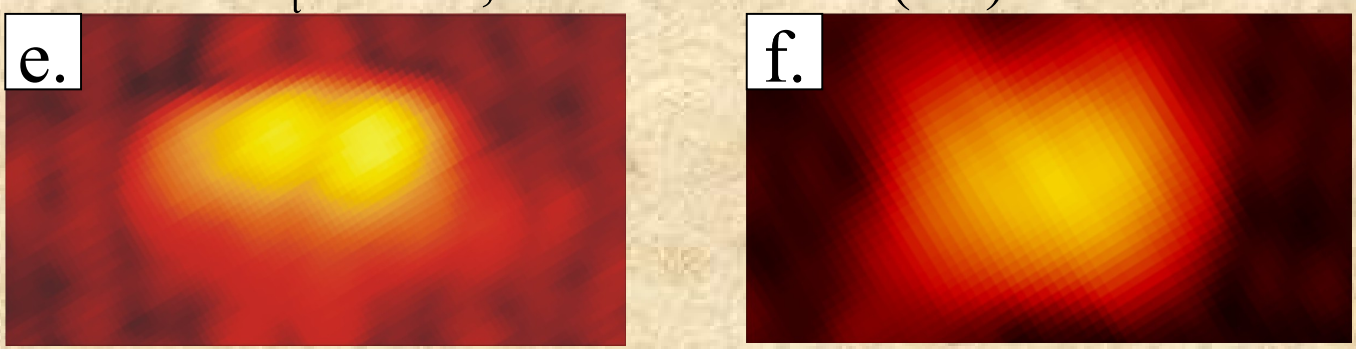
V_t = 884 mV, I_t = 0.16 nA

Dimers: Theory vs. Experiment

Ortho dimer - Dimer A   Para dimer - Dimer B



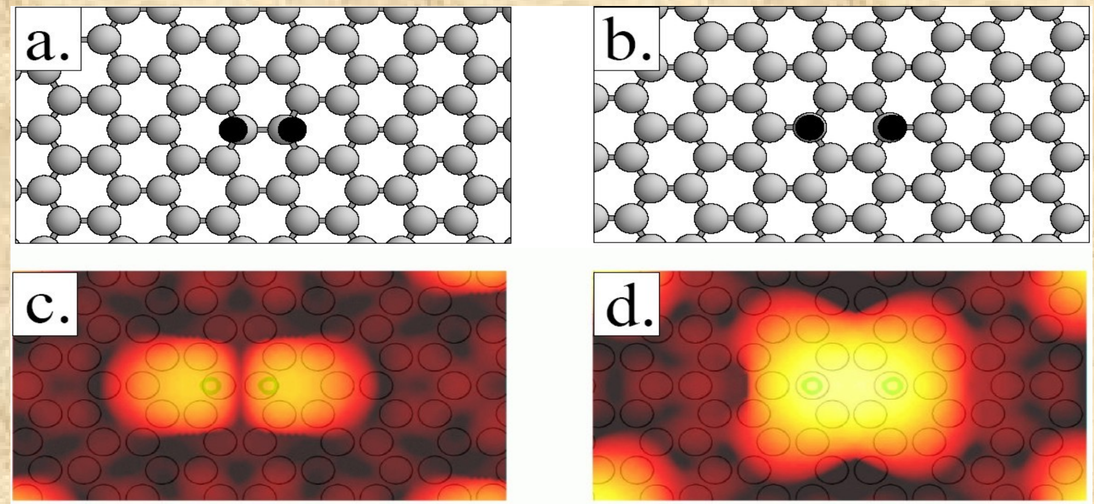
V_t=0.9 V, LDOS=1x10^{-6} (eV)$^{-1}$ Å^{-3}



V_t = 884 mV, I_t = 0.16 nA

Dimers: Theory vs. Experiment

Ortho dimer - Dimer A   Para dimer - Dimer B



V_t=0.9 V, LDOS=1x10^{-6} $(eV)^{-1}$ Å^{-3}

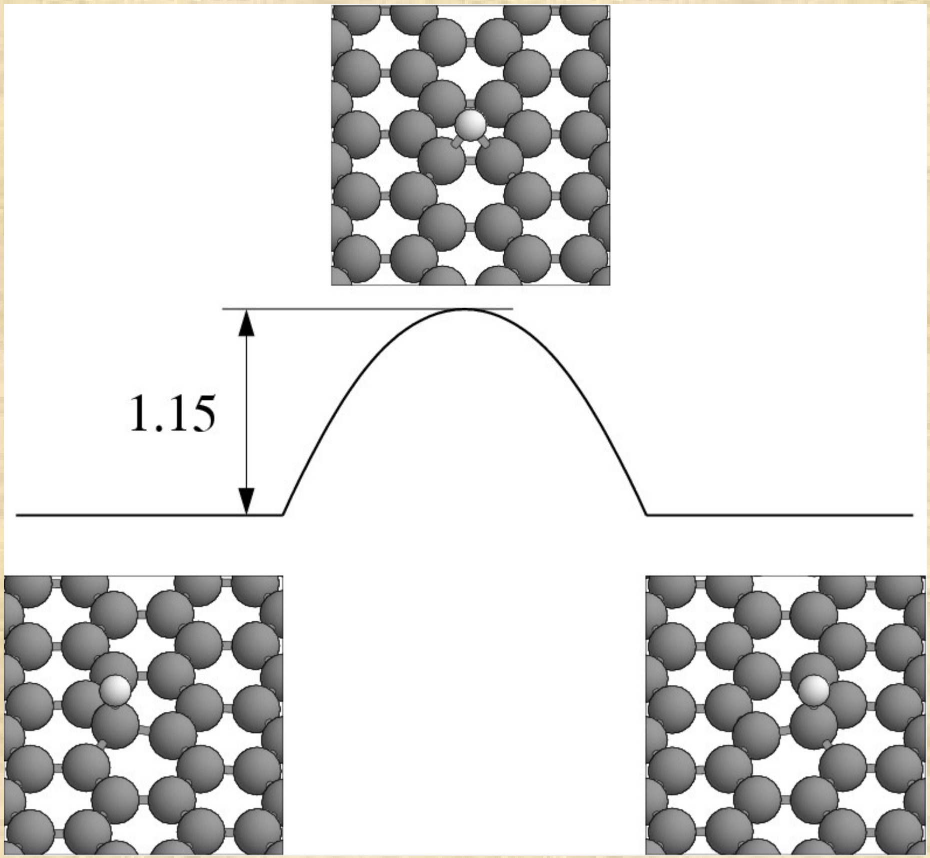
V_t = 884 mV, I_t = 0.16 nA

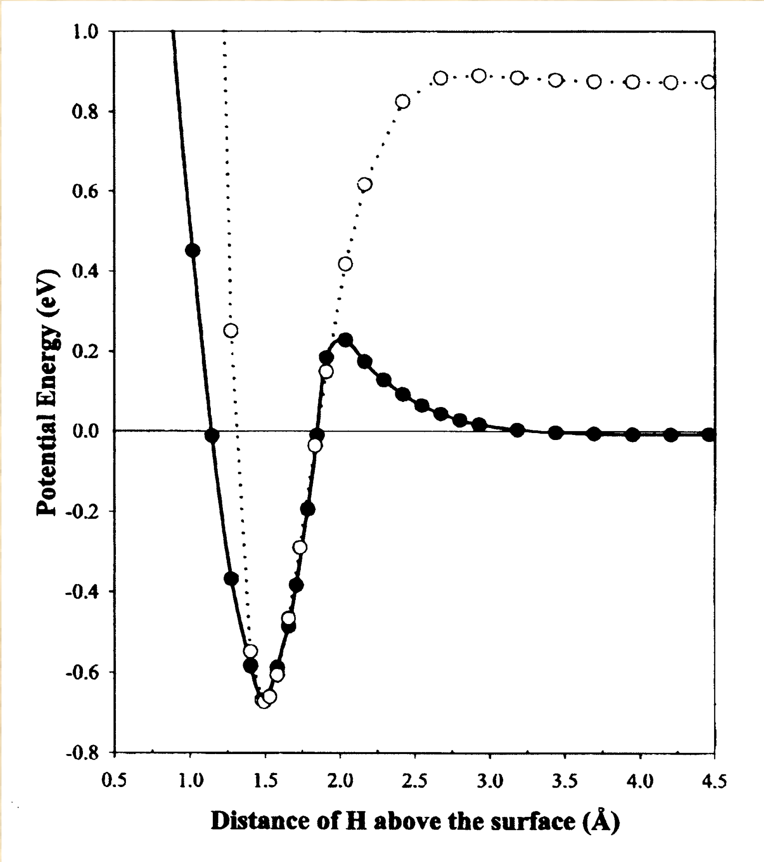
In agreement with: Y. Ferro et al., Chem. Phys. Lett. **368**, 609 (2003).
Partial agreement with: Y. Miura et al. J. Appl. Phys. **93**, 3395 (2003).

Diffusion

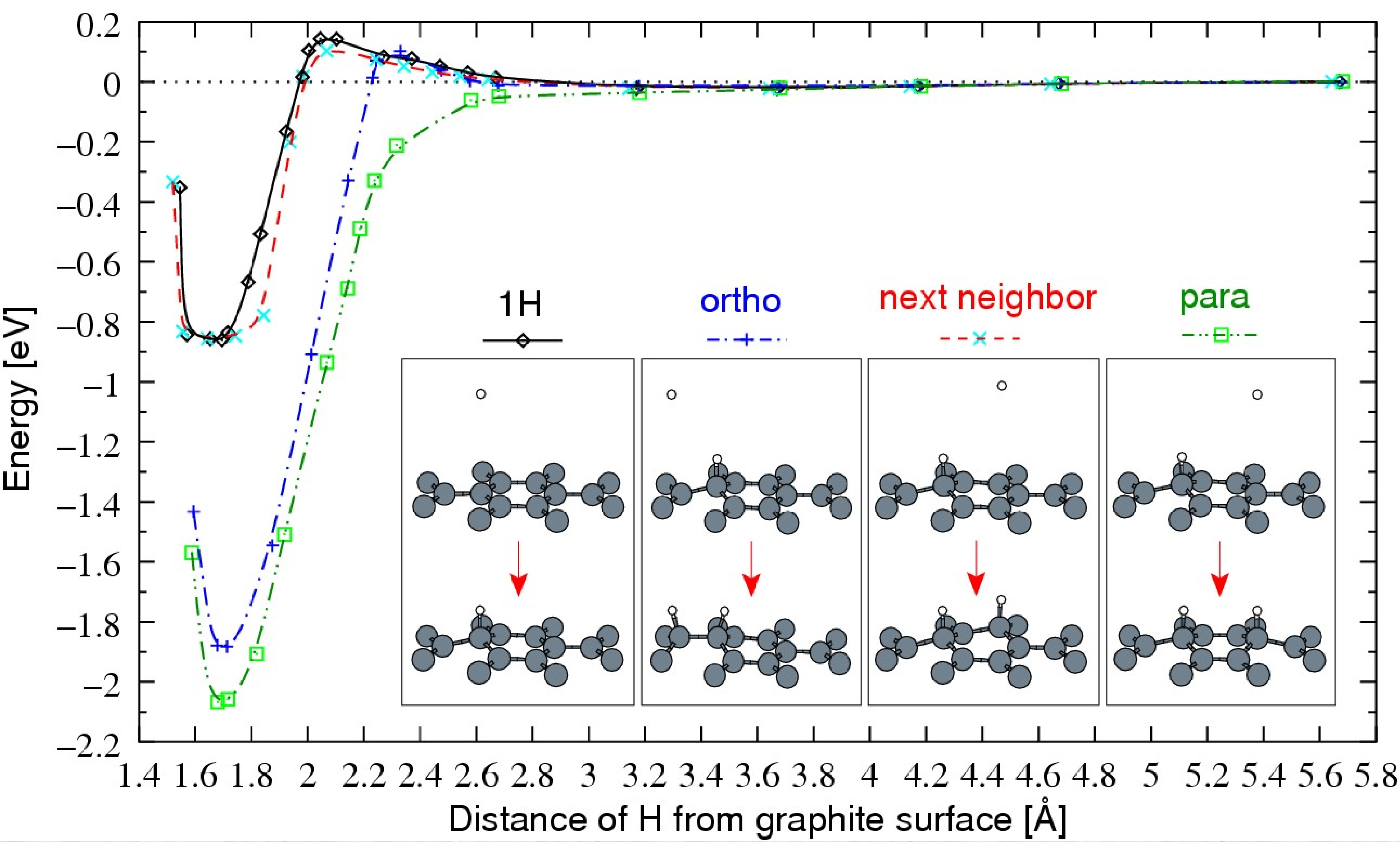
Barrier to diffusion for an isolated H atom: 1.15 eV

Barrier to desorption for an isolated H atom: 0.9 eV





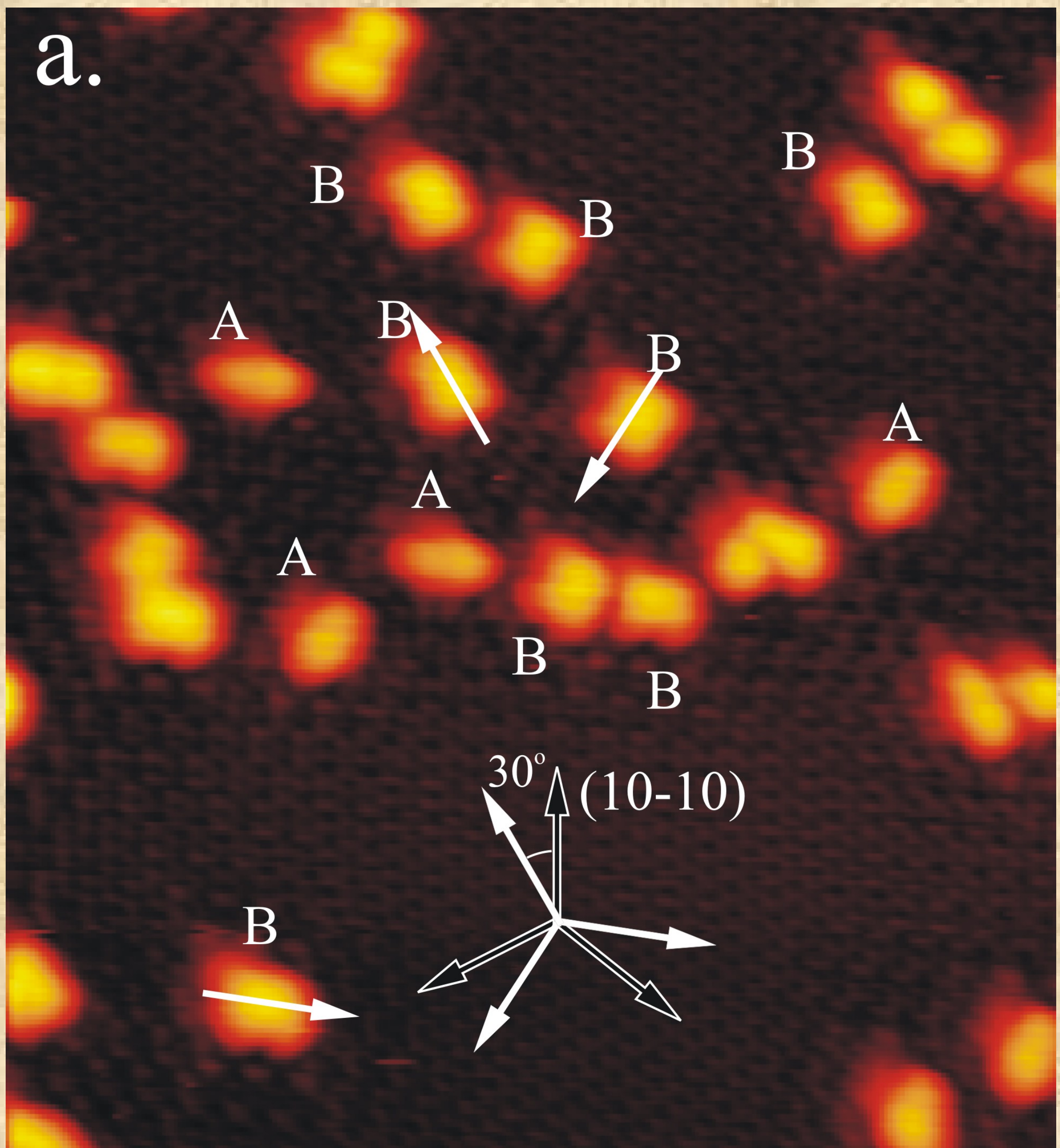
Dimer formation



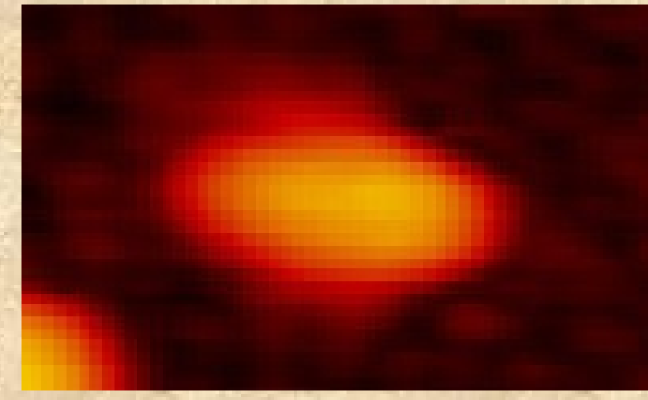
Hornekær et al. Phys. Rev. Lett. **97,** 186102 (2006)

H-Dimers on graphite

103 x 114 Å^2



A: Ortho–dimer

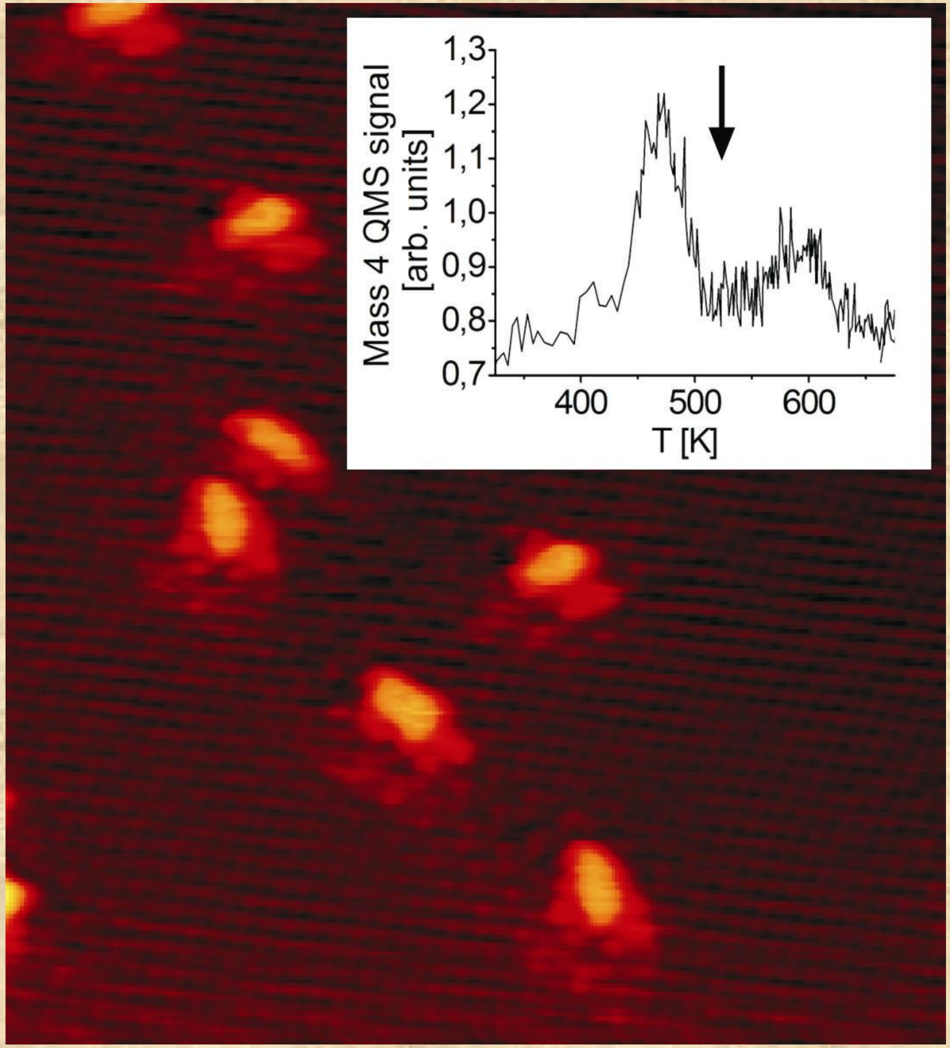


B: Para-dimer

V_t = 884 mV, I_t = 0.16 nA

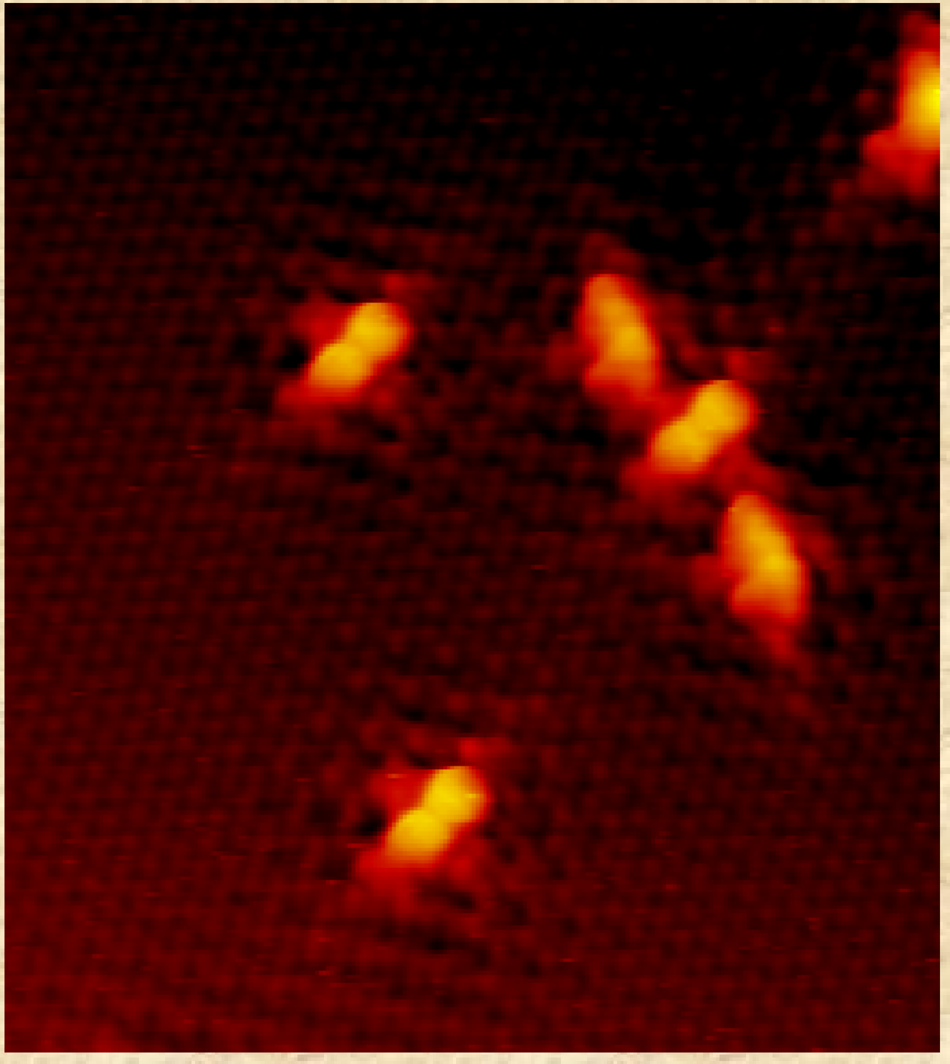
Dimers after Anneal

103 x 114 Å^2



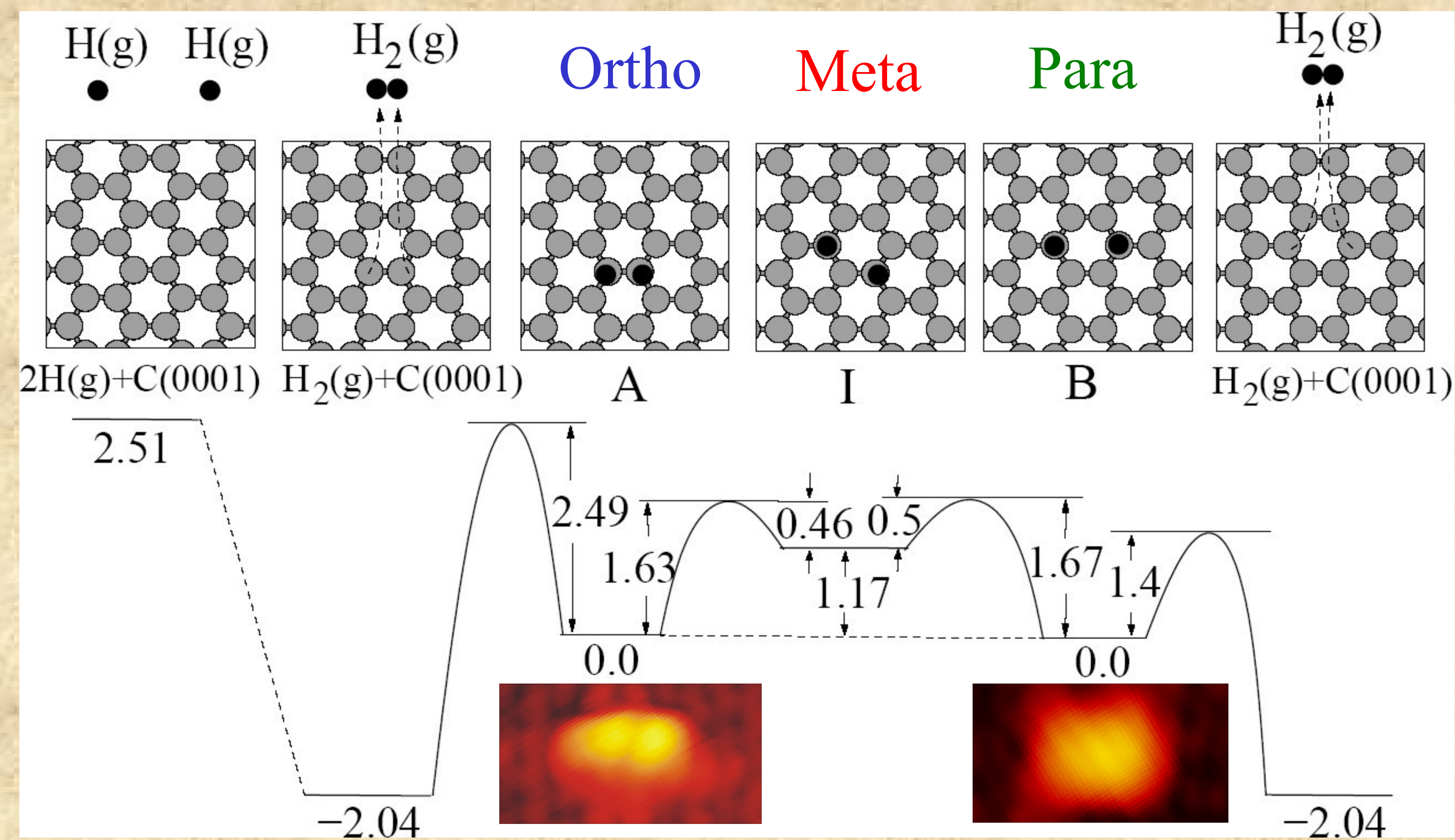
V_t = 884 mV, I_t = 0.19 nA

80 x 72 Å^2



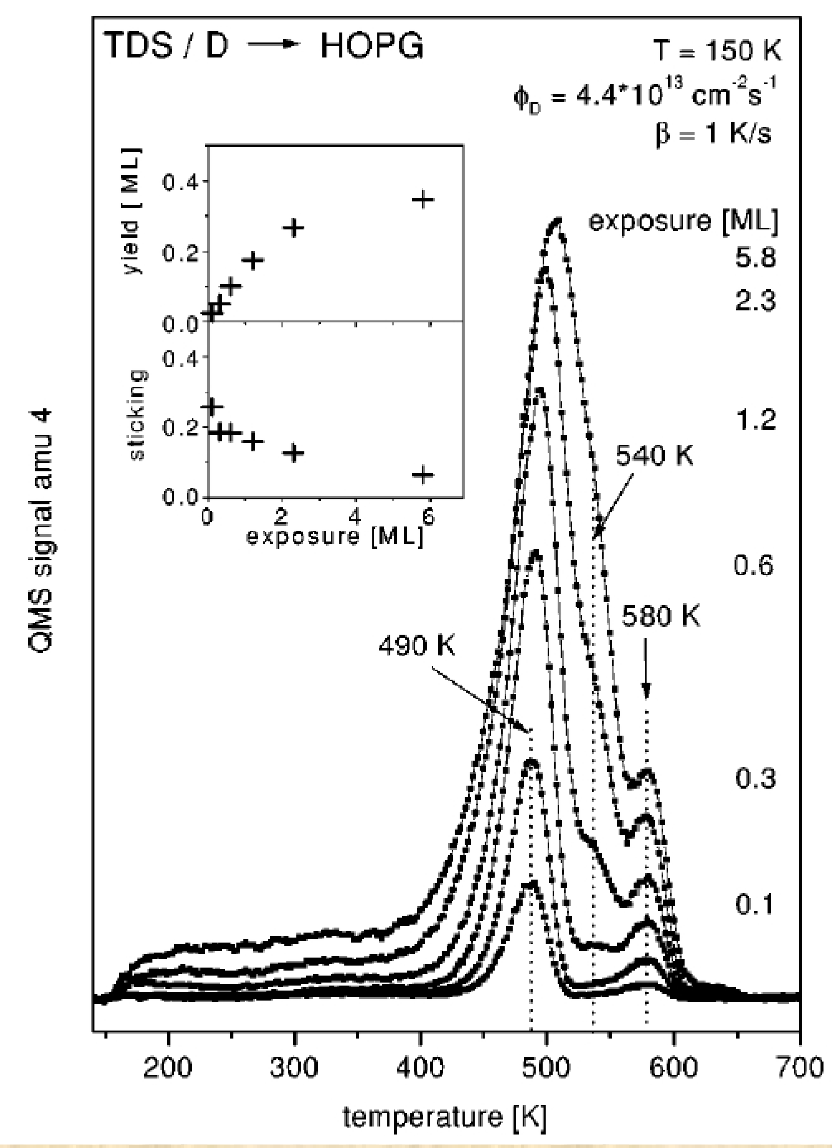
V_t = 884 mV, I_t = 0.36 nA

Recombination pathways



Hornekær et al. Phys. Rev. Lett. ***96****, 156104 (2006)*

Explaining the TPD?



$$\frac{d\Theta}{dt} = -k_0\, e^{-E_B/k_B T}\, \Theta^n$$

n=1 => First order desorption

Barrier to diffusion: 1.3 eV

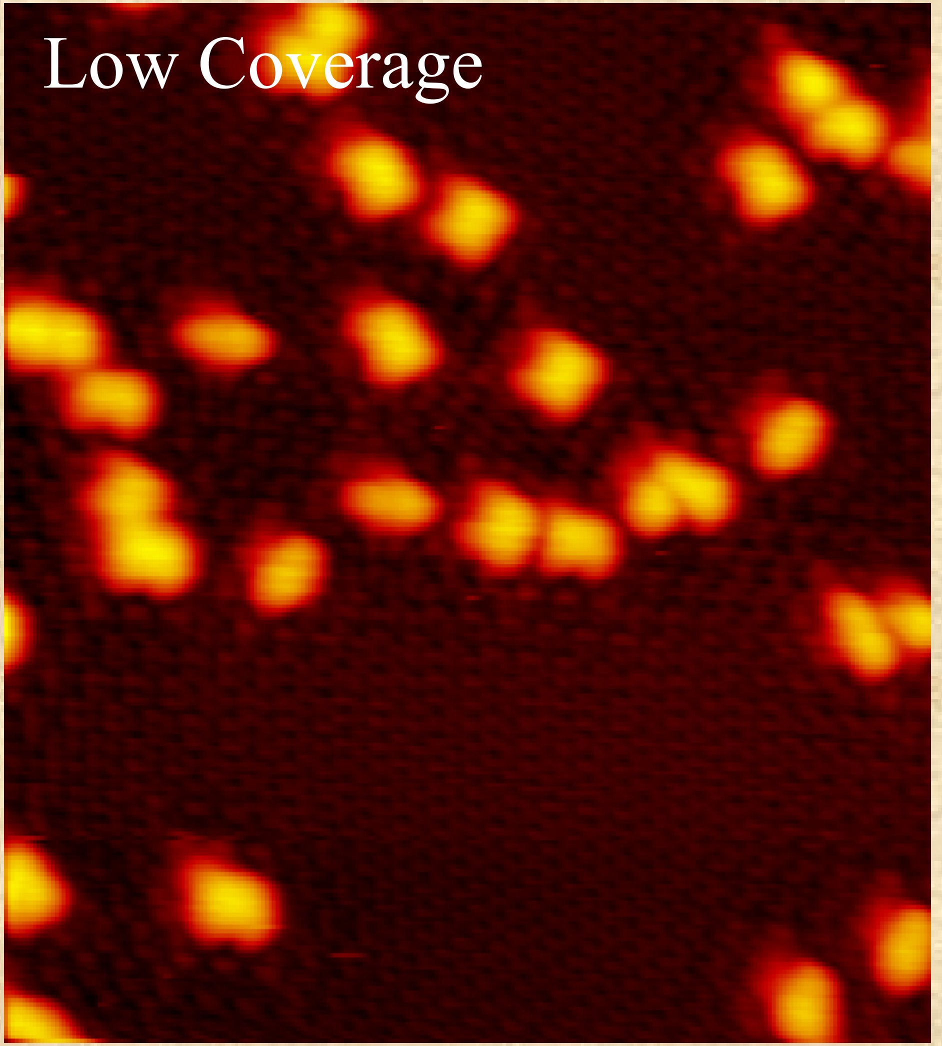
Barrier to desorption: 0.9 eV

490 K => 1.4 eV

580 K => 1.6 eV

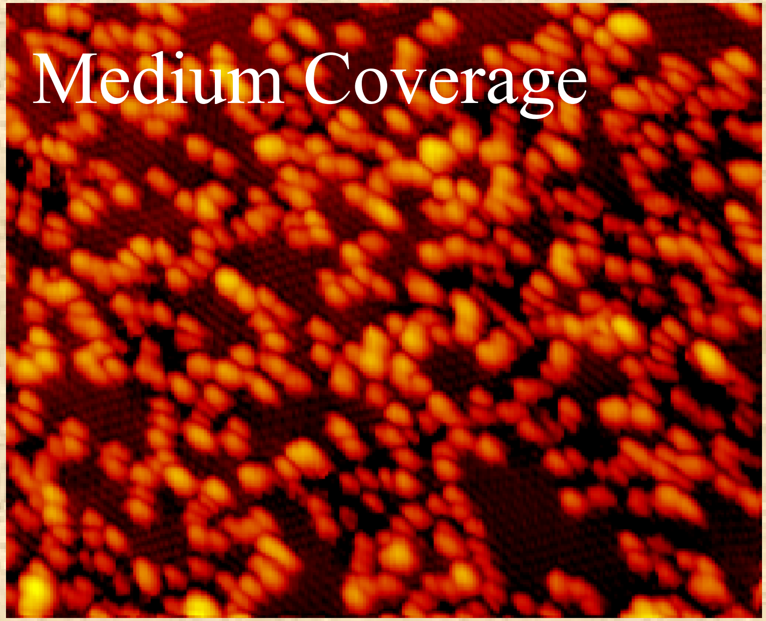
H on HOPG

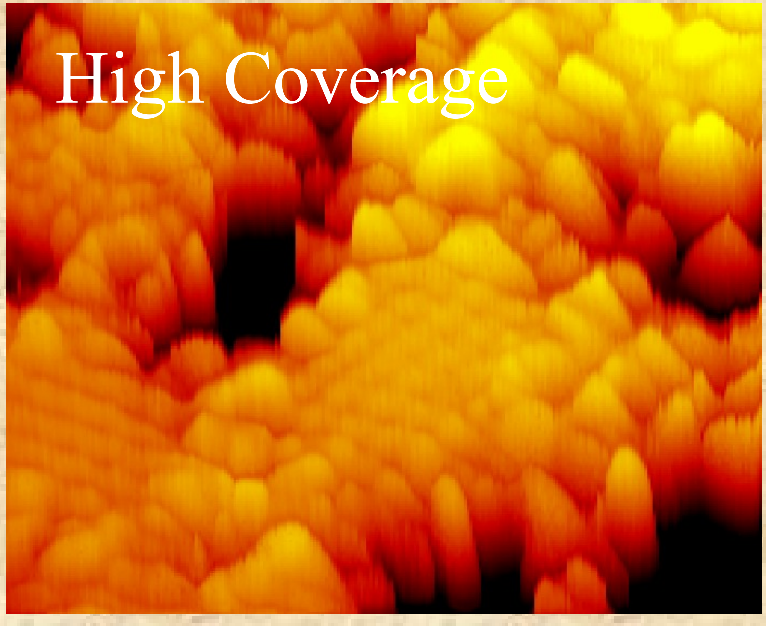
171 x 155 Å^2



103 x 114 Å^2

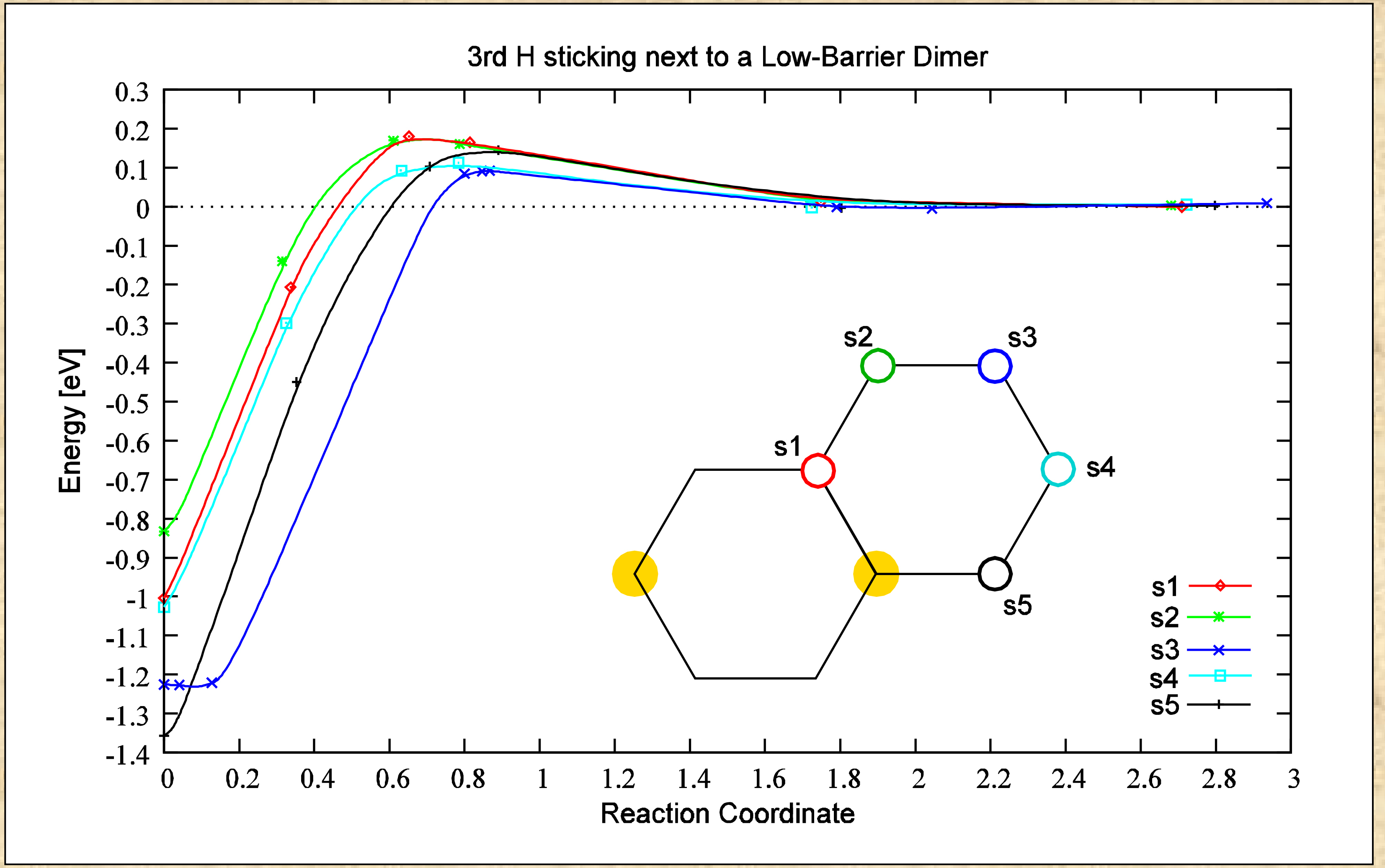
V_t~800mV, I_t~0.15-0.2nA



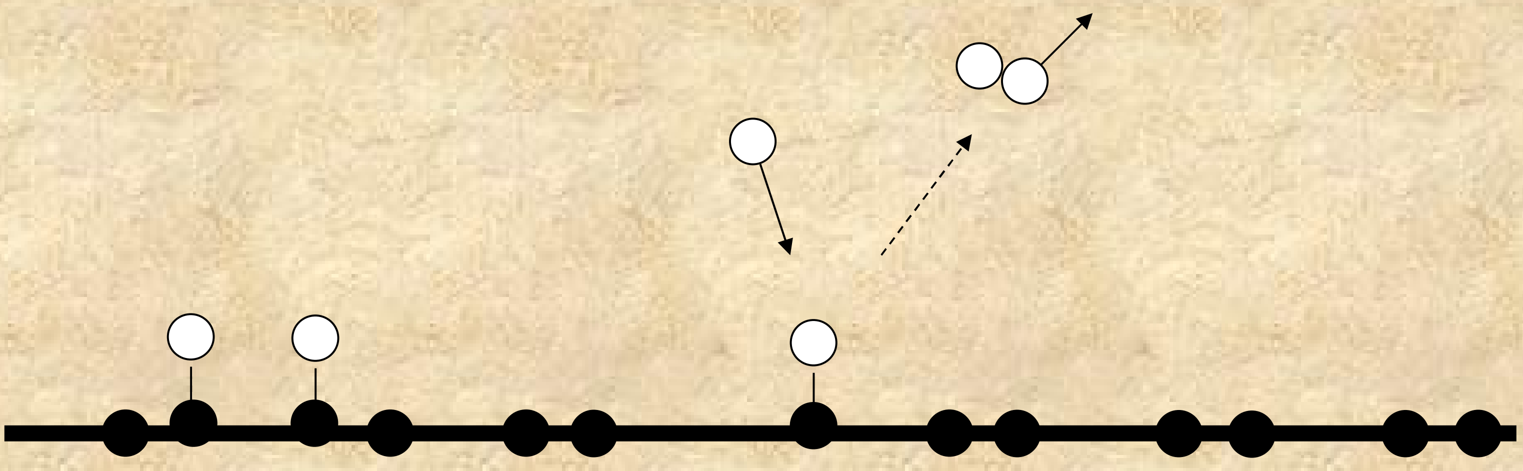


80 x 72 Å^2

Preferential sticking and clustering



Eley Rideal - Abstraction



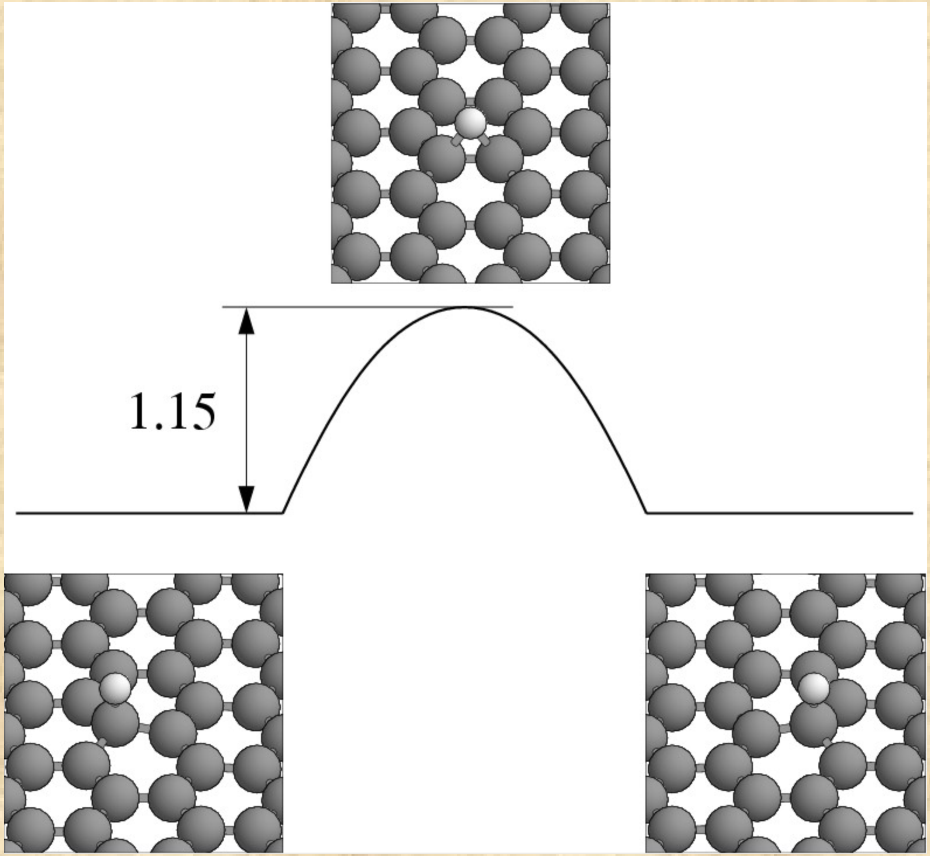
Jeloaica & Sidis (2001)

Sha et al (2002)

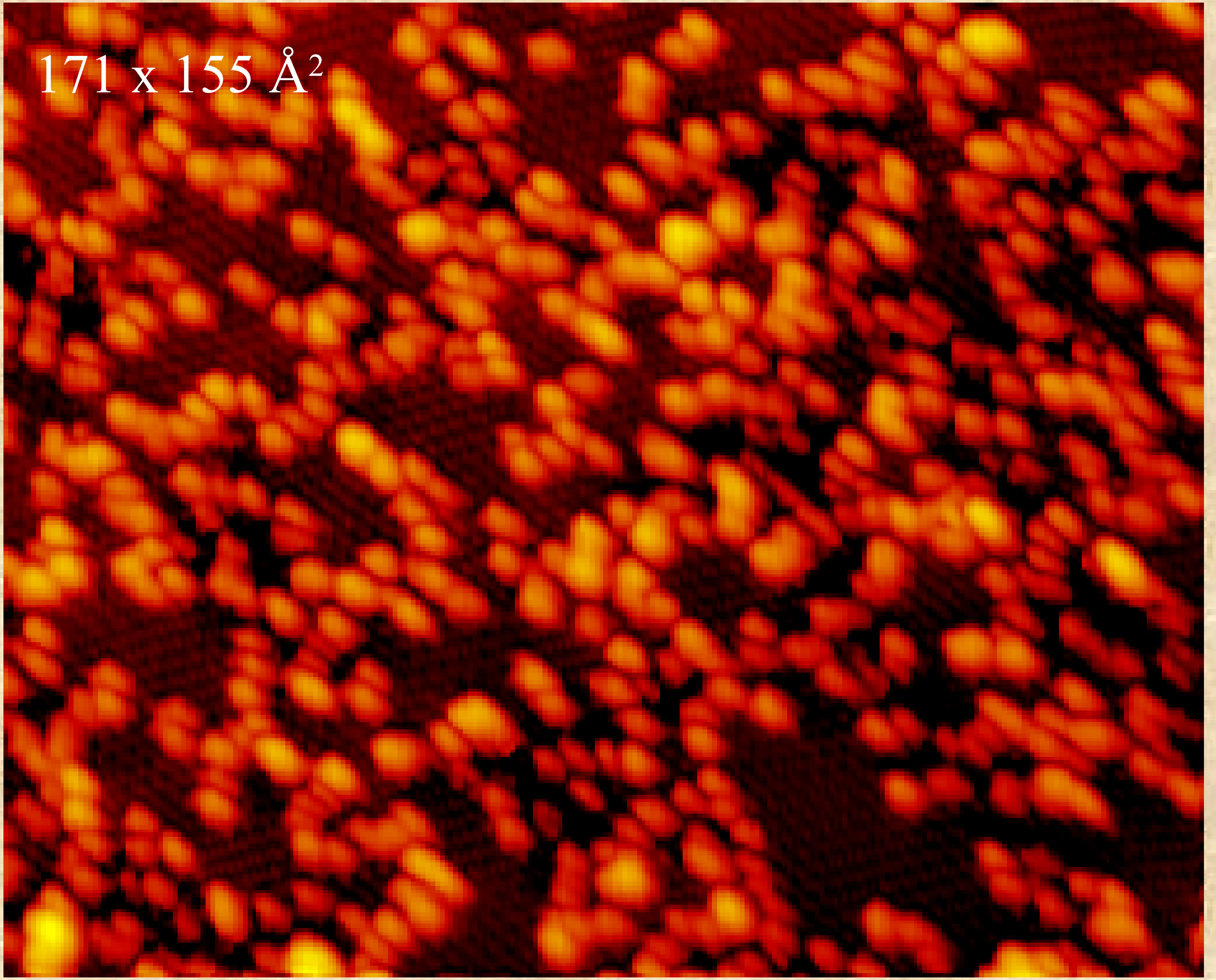
Zecho et al (2002)

Diffusion

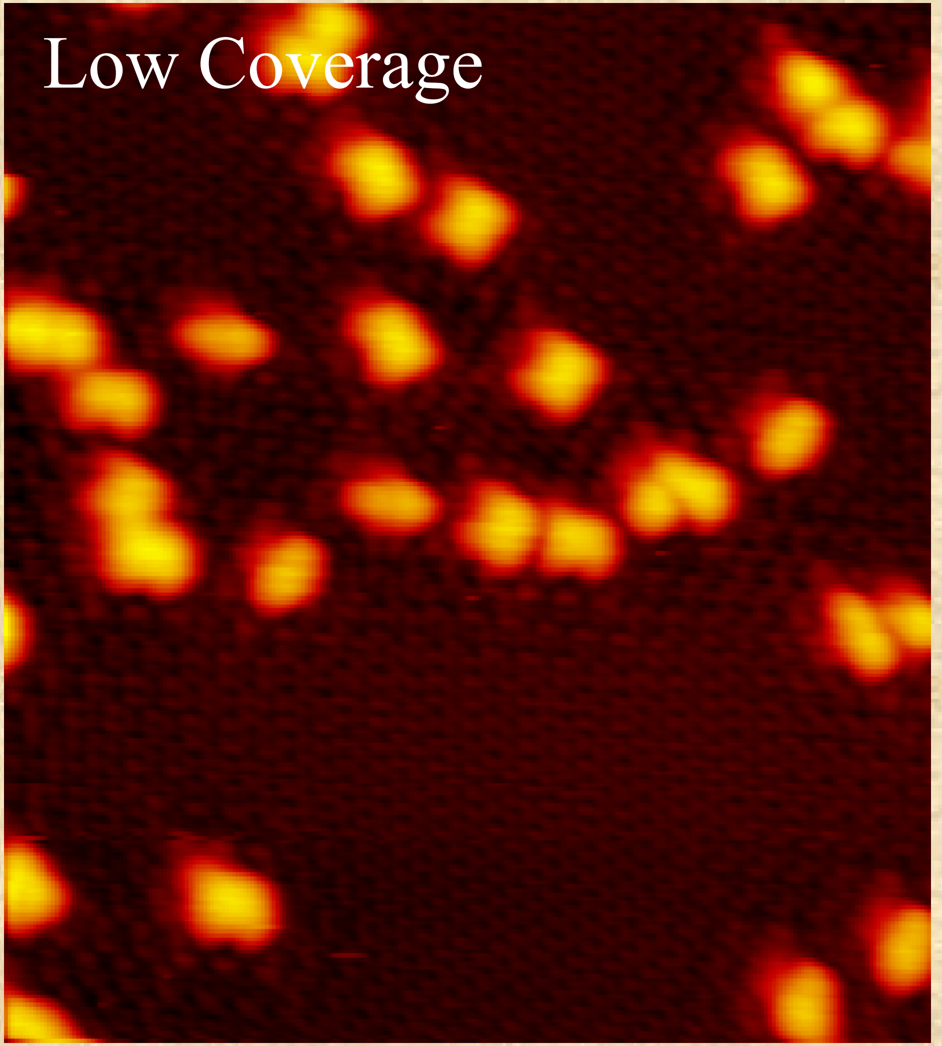
Barrier to diffusion for an isolated H atom: 1.15 eV



Random adsorption



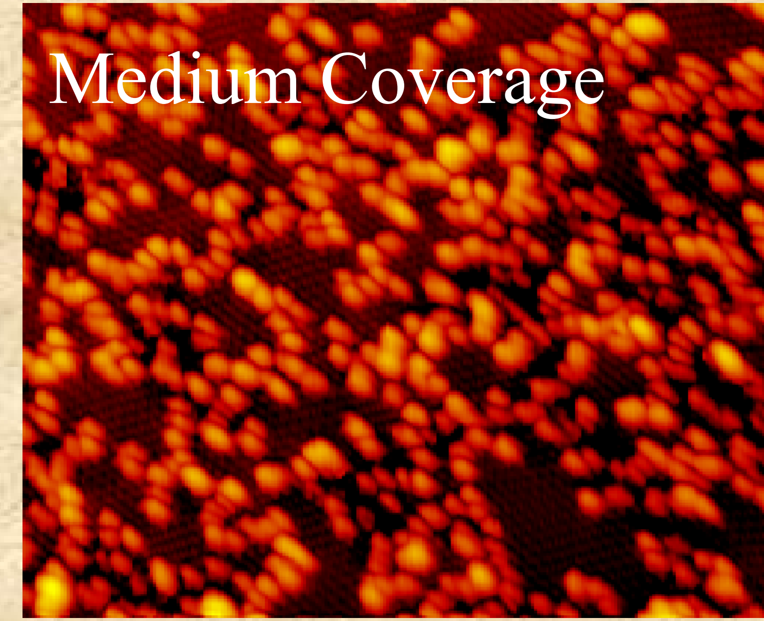
H on HOPG

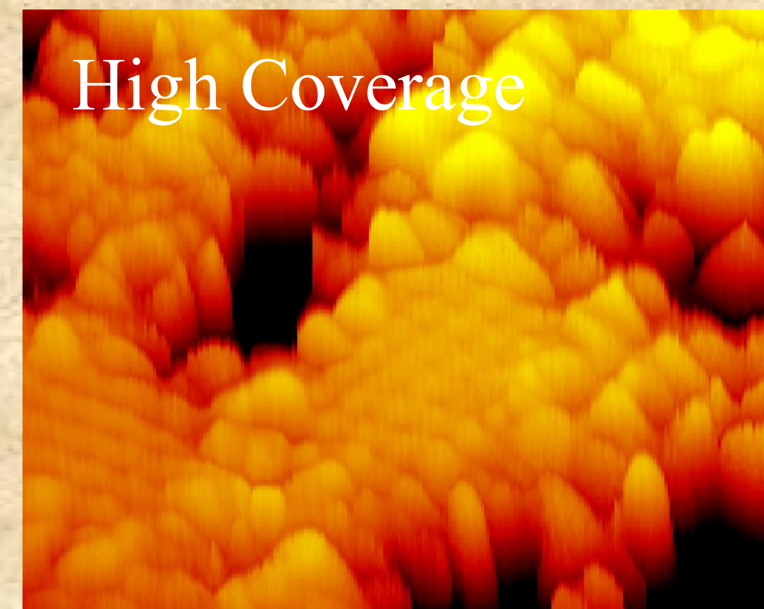


103 x 114 Å^2

V_t~800mV, I_t~0.15-0.2nA

171 x 155 Å^2





80 x 72 Å^2

Comparison to H-Si (100)

H-Si (100):

1st order desorption

Non-langmuirian adsorption

Complete pairing observed in STM down to Θ~20%

Suggested mechanism:

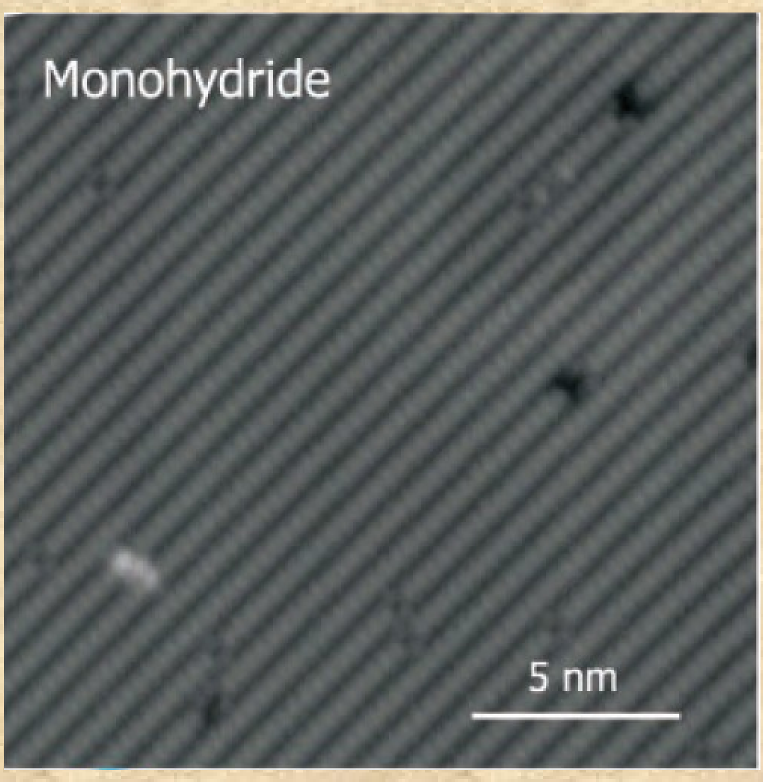
Hot atom precursor mediated adsorption

Theory predicts precursor states with E_b~1-2 eV

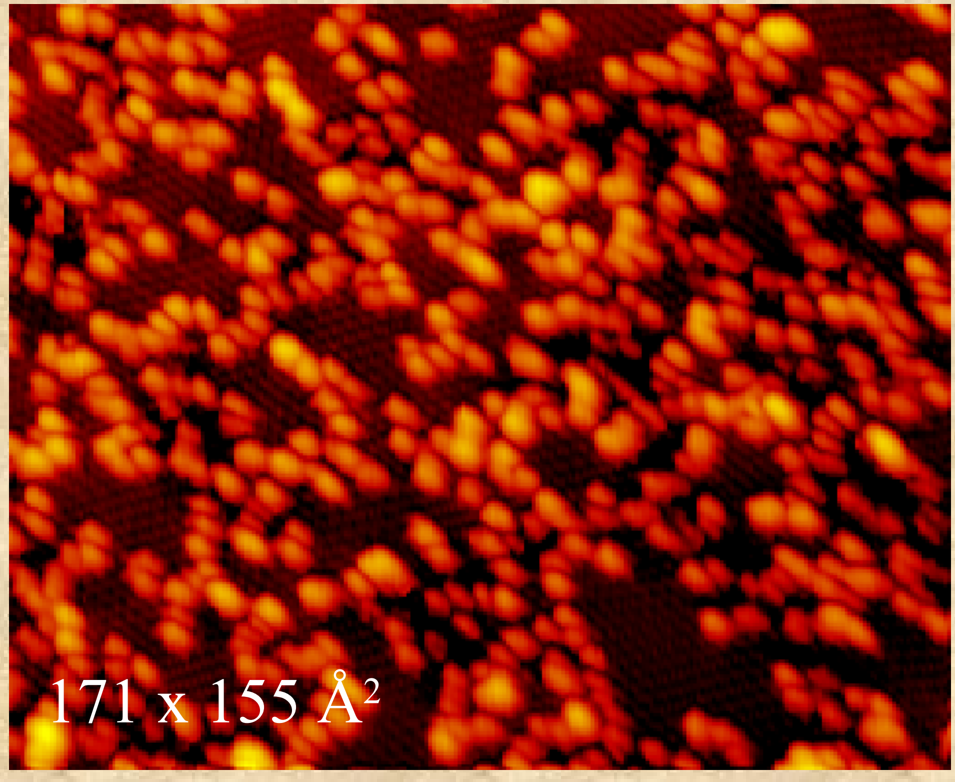
*Widdra et al., PRL **74**, 2074 (1995)*

*Tok et al, JCP **118**, 3294 (2003)*

Comparison to H-Si (100)

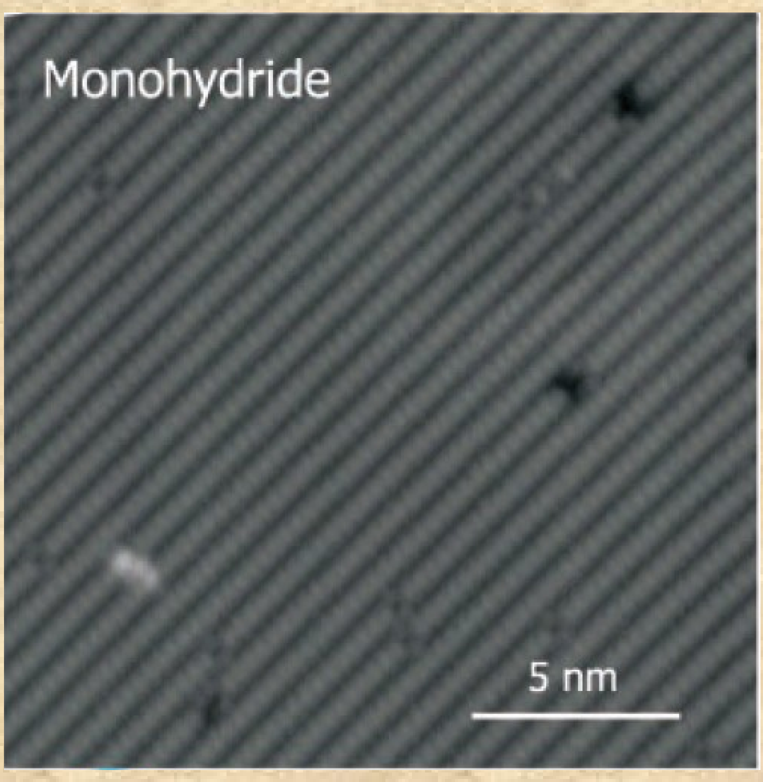


H-Si (100)

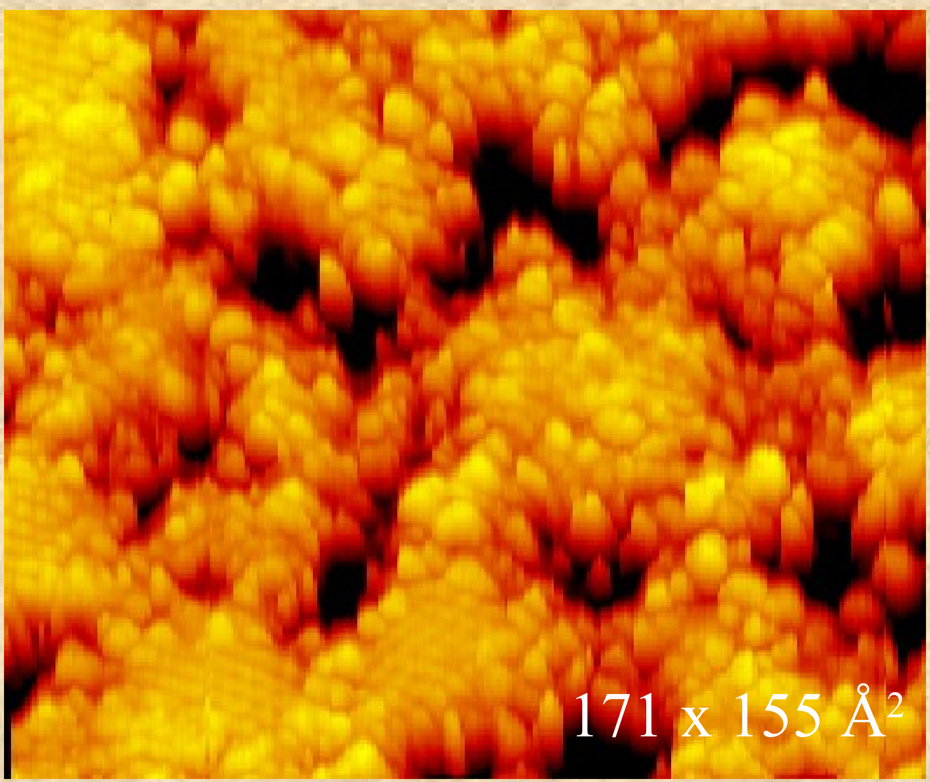


H-HOPG (0001)

Comparison to H-Si (100)

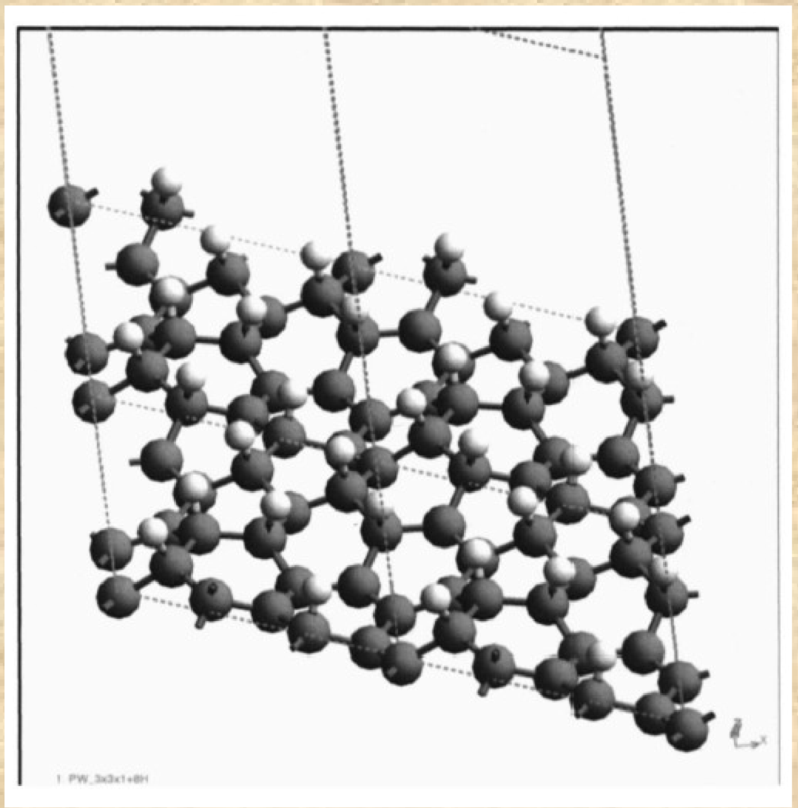


H-Si (100)

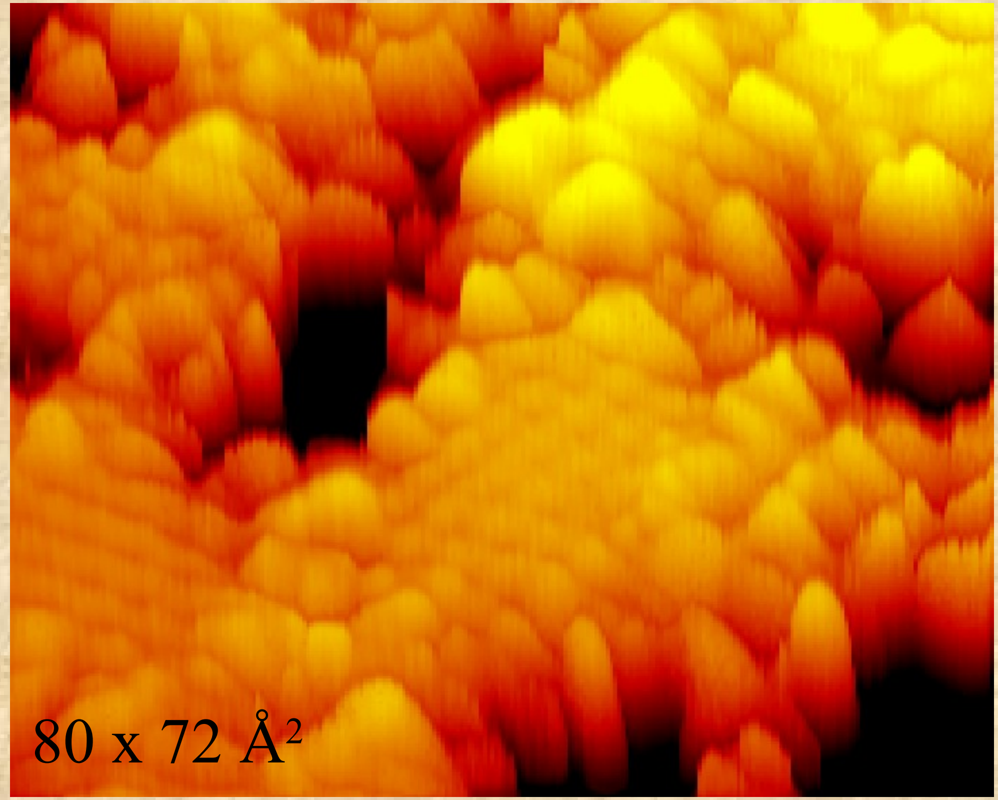


H-HOPG (0001)

High coverage



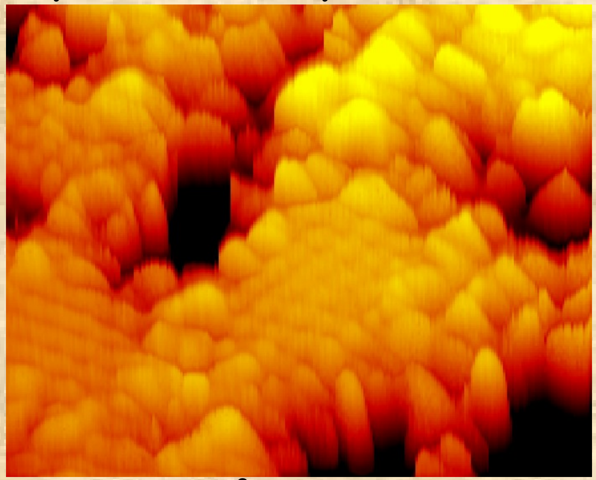
Allouche et al., J. Chem. Phys.
***123**, 124701 (2005)*



Hornekær et al. Phys. Rev. Lett.
97, 186102 (2006)

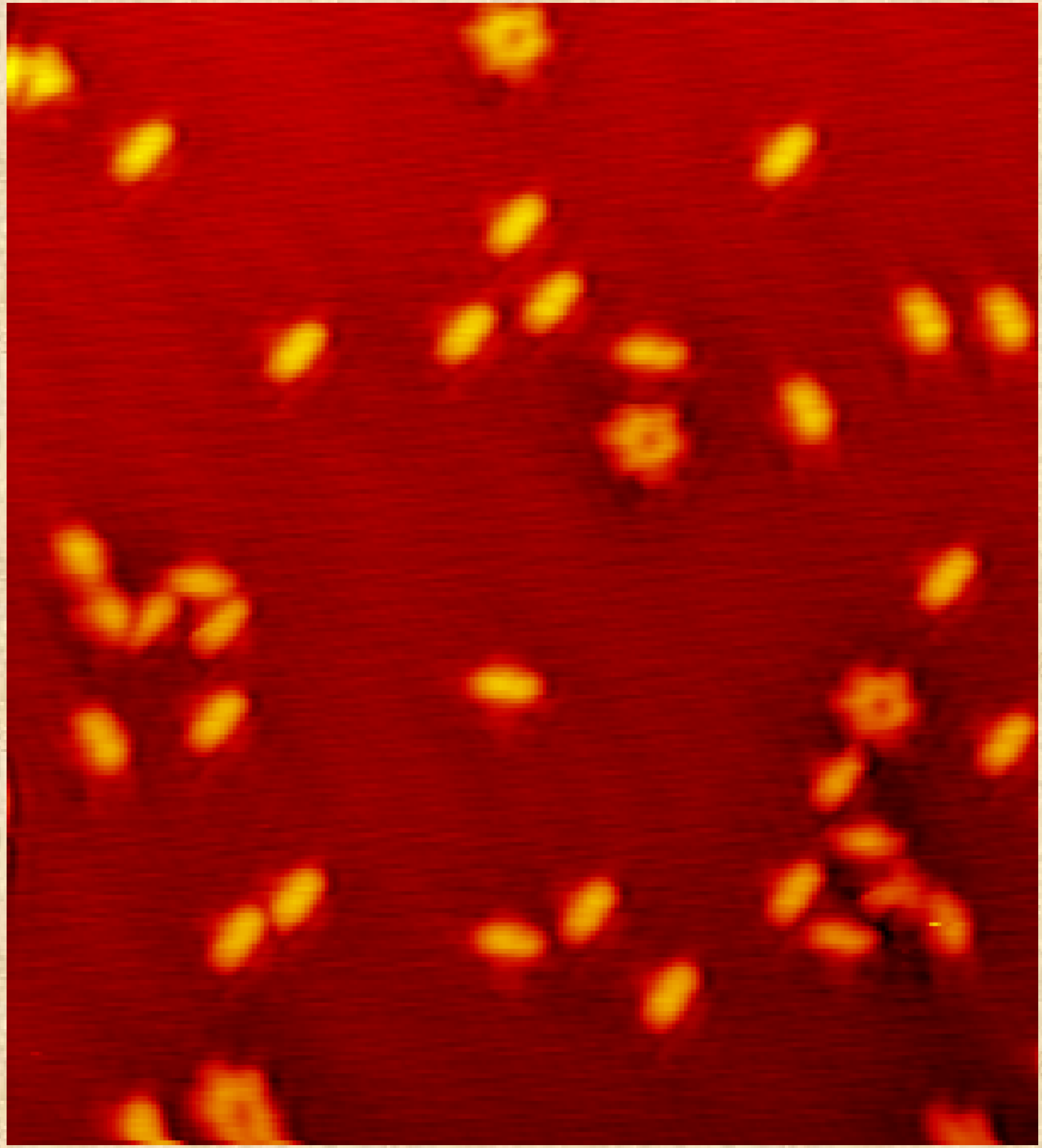
High Coverage

$V_t = -1.05$ V, $I_t = -0.55$ nA

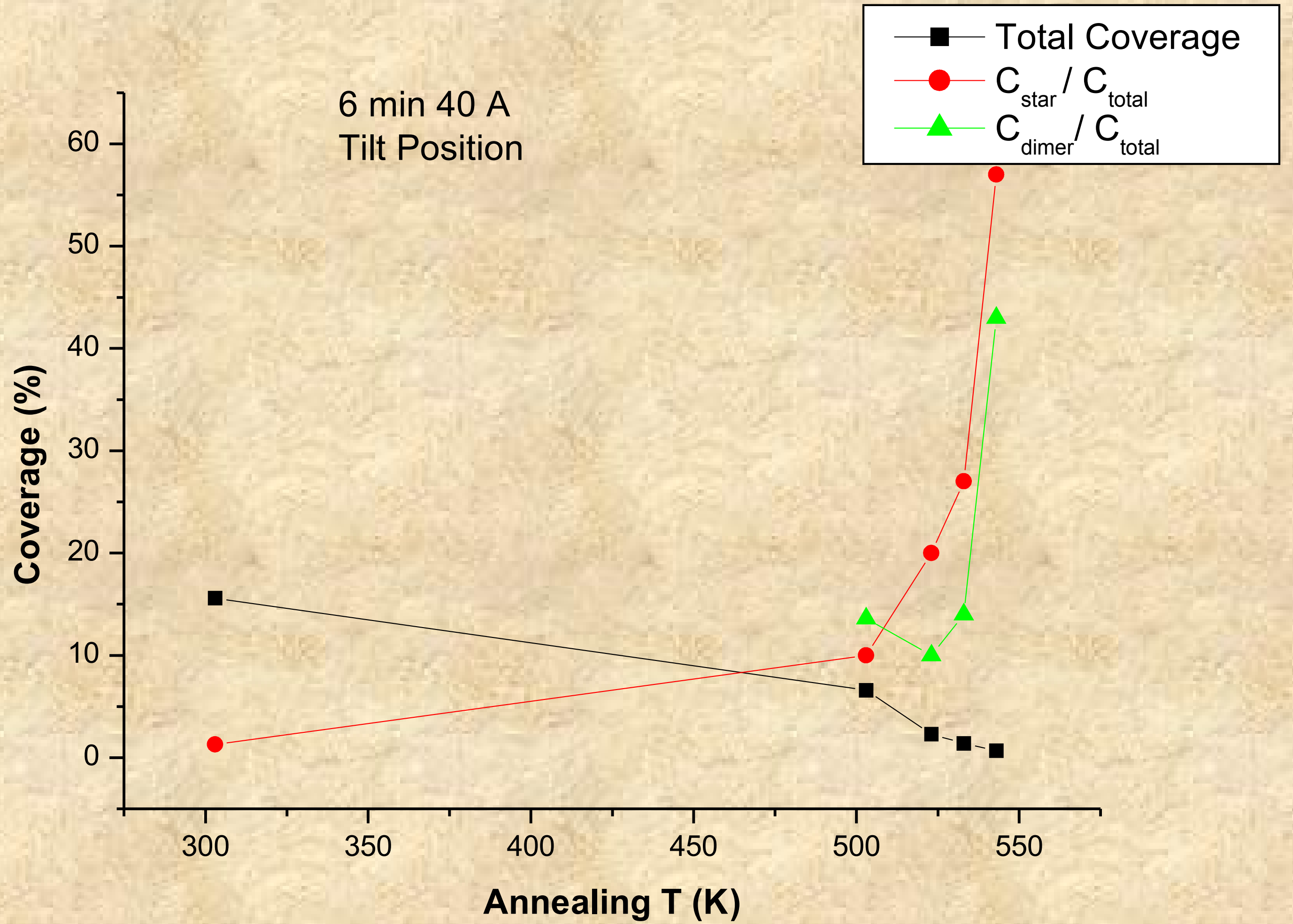


80 x 72 Å^2

525K anneal



$V_t = -1.05$ V, $I_t = -0.18$ nA, 171 x 155 Å^2

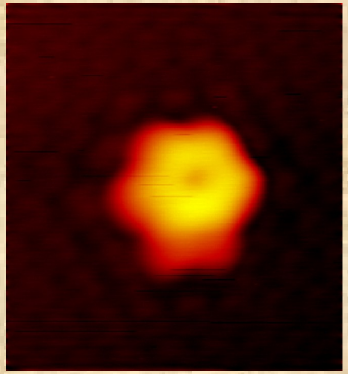


6 min 40 A
Tilt Position
Total Coverage
C_{star} / C_{total}
C_{dimer}/ C_{total}
Coverage (%)
0
10
20
30
40
50
60
300
350
400
450
500
550
Annealing T (K)

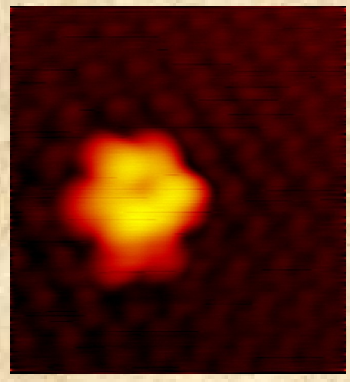
Stars / trimers

Negative voltages:

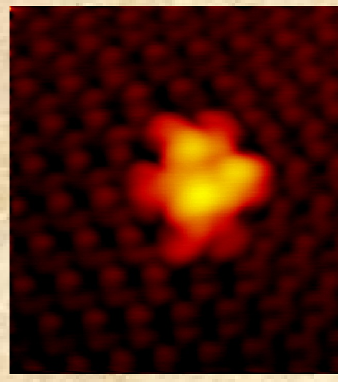
31 x 34 Å^2



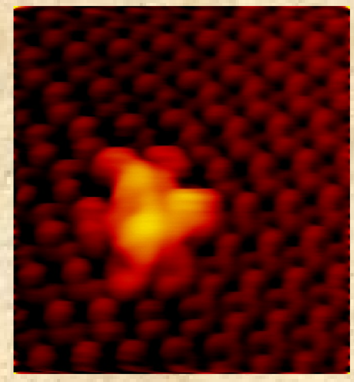
I=-0.16nA, V=-874mV
0512020424



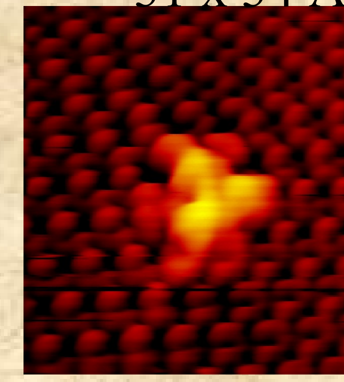
I=-0.15nA, V=-309mV
0512020422



I=-0.16nA, V=-109mV
0512020408

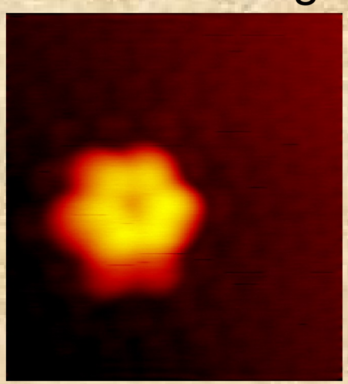


I=-0.16nA, V=-46mV
05120204210

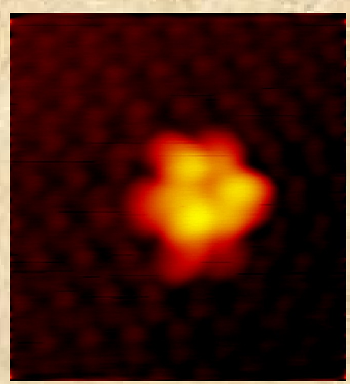


I=-0.15nA, V=-23mV
0512020437

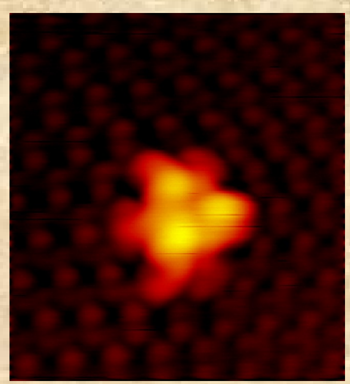
Positive voltages:



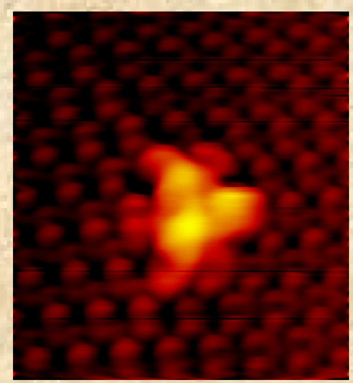
I=0.15nA, V=874mV
0512020435



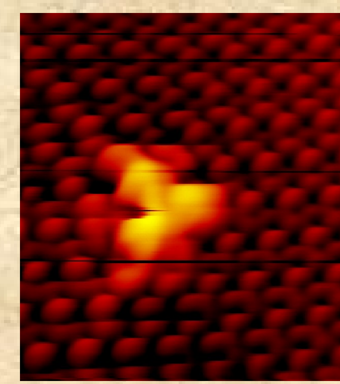
I=0.15nA, V=367mV
0512020429



I=0.15nA, V=154mV
0512020431

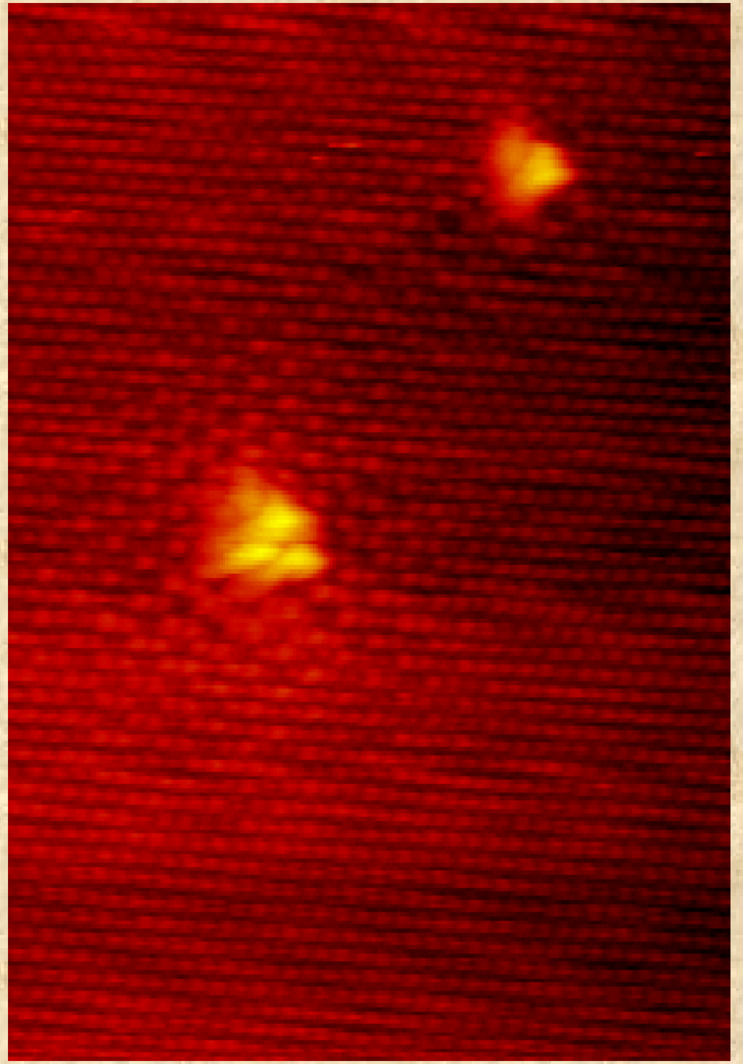


I=0.15nA, V=46mV
0512020434



I=0.15nA, V=23mV
0512020438

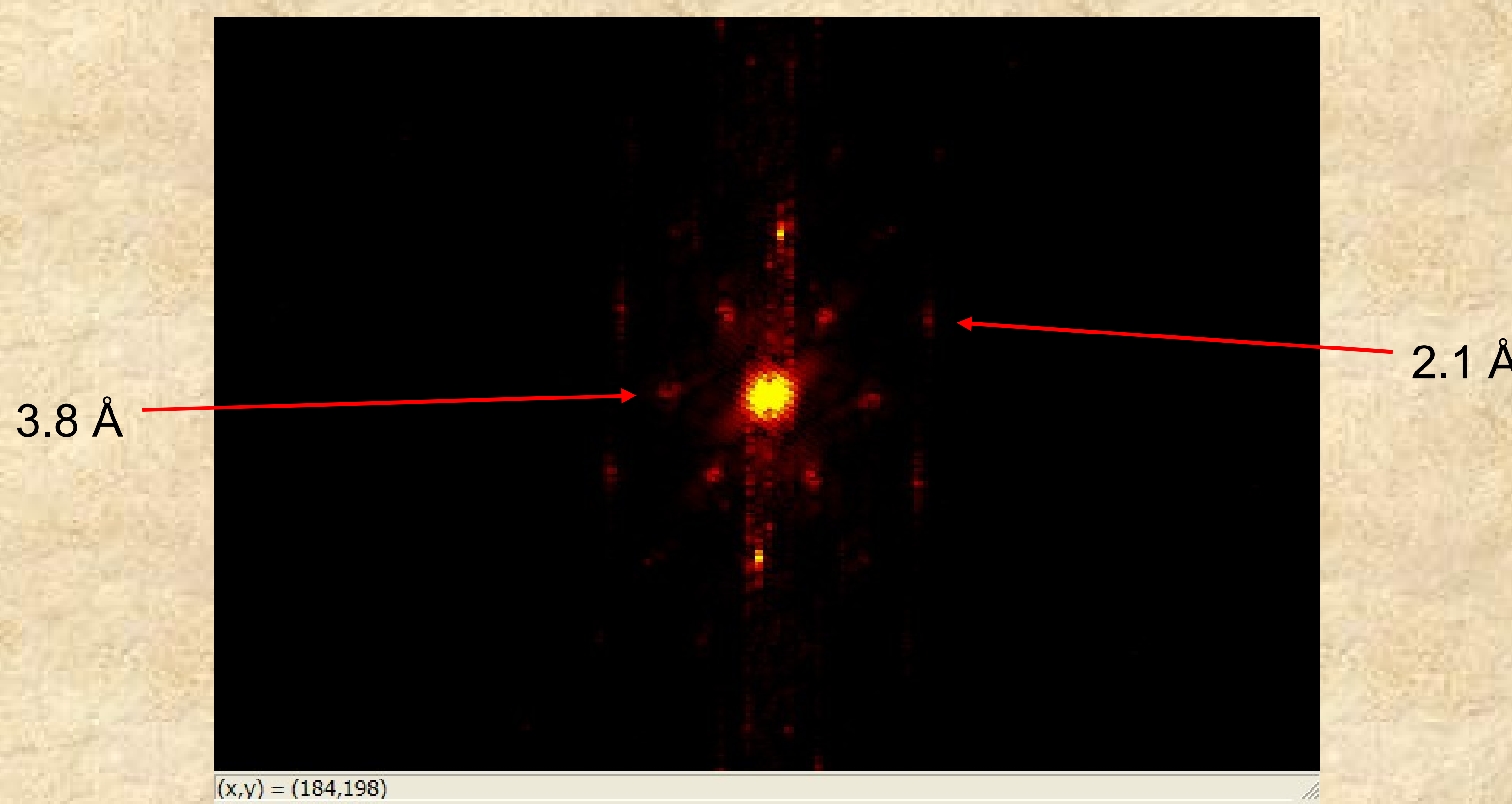
Trimers



85 Å

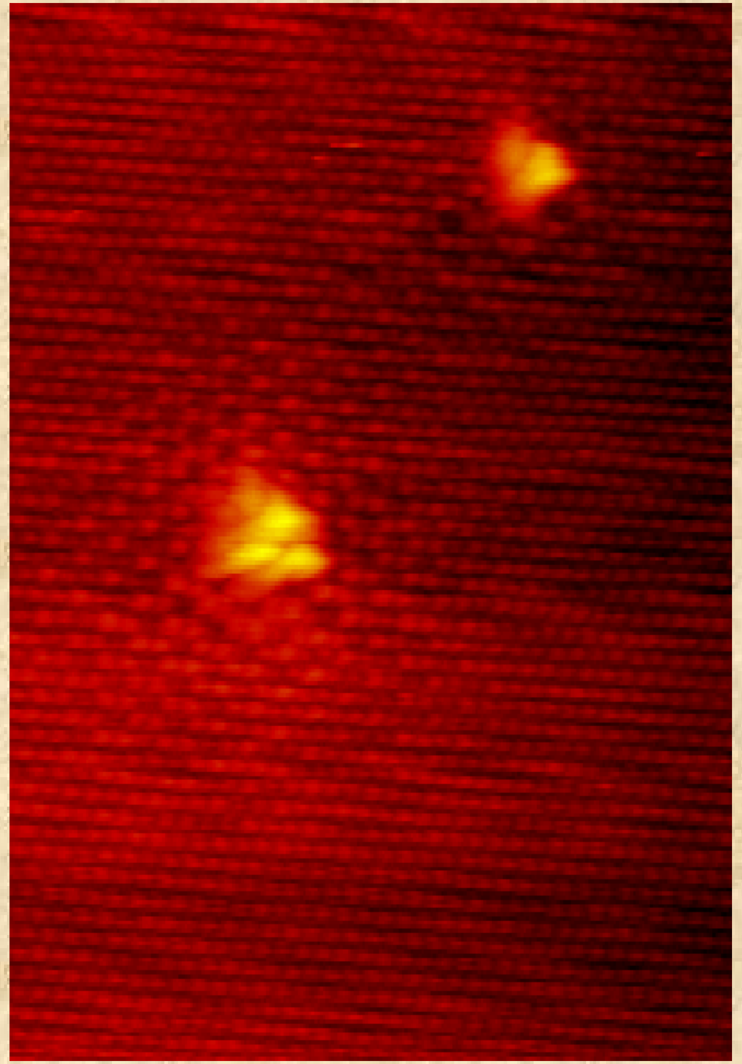
0421-8-27
I_t = -0.220nA
Vt = -625mV

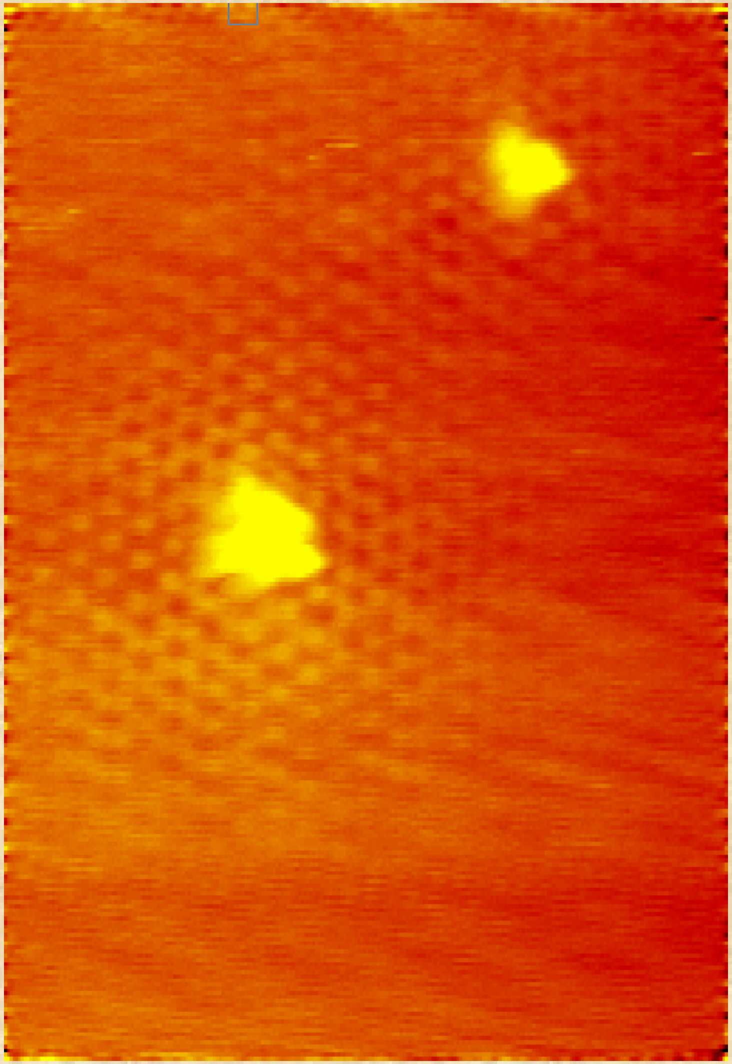
Trimers - superstructure



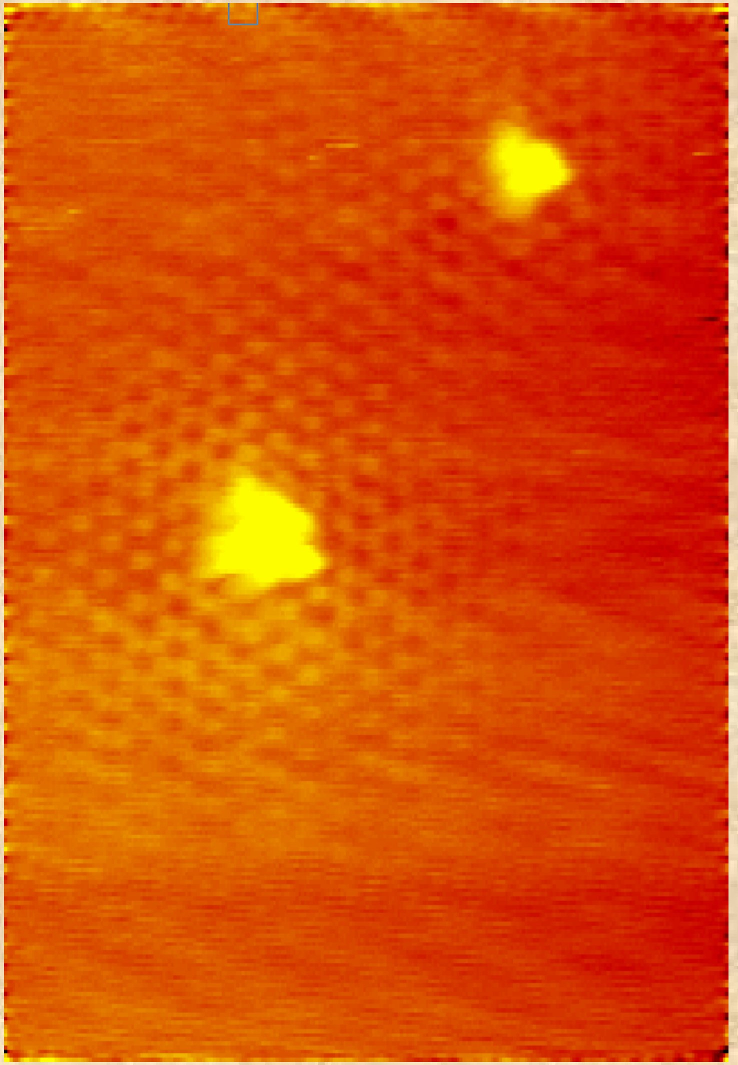
Squareroot(3) reconstruction

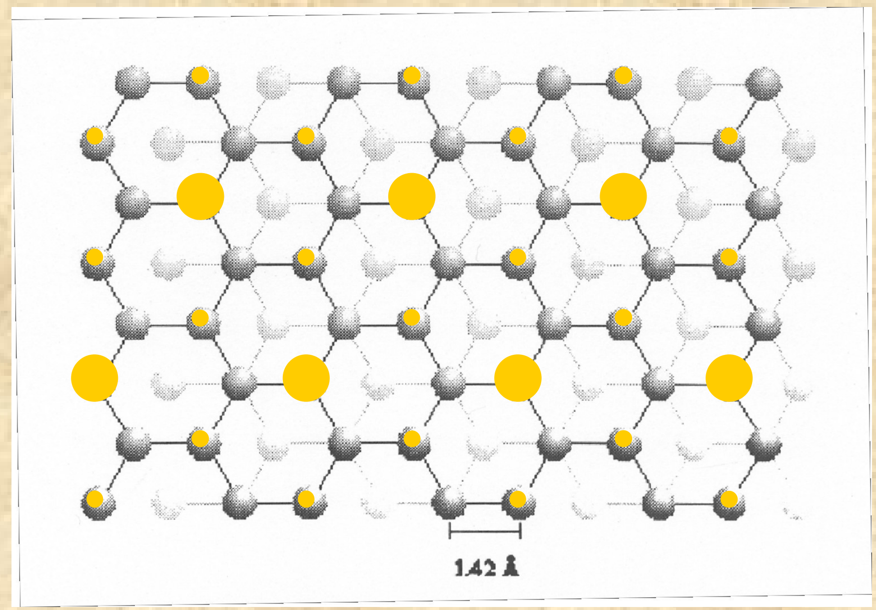
Trimers - superstructure



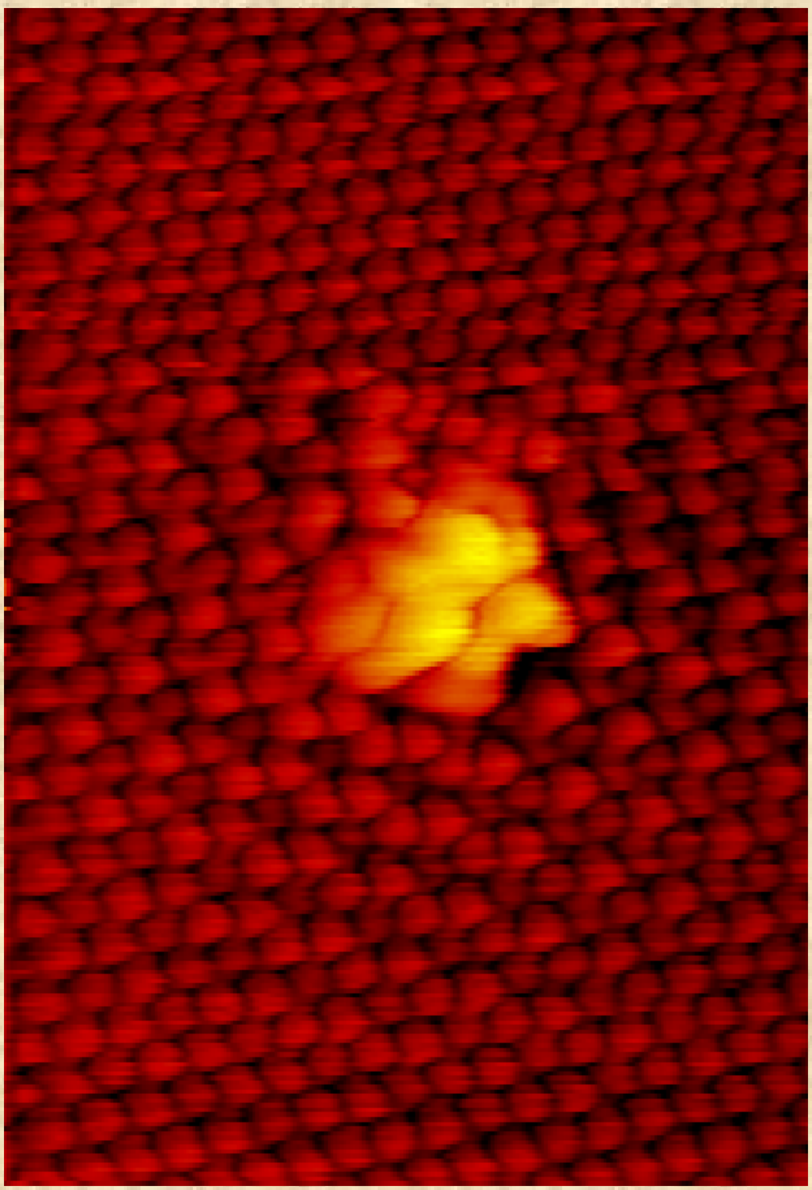


Trimers - superstructure





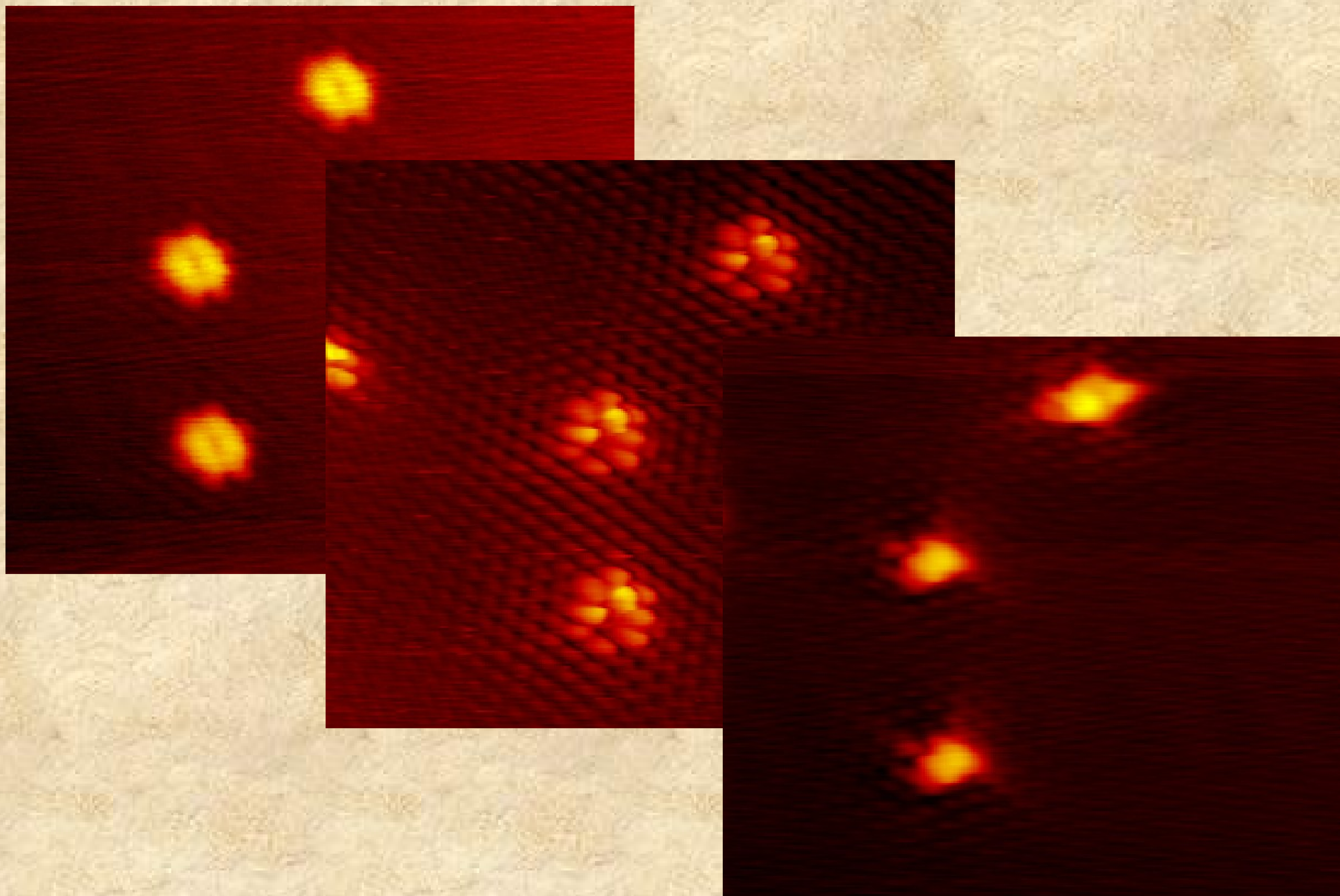
Tip induced desorption



42 Å

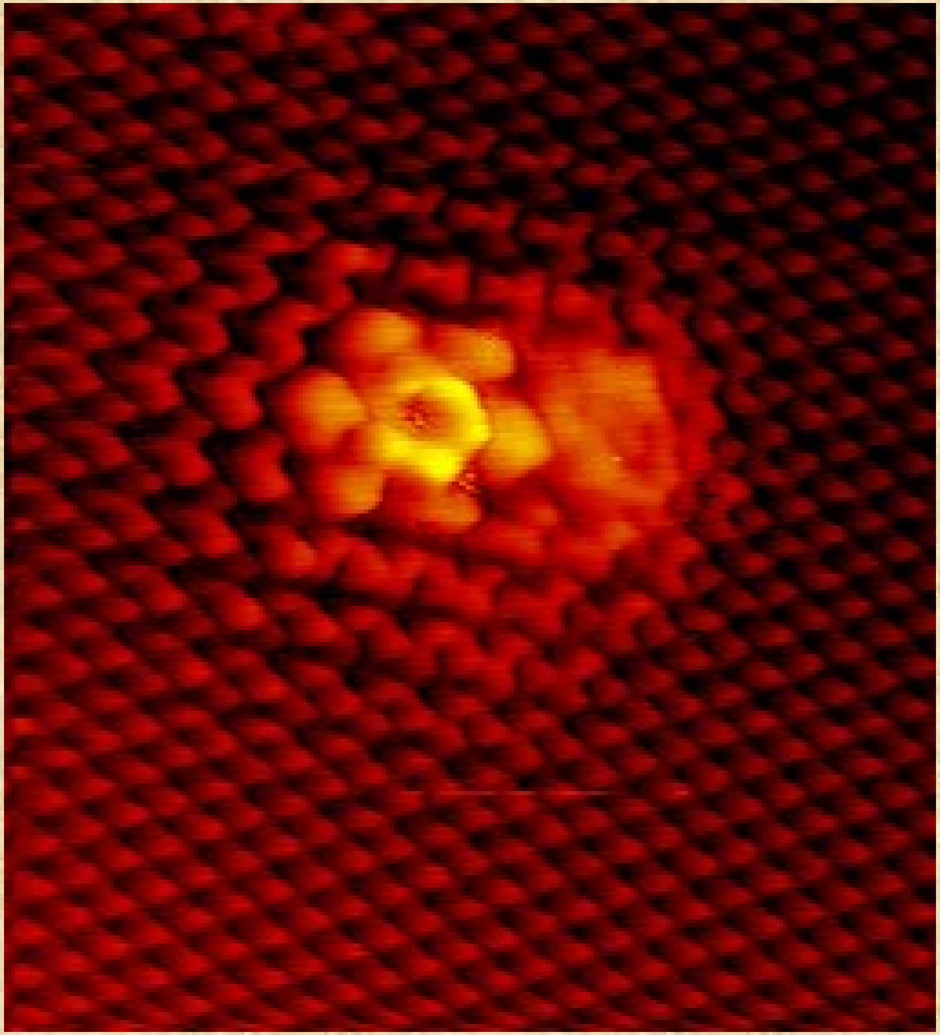
0420-7-5
I_t = -0.150nA
Vt = -442mV

Manipulation

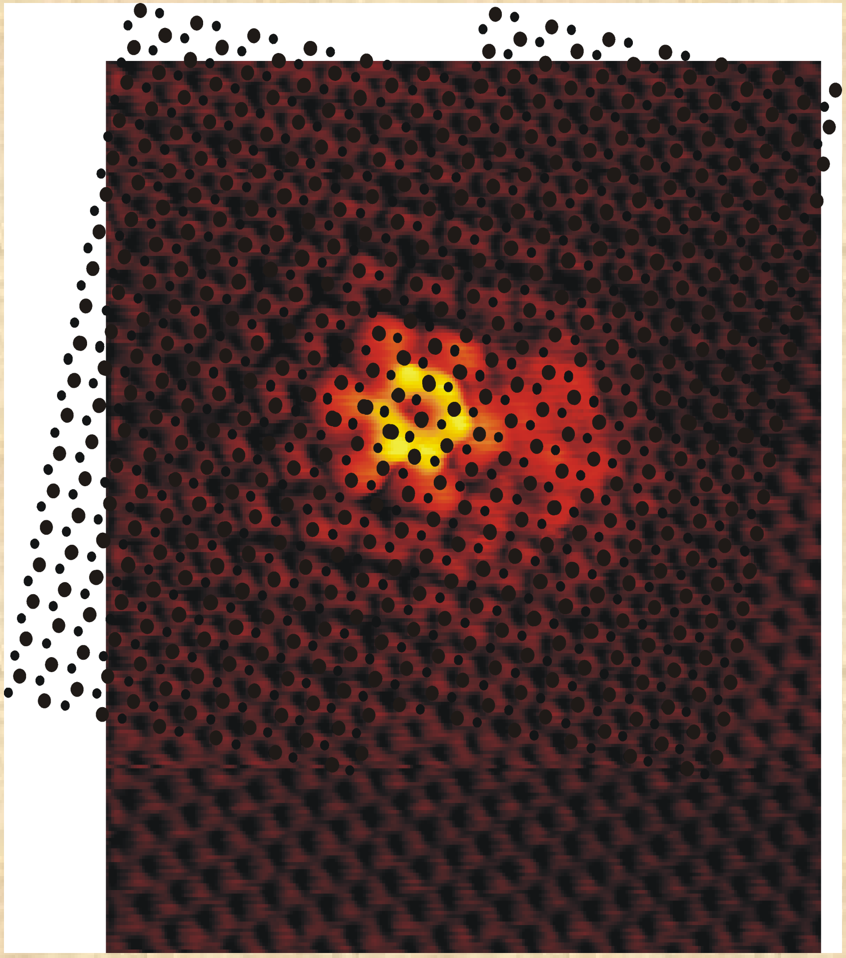


Star-structure

52 x 57 Å^2

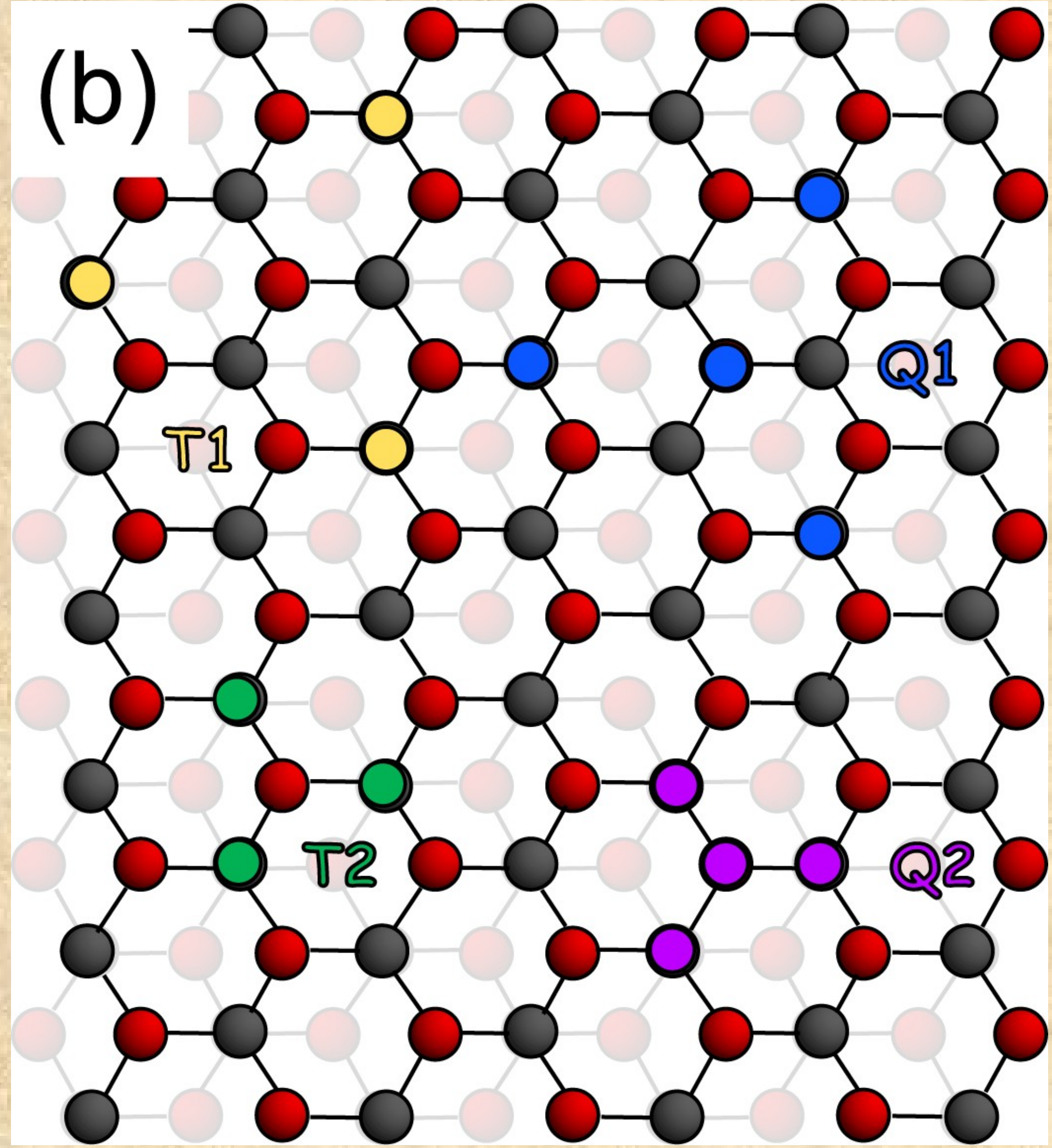


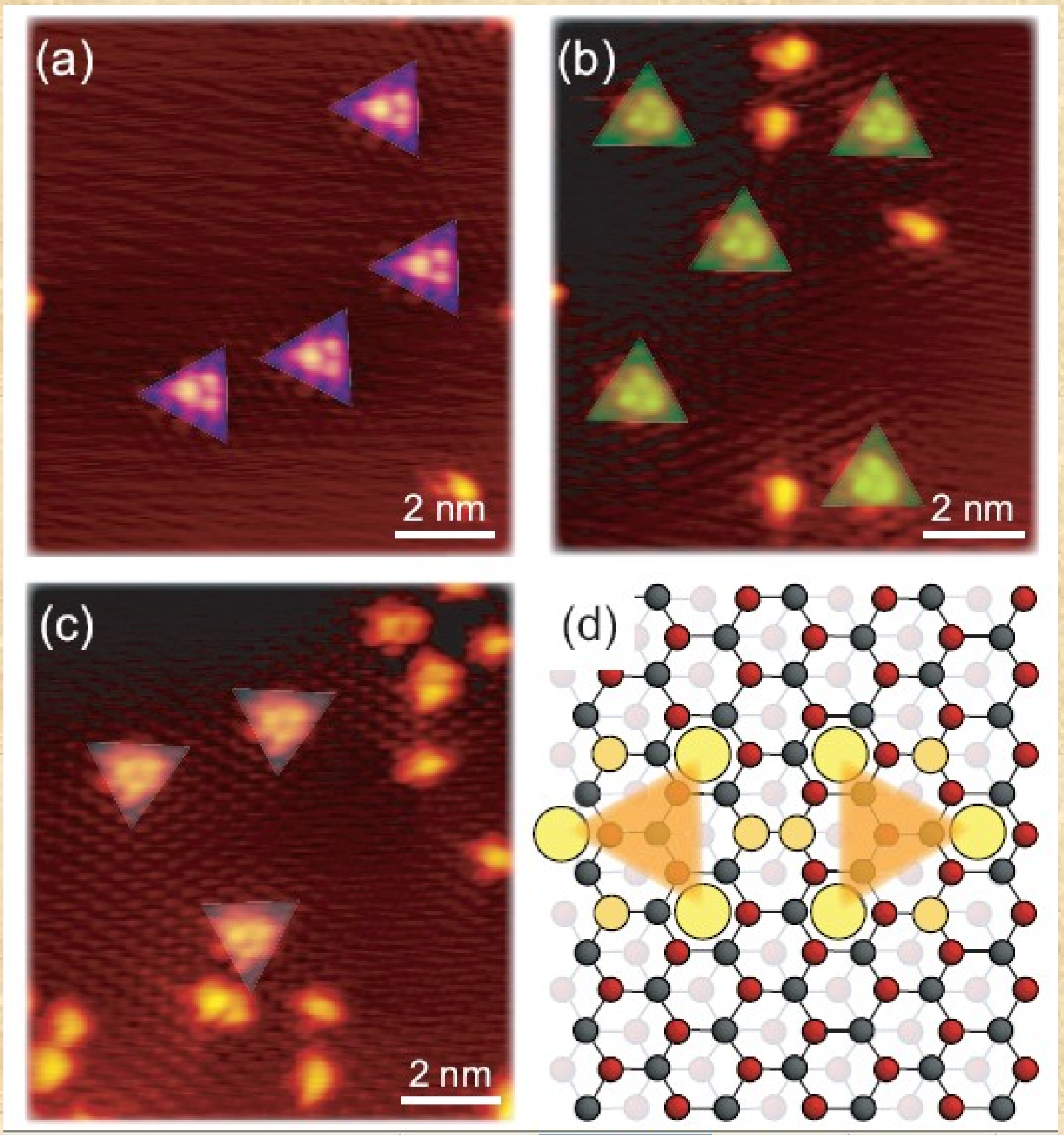
V_t = -743 mV, I_t = -0.62 nA



Stars – superimposed graphite network

Star structure?

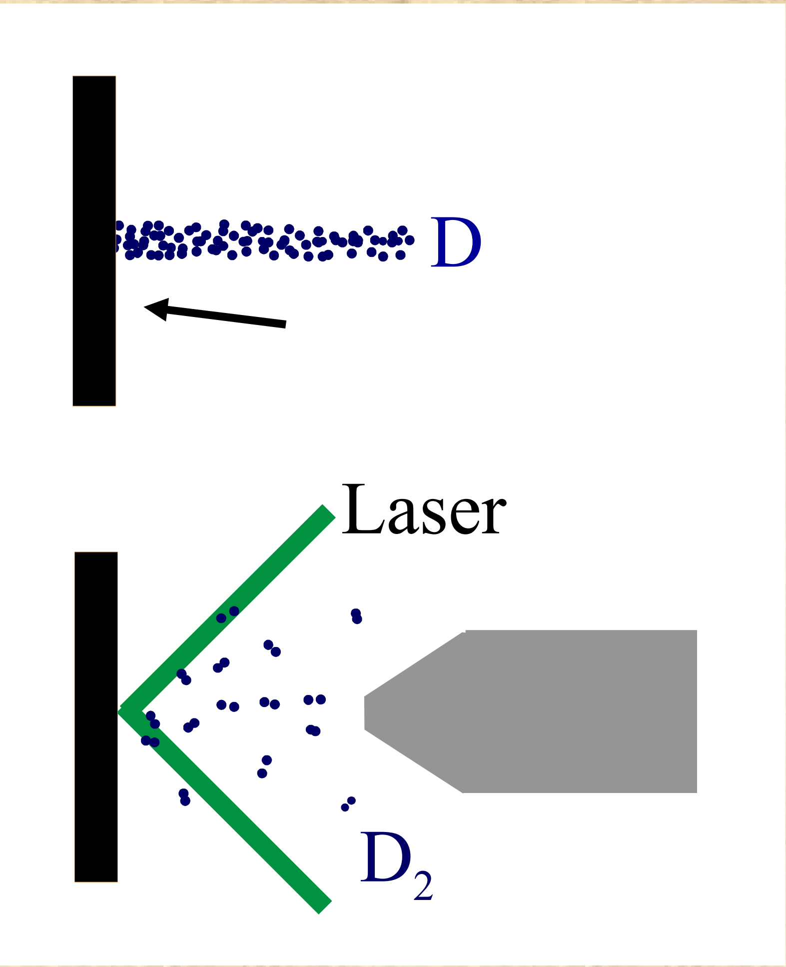



(a)
2 nm
(b)
2 nm
(c)
2 nm
(d)

Eagle-Nebula

10-1000 K, 100-10.000 atoms/cm^3

Measuring the kinetic energy of formed molecules



Laser Induced
Thermal Desorption
(LITD)

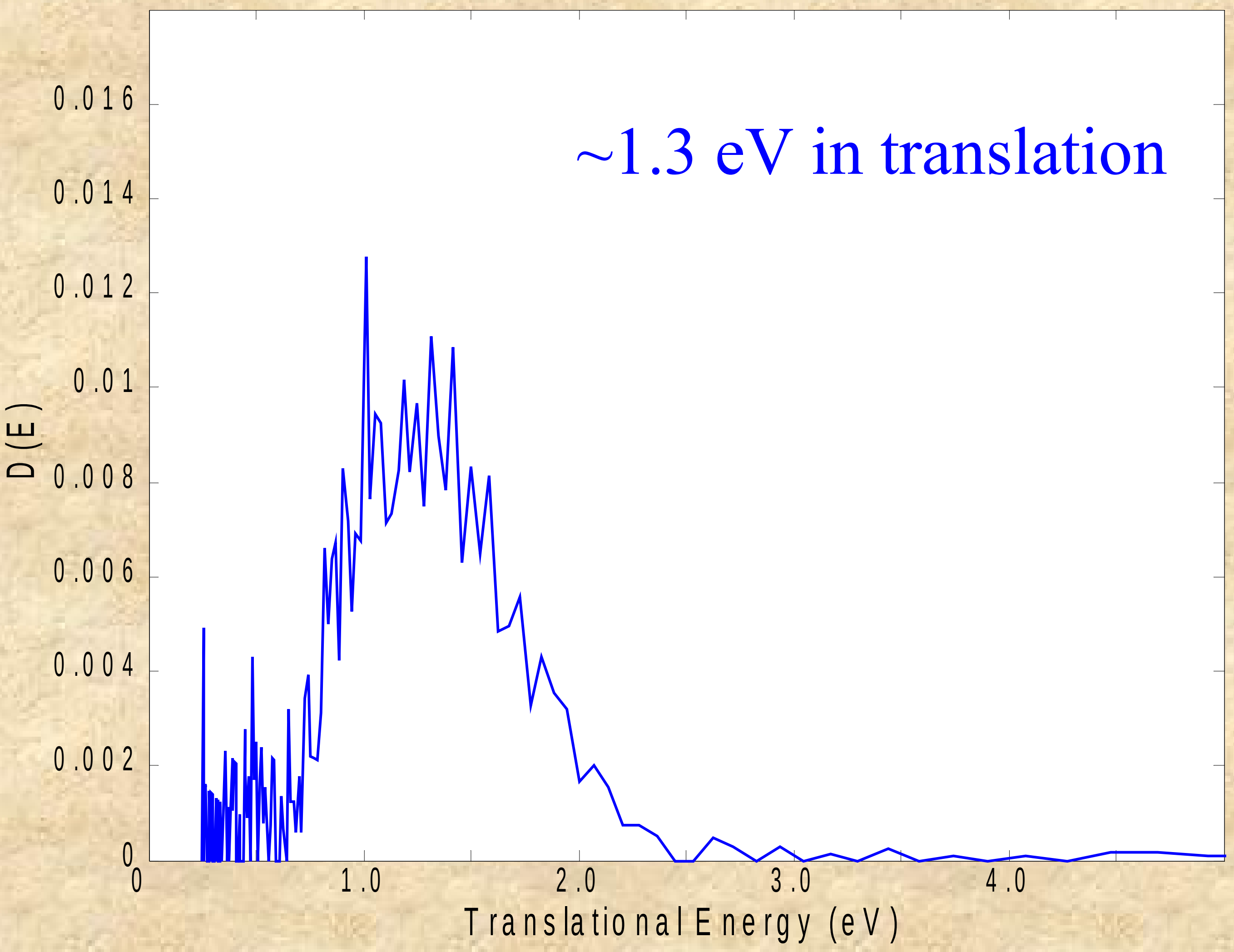
Alexandrite
Laser

4 mJ
100 ns pulse

↓

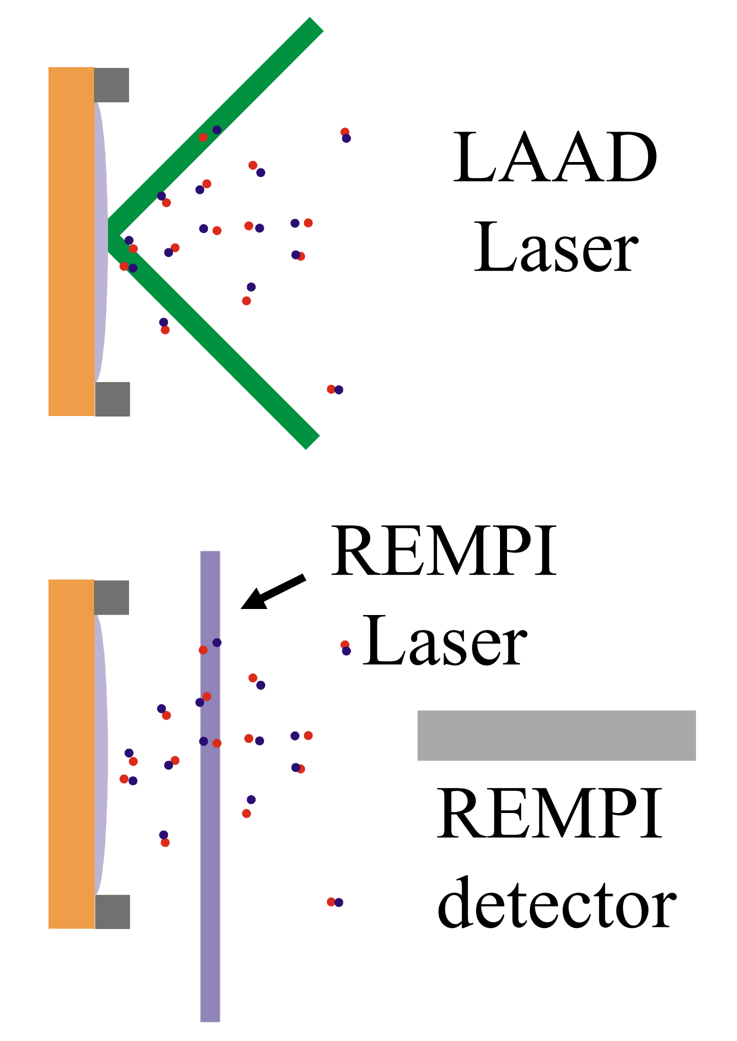
Time of Flight Measurement

Kinetic energy of D_2 formed on graphite



S. Baouche et al, J. Chem. Phys. 2006

Measuring internal state distributions



3.4 eV liberated

~1.3 eV in translation

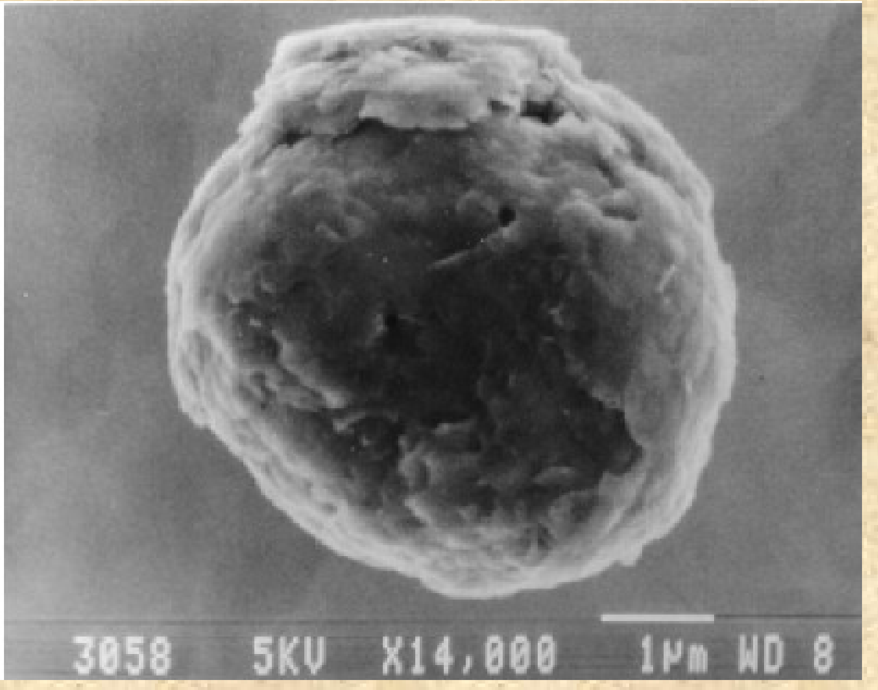
0-1.4 eV in surface heating

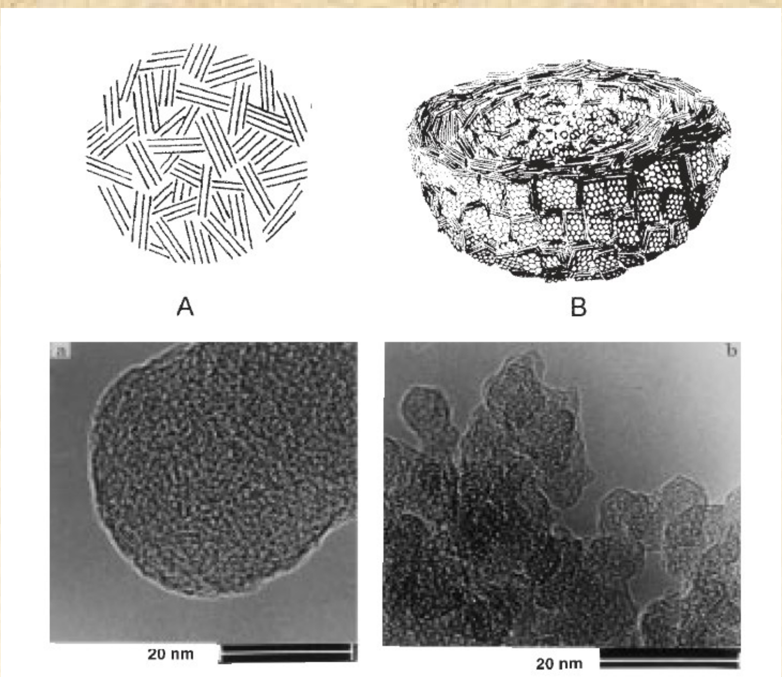
0.7 - 2.1 eV in ro-vibration

Talk by Saoud Baouche

Real carbonaceous surfaces

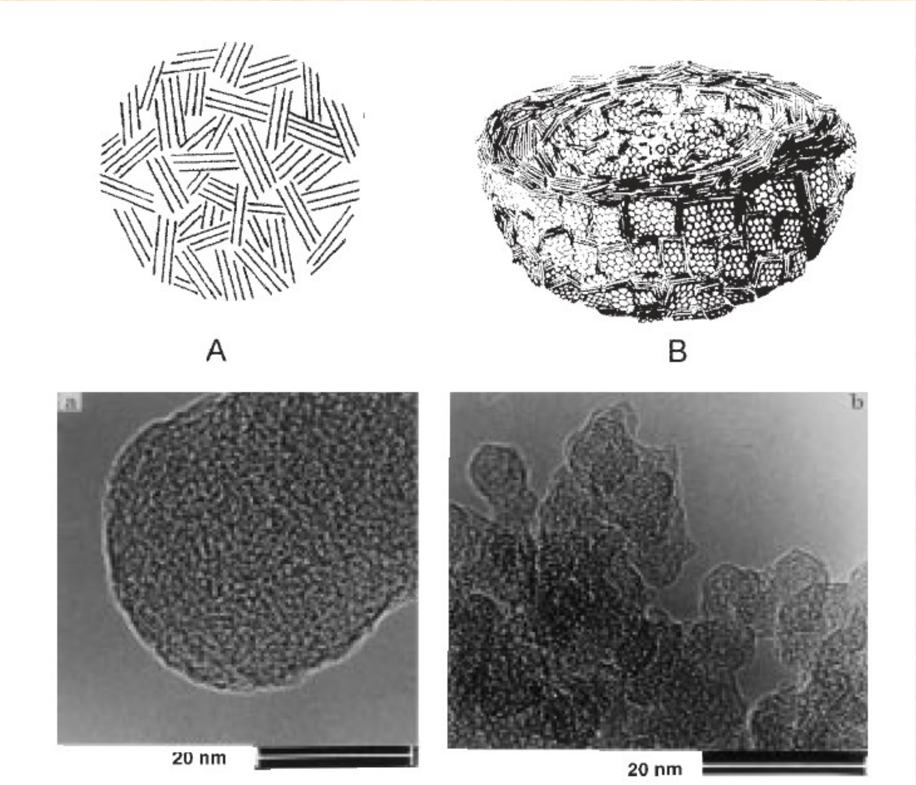
Onions



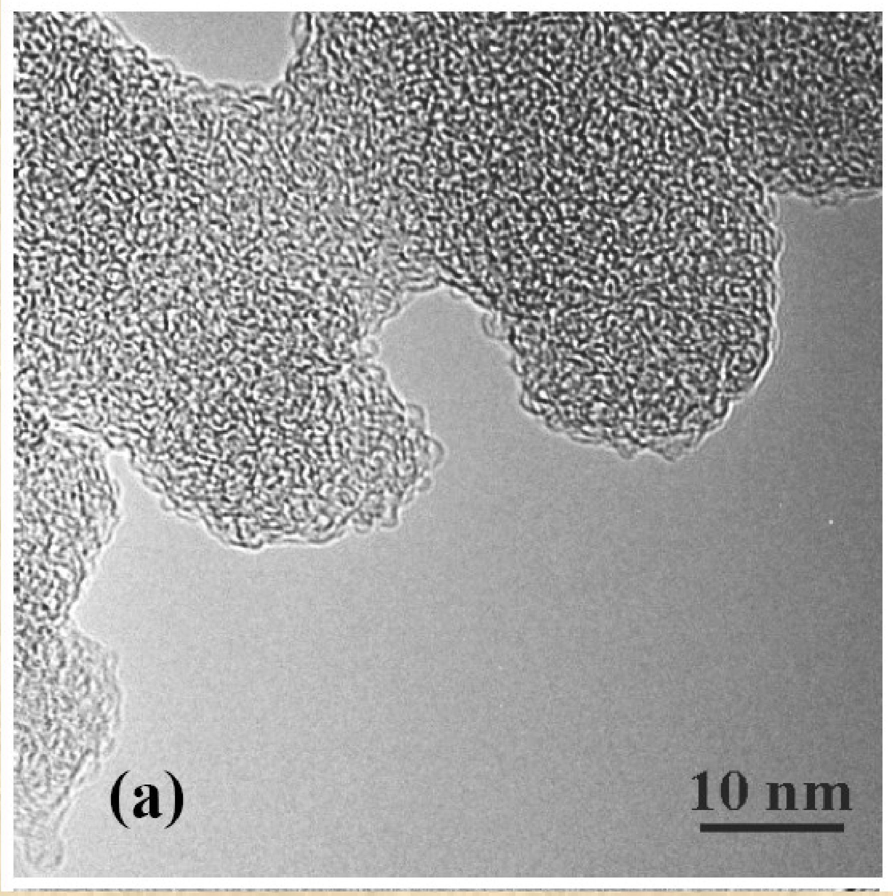


Th. Henning and F. Salama,
Science 282, 2204 (1998)

Porous carbonaceous surfaces



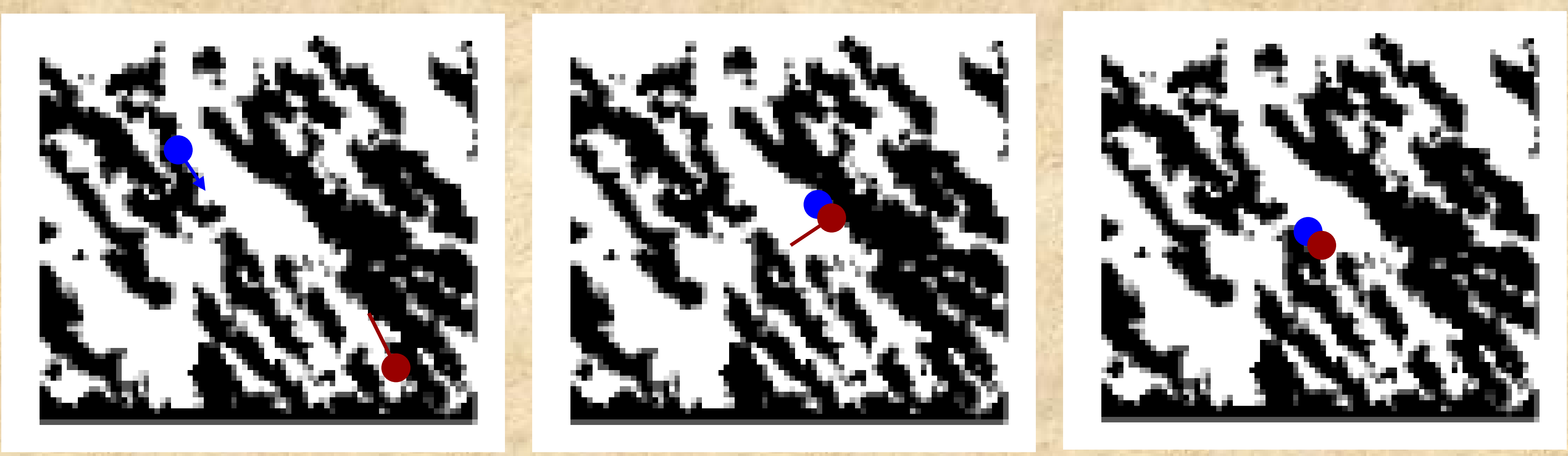
Th. Henning and F. Salama,
Science **282**, 2204 (1998)



Schnaiter et al. Ap. J. **519**, 687 (1999)

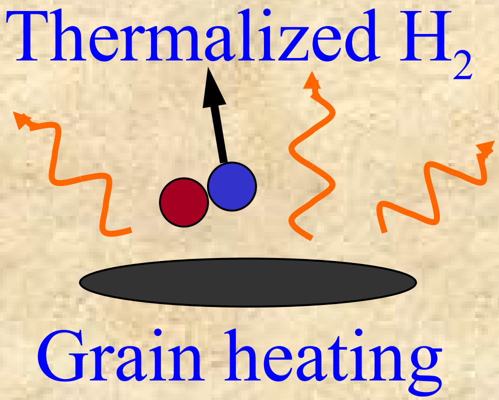
H_2 formation on ASW grown at 10 K:

Physical (Cartoon) picture

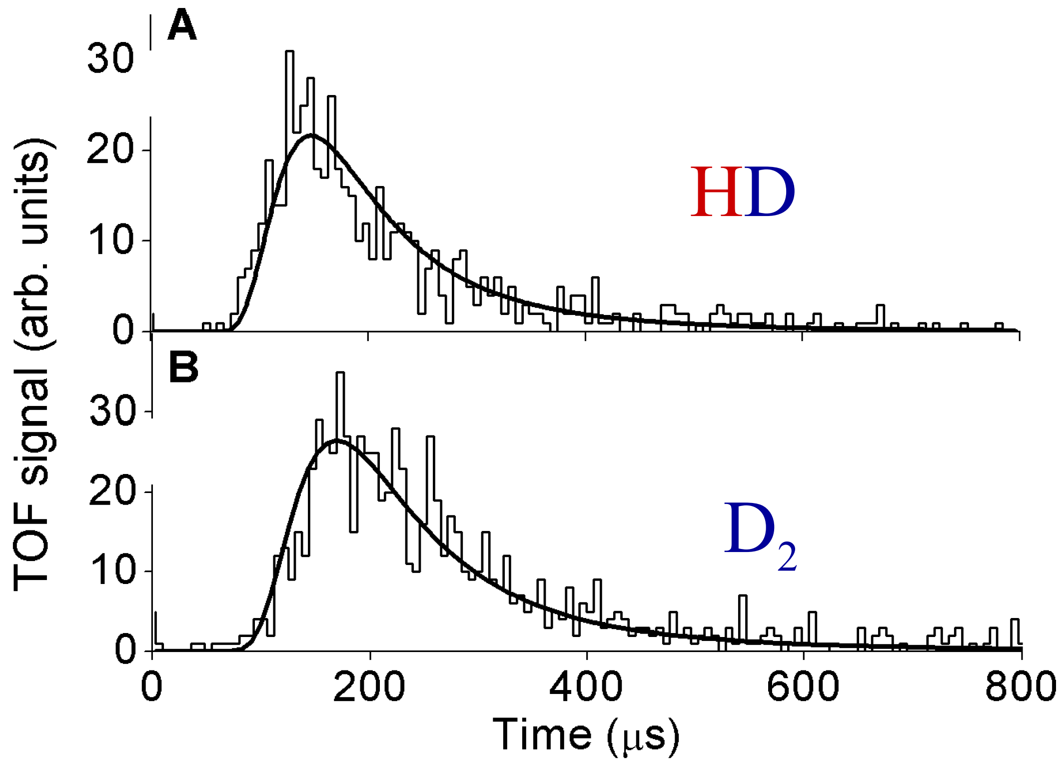


ASW figure from Kimmel et al, JCP 114 p.5295 (2001)

Due to morphology:



Kinetic energy of HD formed on porous water ice (ASW)

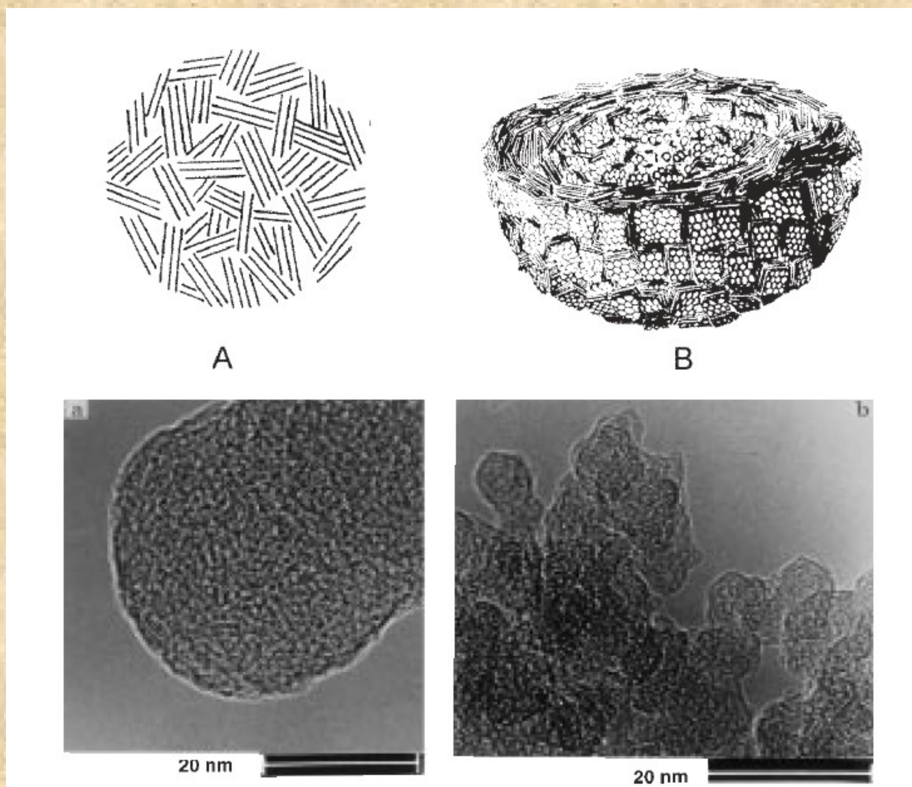


Solid line:

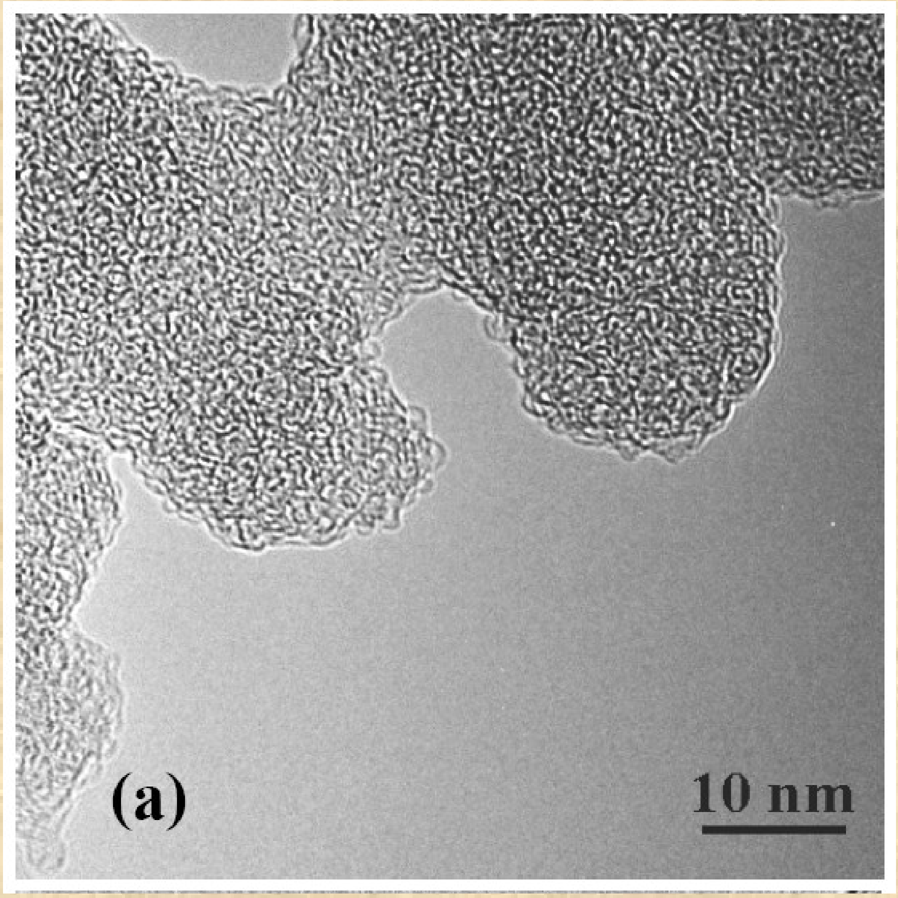
45 K Maxwell-Boltzmann velocity dist.

L. Hornekær et al., Science, **302**, 1943 (2003)

Porous carbonaceous surfaces

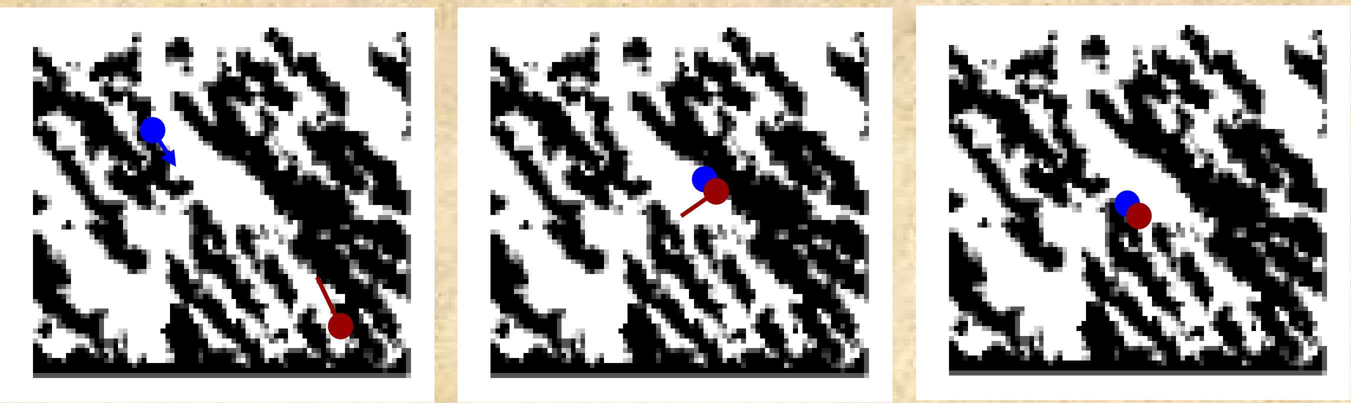


Th. Henning and F. Salama,
Science **282**, 2204 (1998)



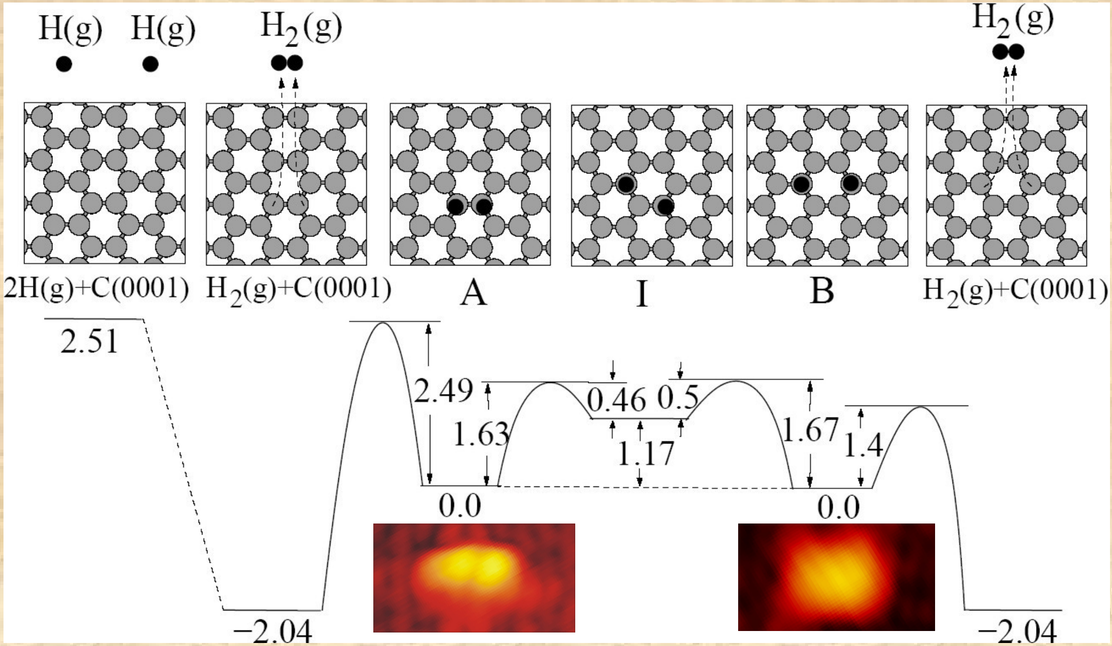
Schnaiter et al. Ap. J. **519**, 687 (1999)

Surface astrochemistry: Morphology is a key issue



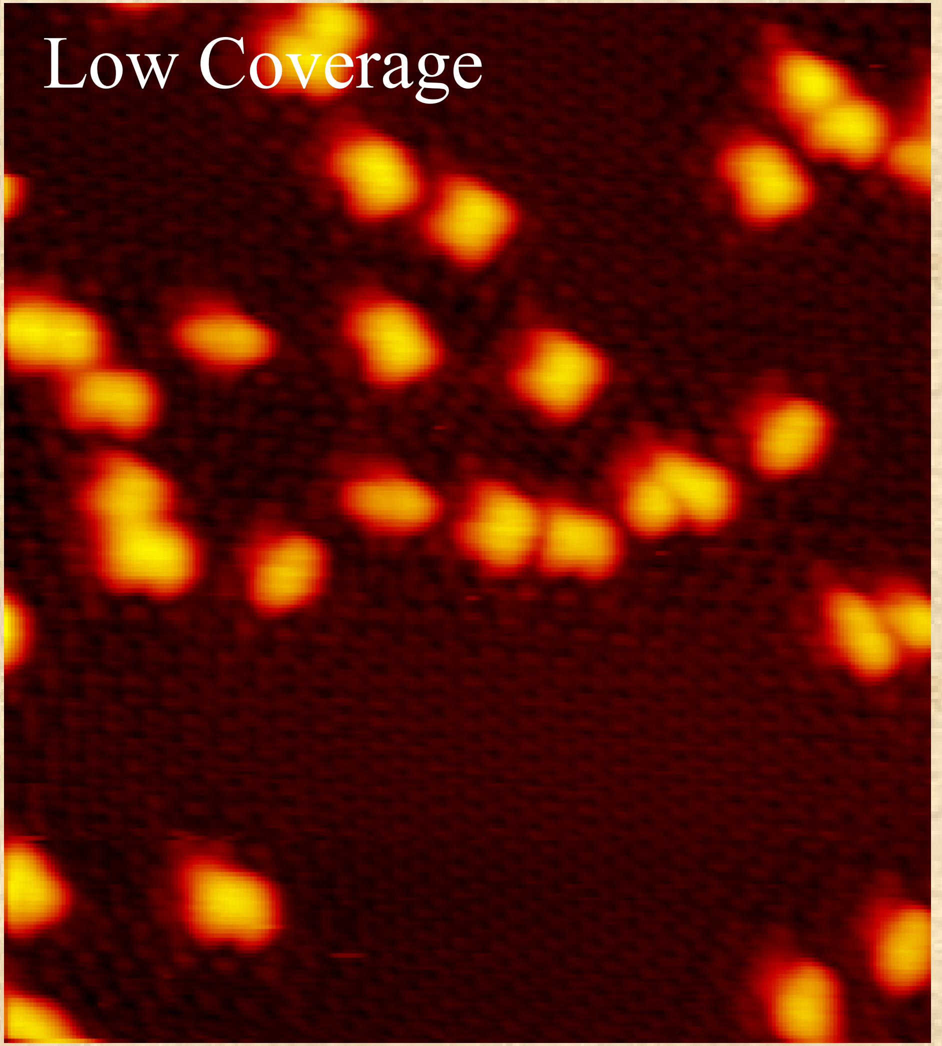
H_2 formation on water ice

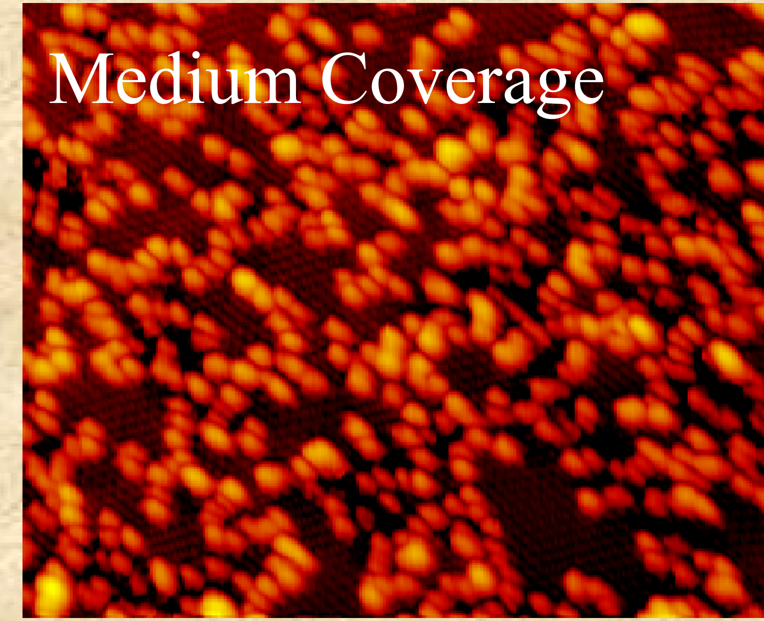
H_2 formation on graphite

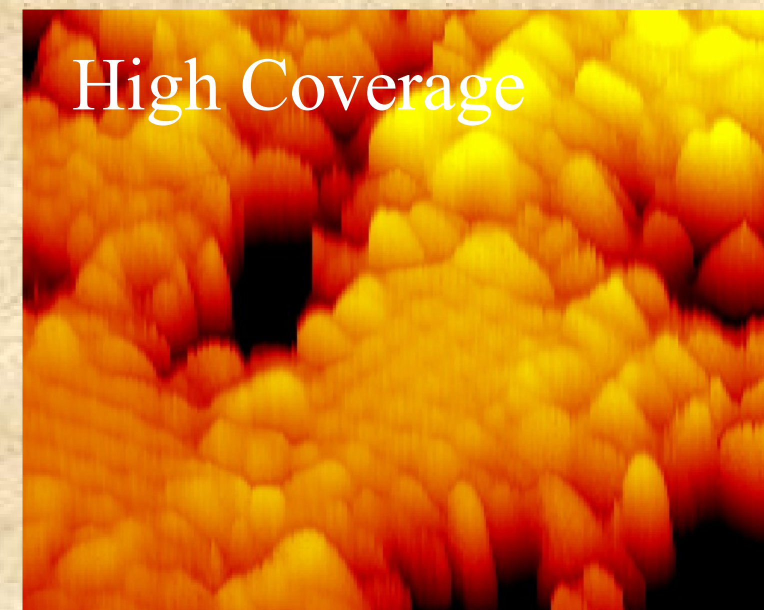


H on HOPG

171 x 155 Å^2







103 x 114 Å^2

V_t~800mV, I_t~0.15-0.2nA

80 x 72 Å^2

People involved

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EPFL

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Arnd Baurichter
Victor Petrunin
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Dept. Phys. SDU

Thomas Zecho
Univ. Bayreuth
and MPG Plasma