H-graphite: Adsorption / desorption / recombination

Liv Hornekær
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Tokamac plasma facing materials

Interstellar Catalysis

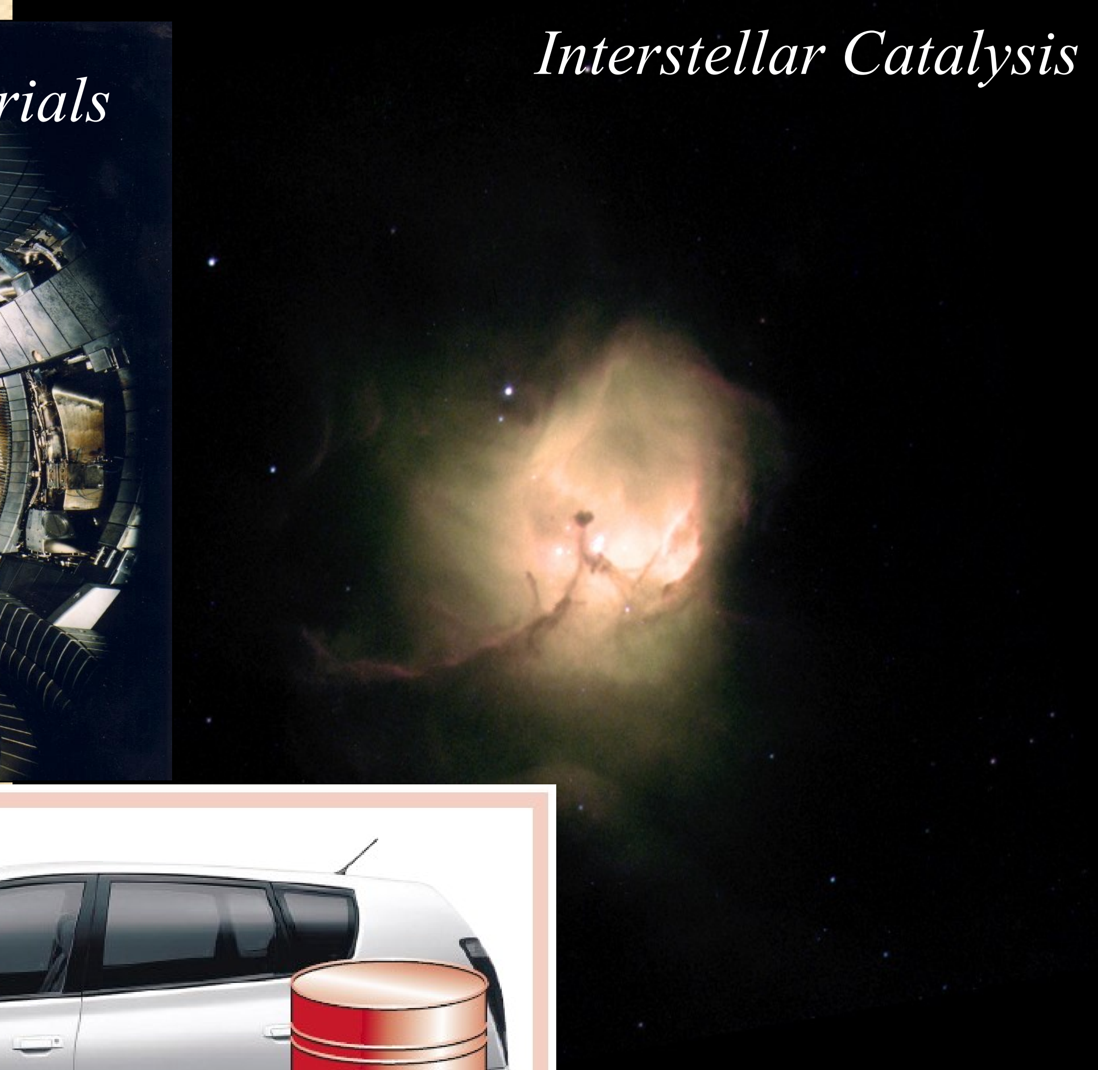
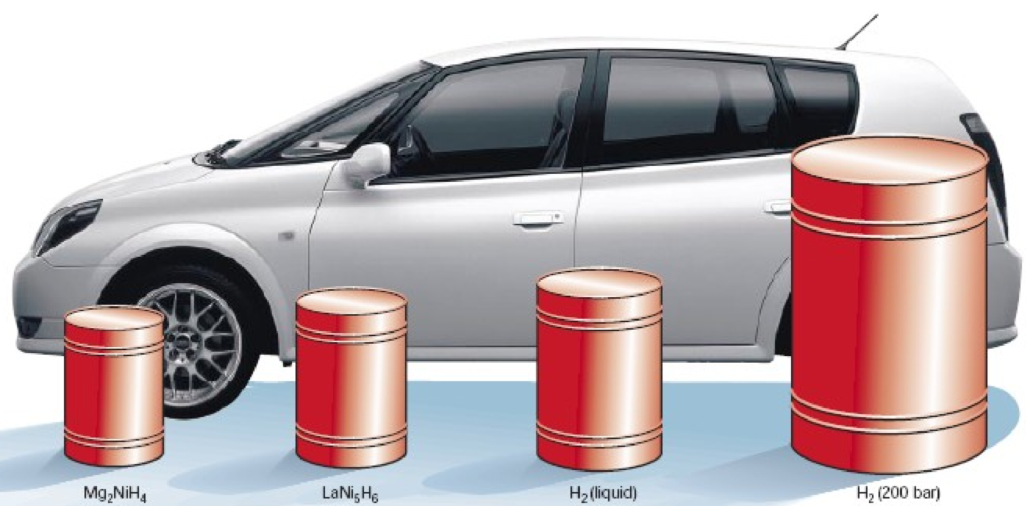


Figure 1 Volume of 4 kg of hydrogen compacted in different ways, with size relative to the size of a car. (Image of car courtesy of Toyota press information, 33rd Tokyo Motor Show, 1999.)

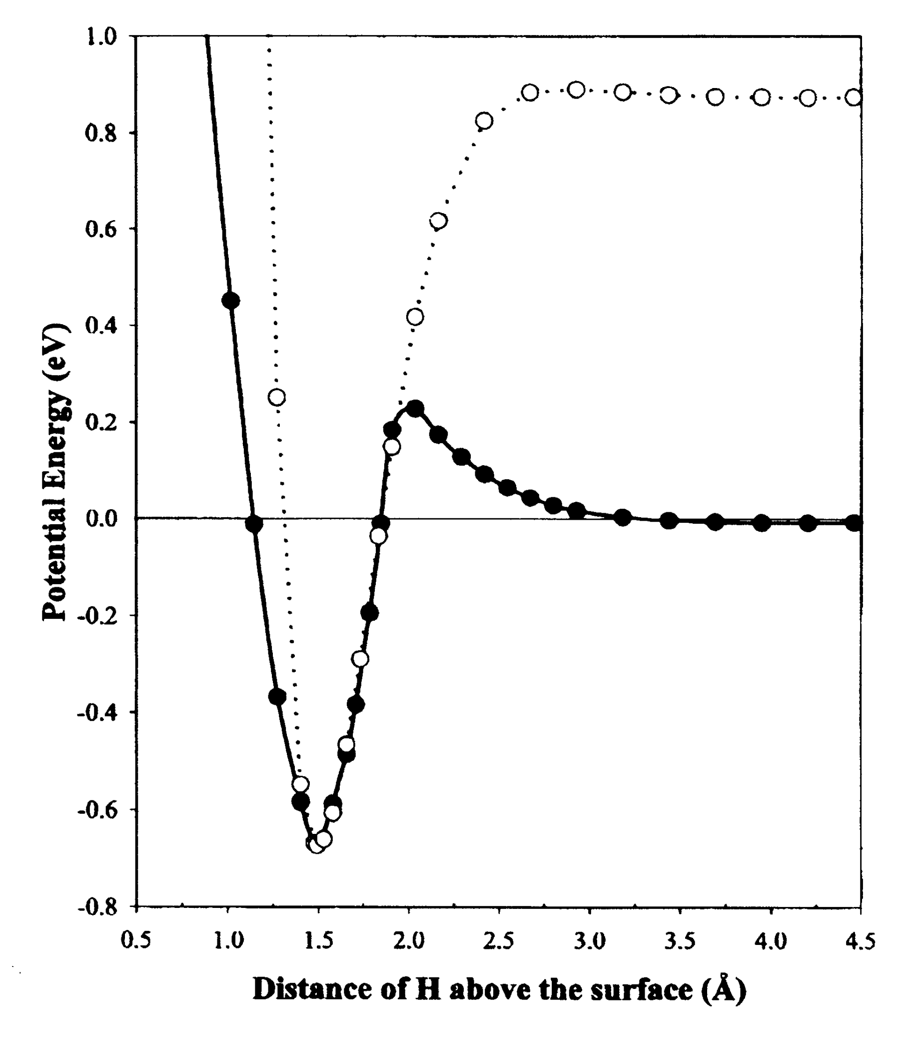


Hydrogen storage for automotive applications

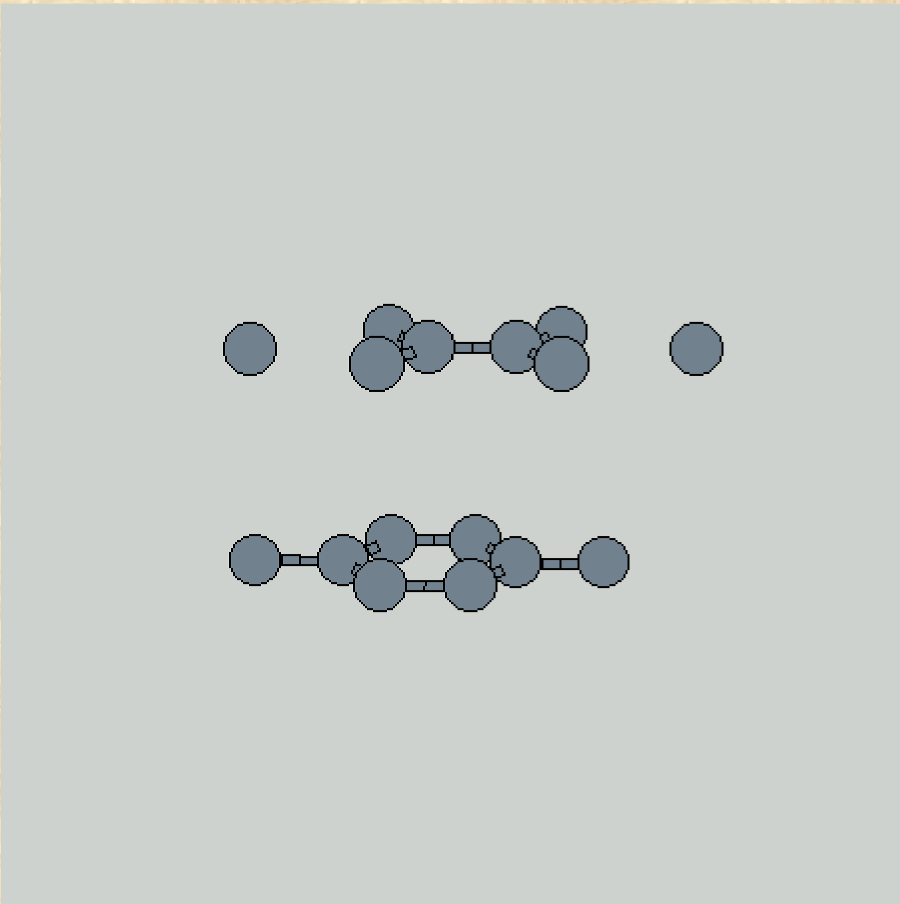
H chemisorbed on graphite

Neumann et al. Appl. Phys. A ***55****, 489 (1992)*

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

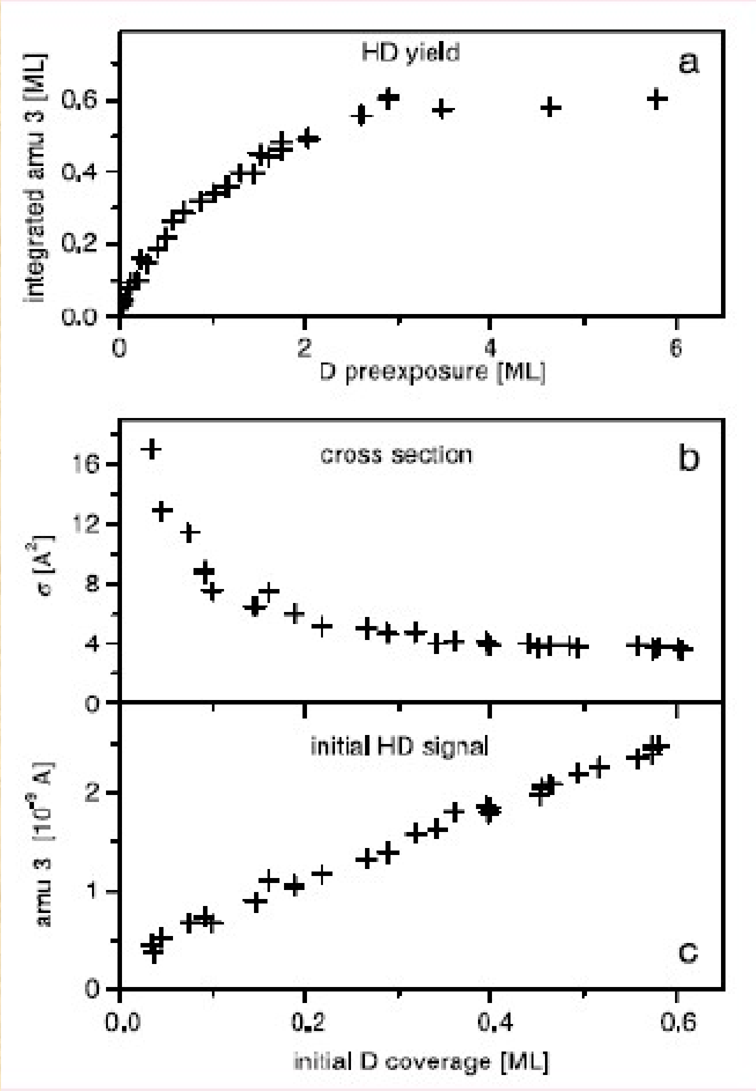


Sha et al, Surface Science 496, 318 (2002)



Eva Rauls

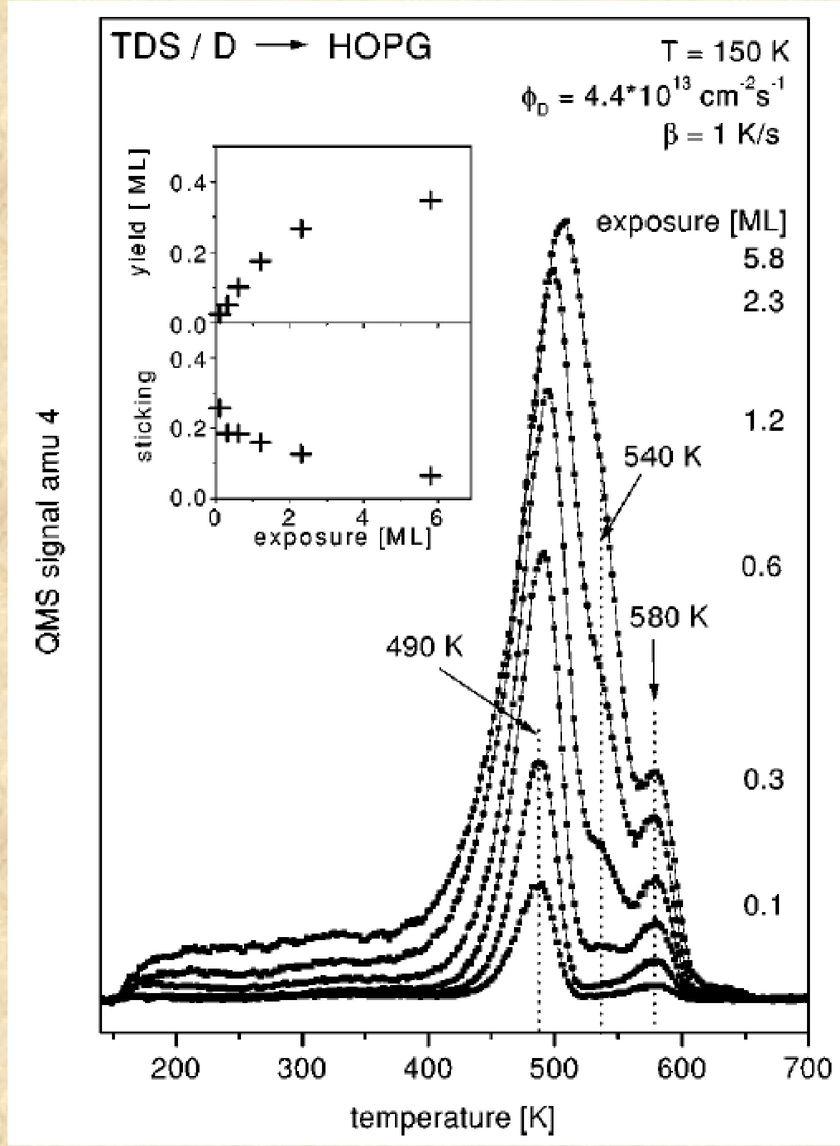
H_2 (HD) formation on graphite – Eley-Rideal Abstraction



Zecho et al, Chem. Phys. Lett. 366, 188 (2002)

Jeloaica & Sidis (2001),
Meijer et al. (2001),
Sha et al. (2002),
Morisset et al. (2004),
Matinazzo & Tantardini (2006),
Bachellerie et al. (2007),
Thomas et al. (2008)

H_2 formation on graphite - TDS



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

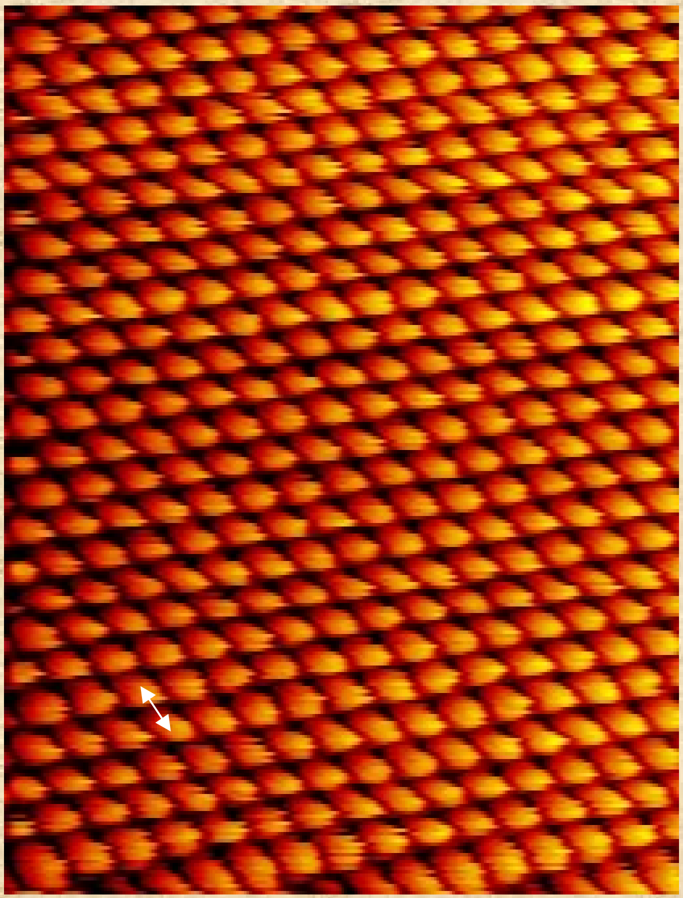
n=1 => First order desorption

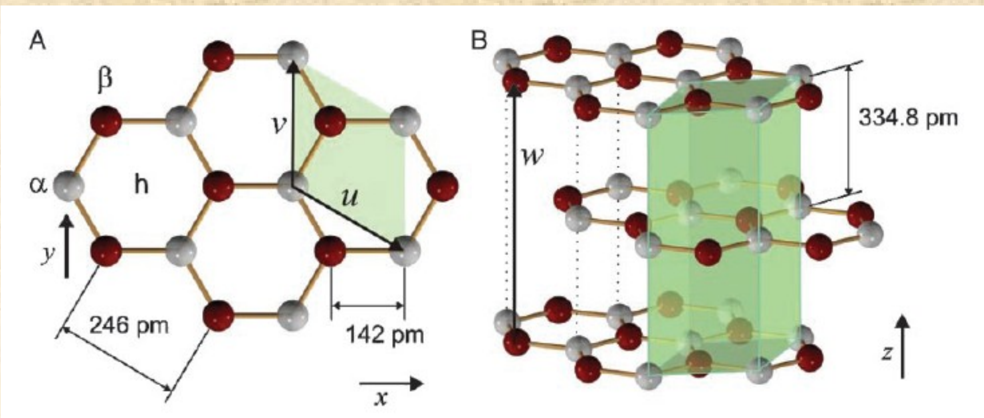
490 K => 1.4 eV

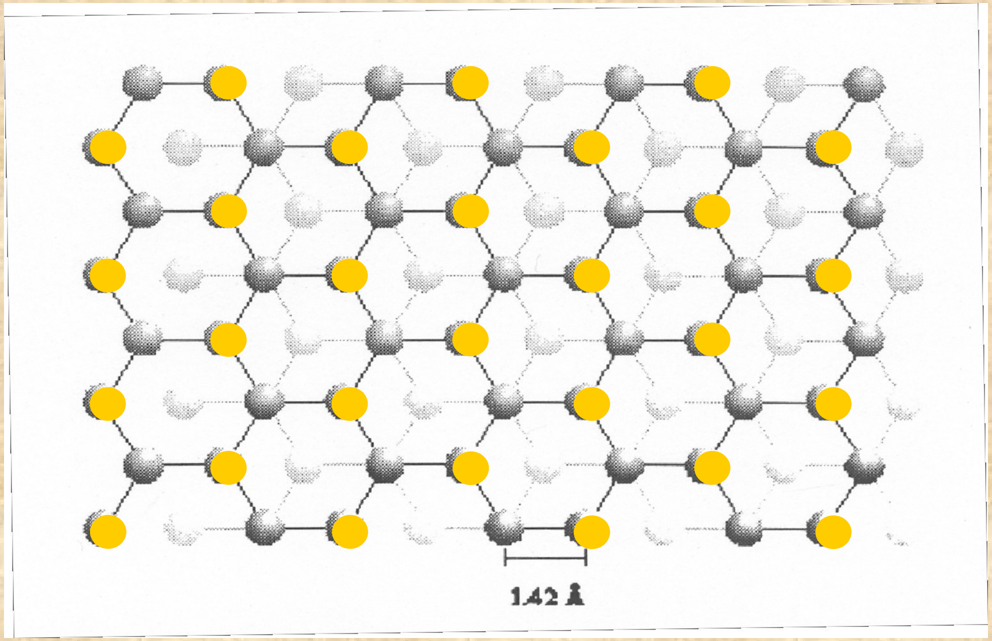
580 K => 1.6 eV

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

STM on graphite

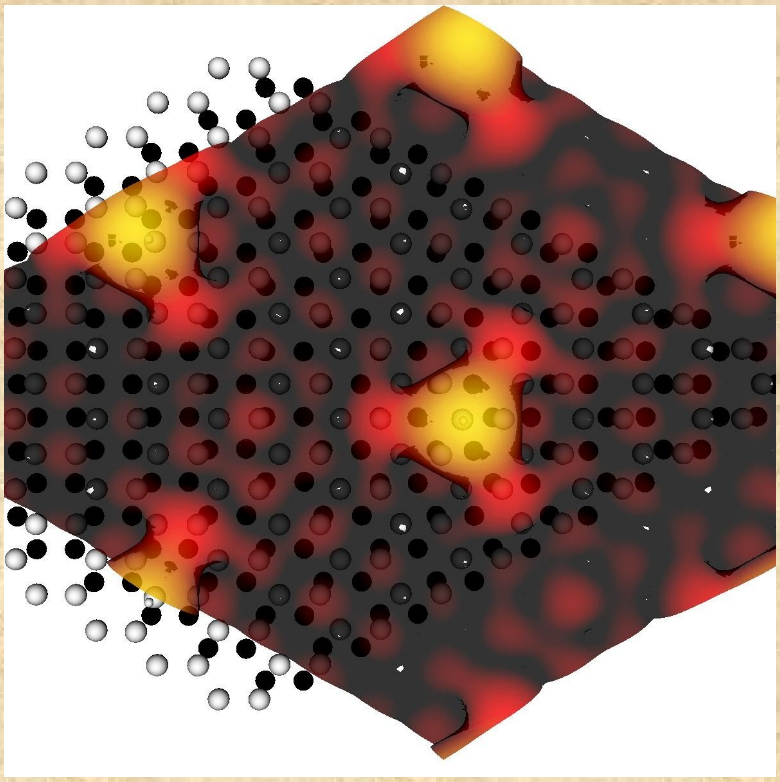




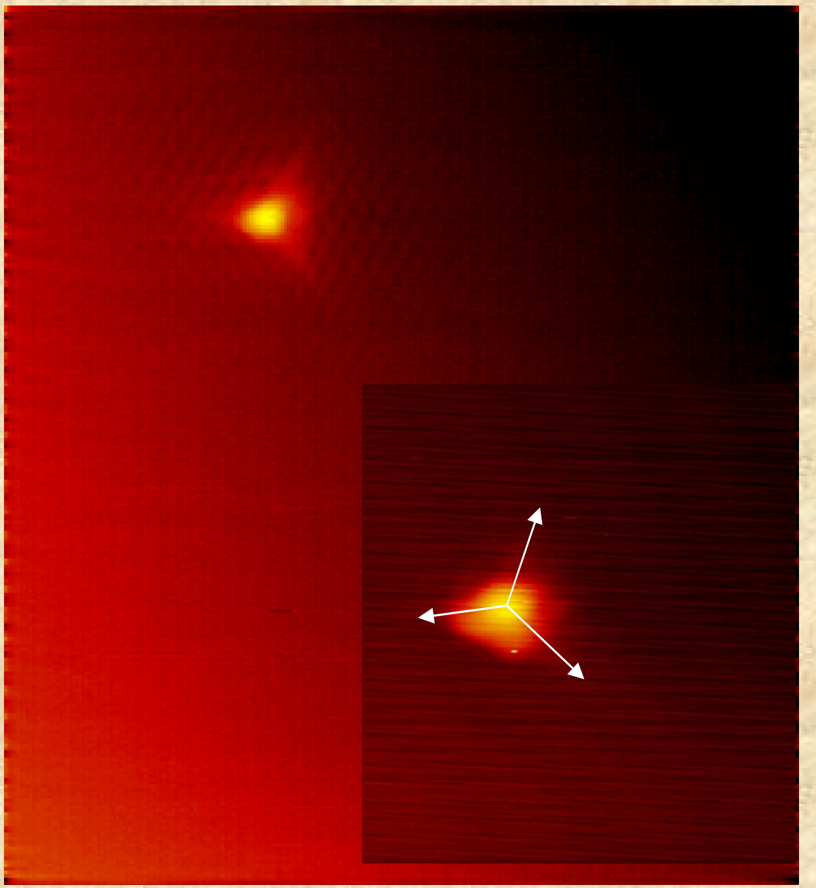


↕ 2.46 Å

Hydrogen on graphite –Monomers



Zeljko Sljivancanin

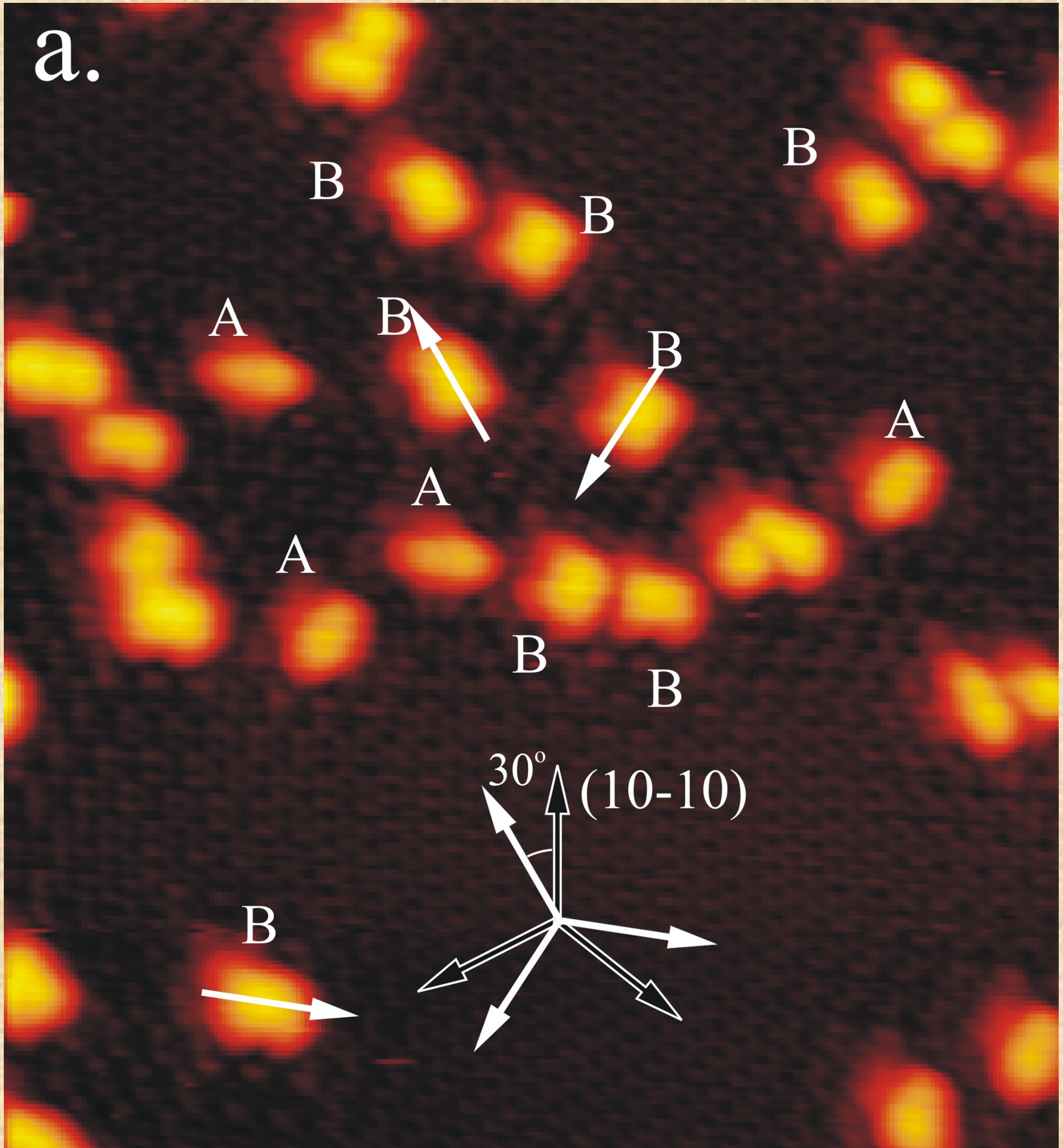


155 x 171 Å^2 , 180 K

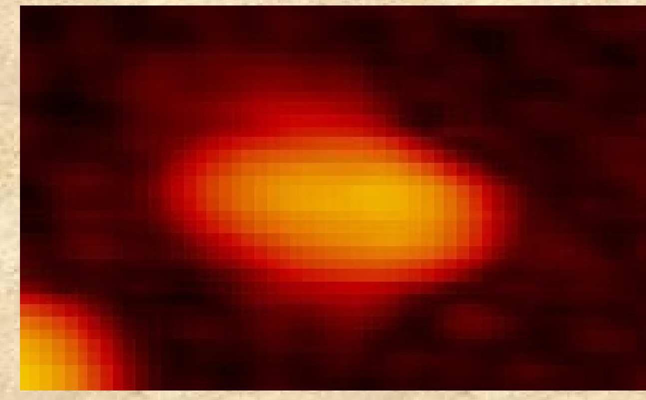
V_t~ -710mV, I_t~ -0.16nA

H-Dimers on graphite

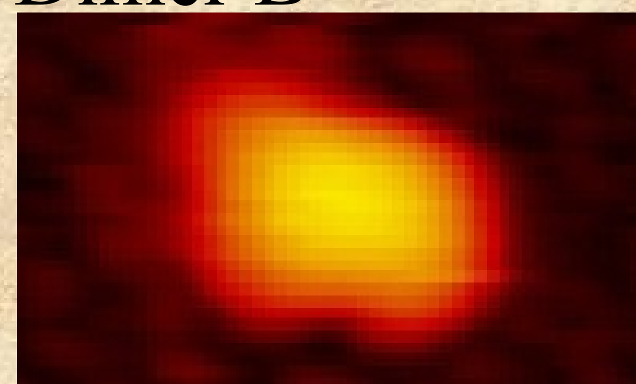
103 x 114 Å^2



Dimer A



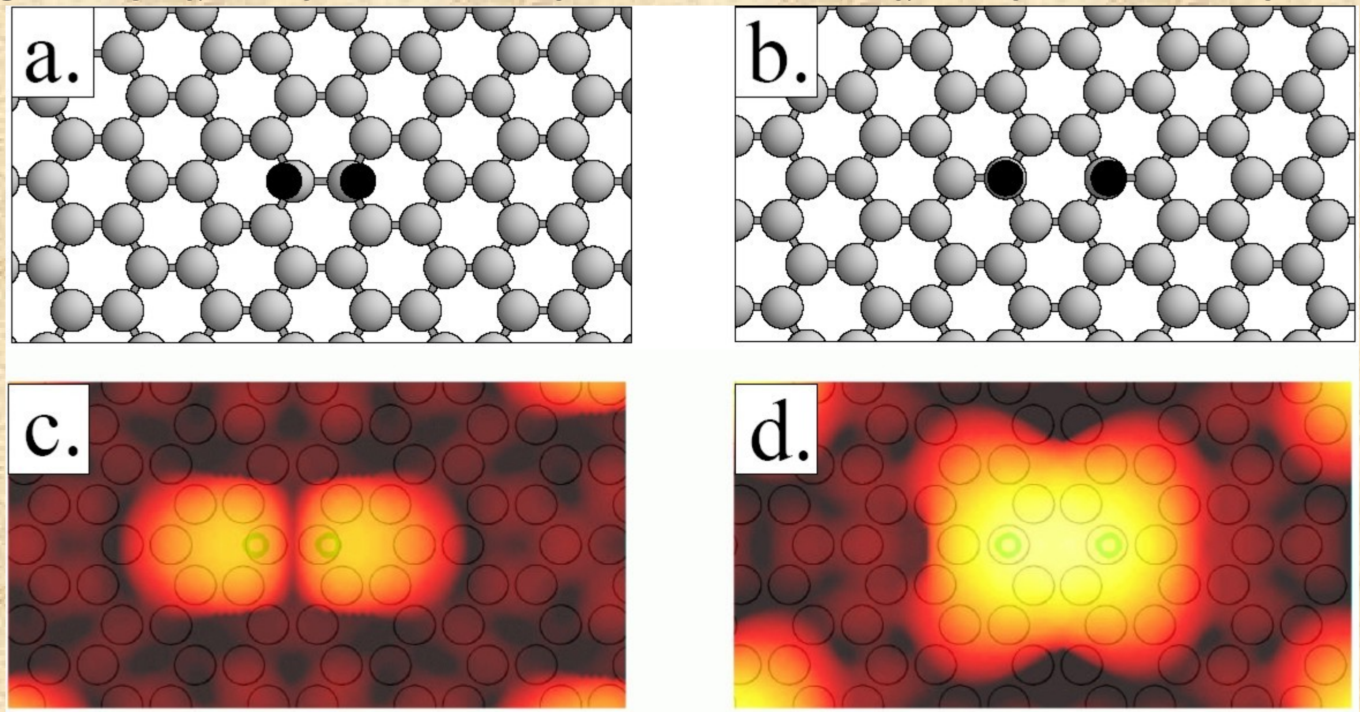
Dimer B



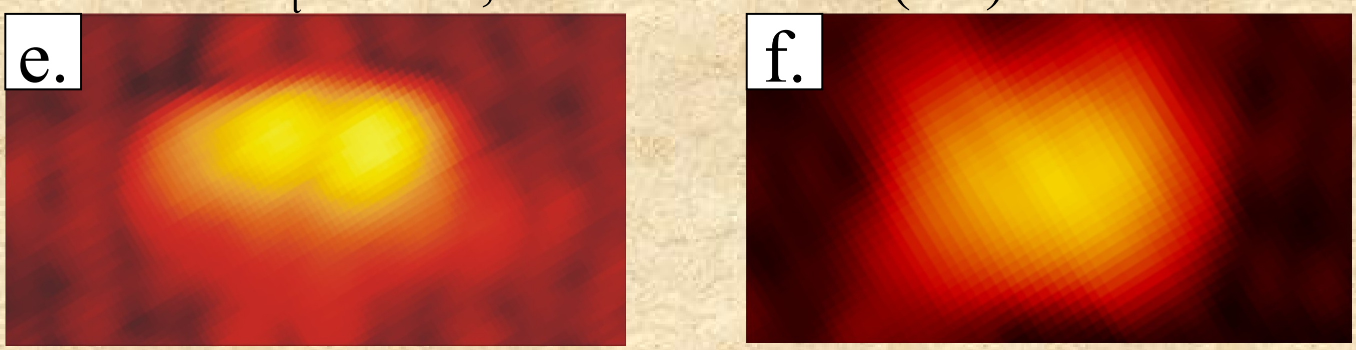
$V_t = 884$ mV, $I_t = 0.16$ nA

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

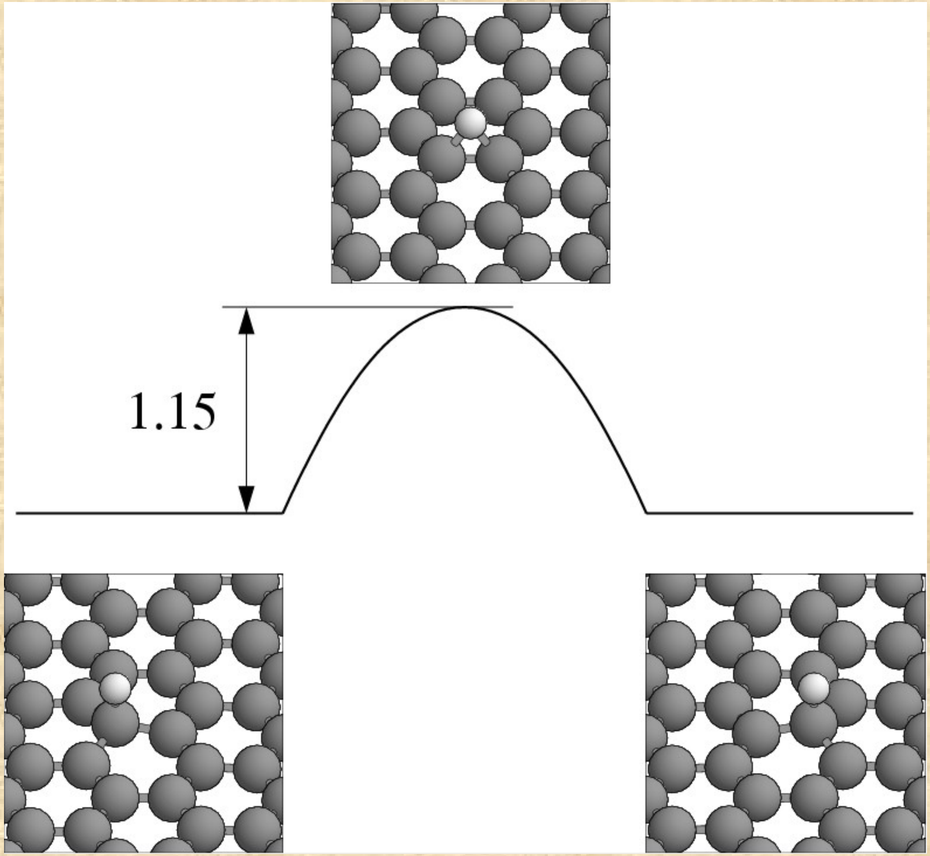
Hornekær et al. Phys. Rev. Lett. ***96****, 156104 (2006)*

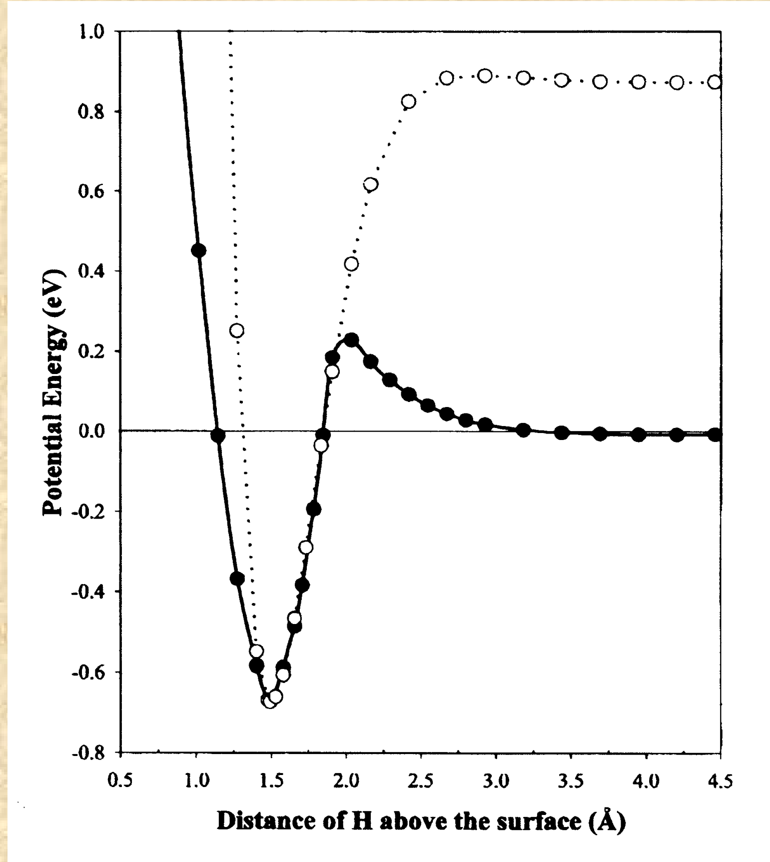
Similar results for ortho dimer:
Ferro et al. Chem. Phys. Lett. ***368****, 609 (2003).*
Y. Miura et al. J. Appl. Phys. ***93****, 3395 (2003).*

Diffusion

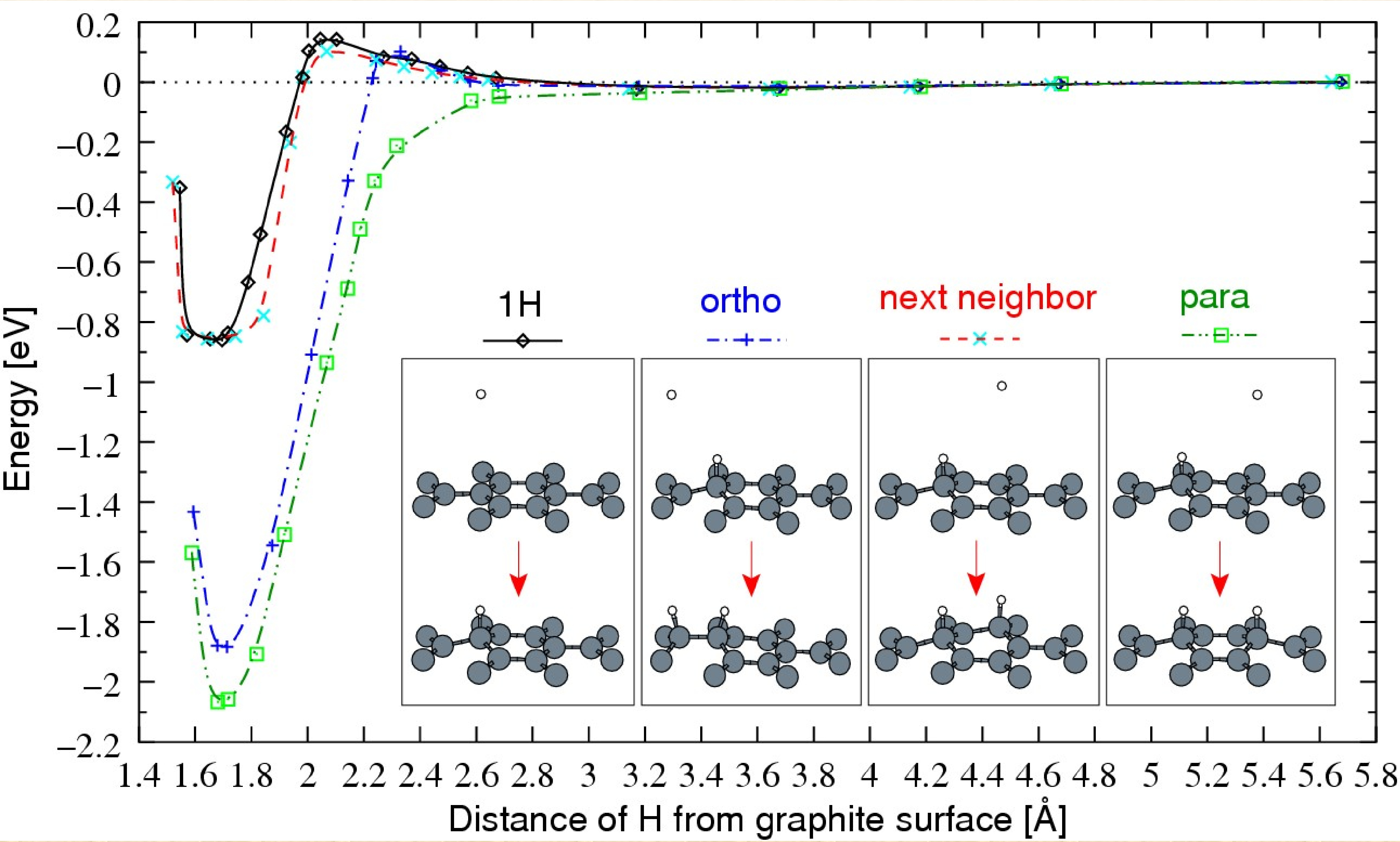
Barrier to diffusion for an isolated H atom: 1.15 eV

Barrier to desorption for an isolated H atom: 0.9 eV





Dimer formation

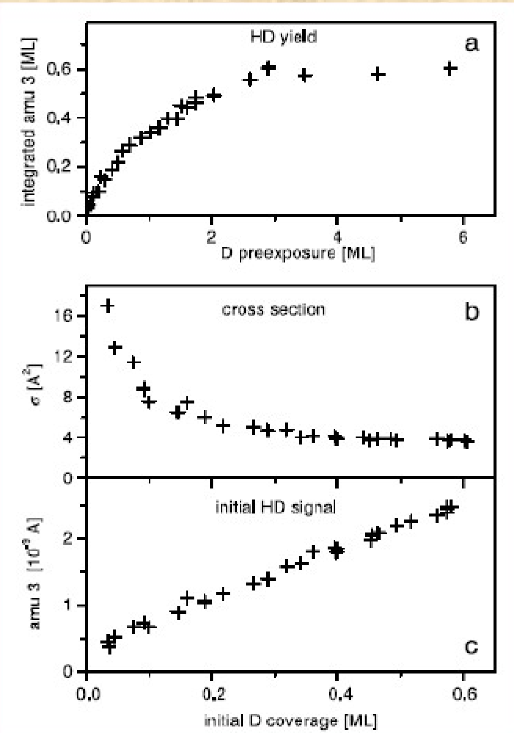


Hornekær et al. Phys. Rev. Lett. **97,** 186102 (2006)

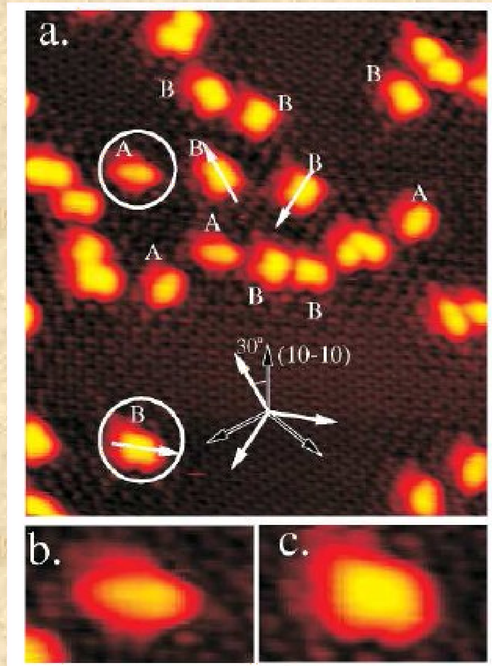
Zero barrier sticking into para-dimer also found by:

Rougeau et al. Chem. Phys. Lett. **431,** 135 (2006)

Kinetic Monte Carlo Simulations -Experimental benchmarks



Zecho et al, Chem Phys Lett, 366 (2002) 188



∼85 % of atoms in dimer conf. at 0.01 ML

Hornekær et al. PRL 96, 156104 (2006)

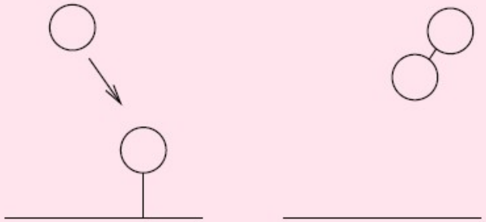
All D abstracted at long H exposure

Thomas et al, Surf. Sci. 602, 2311 (2008)

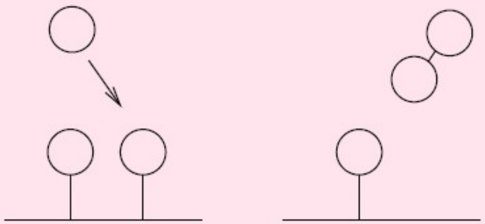
Cuppen & Hornekær, J. Chem. Phys. **128,** 174707 (2008)

Eley-Rideal Abstraction Mechanisms

Direct Eley-Rideal

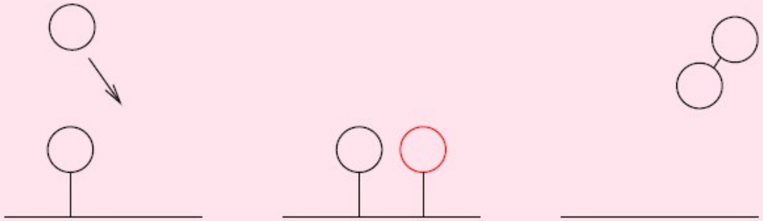


Dimer Eley-Rideal



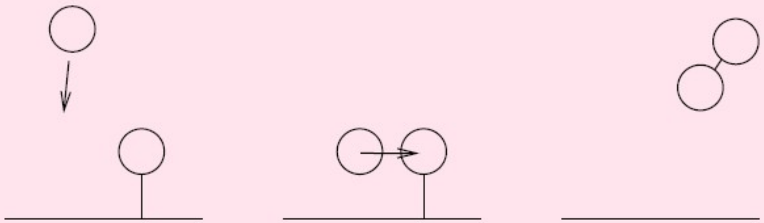
Bachellerie et al., **J.. Phys. Chem. C 111, 5825 (2007)**

Dimer mediated abstraction



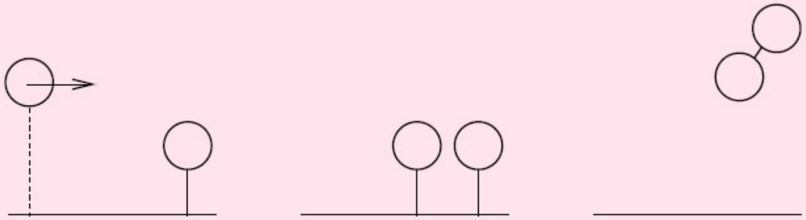
Cuppen & Hornekær, **J. Chem. Phys. 128, 174707 (2008)**

Eley-Rideal with steering



Sha & Jackson, Surf. Sci., 496 (2002) 318

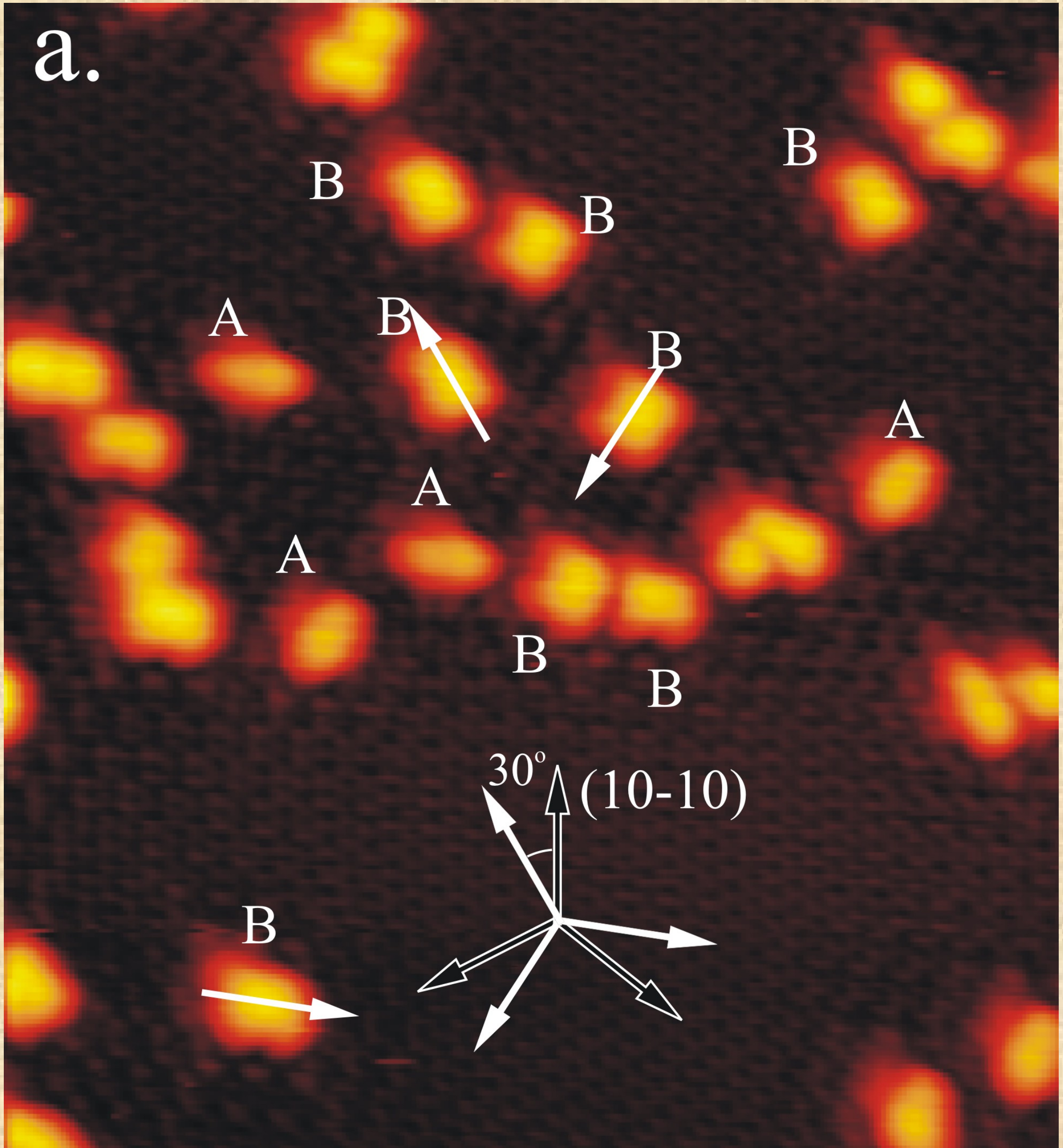
Fast diffusion of physisorbed atoms in combination with direct Eley-Rideal



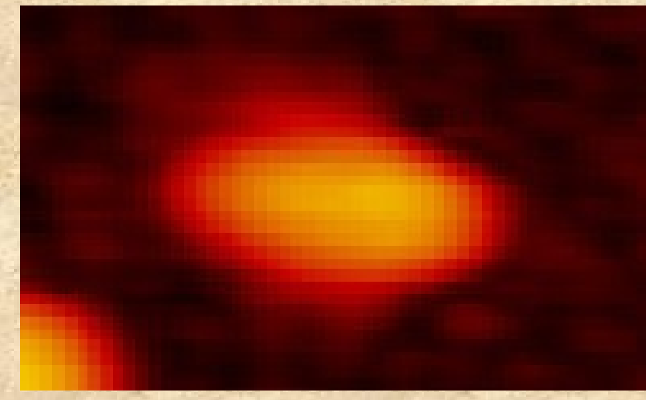
Bonfanti et al., JPC C, 111 (2007) 5825

H-Dimers on graphite

103 x 114 Å^2



A: Ortho–dimer

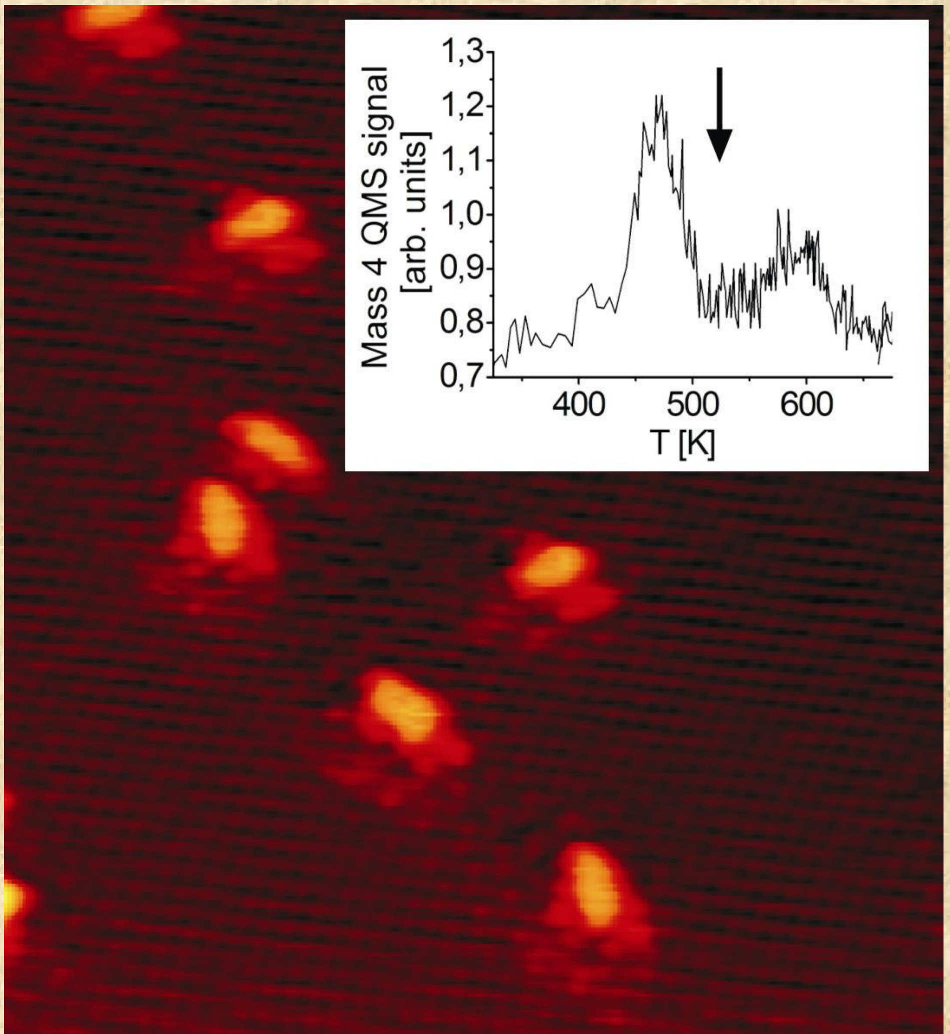


B: Para-dimer

$V_t = 884$ mV, $I_t = 0.16$ nA

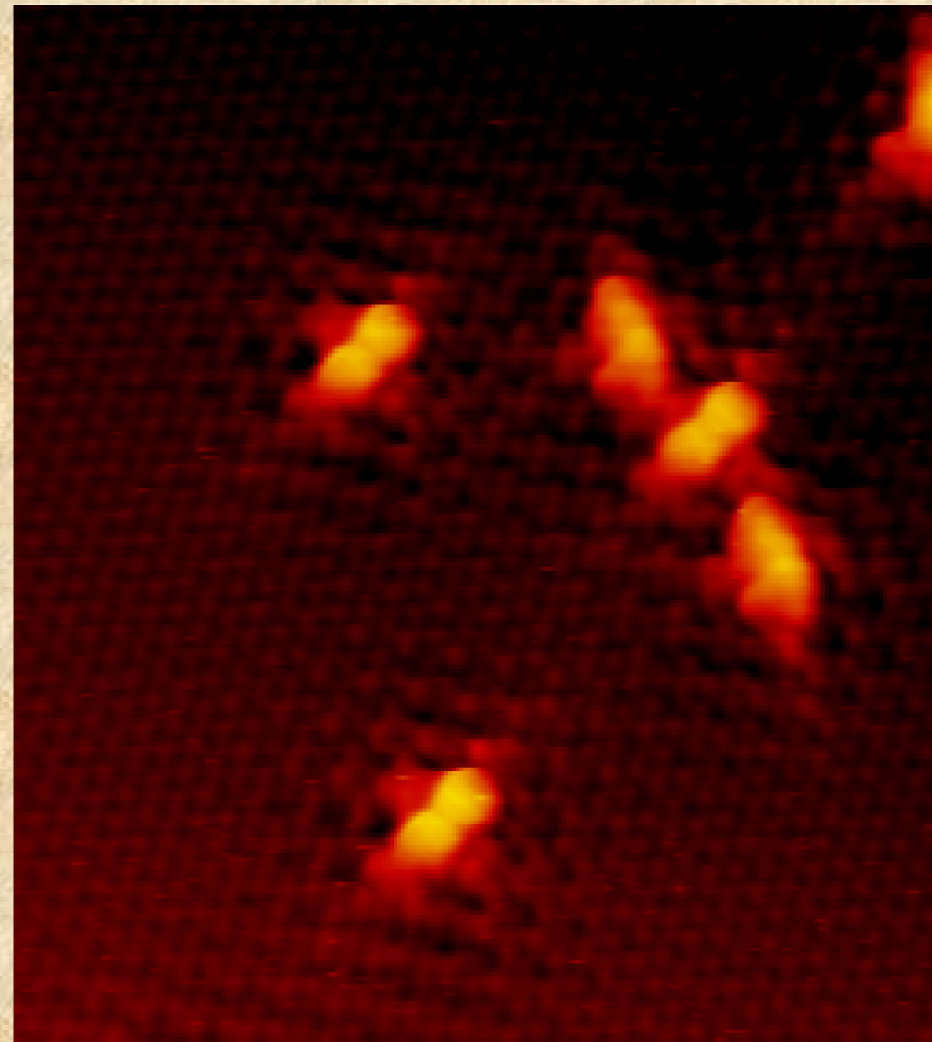
Dimers after Anneal

103 x 114 Å^2



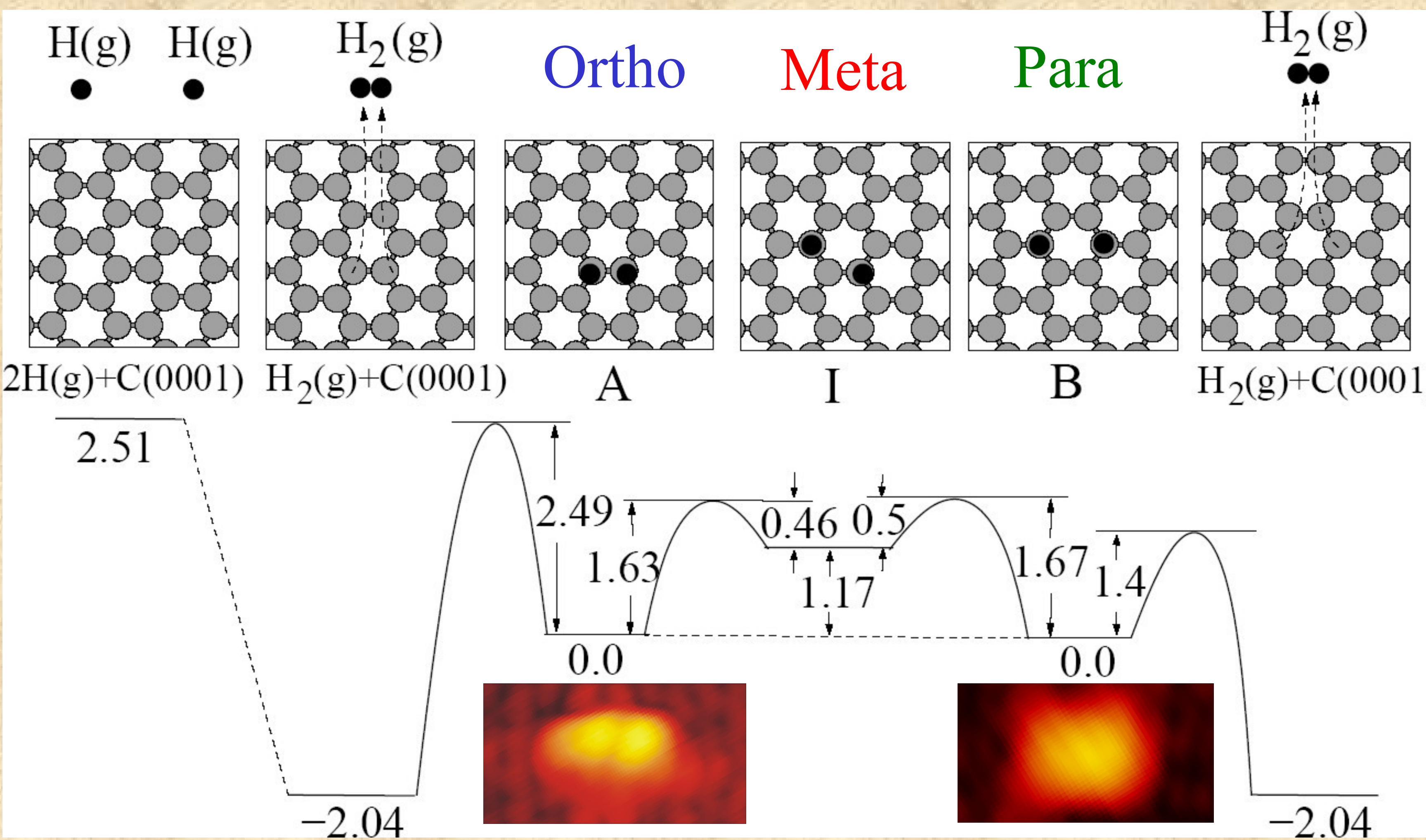
$V_t = 884$ mV, $I_t = 0.19$ nA

80 x 72 Å^2



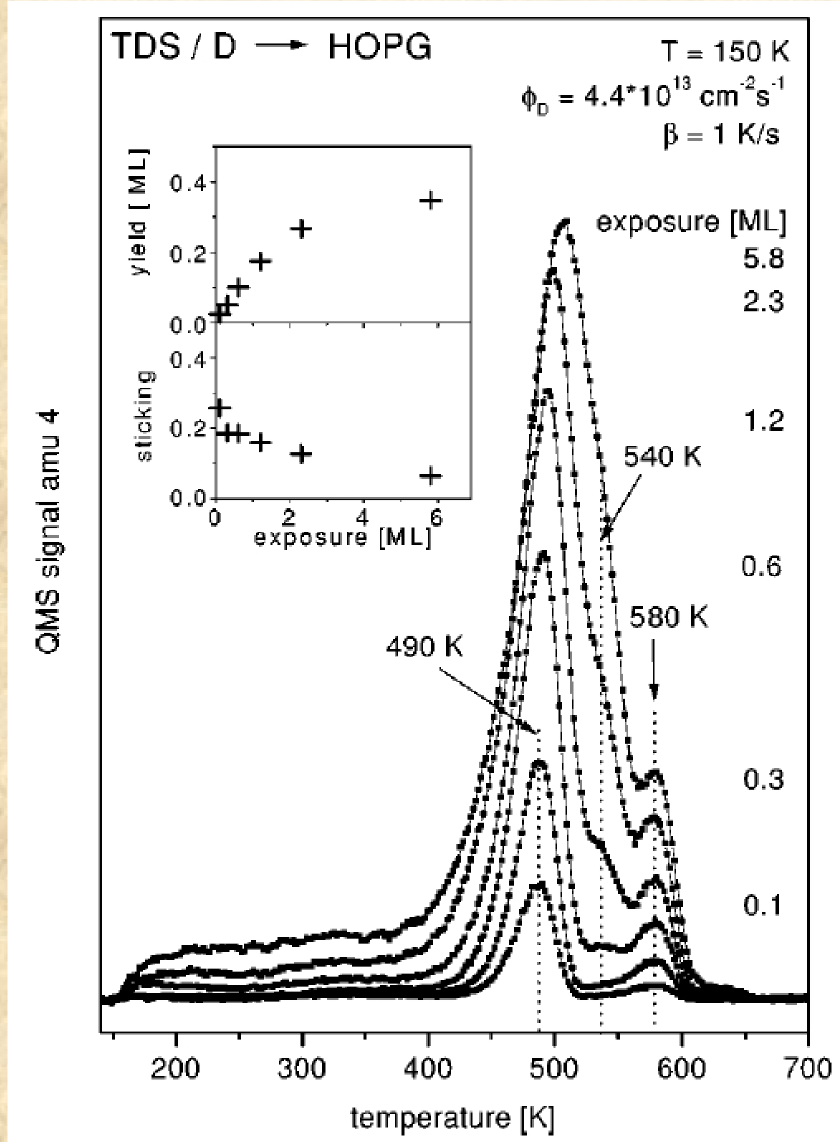
$V_t = 884$ mV, $I_t = 0.36$ nA

Recombination pathways



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

Explaining the TDS/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

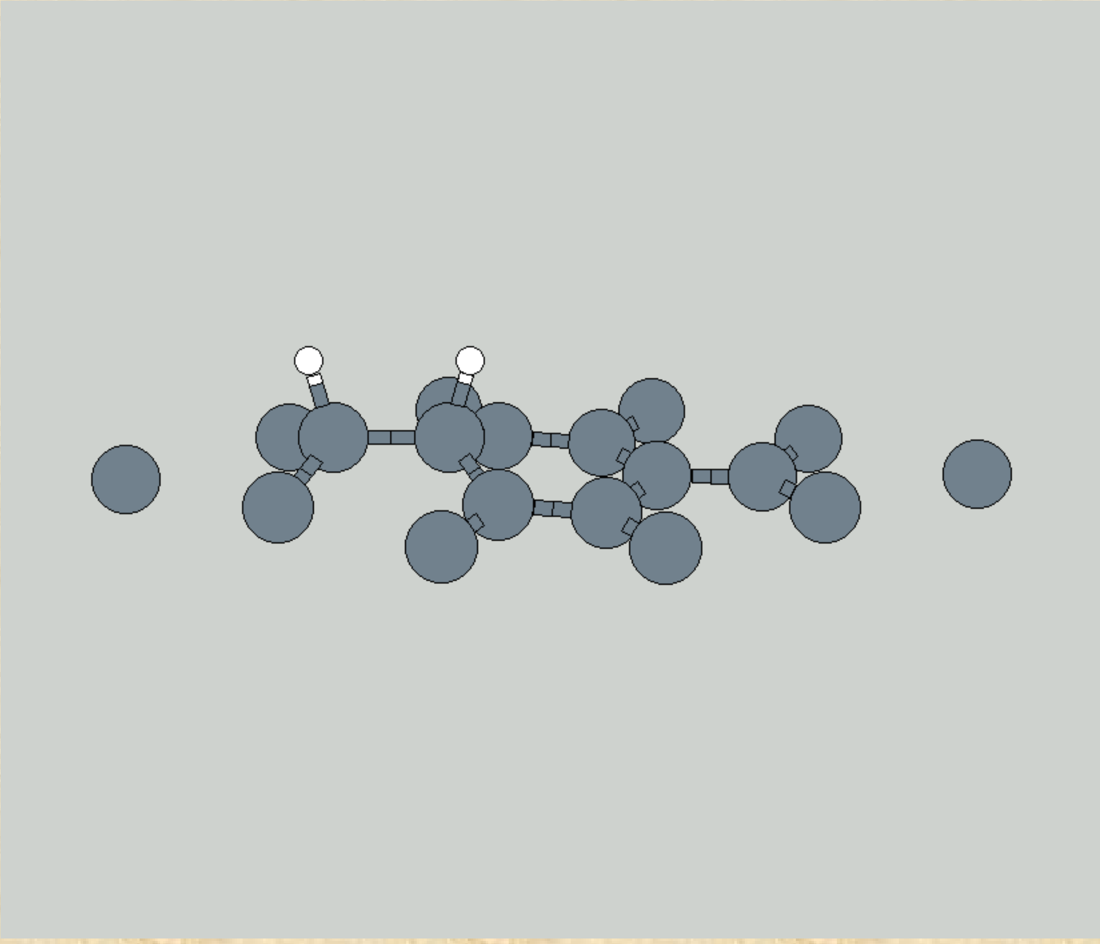
Barrier to desorption: 0.9 eV

490 K => 1.4 eV

580 K => 1.6 eV

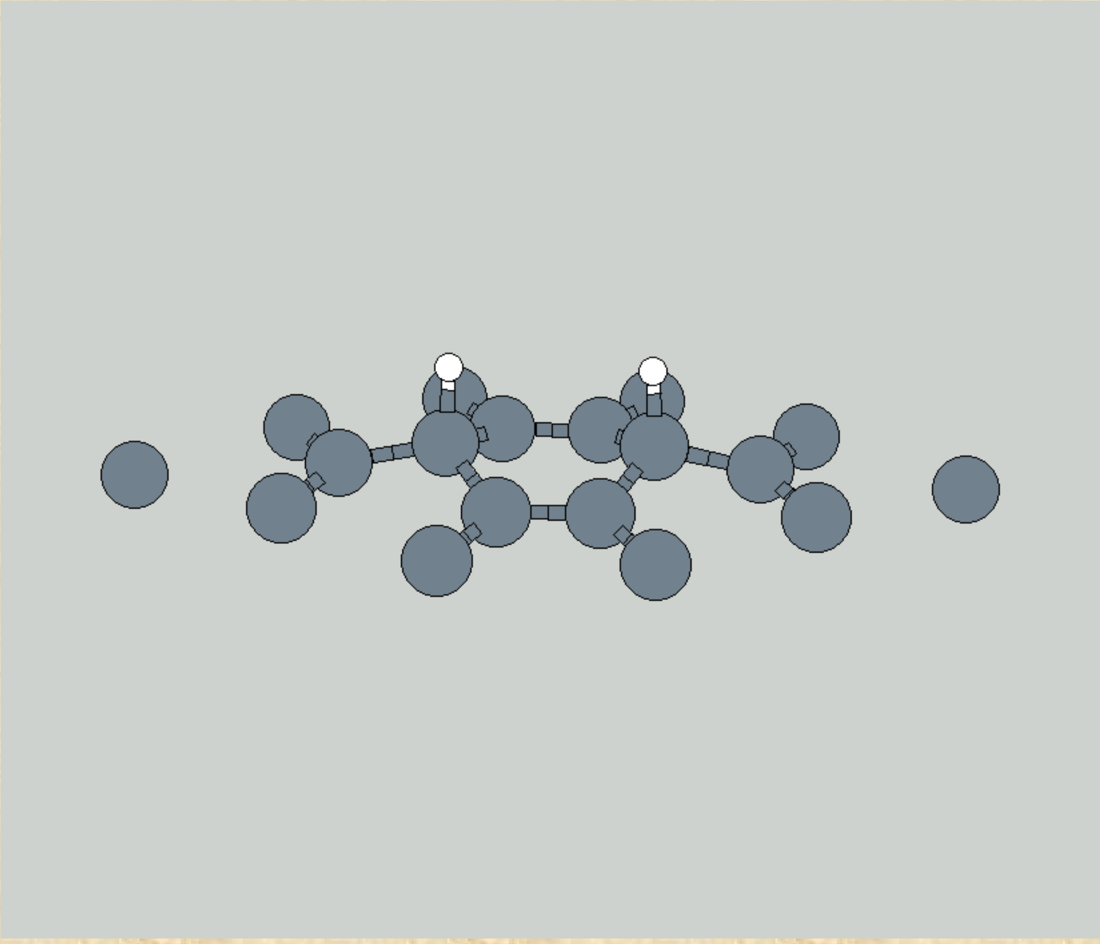
Zecho et al, J. Chem. Phys. 117, 8486 (2002)

Ortho-dimer - high barrier



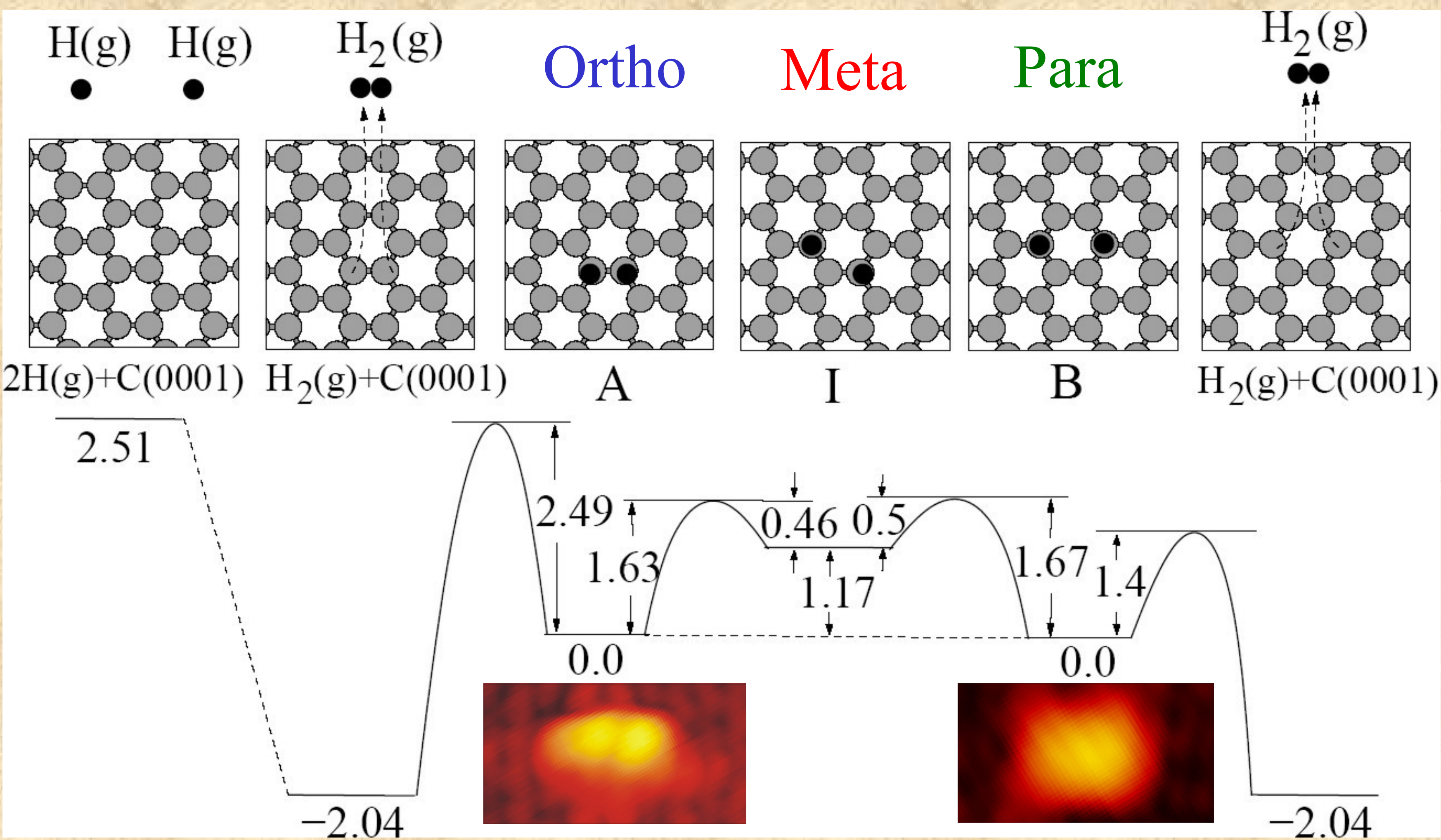
E. Rauls

Para-dimer - low barrier



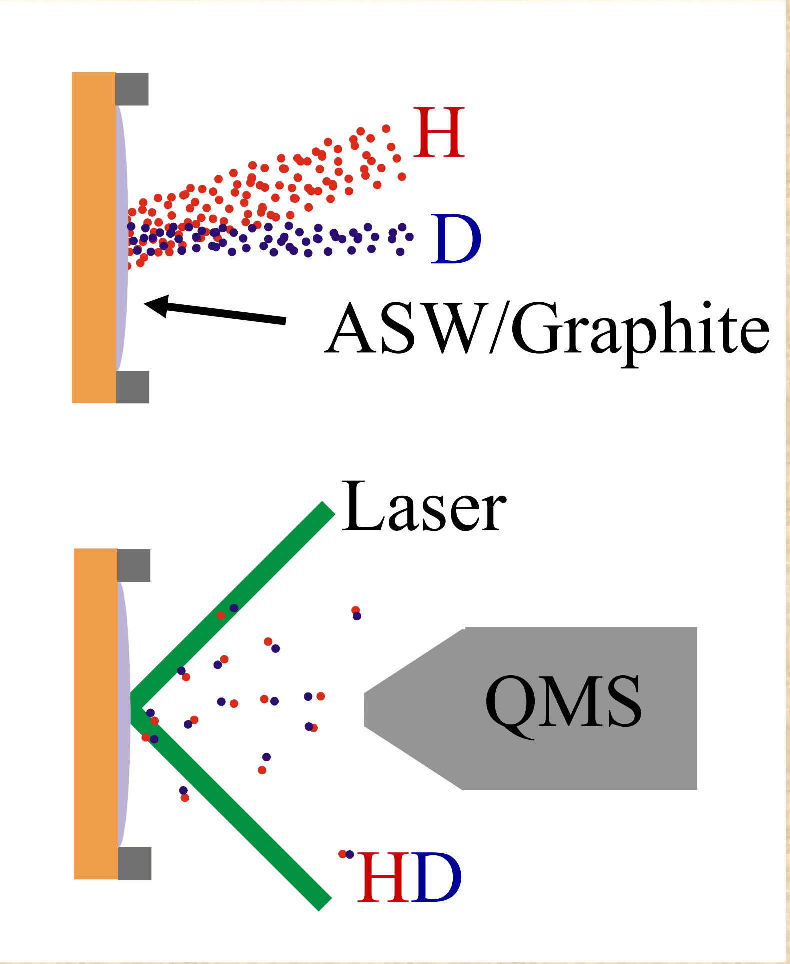
E. Rauls

Recombination pathways



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

Translational energy of formed molecules



Laser Induced
Thermal Desorption
(LITD)

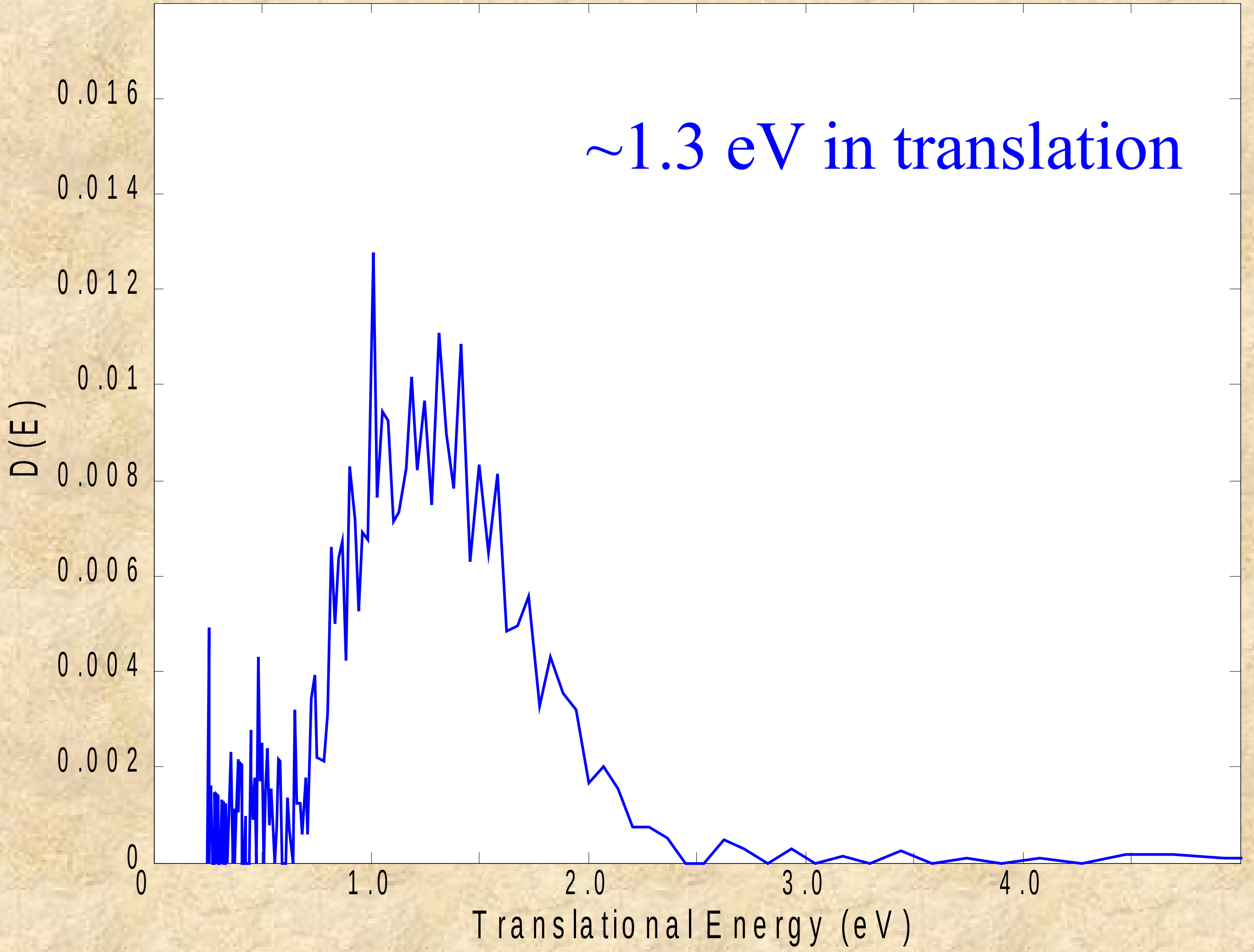
Nd:YAG /Alexandrite
Laser

200 mJ /3 mJ
17 /150 ns pulse

↓

Time of Flight Measurement

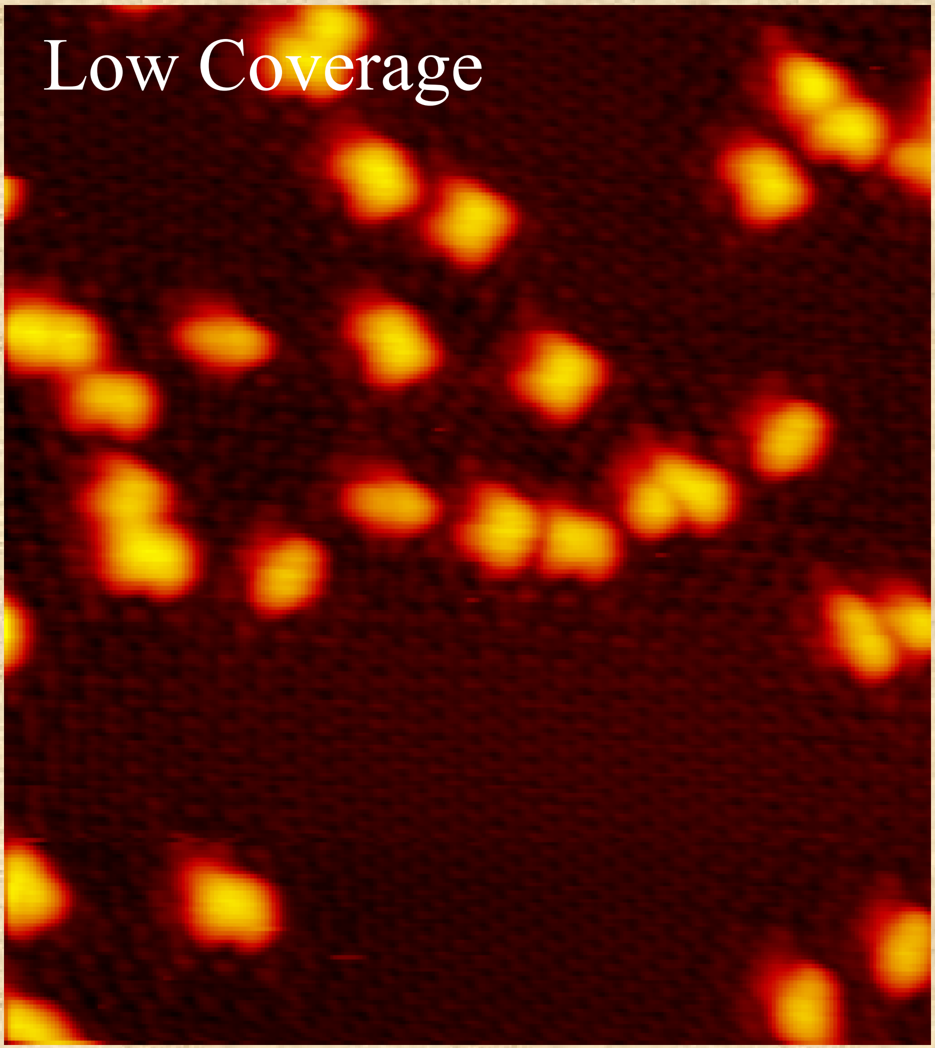
Kinetic energy of D_2 formed on graphite



S. Baouche et al. J. Chem. Phys. ***125****, 084712, 2006*

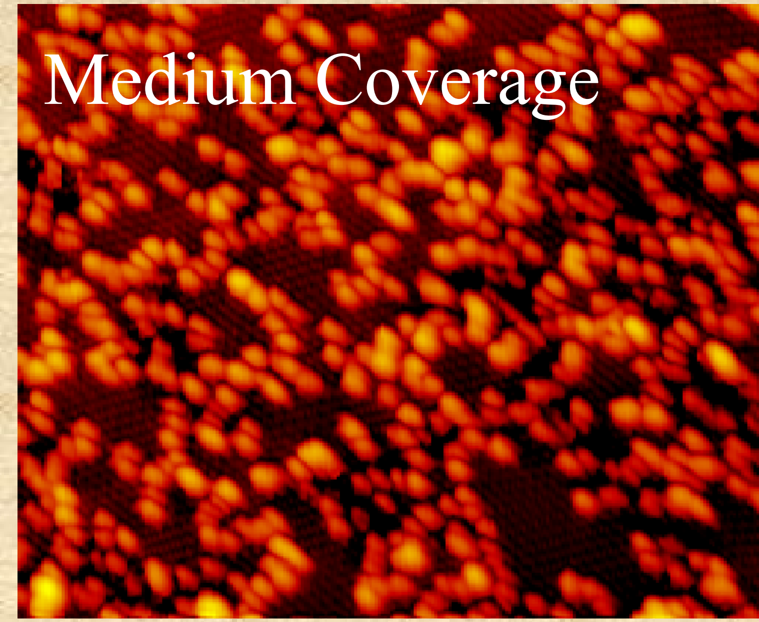
H on HOPG

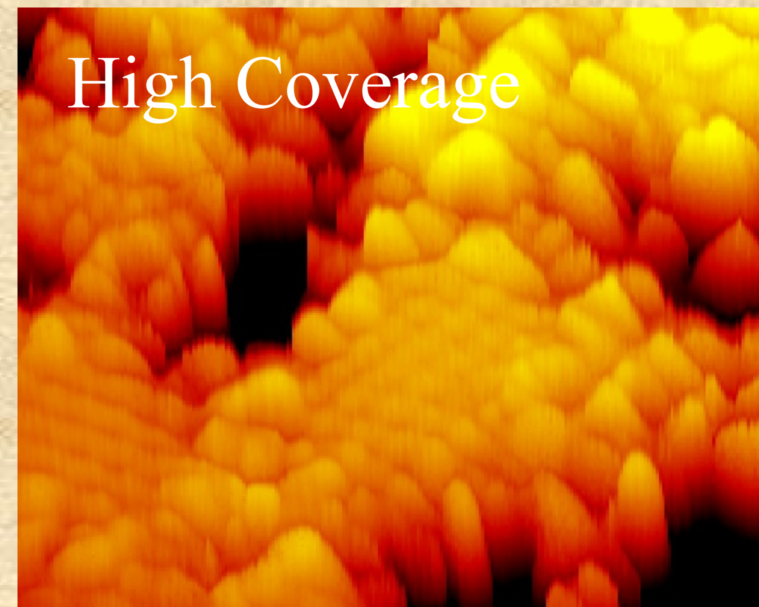
171 x 155 Å²



103 x 114 Å²

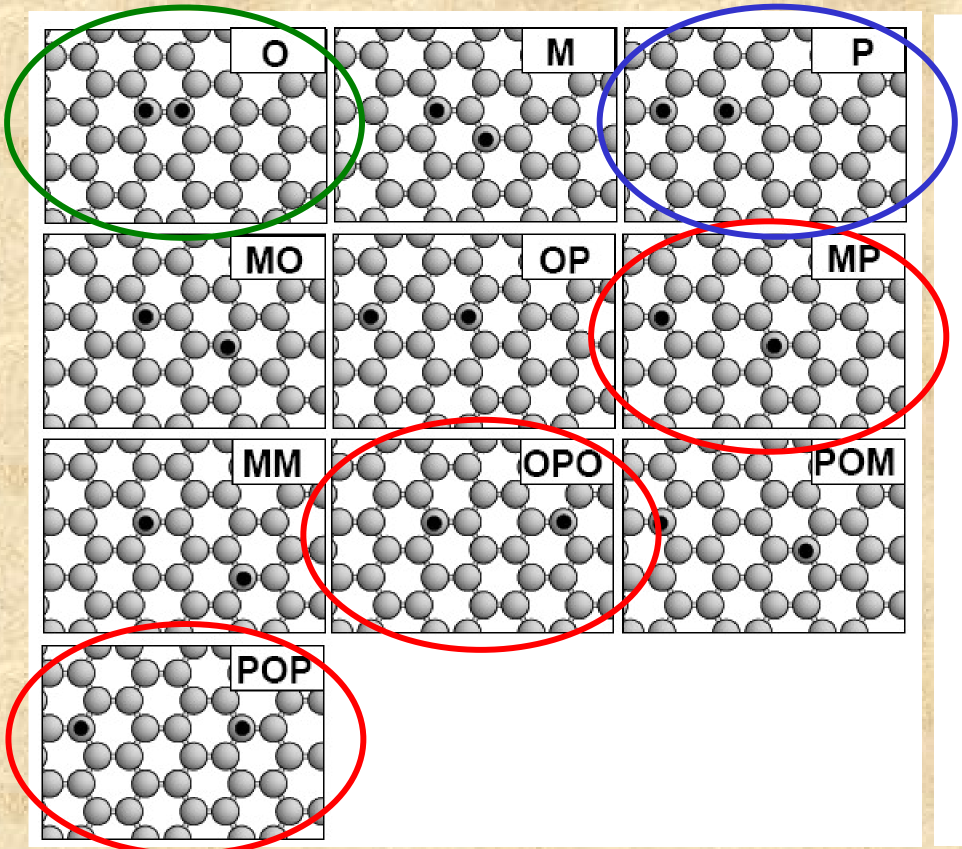
V_t~800mV, I_t~0.15-0.2nA





80 x 72 Å²

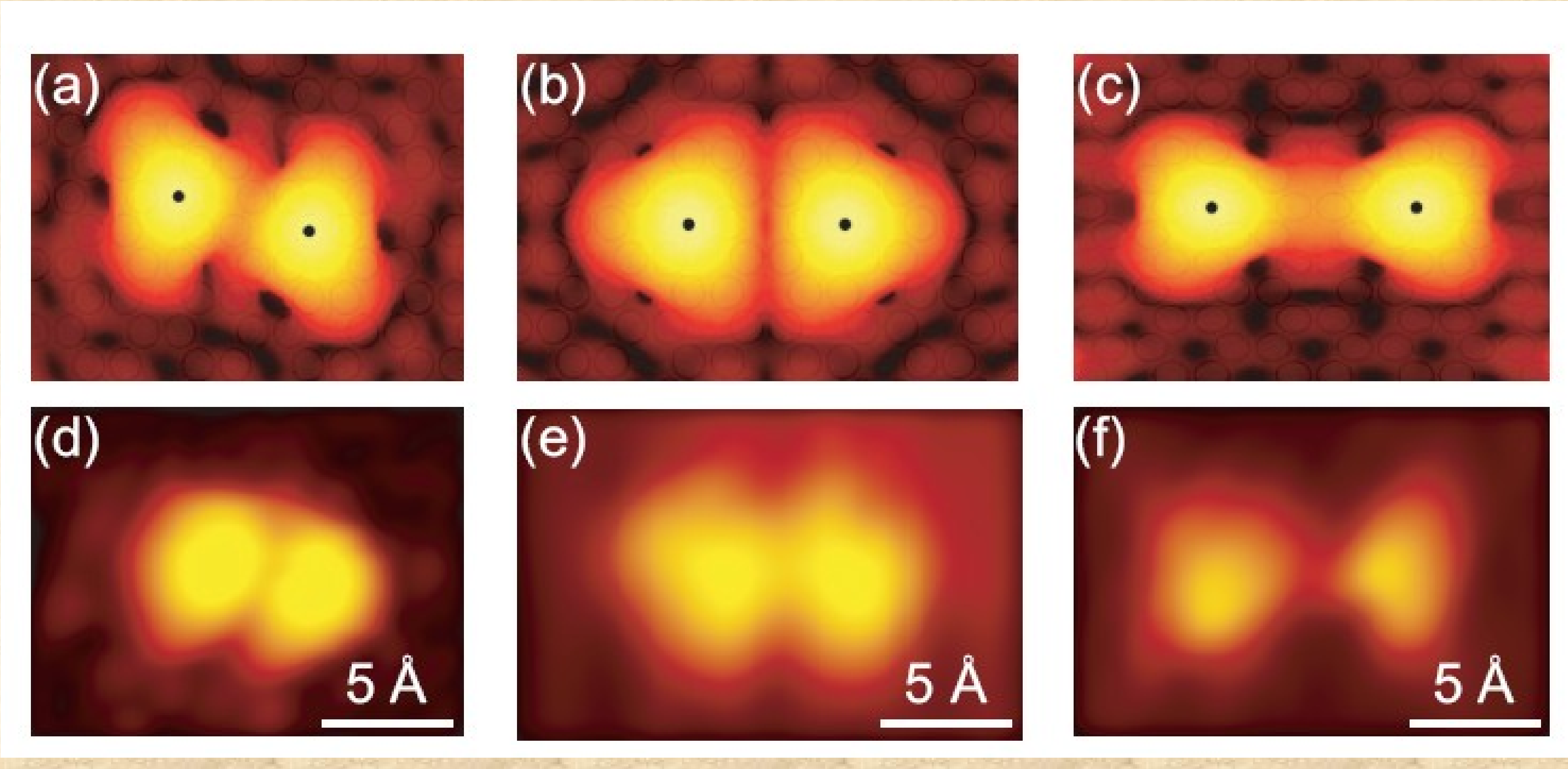
Extended dimers



Config.	6×6 cell # of **k**-points 6	6×6 cell # of **k**-points 18	7×7 cell # of **k**-points 6	7×7 cell # of **k**-points 18
O	0.0	0.0	0.0	0.0
M	1.26	1.22	1.22	1.17
P	0.05	0.04	0.03	0.03
MO	1.01	0.98	0.99	0.94
OP	1.32	1.30	1.27	1.23
MP	0.65	0.63	0.64	0.61
MM	1.22	1.17	1.17	1.12
OPO	0.89	0.88	0.83	0.79
POM	1.23	1.22	1.19	1.15
POP	0.64	0.59	0.69	0.67

Zejlko Sljivancanin

Extended dimers



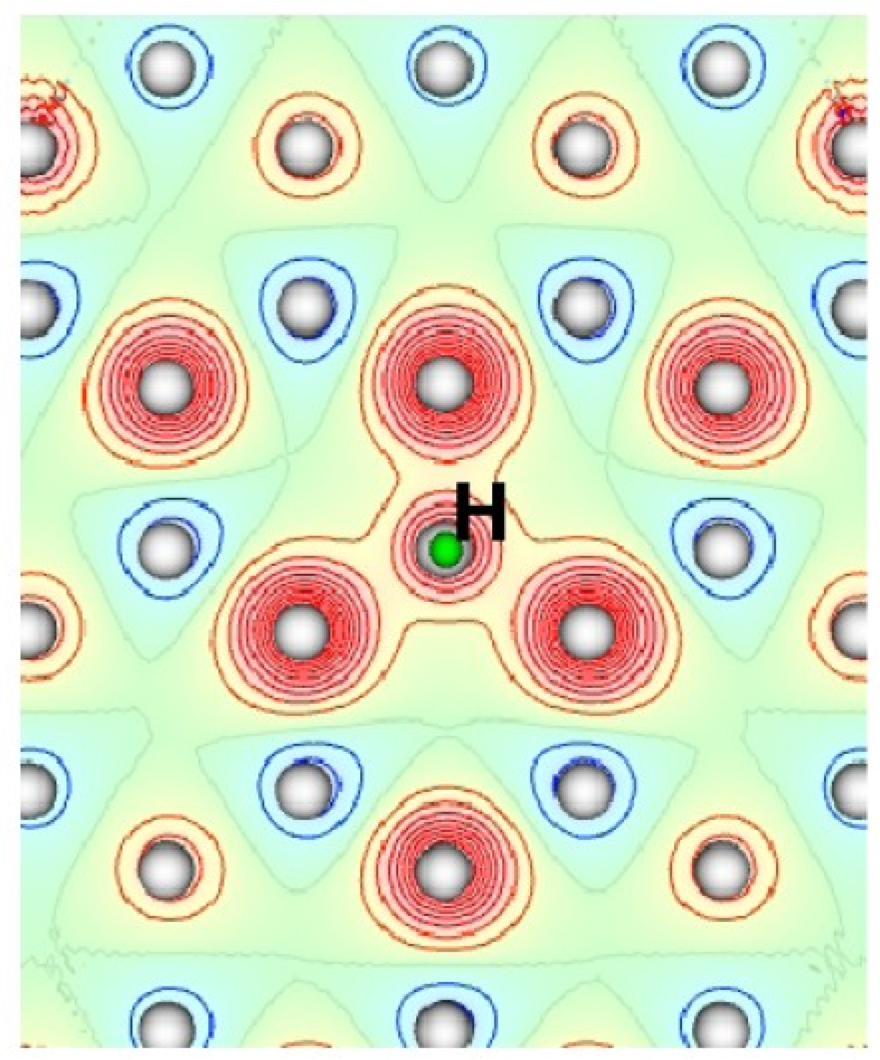
(d) $I_t = -0.58\ nA,\ V_t = -312\ mV$

(e) $I_t = -0.45\ nA,\ V_t = -1250\ mV$

(f) $I_t = -0.43\ nA,\ V_t = -1250\ mV$

Also observed by Andree et al.
Chem. Phys. Lett. **425**, 99 (2006)

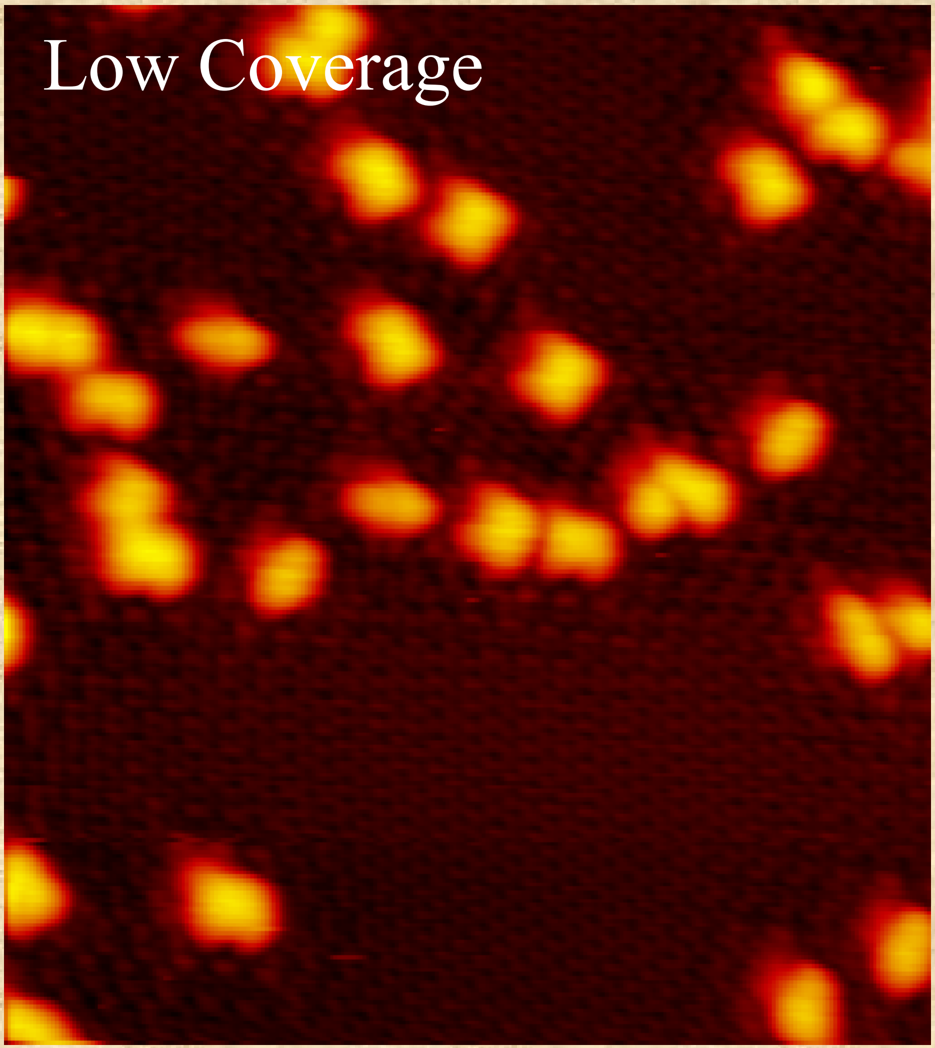
Spin density



Casole et al., arXiv:0808.1312v1

*Similar findings for B-dopants and defects: Ferro et al, J. Nuc. Mat, **363**, 1206 (2007)*

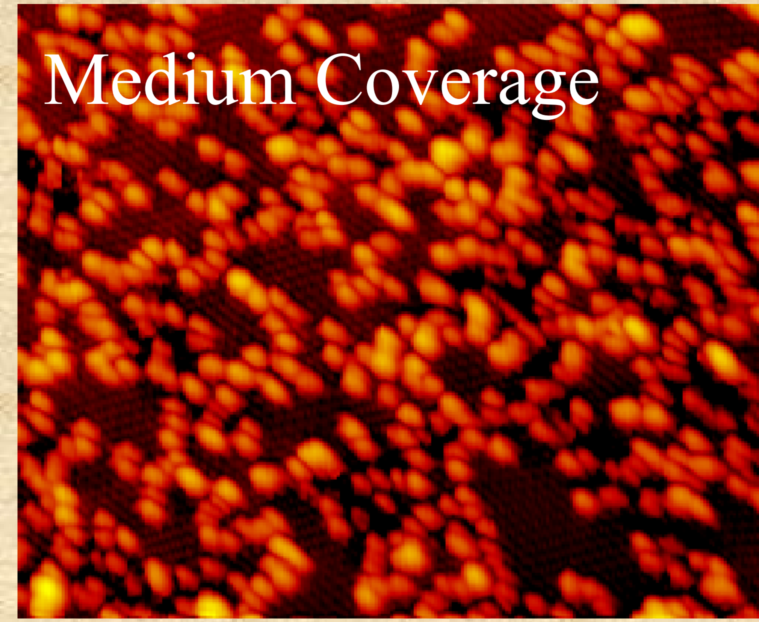
H on HOPG

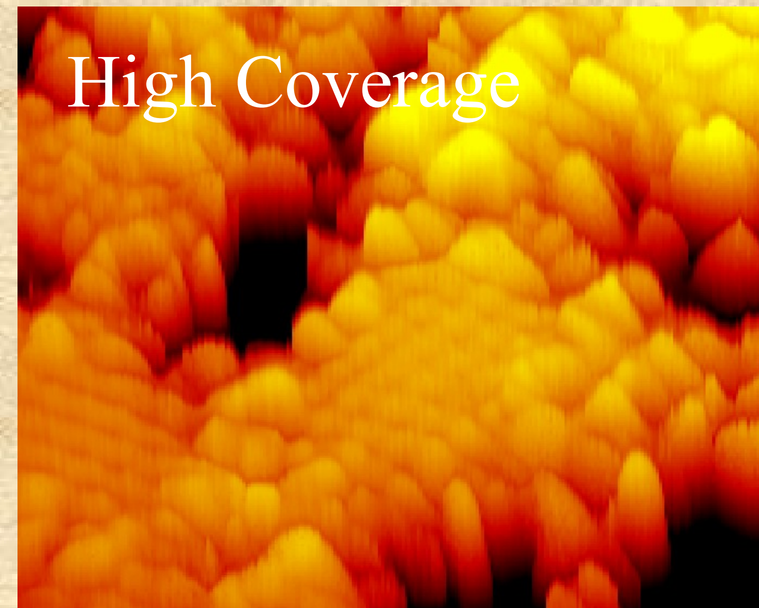


103 x 114 Å^2

V_t~800mV, I_t~0.15-0.2nA

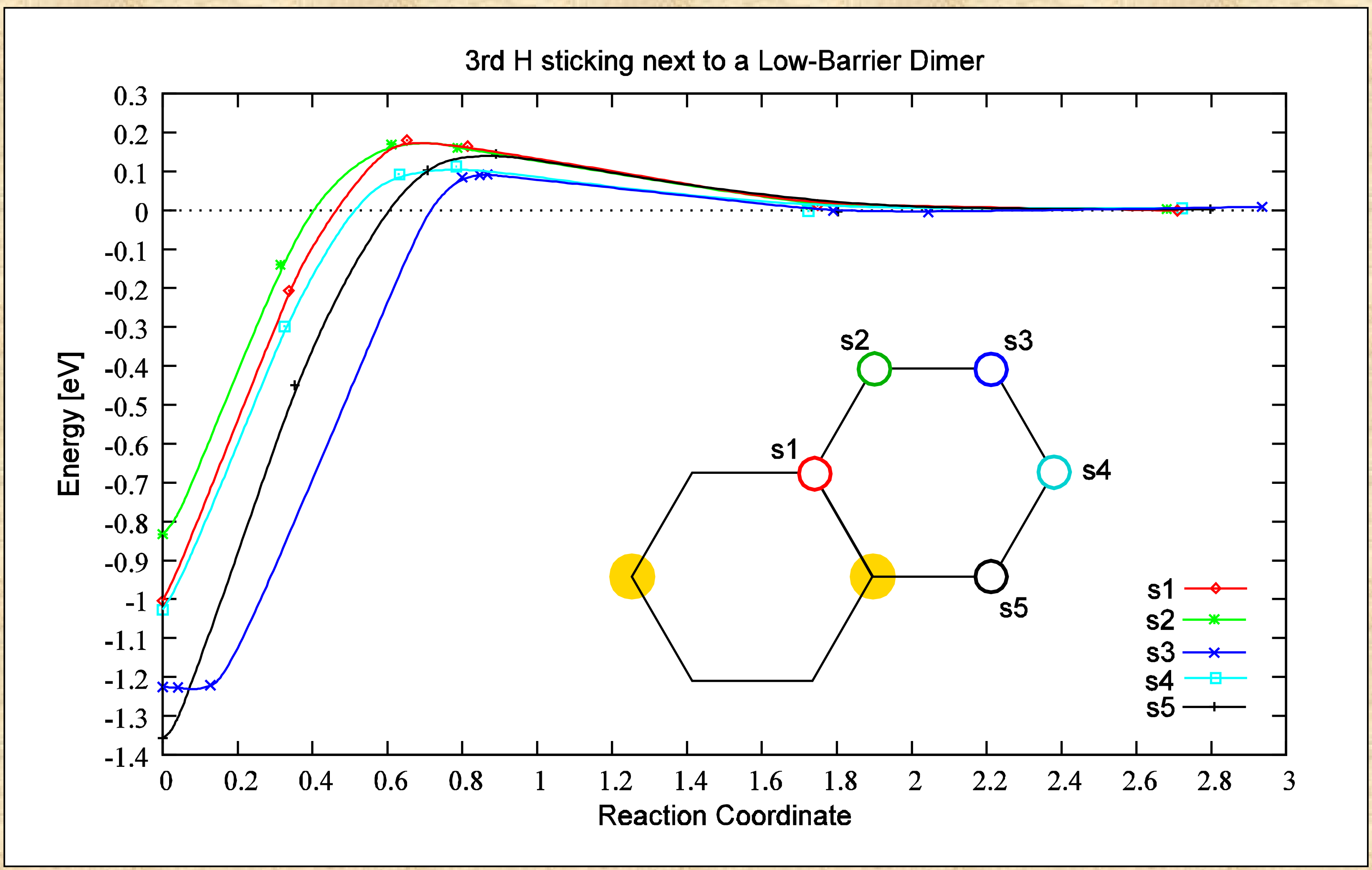
171 x 155 Å^2





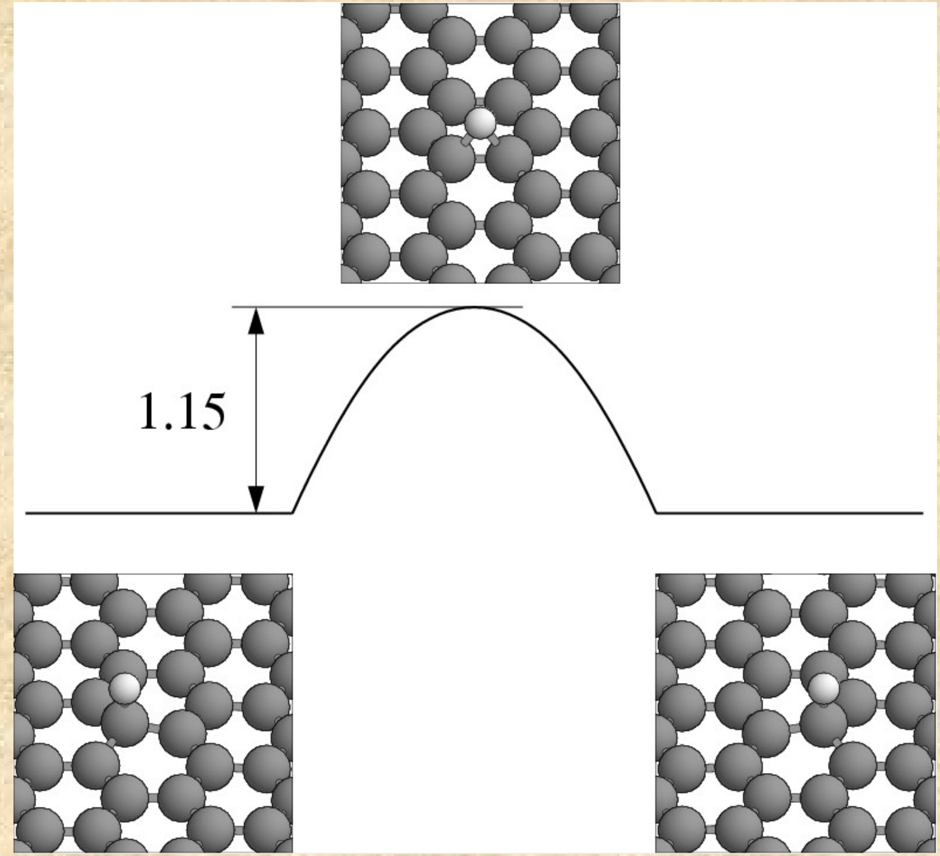
80 x 72 Å^2

Preferential sticking and clustering

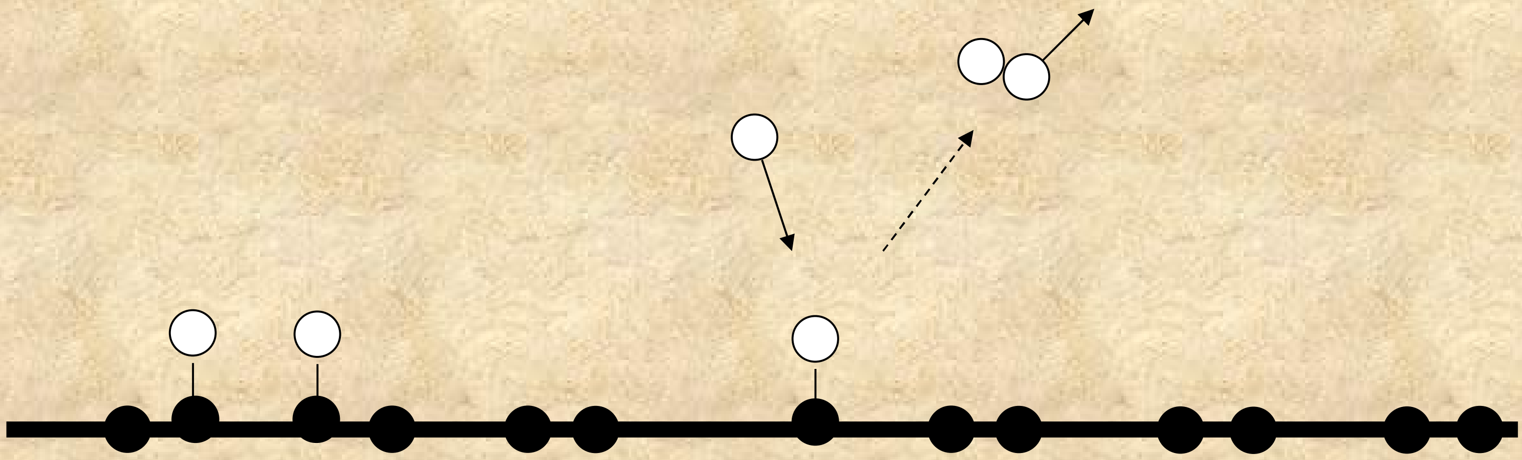


Diffusion

Barrier to diffusion for an isolated H atom: 1.15 eV

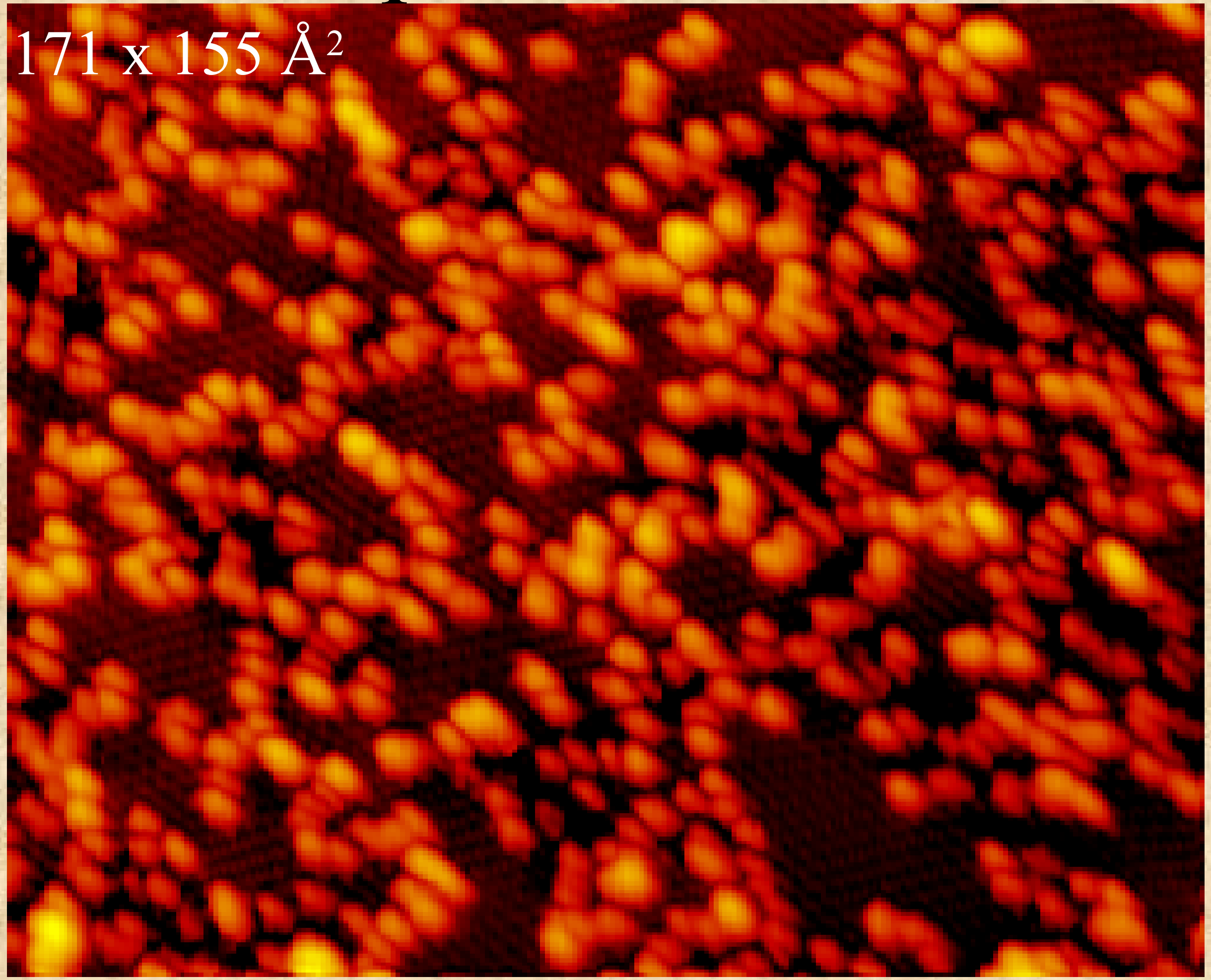


Eley Rideal - Abstraction



Jeloaica & Sidis (2001)
Meijer et al. (2001)
Sha et al. (2002)
Zecho et al. (2002)
Matinazzo & Tantardini (2006)
Morisset et al. (2004)
Bachellerie et al. (2007)
Thomas et al. (2008)

Random adsorption and cluster formation



In accord with LEED and UPS measurements:

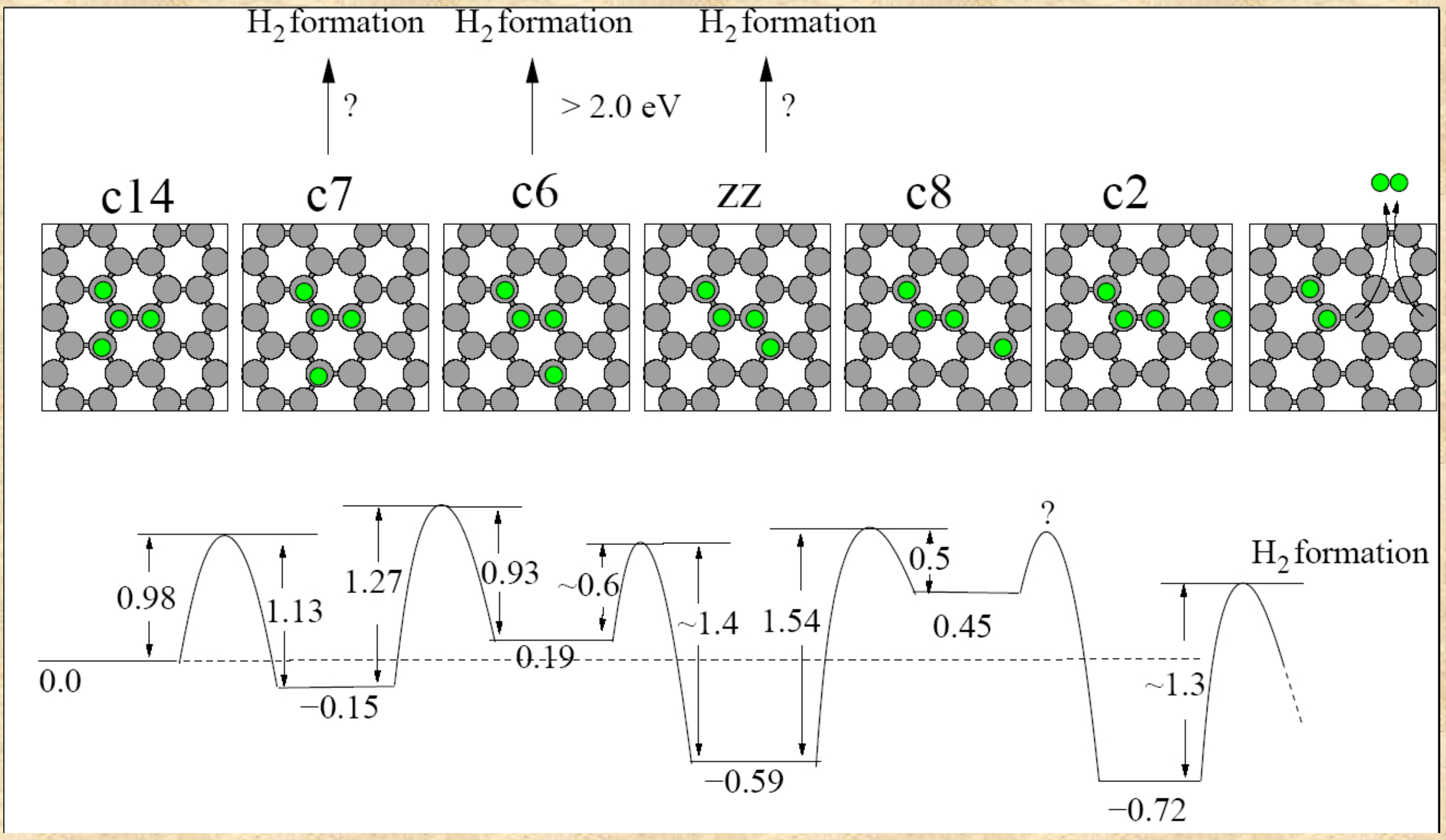
*Neumann et al. Appl. Phys. A **55**, 489 (1992)*

*Guttler et al. Chem. Phys. Lett. **395**, 171 (2004)*

Large cluster formation also found in HREELS and DFT studies:

*Allouche et al, JCP **123**, 124701 (2005)*

Still recombination from dimer like edges (but also atom desorption)



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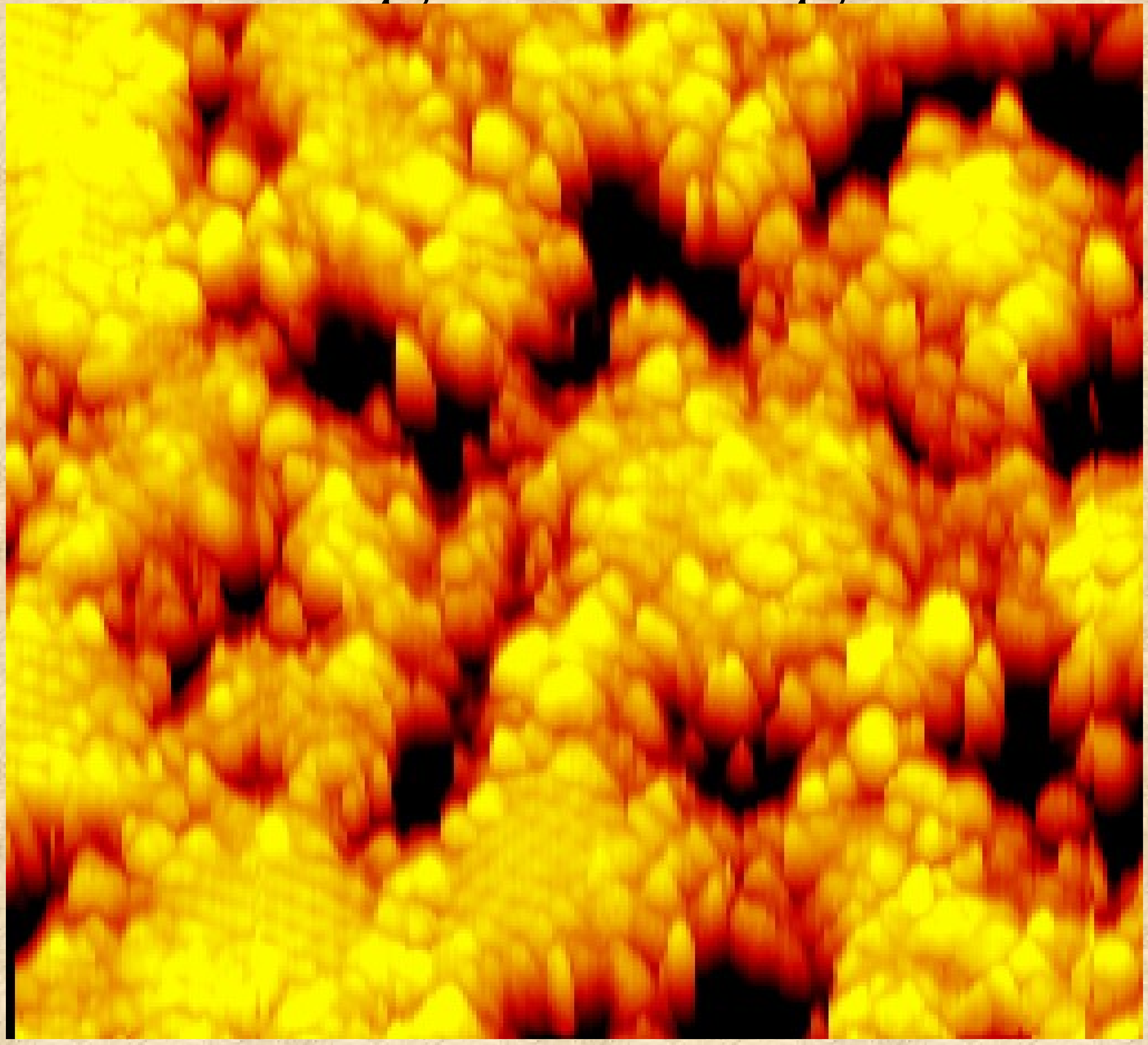
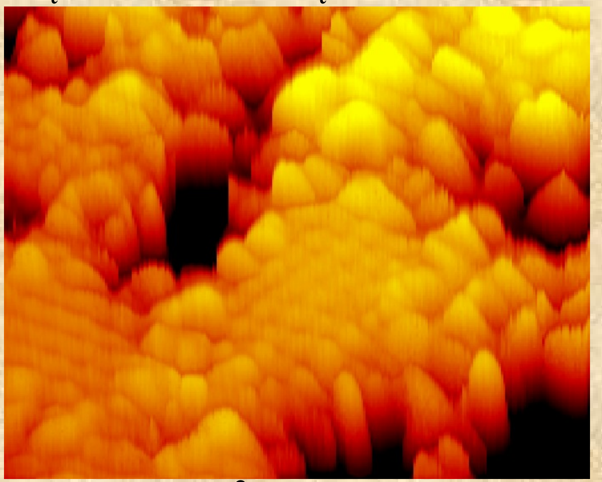
High coverage



171 x 155 Å^2 V_t = -1051 mV, I_t = -0.53 nA

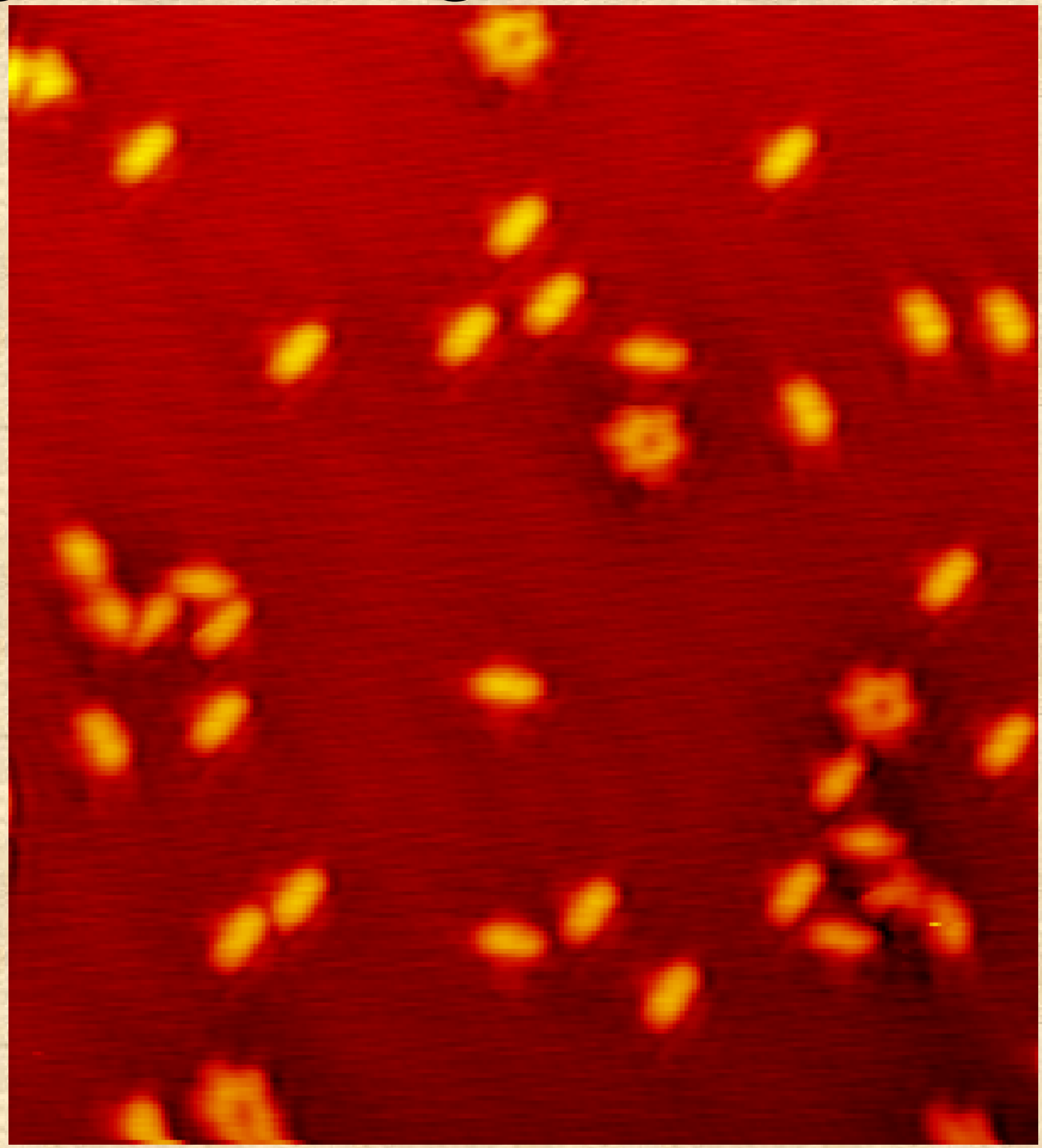
High Coverage

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



80 x 72 Å^2

525K anneal

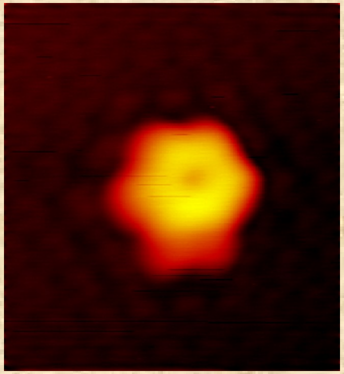


$V_t = -1.05$ V, $I_t = -0.18$ nA, 171 x 155 Å^2

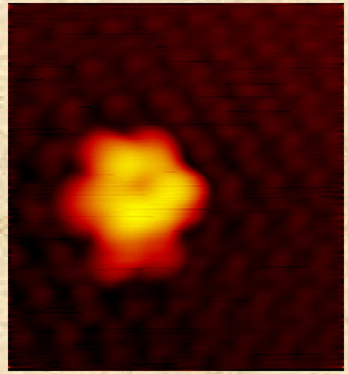
Stars / trimers

Negative voltages:

31 x 34 Å^2



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



I=-0.15nA, V=-309mV
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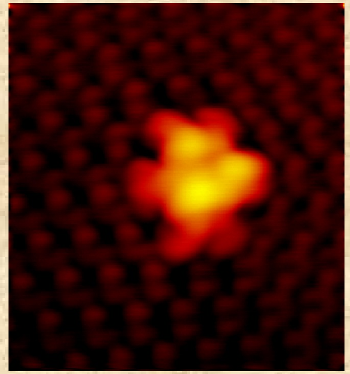
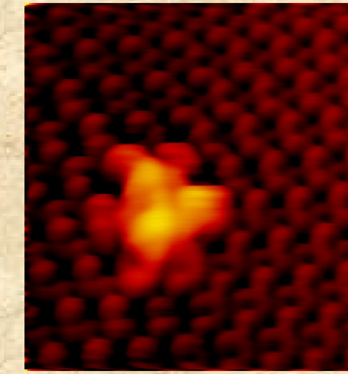
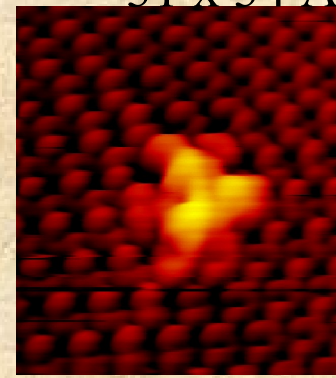


I=-0.16nA, V=-109mV
0512020408

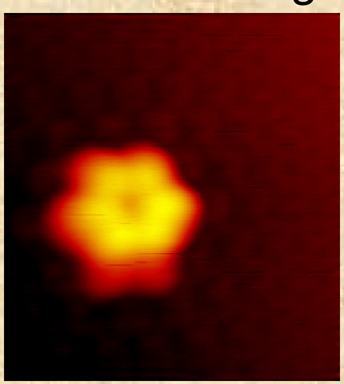


I=-0.16nA, V=-46mV
05120204210

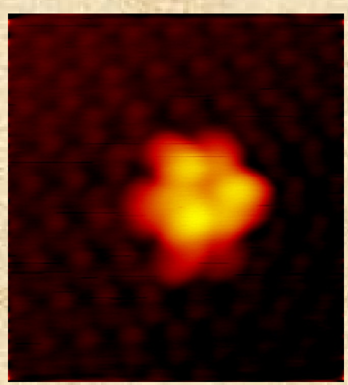


I=-0.15nA, V=-23mV
0512020437

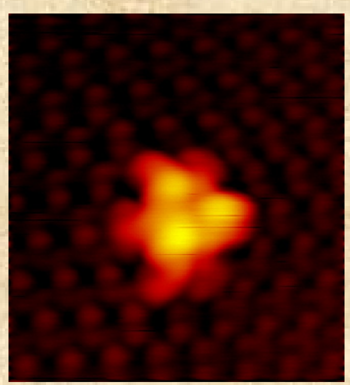
Positive voltages:



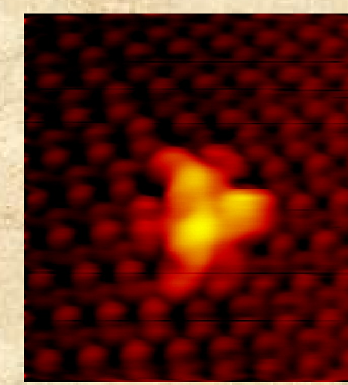
I=0.15nA, V=874mV
0512020435



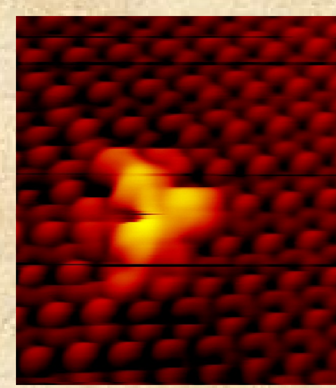
I=0.15nA, V=367mV
0512020429



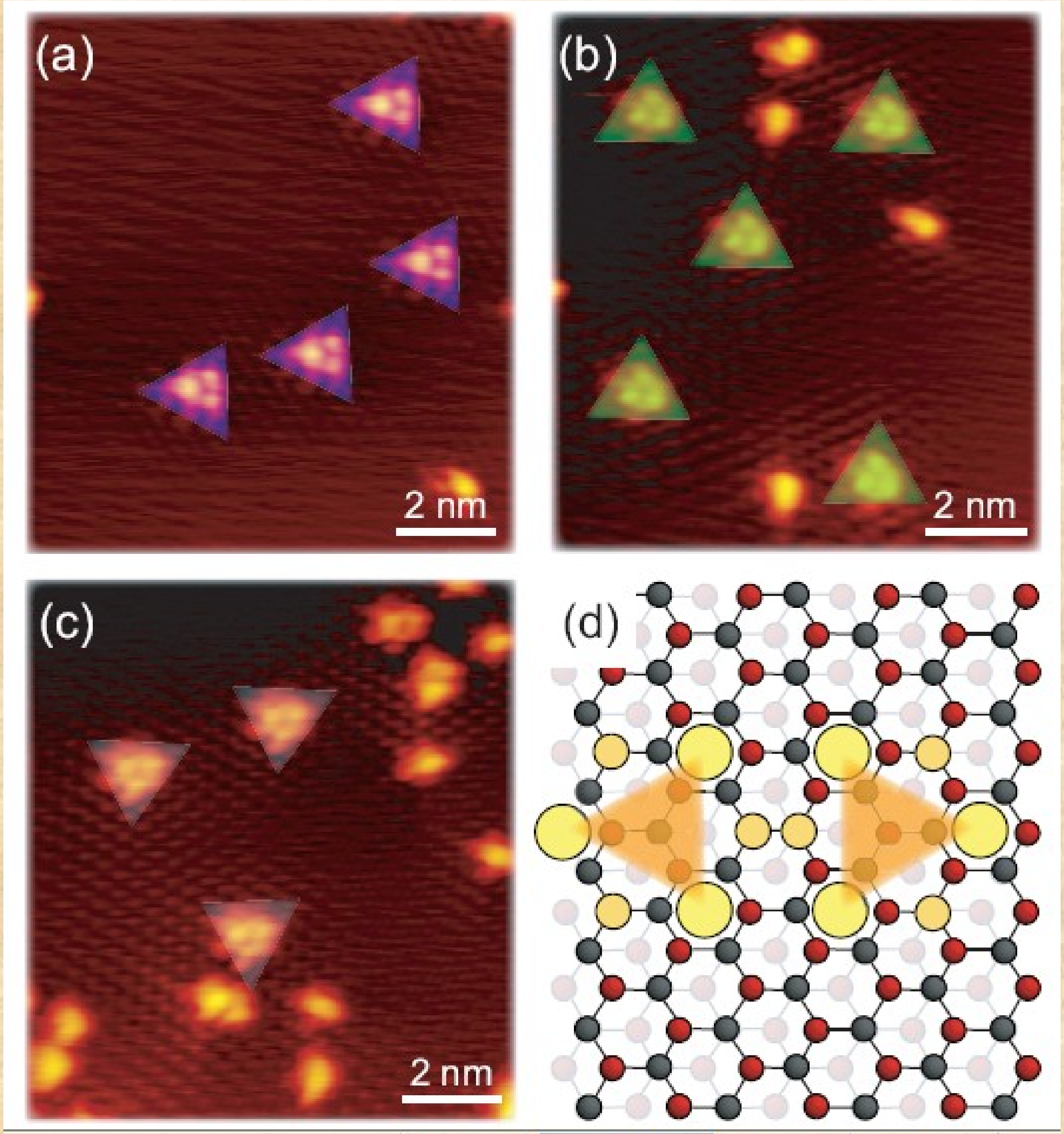
I=0.15nA, V=154mV
0512020431



I=0.15nA, V=46mV
0512020434

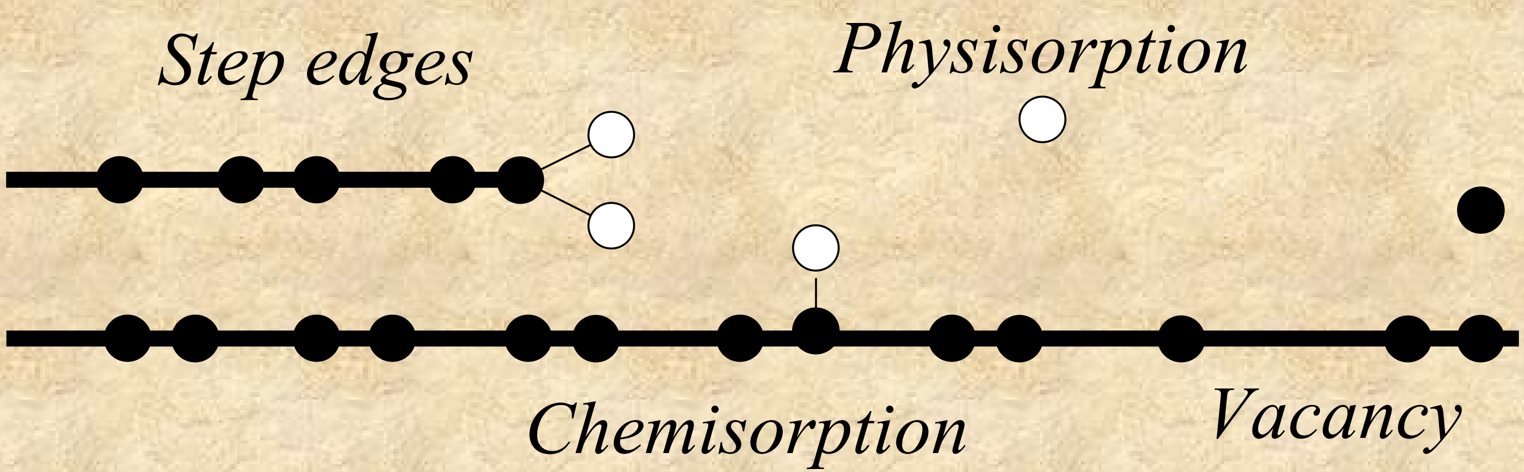


I=0.15nA, V=23mV
0512020438



L. Hornekær et al., Chem. Phys. Lett. (2007)

Binding sites on graphitic surfaces



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

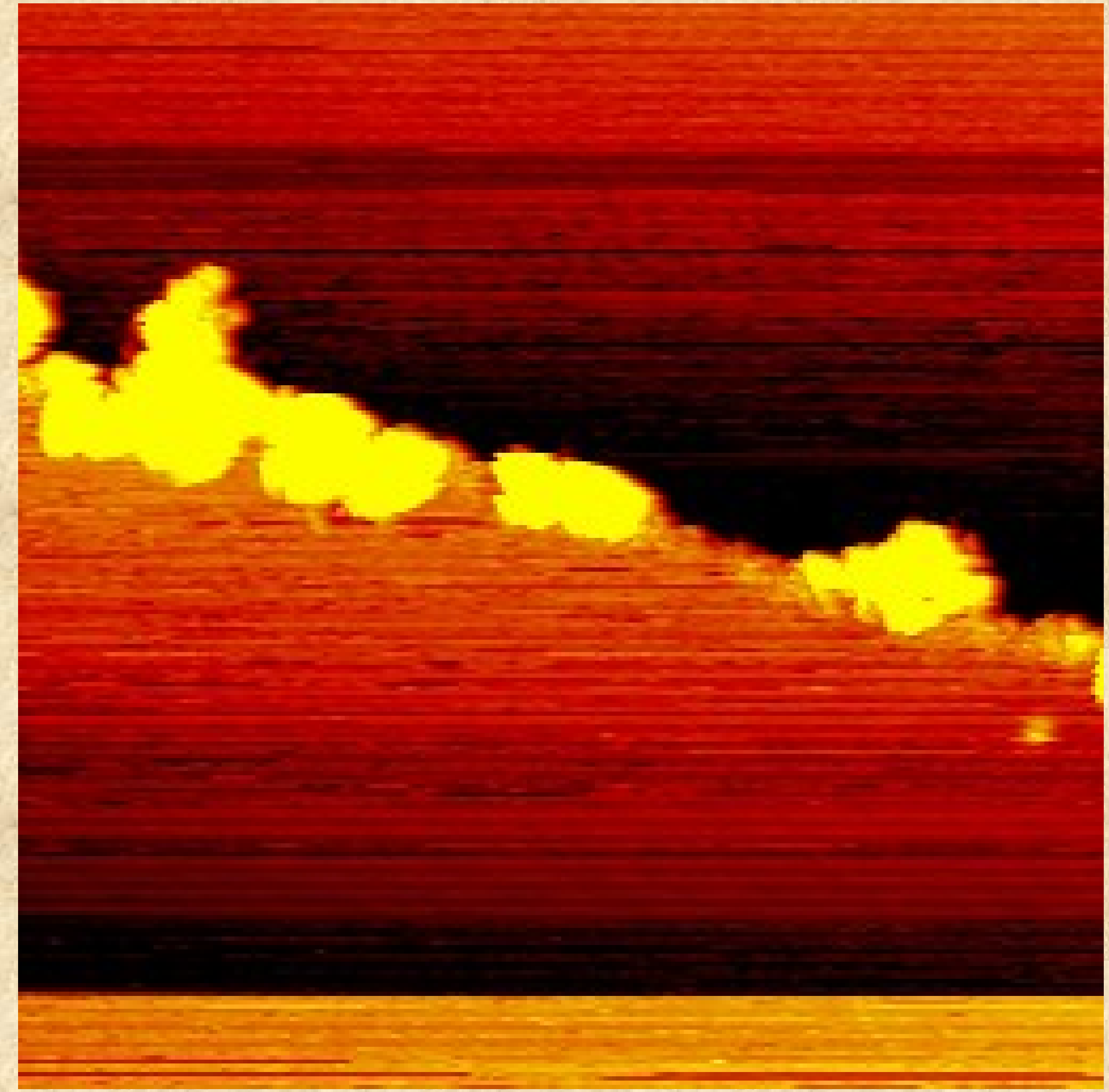
Chemisorption - basal plane: Jeloica & Sidis, Chem. Phys. Lett. 300, 157 (1999)

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

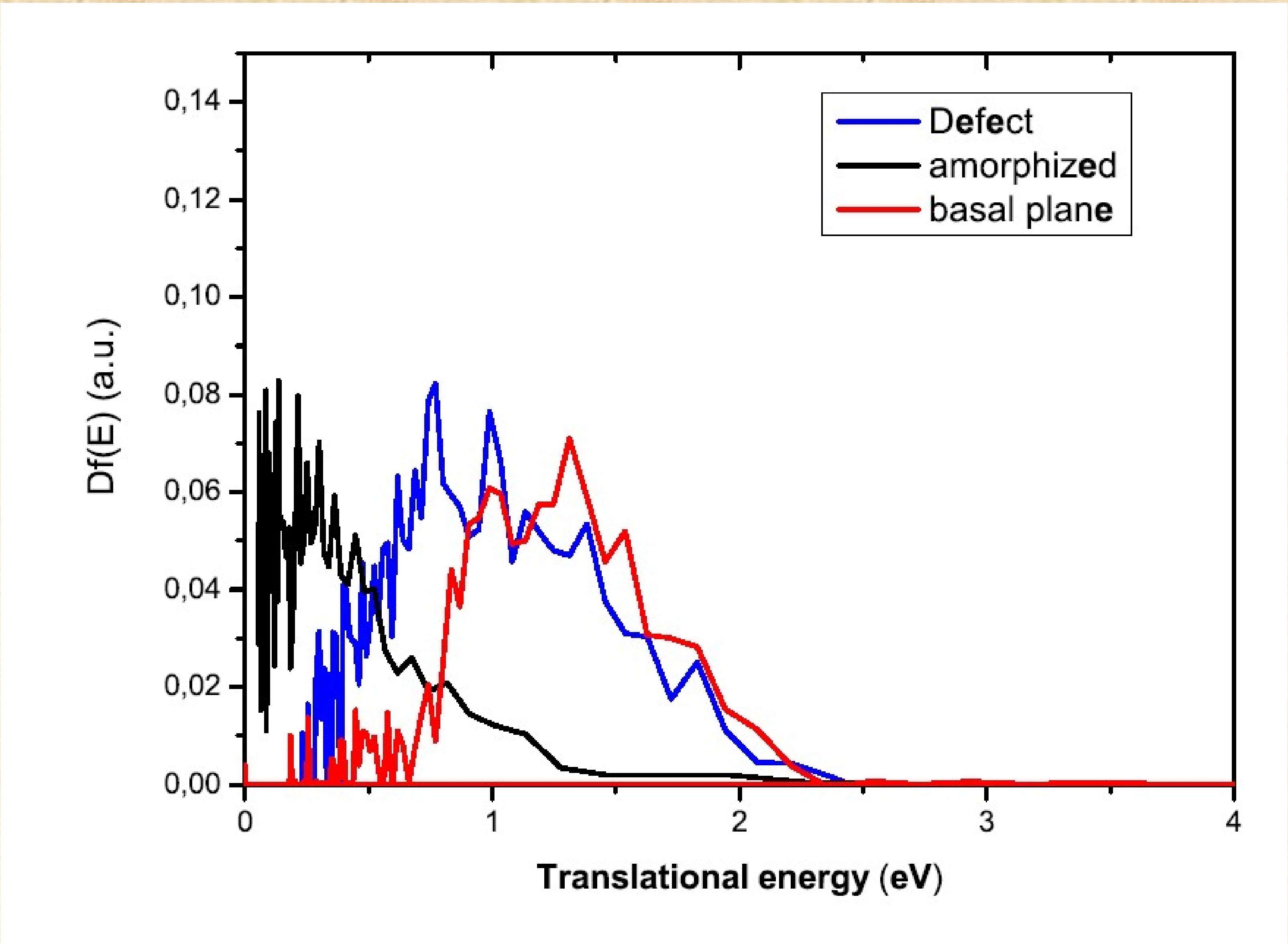
Güttler et al. Surface Science ***570****, 218 (2004)*

*Thomas et al. Surface Science.****602****, 2311 (2008)*

Step edges

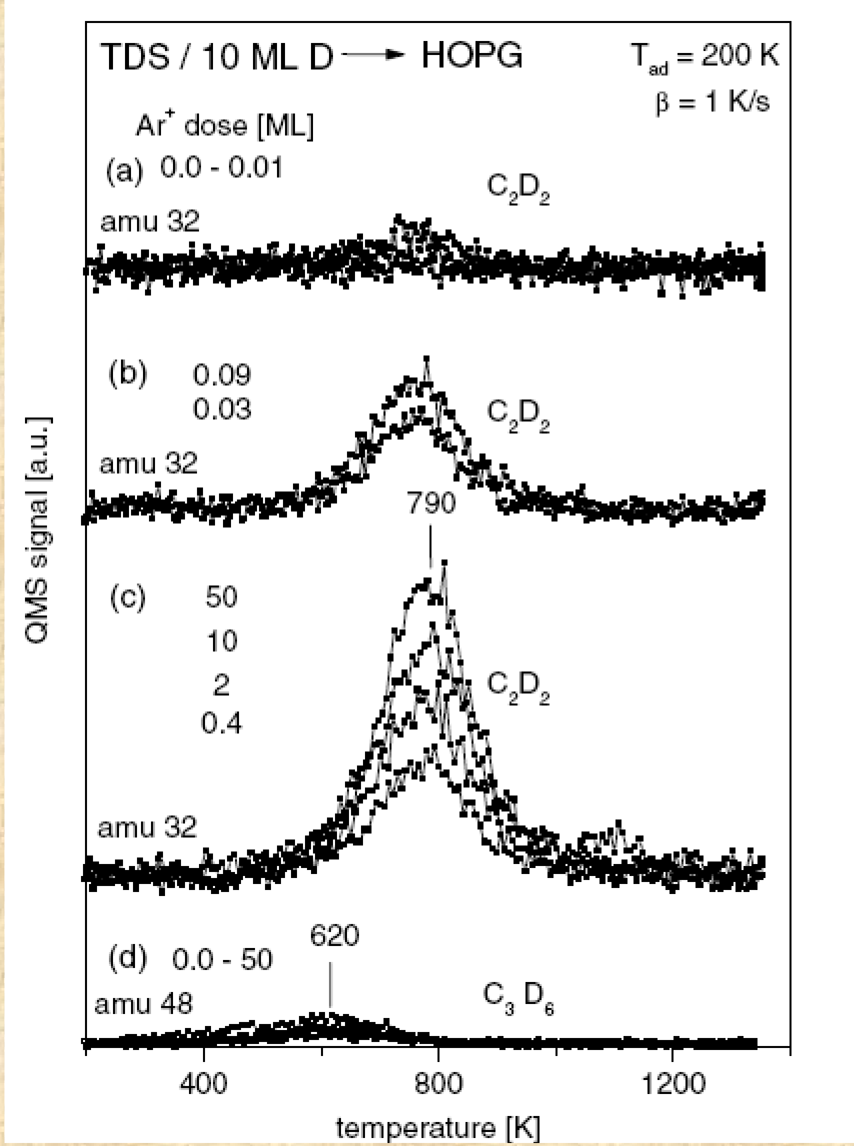


Kinetic energy distribution



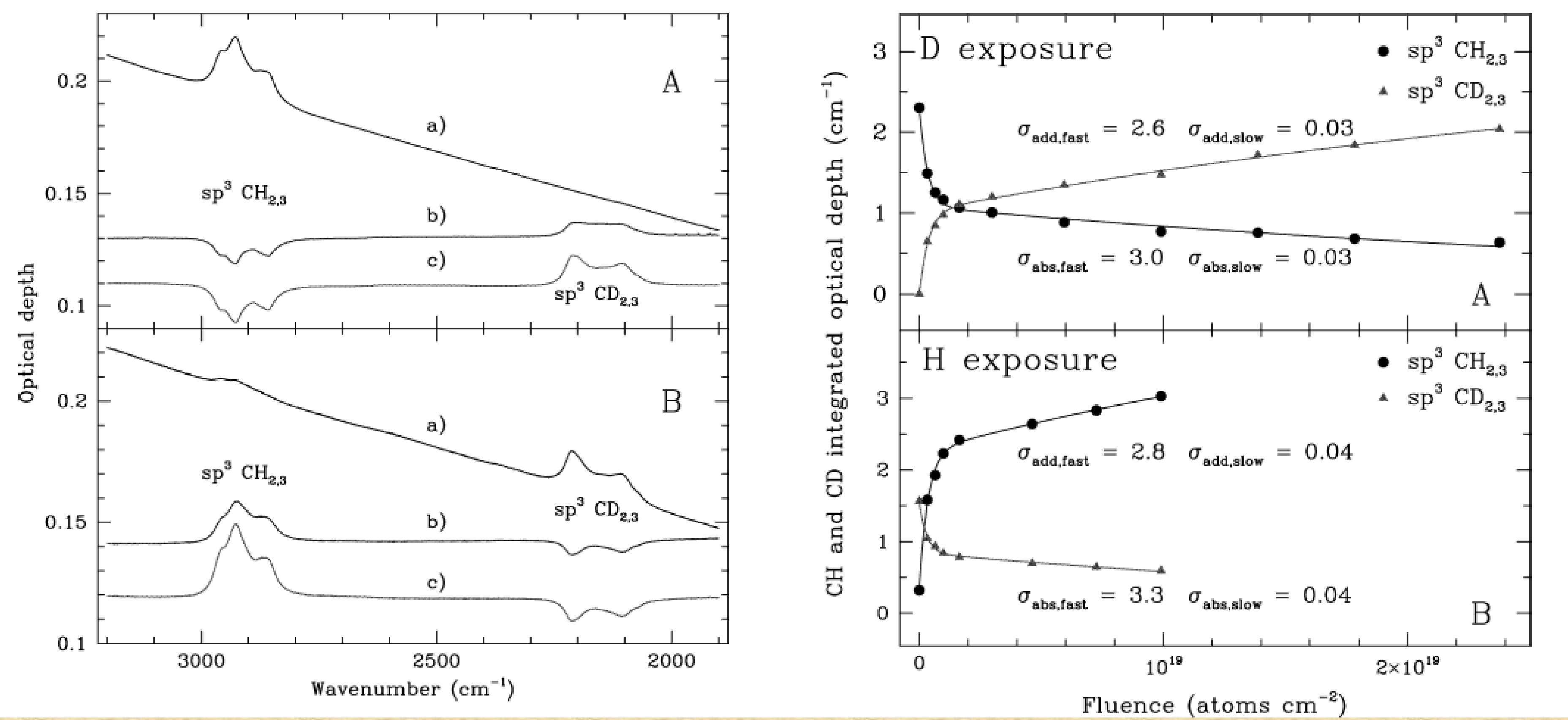
S. Baouche et al.

Hydrocarbon formation



A. Güttler et al., Surface Science **570**, 218 (2004)

H_2 Formation on hydrogenated carbon nanograins



*Menella, ApJ **684**, L25 (2008)*

Talk by Vito Menella

H on other carbonaceous materials:

Graphene
Carbon nanotubes
C60
PAHs

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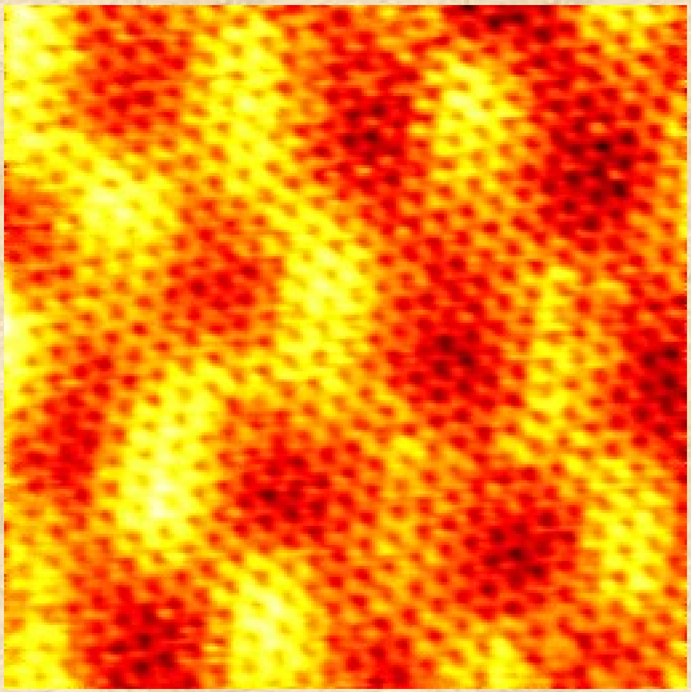

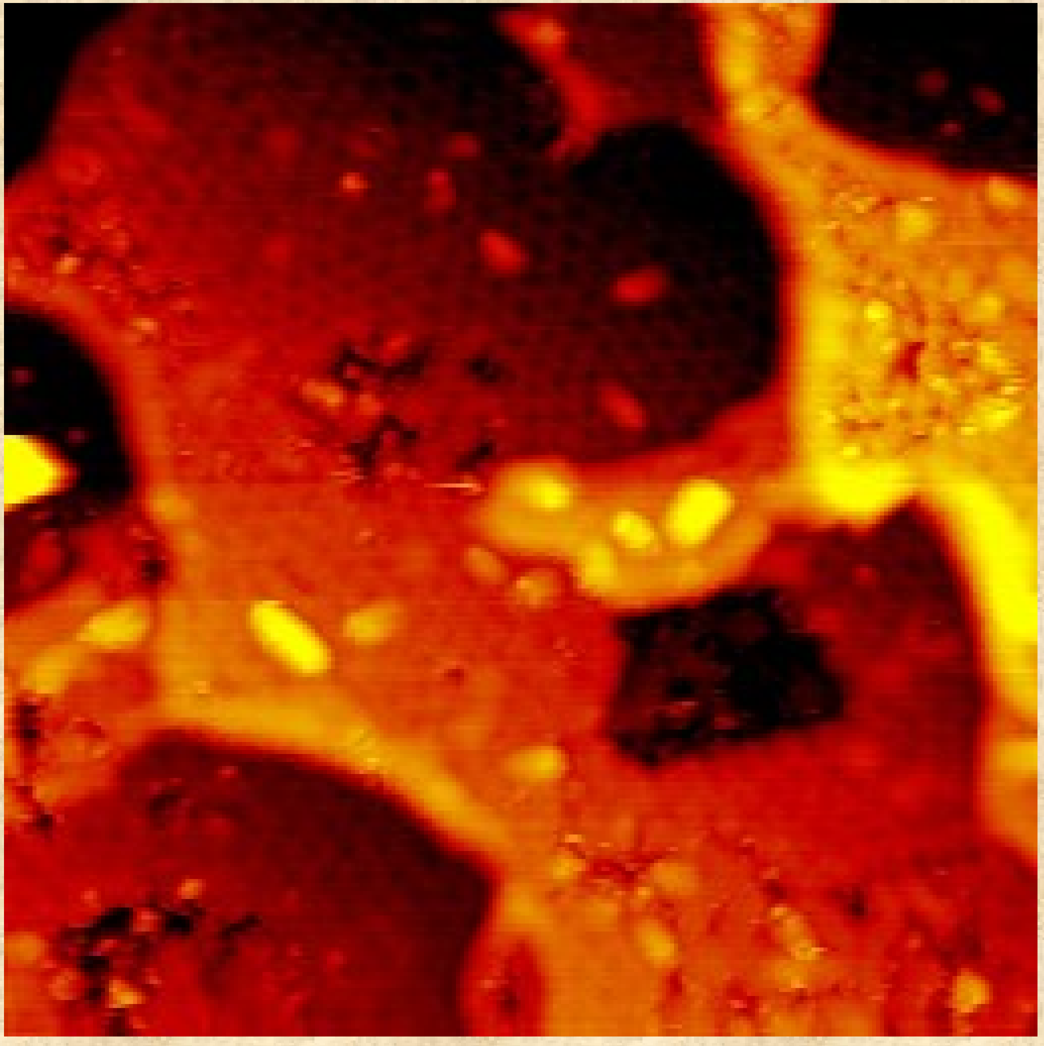

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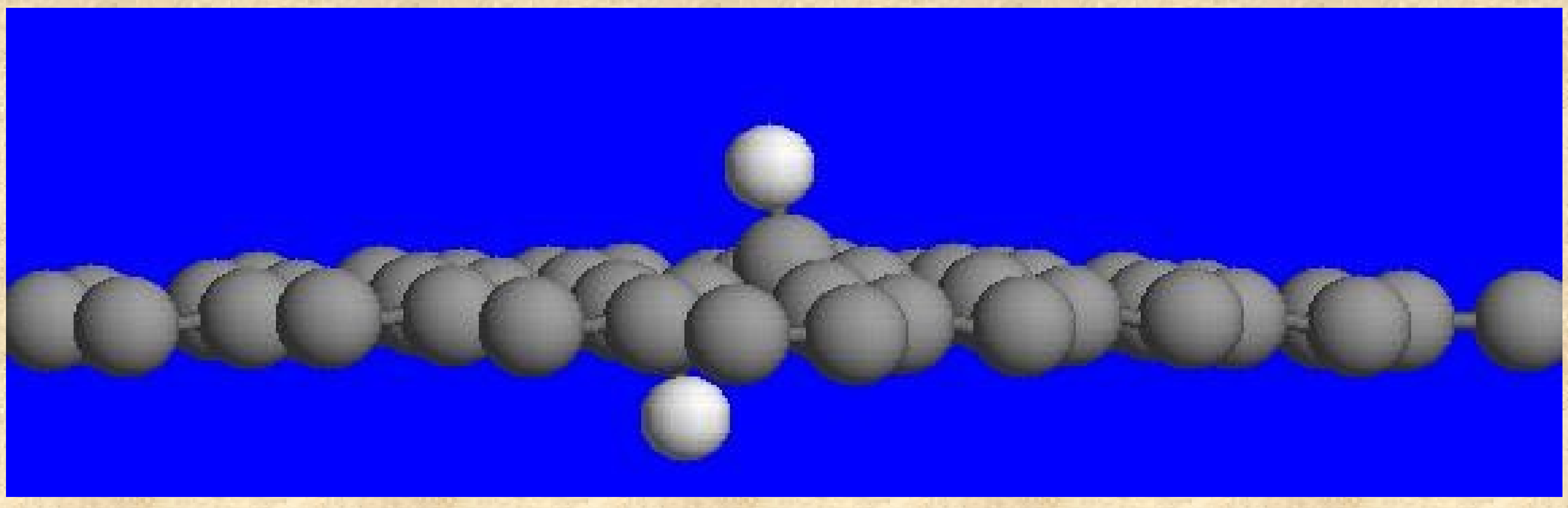
C60
PAHs



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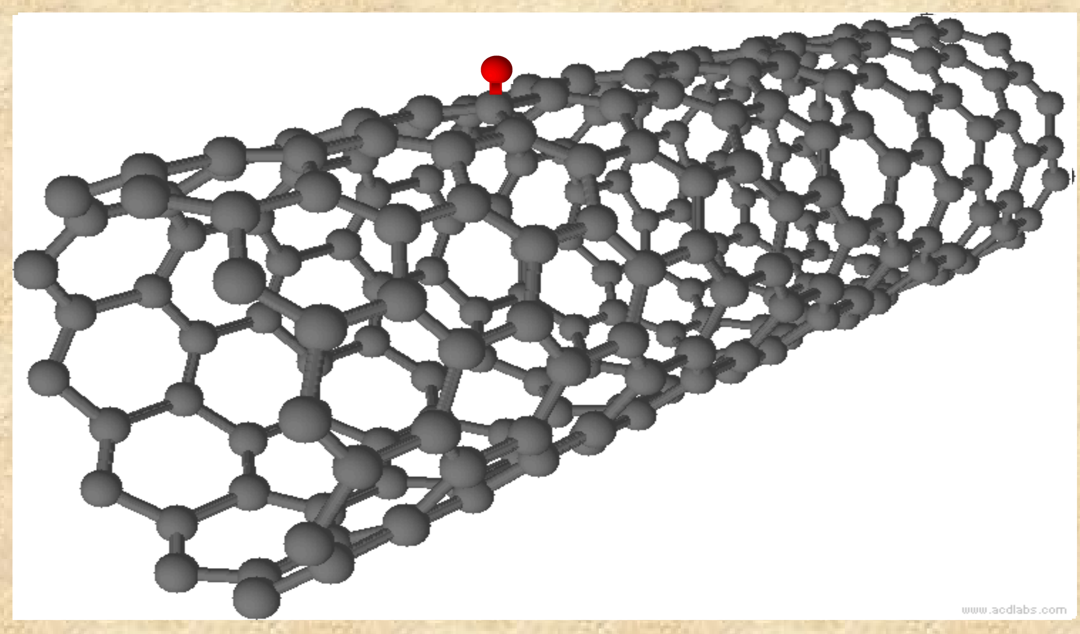

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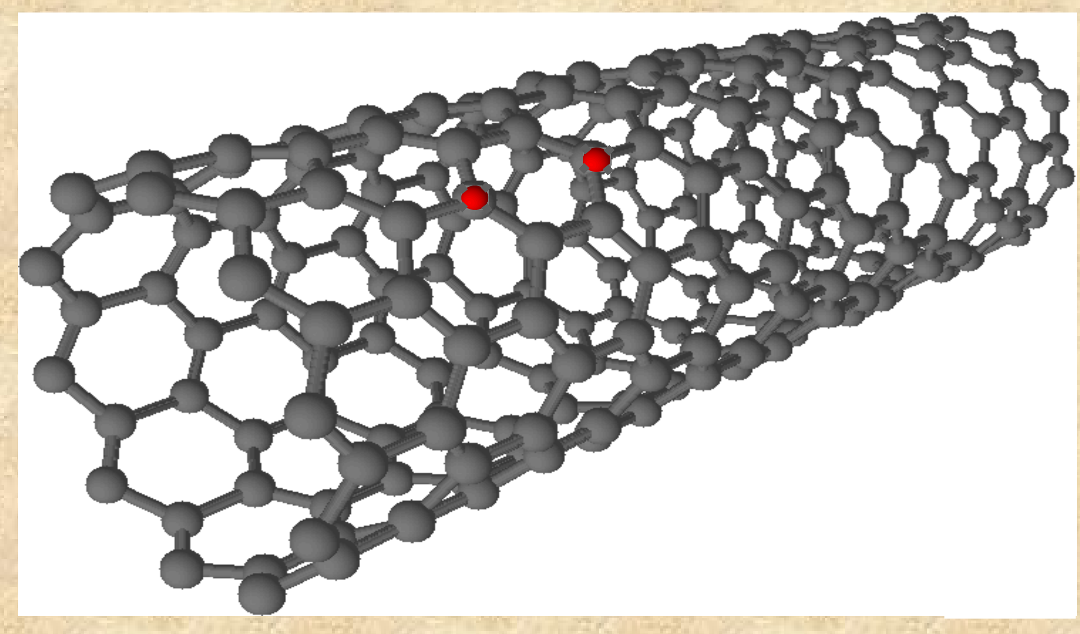

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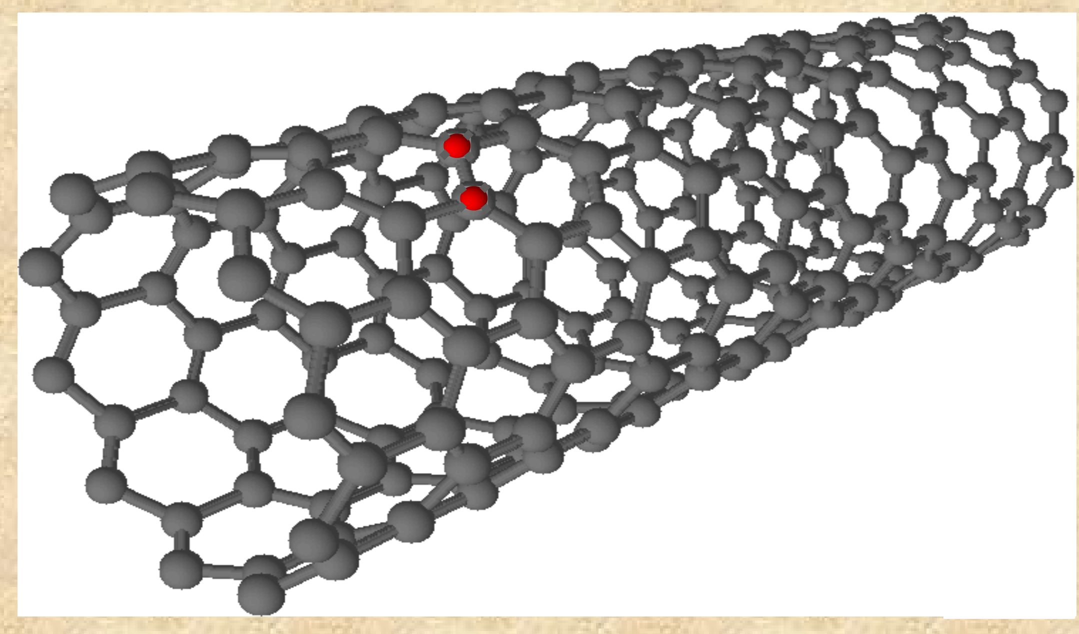

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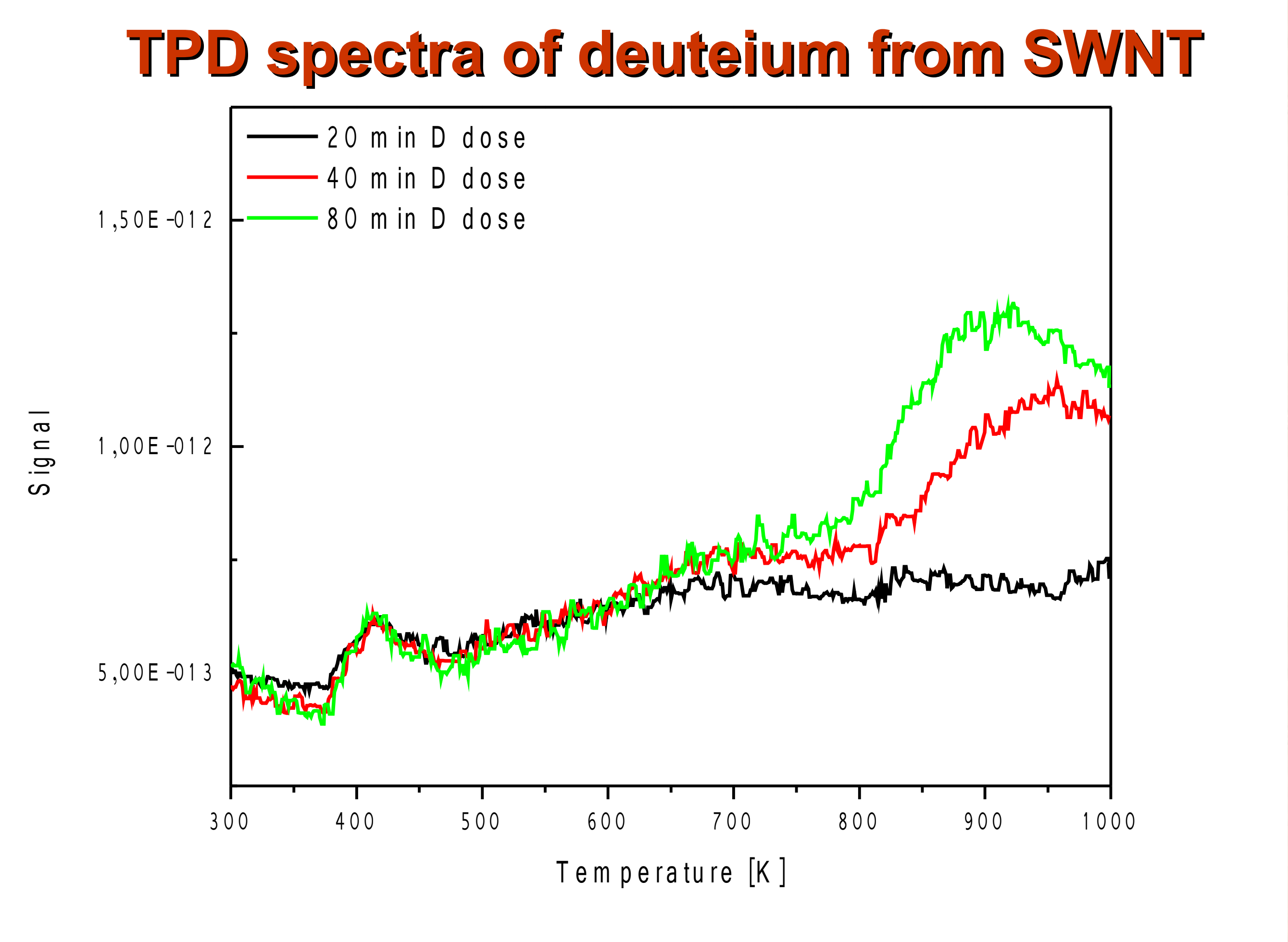

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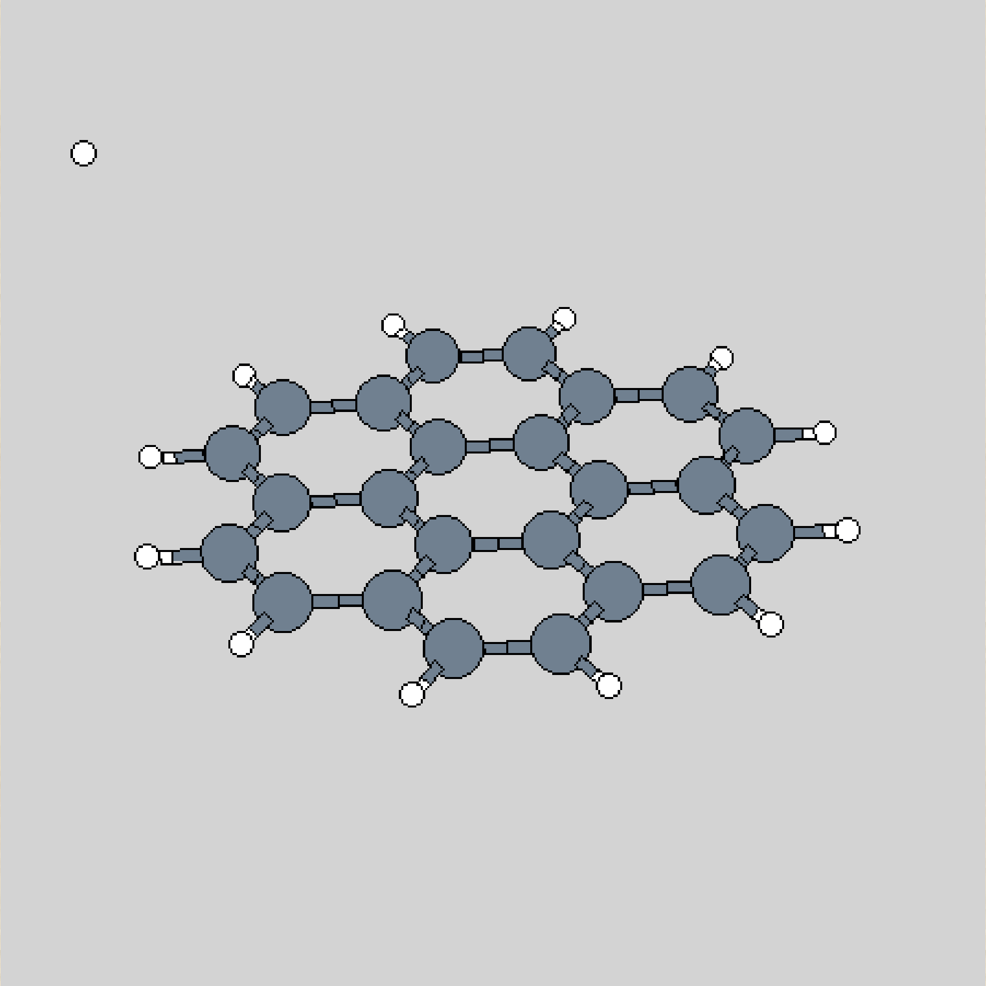

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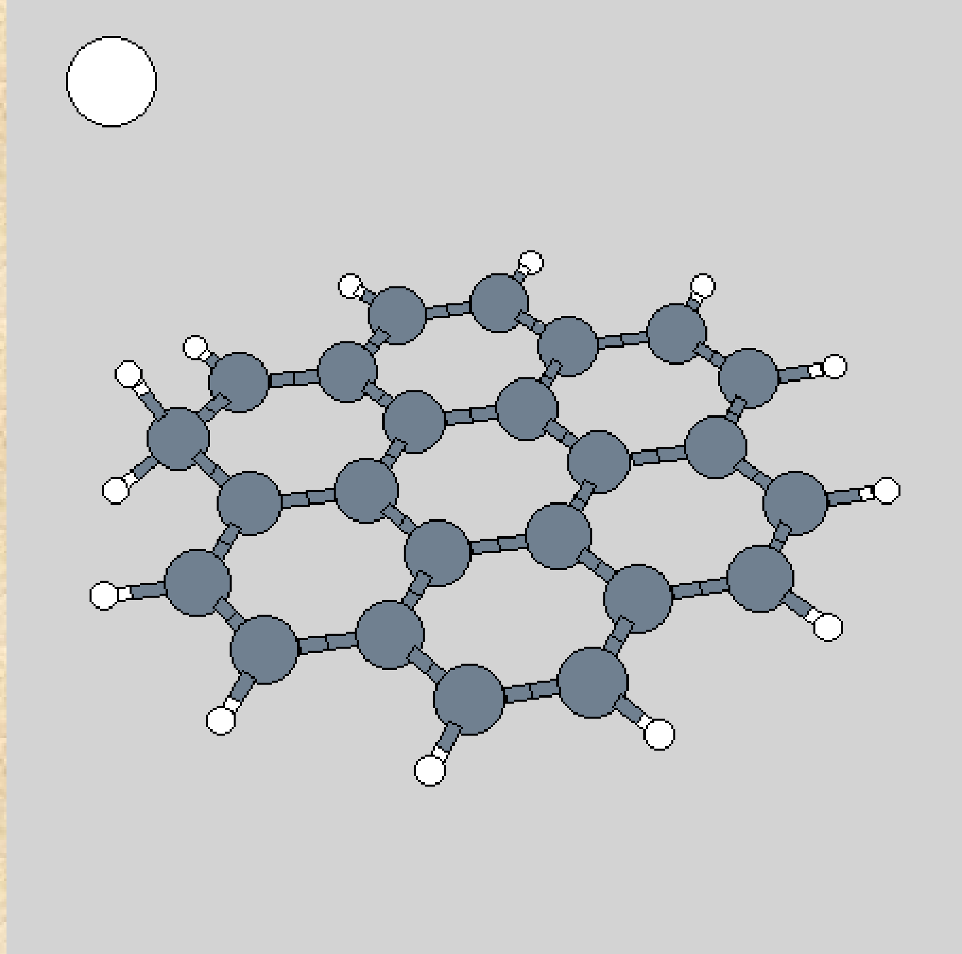

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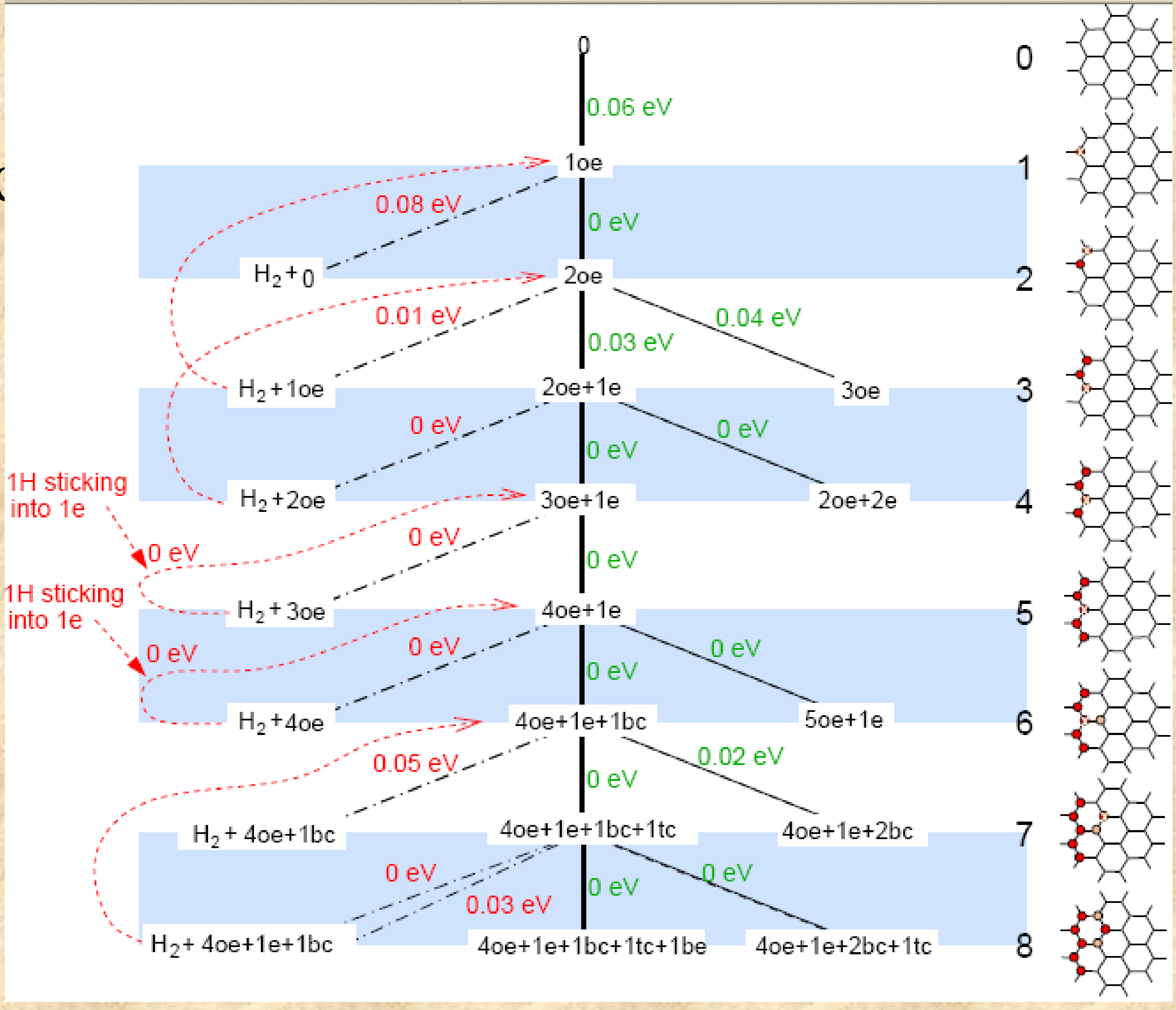
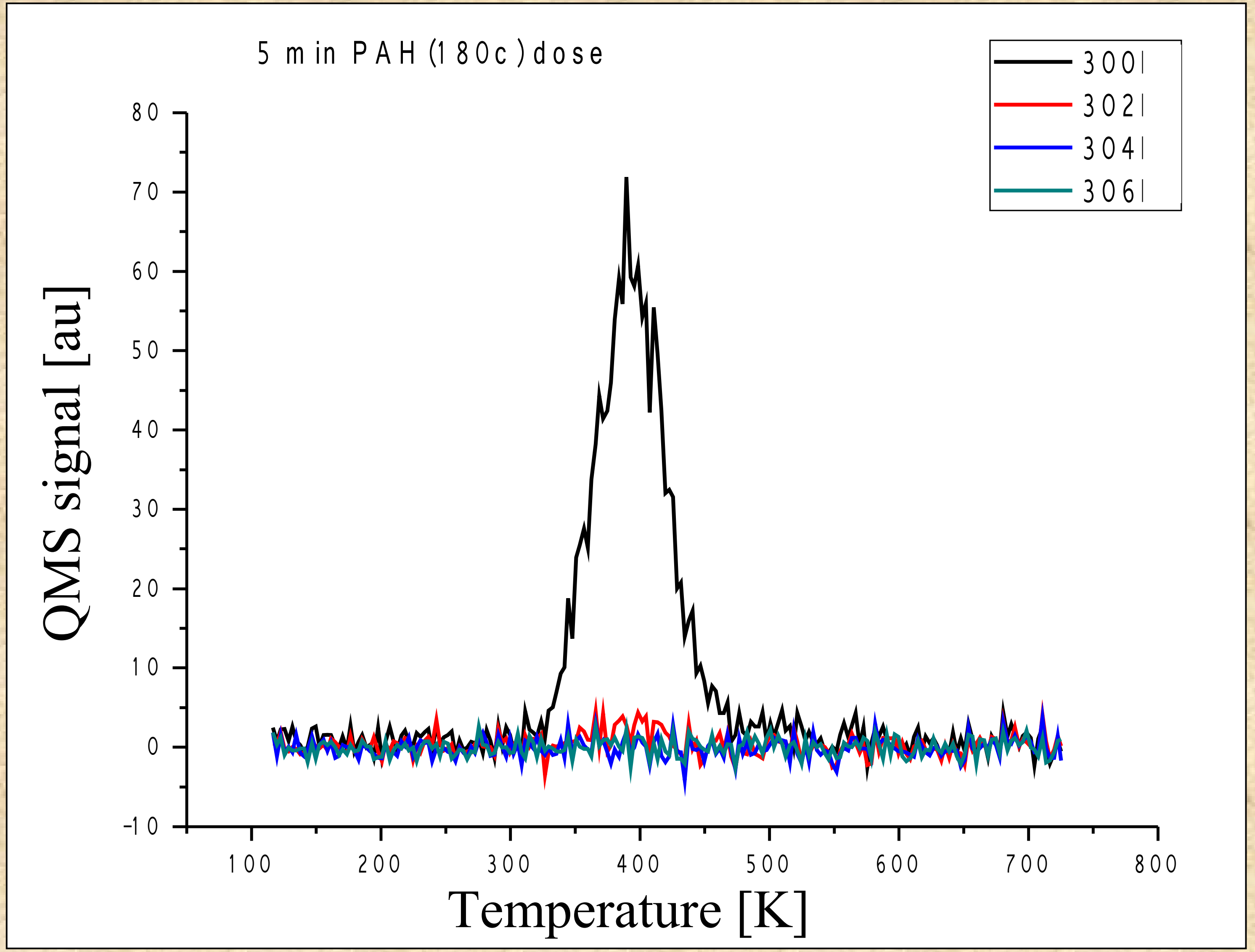
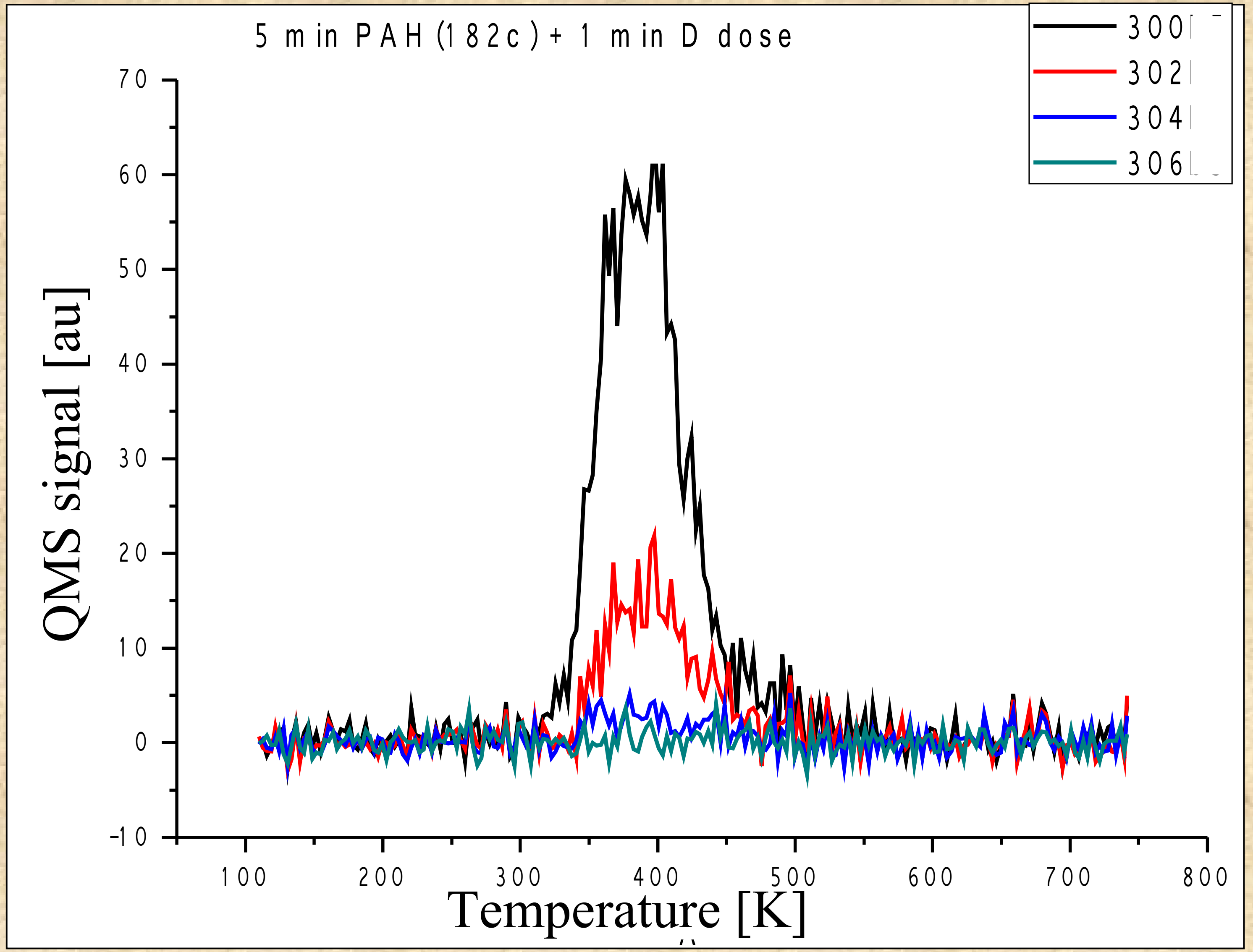
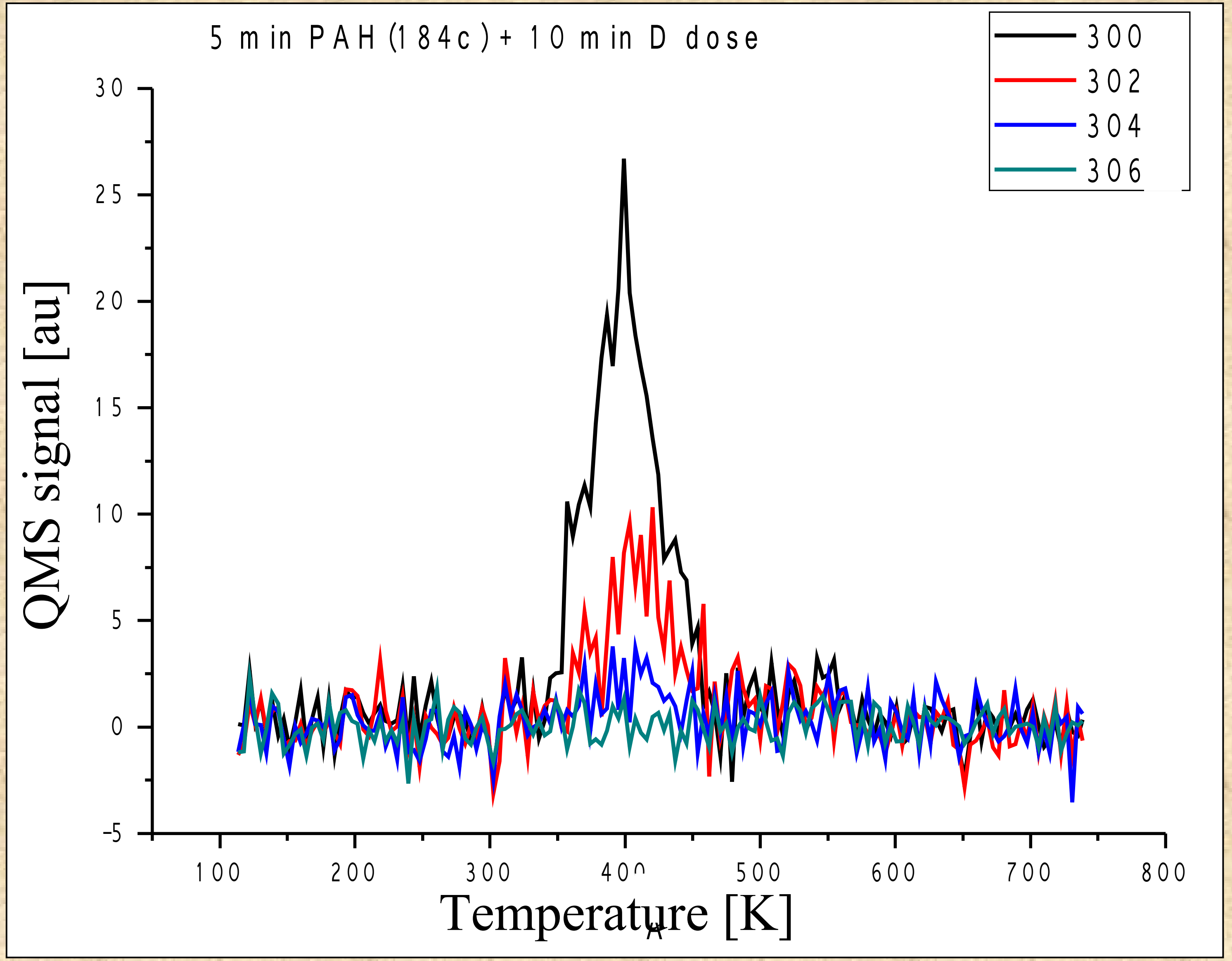


Rauls and Hornekær, Ap. J. **679**, 531 (2008


5 min in PAH (180c) dose
3001
3021
3041
3061
QMS signal [au]
Temperature [K]
80
70
60
50
40
30
20
10
0
-10
100
200
300
400
500
600
700
800



5 min PAH (182c) + 1 min D dose
300
302
304
306
QMS signal [au]
70
60
50
40
30
20
10
0
-10
100
200
300
400
500
600
700
800
Temperature [K]


5 min PAH (184c) + 10 min D dose
300
302
304
306
QMS signal [au]
30
25
20
15
10
5
0
-5
100
200
300
400
500
600
700
800
Temperature [K]

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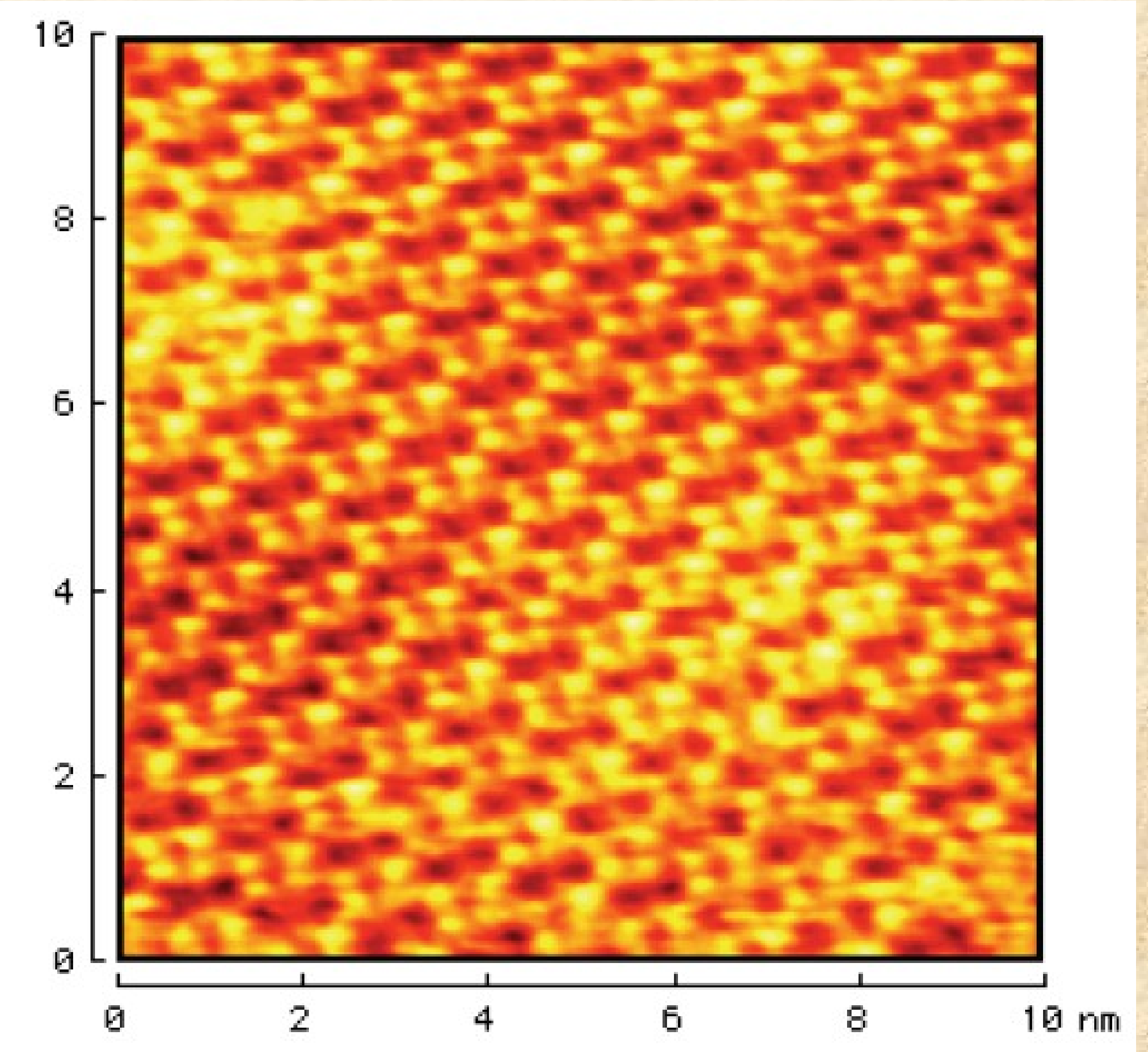

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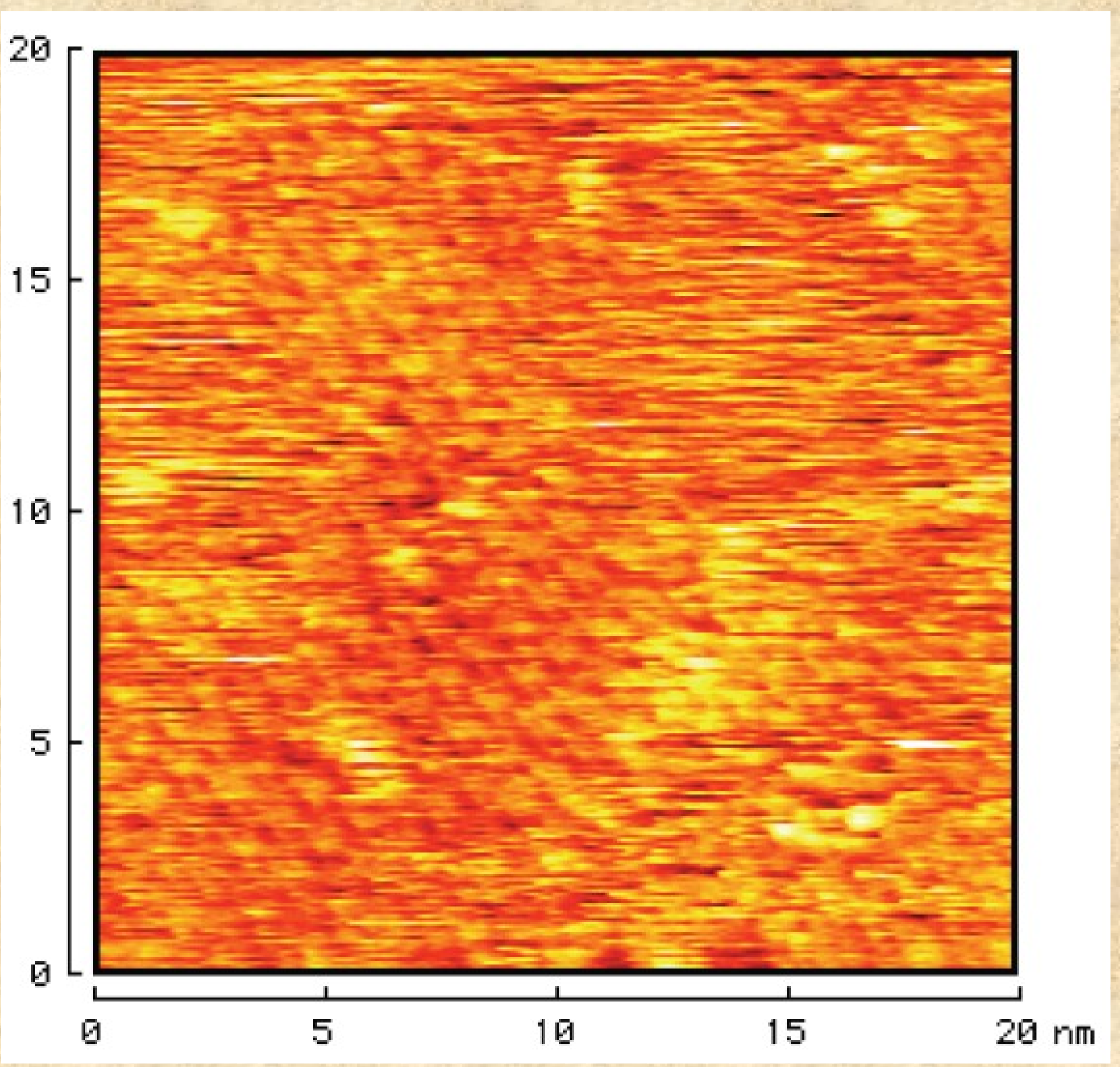
Talk by
Christine Joblin



People involved

STM :
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Richard Balog
Wei Xu
Roberto Ortero
Flemming Besenbacher

Surface dynamics:
Bjarke Jørgensen
Saoud Baouche
Alan Luntz

DFT:
Zeljko Sljivancanin
Eva Rauls
Bjørk Hammer

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Interdisciplinary Nanoscience Center (iNANO)
University of Aarhus