Molecular Hydrogen Formation in the laboratory - Simple or complex?

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Efficient H_2 formation under a wide range of interstellar conditions

Dense clouds	
Diffuse clouds	~$3 \times 10^{-17} cm^3 s^{-1}$ Jura 1975, Gry 2002
PDRs	$3 \times 10^{-17} - 2 \times 10^{-16} cm^3 s^{-1}$ Habart 2004
Post-shock gasses	

Efficient formation of H_2 on dust grains from T_{gas}= 10 – 1000 K, T_{grain}= 10 – 100 K

But not by the same reaction mechanism !

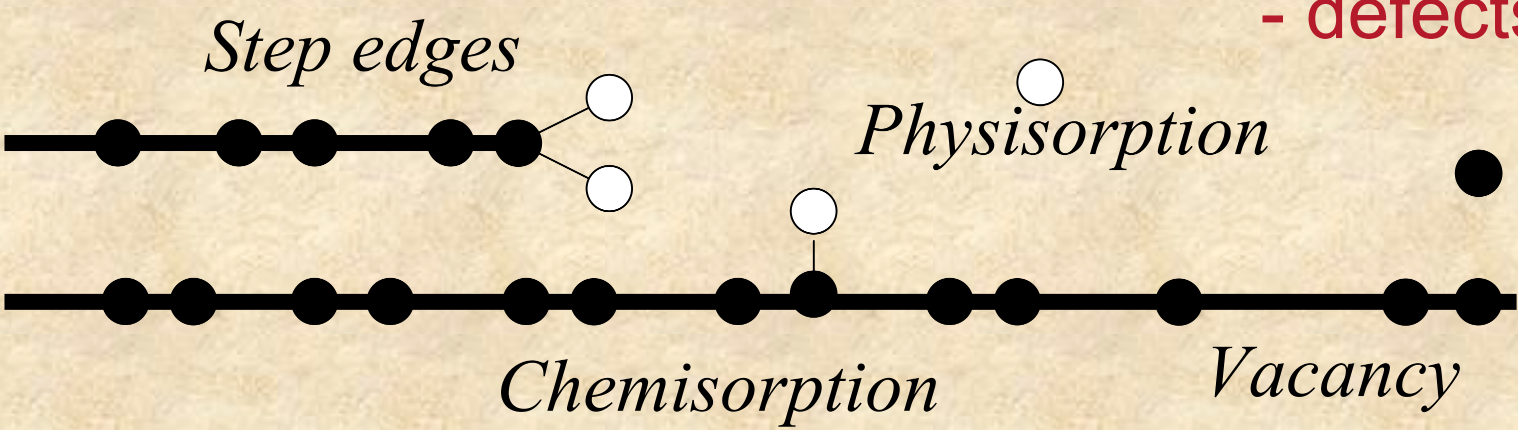
*grain surfaces are not the same

*Different surface reactions are
active at different temperatures

What are the parameters ?

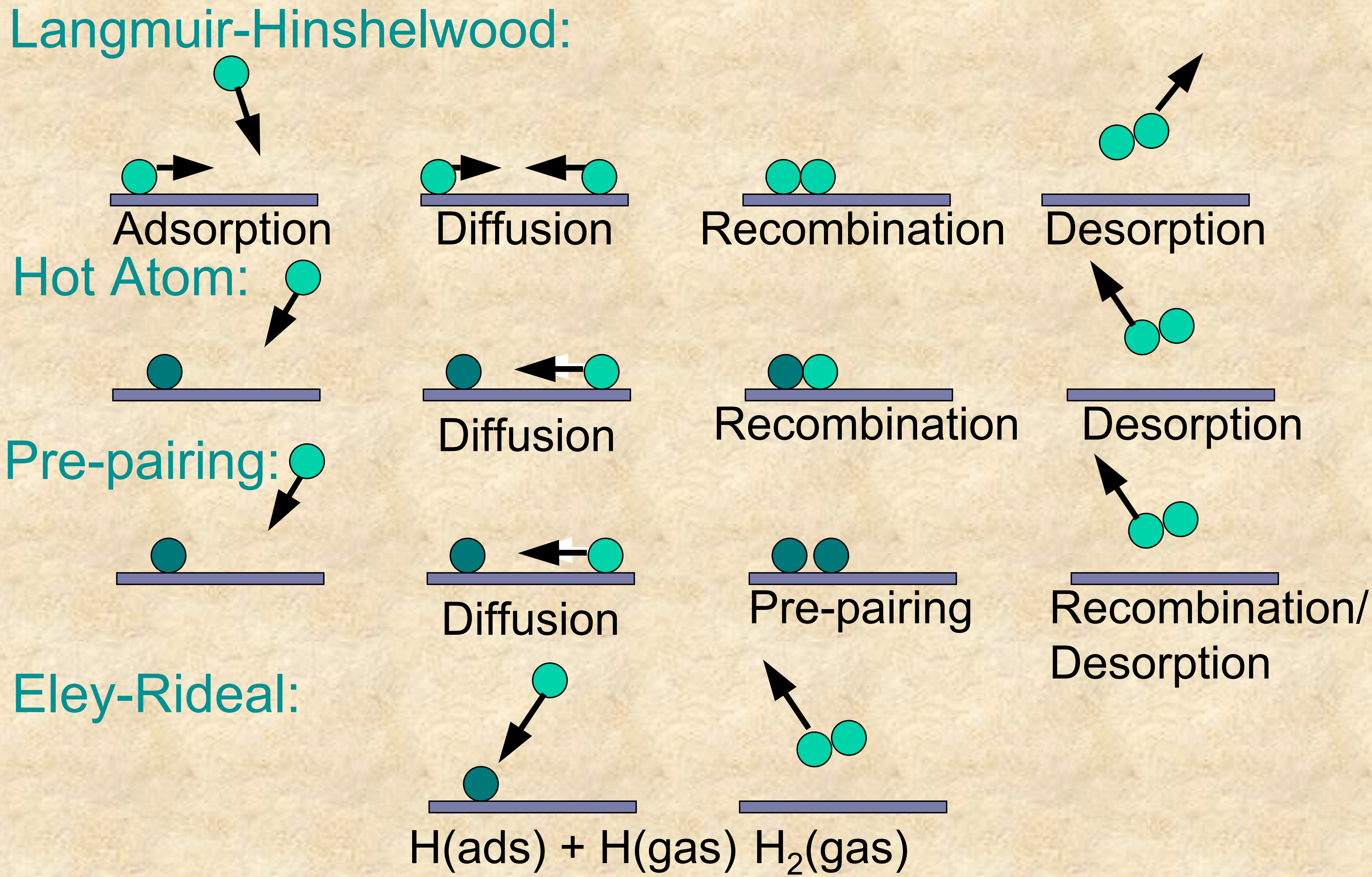
Grain surfaces: Chemical composition
Morphology: Roughness
Porosity
(Grain size)

Surface binding sites: Physisorption - basal plane
(- defects)
Chemisorption - basal plane
- defects



What are the parameters ?

Surface reactions:

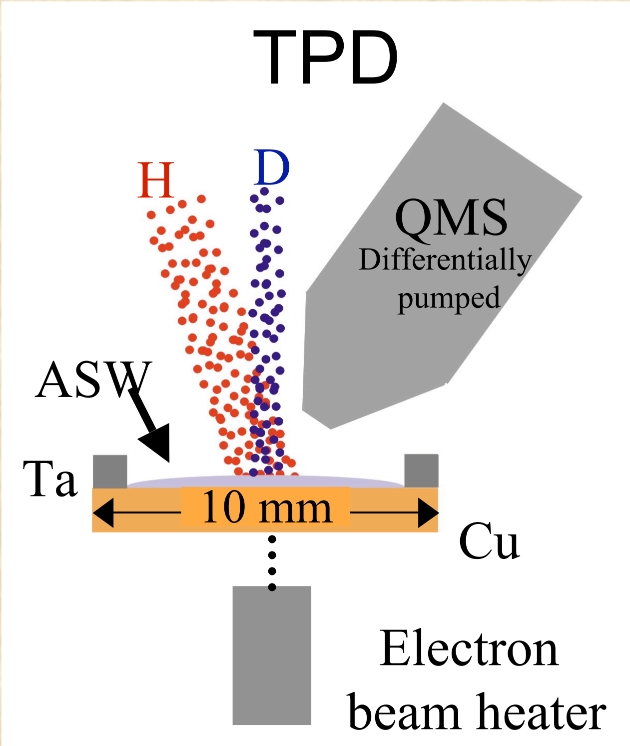


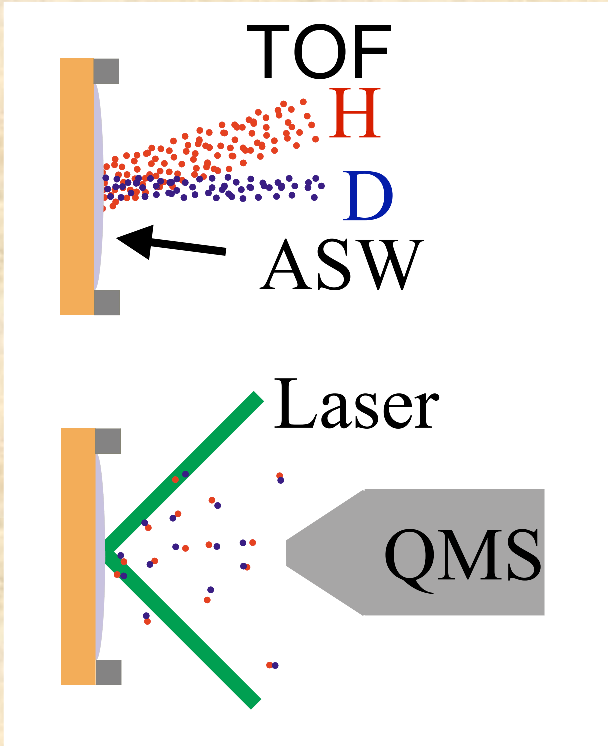
Dense cloud conditions:

Ice covered surfaces at 10 K

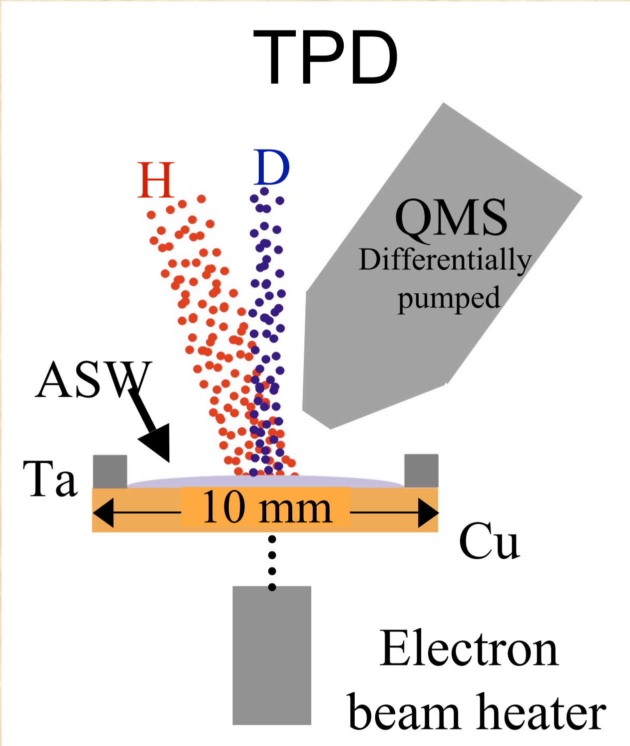
Experiments:
Vidali (Manico 2001, Roser 2002, 2003)
Hornekær (Hornekaer 2003, 2005)
Lemaire/Dulieu (Dulieu 2005, Amiaud 2006, 2007)

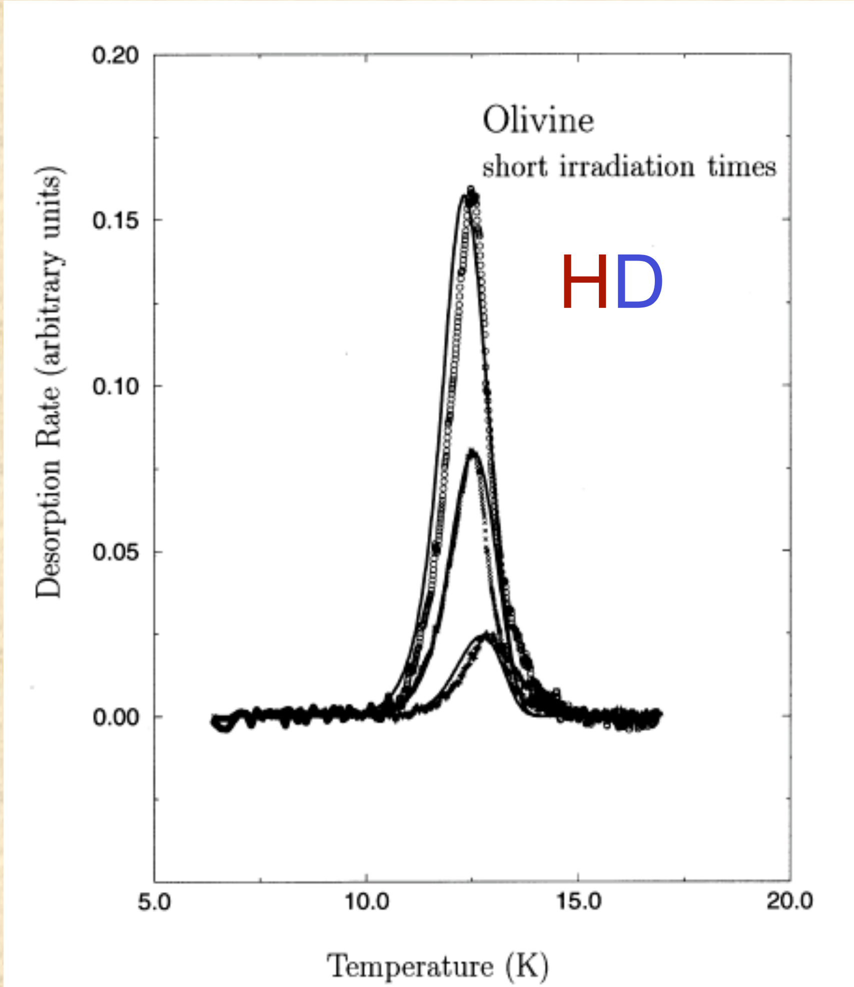
Types of experiments:





Temperature Programmed Desorption

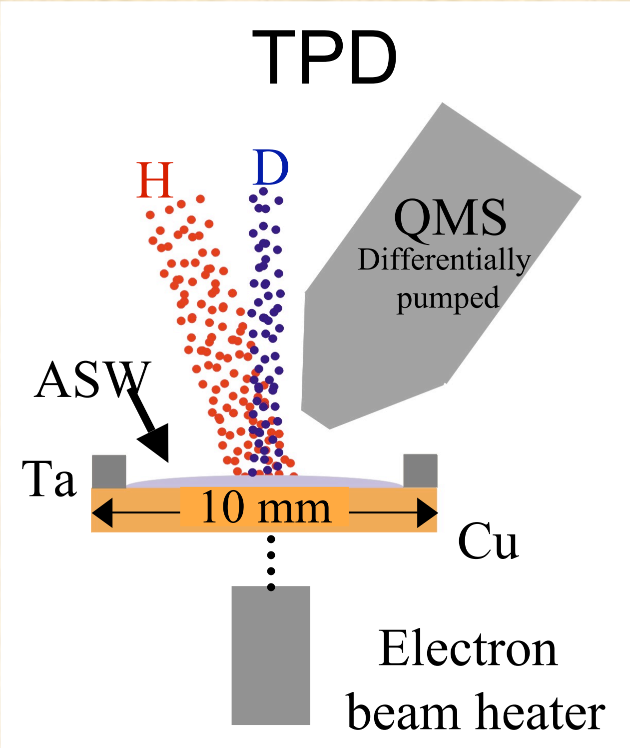


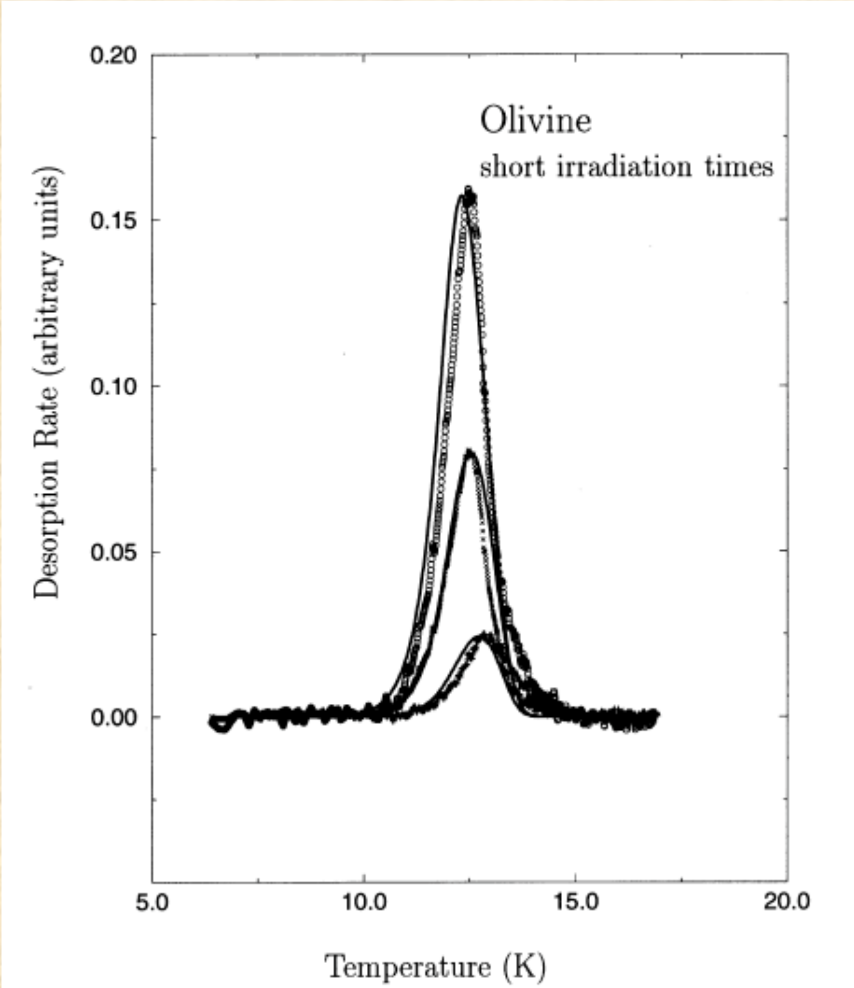


Katz 1999

Temperature Programmed Desorption

$$\frac{d\Theta}{dt} = -k_0\, e^{-E_B/k_B T}\, \Theta^n \qquad n=2\ ?$$

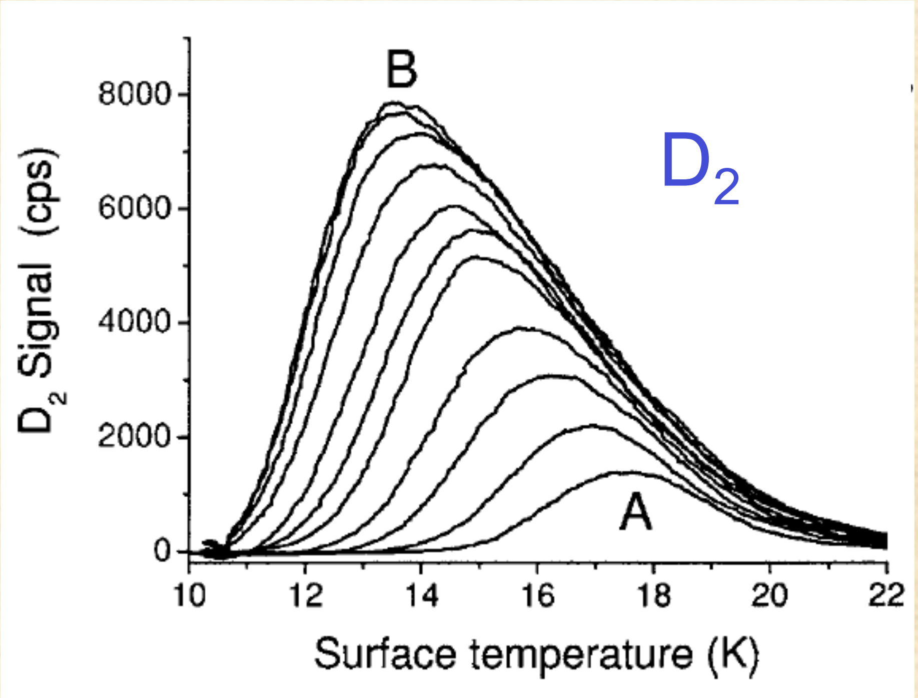




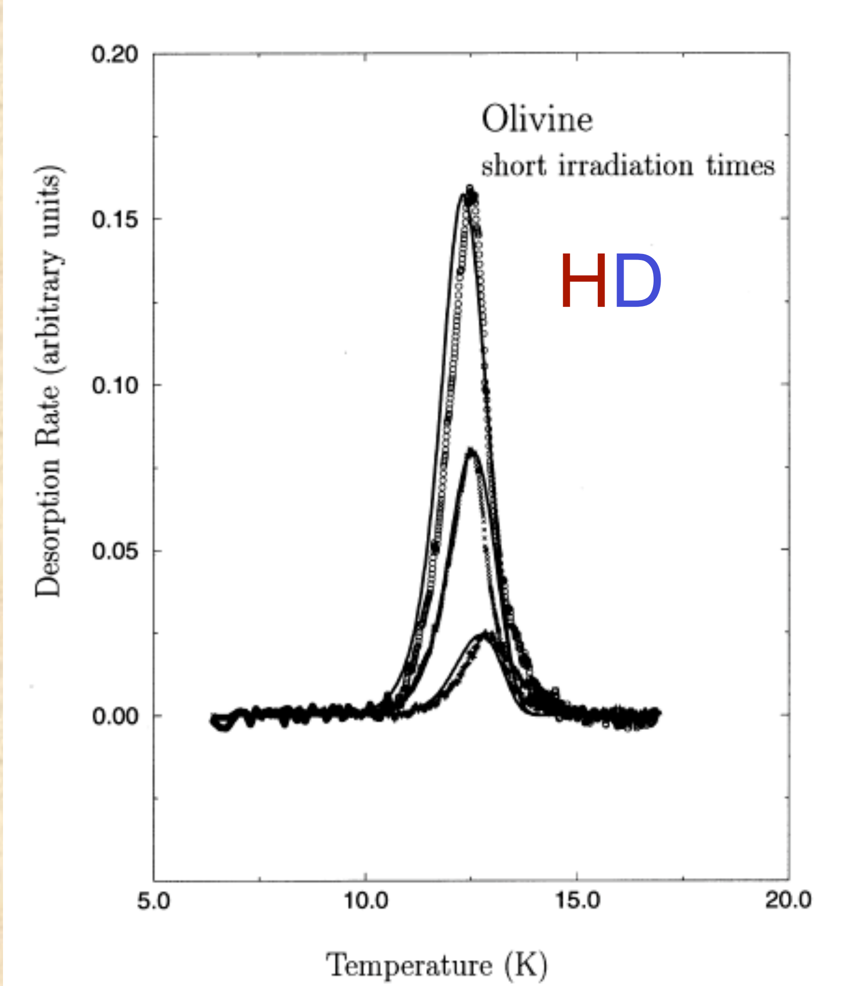
Katz 1999

Temperature Programmed Desorption

E_b a distribution $\quad \frac{d\Theta}{dt} = -k_0\, e^{-E_B/k_BT}\, \Theta^n \quad$ or is E_b really a distribution ?



Amiaud 2007

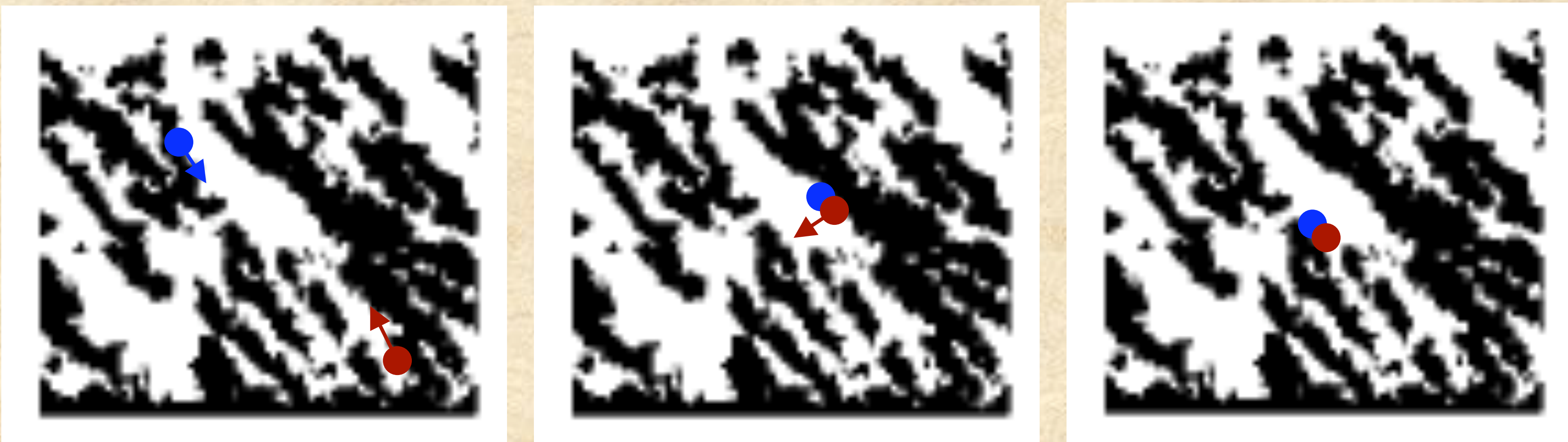


Katz 1999

Grain Morphology

Roughness: Not one E_b,
but a distribution of binding energies

Porosity:



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

What do we know from experiments about H_2 formation under dense cloud conditions?

In the lab: H_2 formation is efficient (~0.2-0.5)
for 7-18 K (Hornekaer 2003, Vidali 2005)

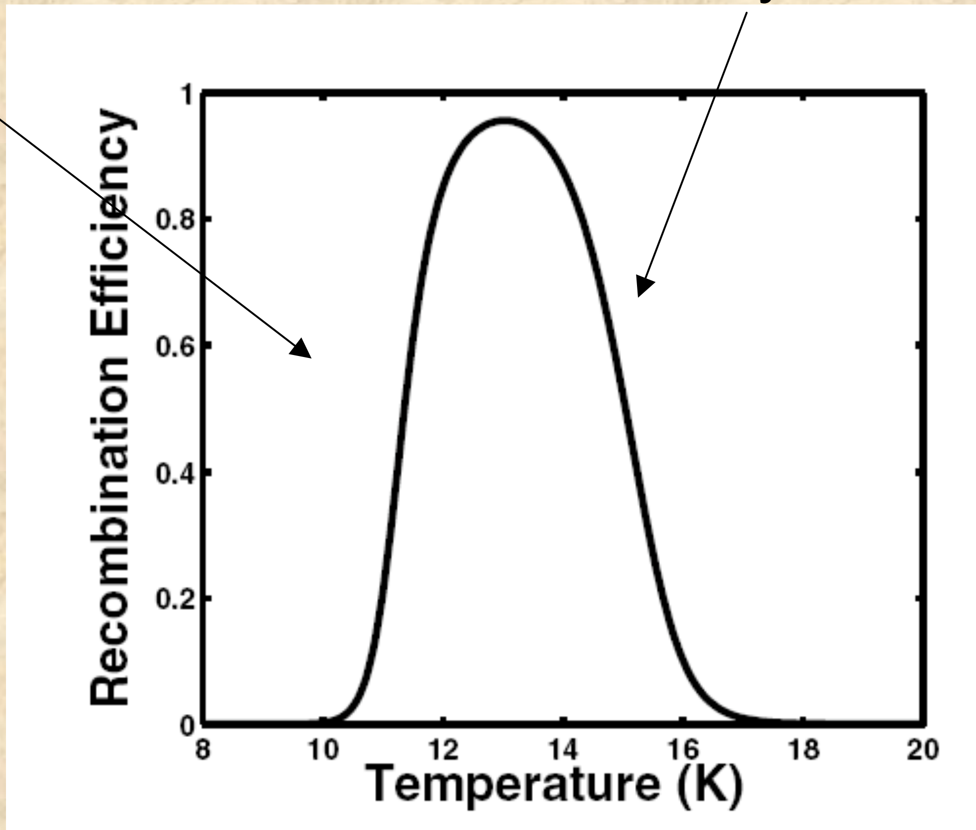
Mechanism: Langmuir-Hinshelwood or Hot atom

Controversy: Low temperature mobility

Model extrapolations to the ISM

Controversial
-But probably unimportant

Given by the H atom desorption barrier.
Uncertain due to simplified analysis models.



Perets 2005,Vidali 2005

Status on surface reactions under dense cloud conditions:

High efficiency in relevant temperature range

But:

Surface parameters: All done on H_2O ASW ice
H_2O deposited as molecules
No calculation of efficiency range taking surface morphology correctly into account.
Grain size.

Further complications: Poisoning (Catalysis)
Isotope effects (Dulieu)

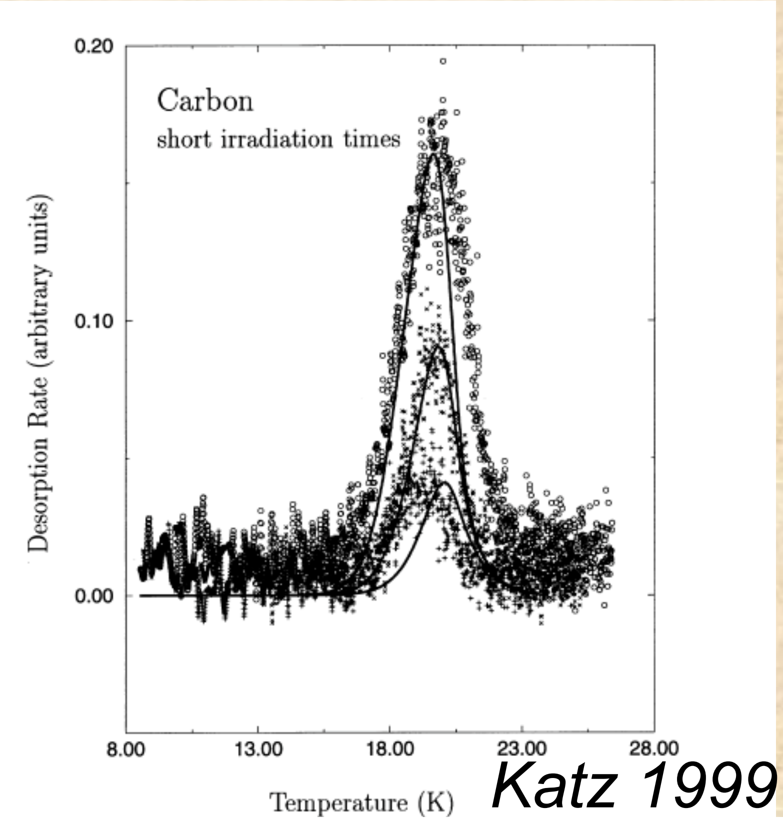
Diffuse cloud conditions

Bare grain at 15-20 K, gas temperature: 30-100 K

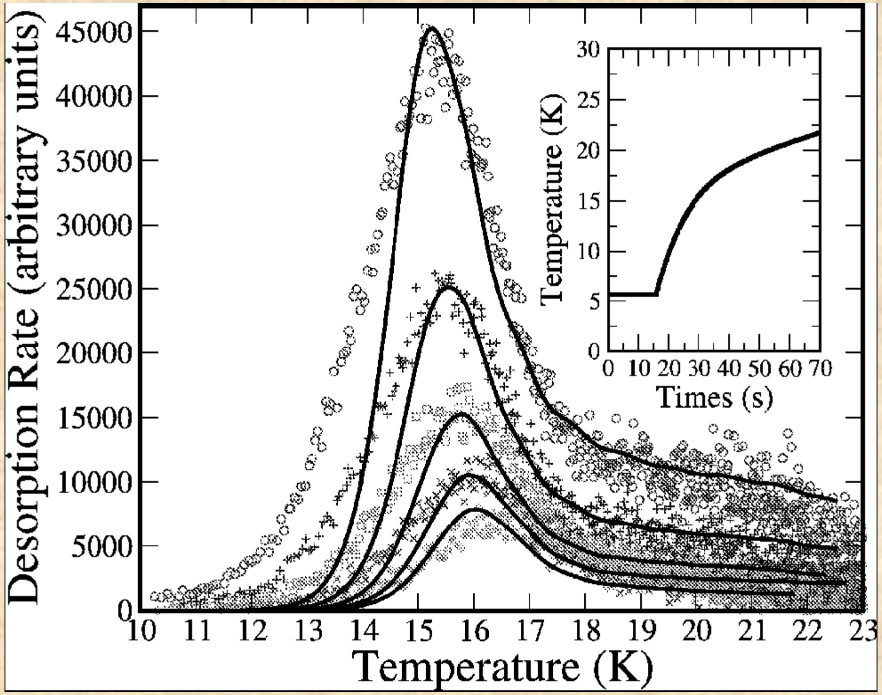
Experiments: TPD by Vidali et al.

Polycrystalline and amorphous silicates

Amorphous carbon



Katz 1999

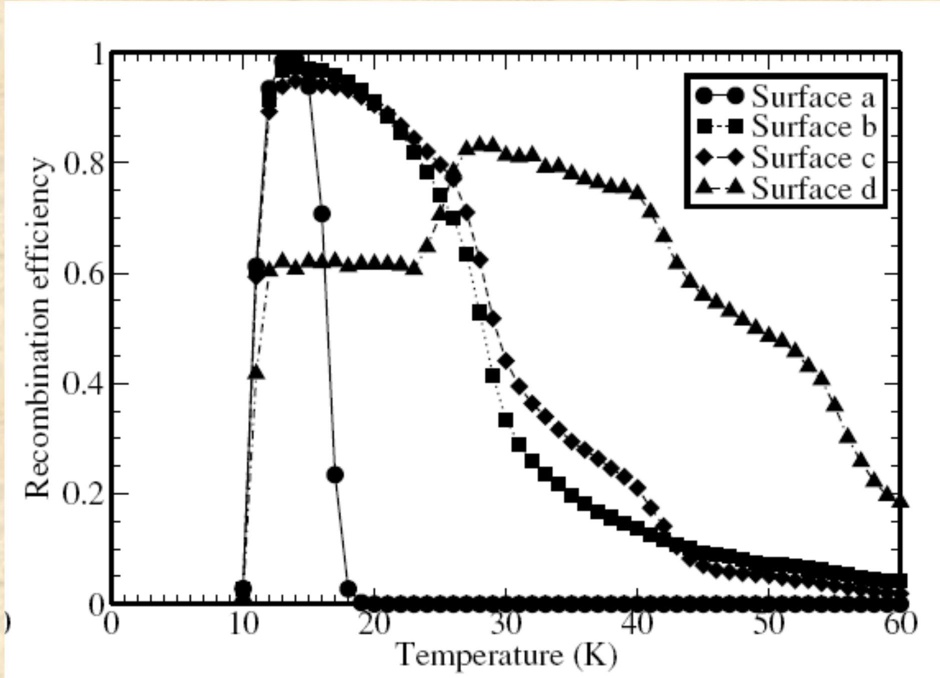


Perets 2007

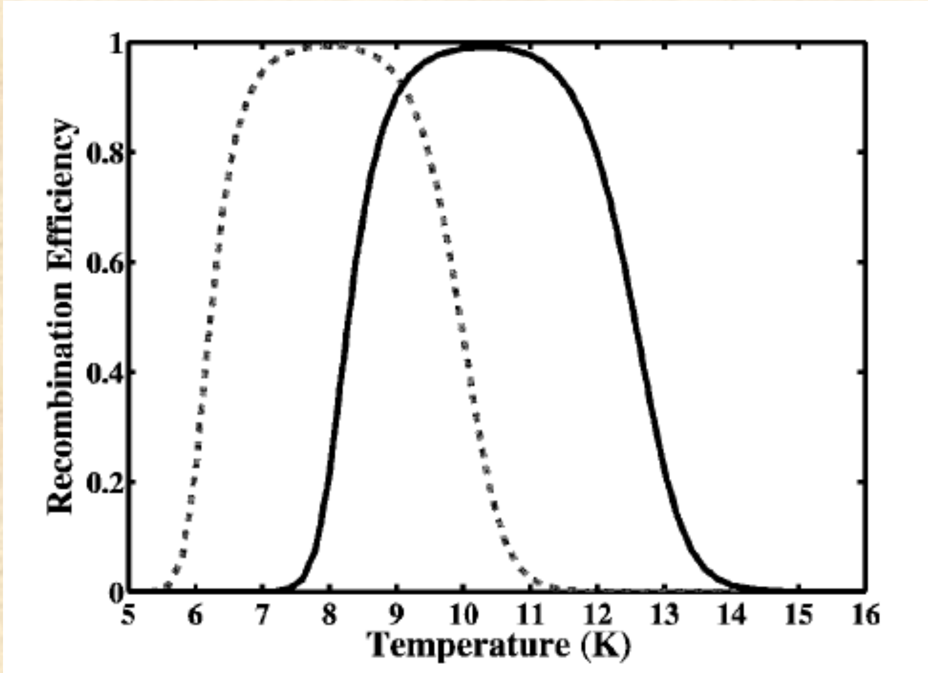
Extrapolation to interstellar H_2 formation efficiency

Amorphous Carbon

Silicates



Cuppen 2005



Perets 2007

A problem for interstellar H_2 formation under diffuse cloud conditions ?

In the analysis of these data the roughness of the surface was not sufficiently accounted for.

If we disregard this and accept derived parameters:

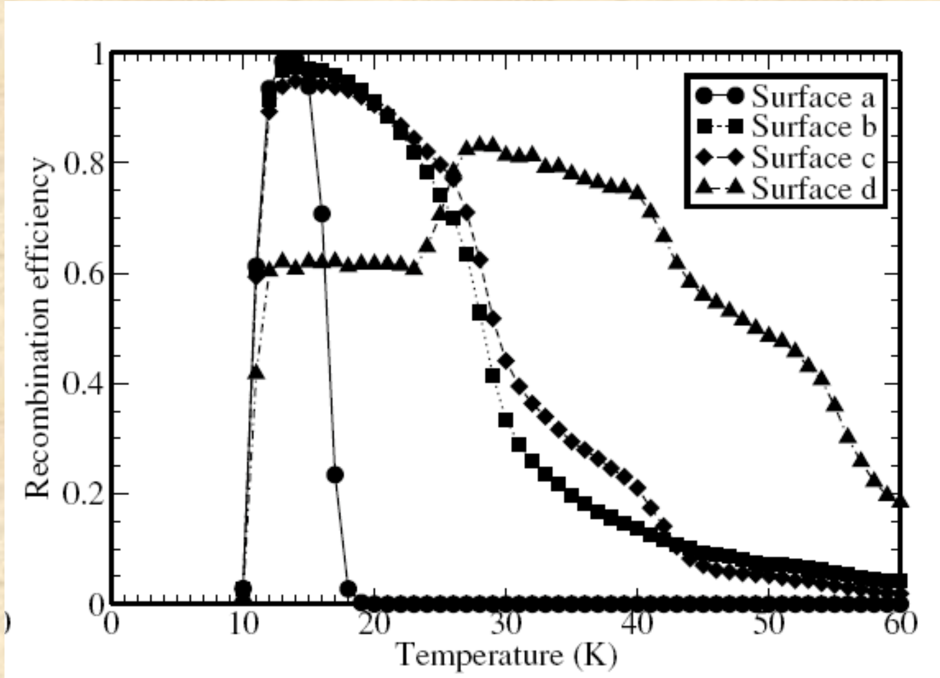
Then there is a problem.

But:
Surface roughness can save the day by bringing the High efficiency interval up to 20-50 K depending on the degree of roughness.

Cuppen 2005

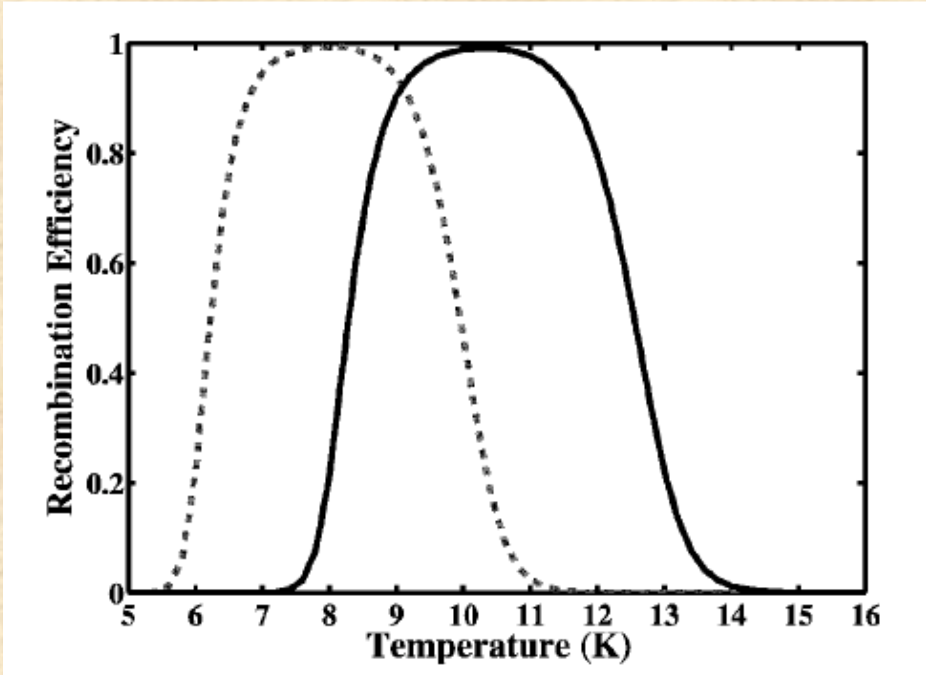
Extrapolation to interstellar H_2 formation efficiency

Amorphous Carbon



Cuppen 2005

Silicates



Perets 2007

Status on H_2 formation under diffuse cloud conditions:

Surface parameters are critical:

Surface roughness determines efficient temperature window

Again, low temperature cut-off probably not important due to Eley-Rideal

Surface roughness has to be correctly accounted for both in data analysis and models.

Grain surfaces => reaction rates

Reaction rates => grain surfaces

PDR / Shocked-gasses

Bare grains at 10-300 K, gas temperature: 100-1000 K

Few experiments:

Zecho (Zecho 2002)

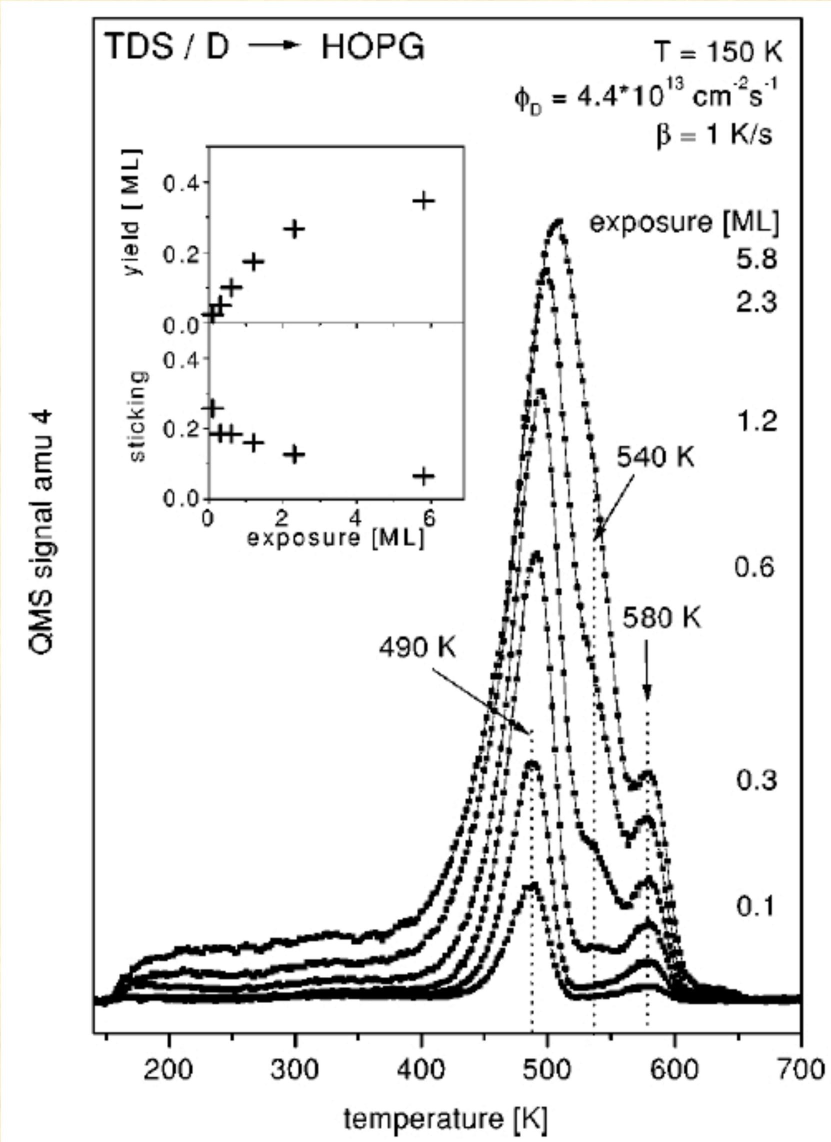
Hornekaer (Hornekaer 2006, Baouche 2006)

On graphite and amorphized graphitic surfaces

Many experimental methods:

TPD, STM, EELS, QMS, LITD-TOF

TPD of D_2 formation on graphite

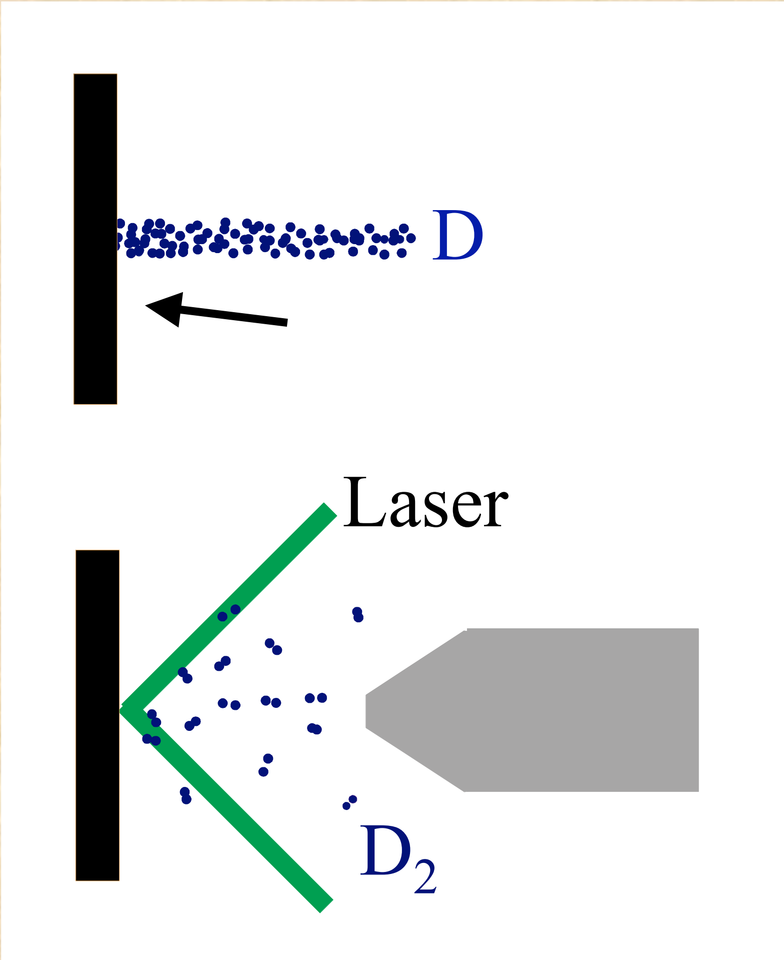


$$\frac{d\Theta}{dt} = -k_0\, e^{-E_B/k_B T}\, \Theta^n$$

n=1 => First order desorption

Zecho et al, J. Chem. Phys. 117, 8486 (20

LITD TOF



Laser Induced
Thermal Desorption
(LITD)

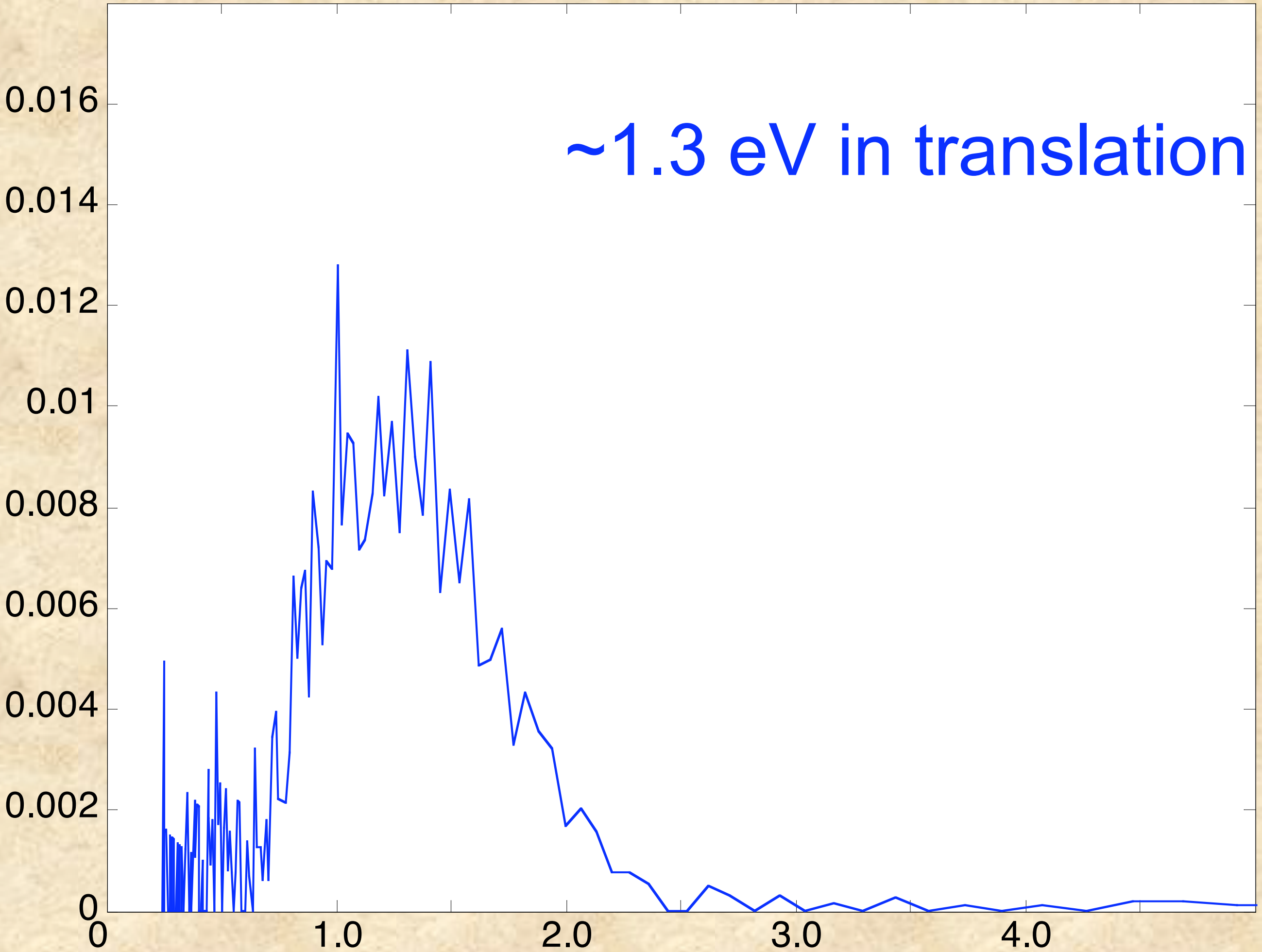
Alexandrite
Laser

4 mJ
100 ns pulse

↓

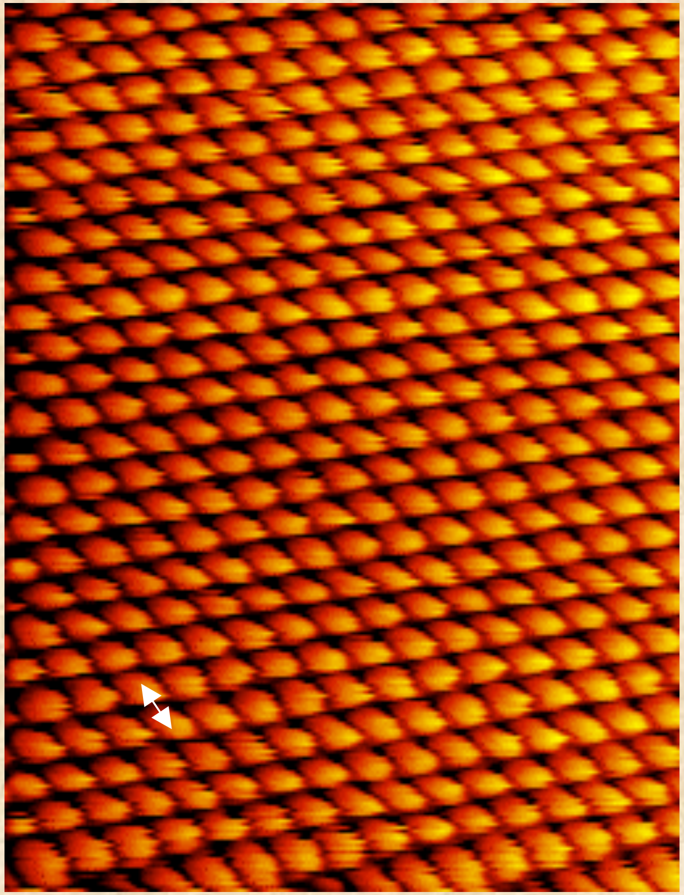
Time of Flight Measurement

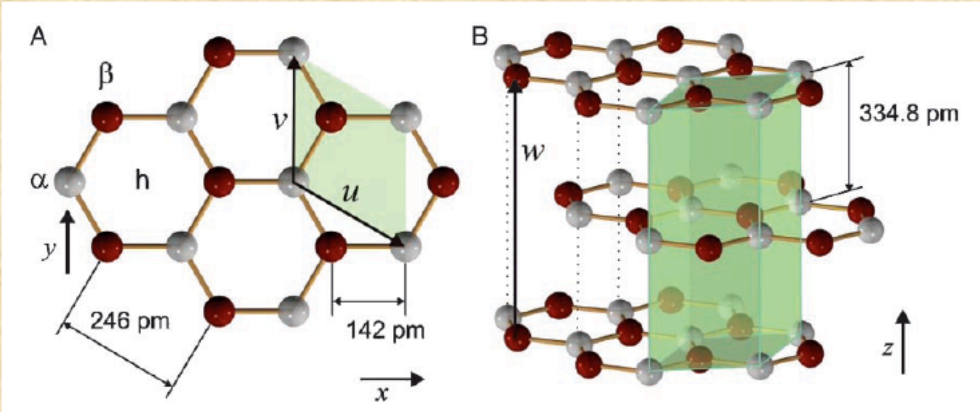
Kinetic energy of D_2 formed on graphite

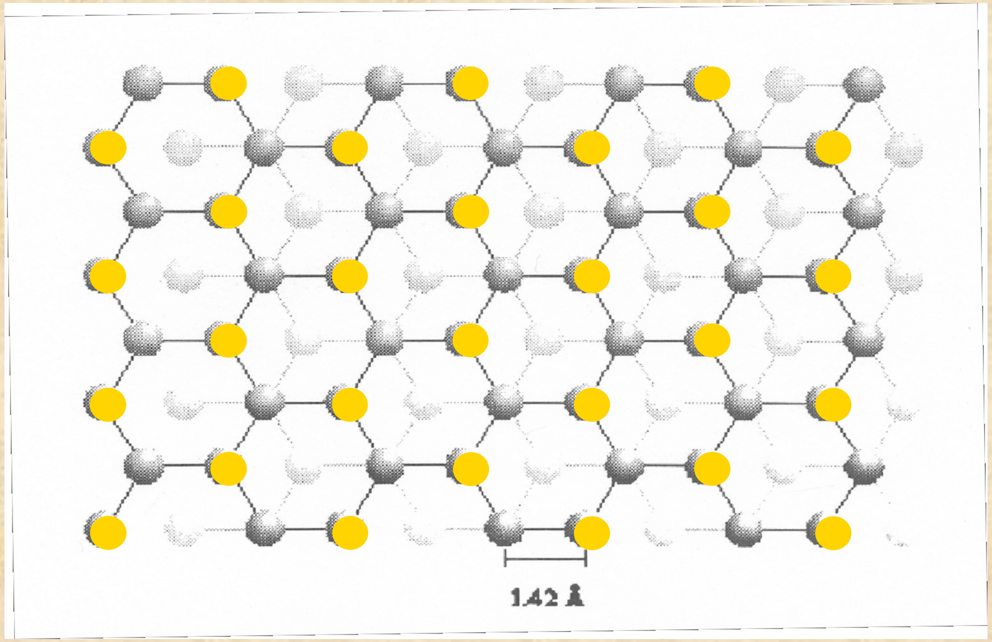


Baouche 2006

STM on graphite

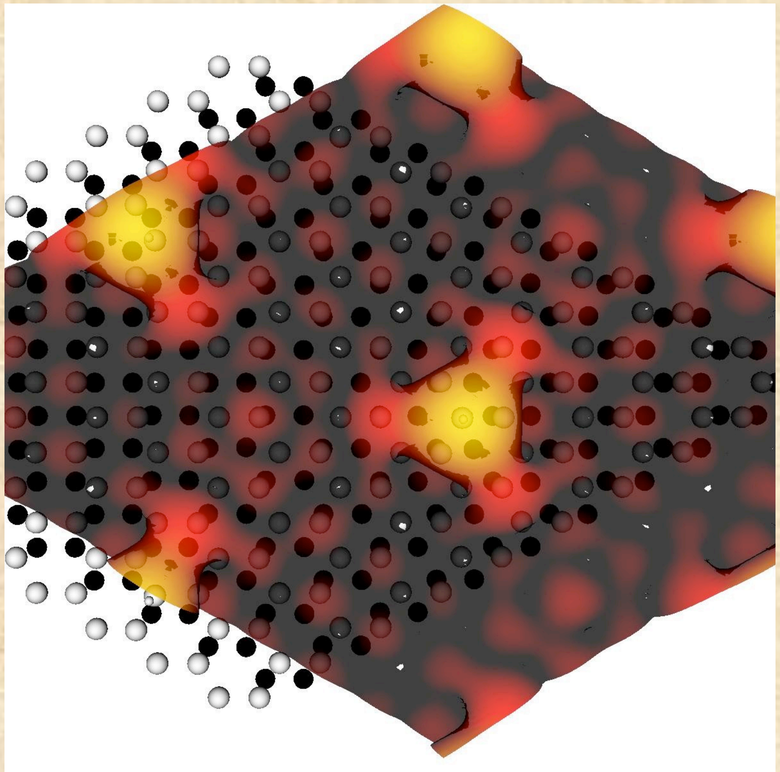




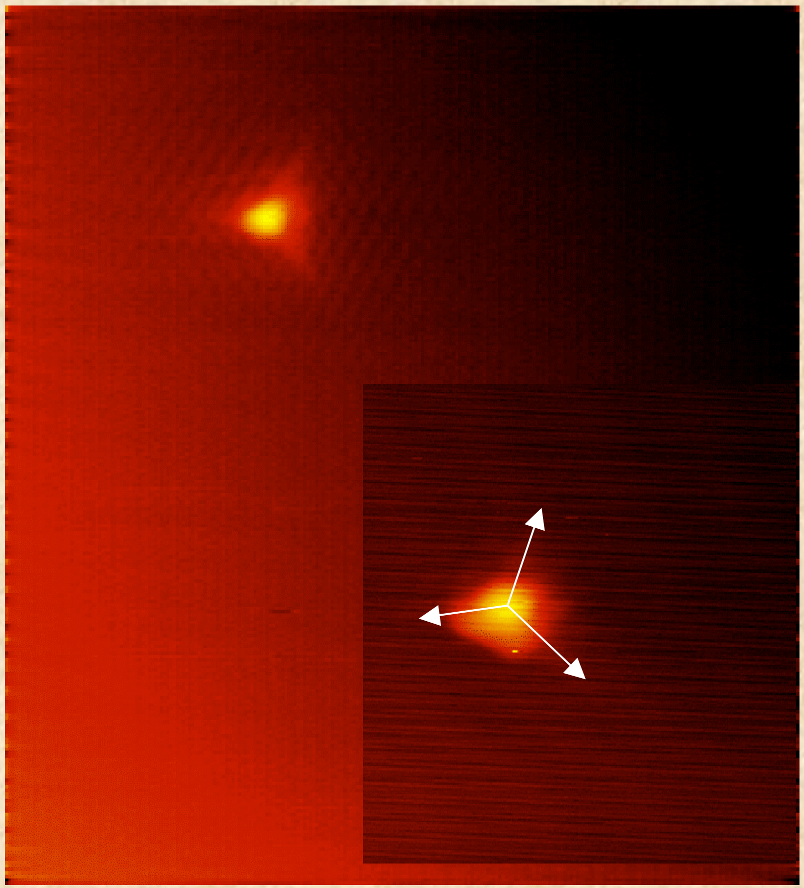


↕ 2.46 Å

Hydrogen on graphite –Monomers



Zeljko Sljivancanin

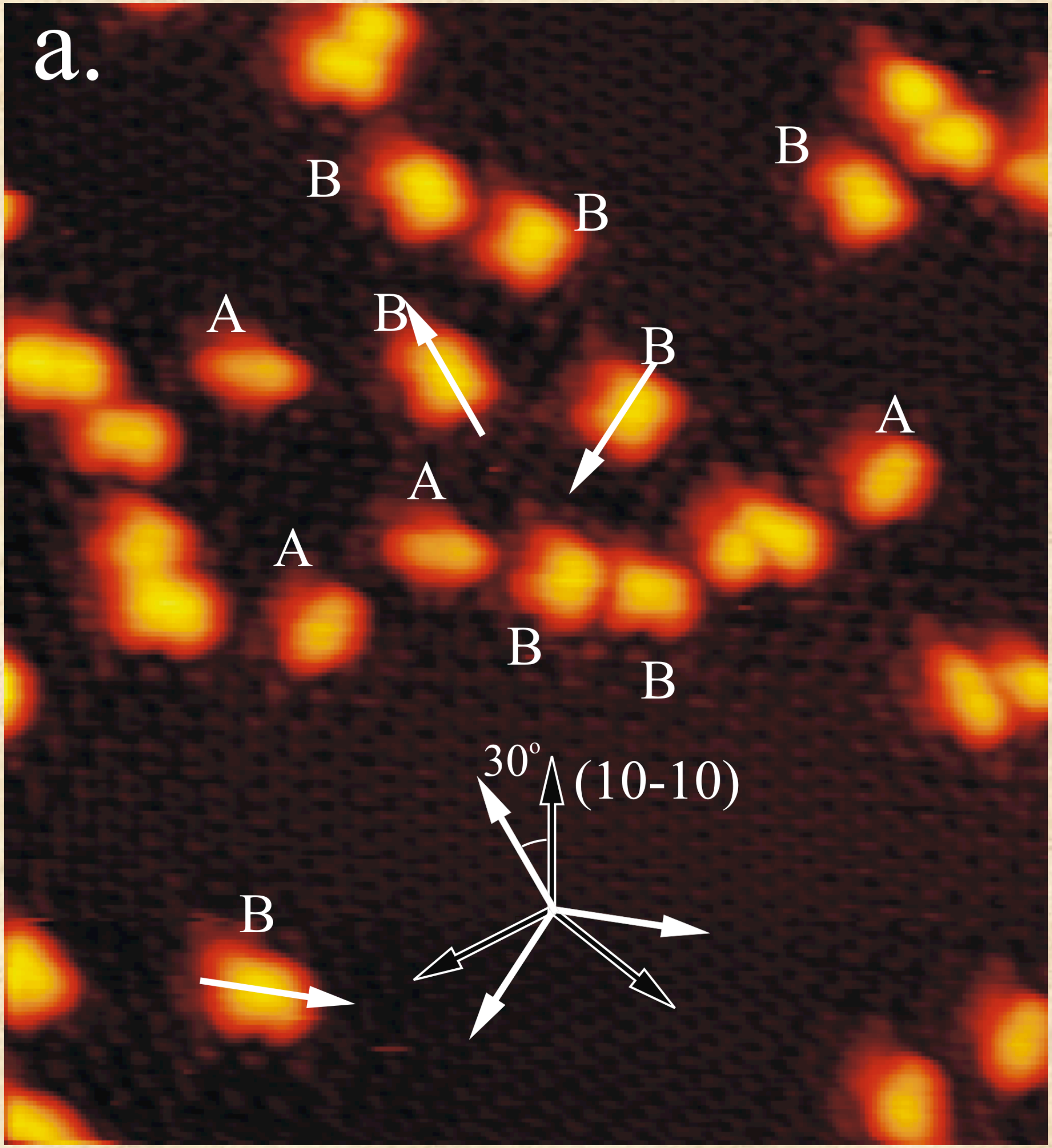


155 x 171 Å^2 , 180 K

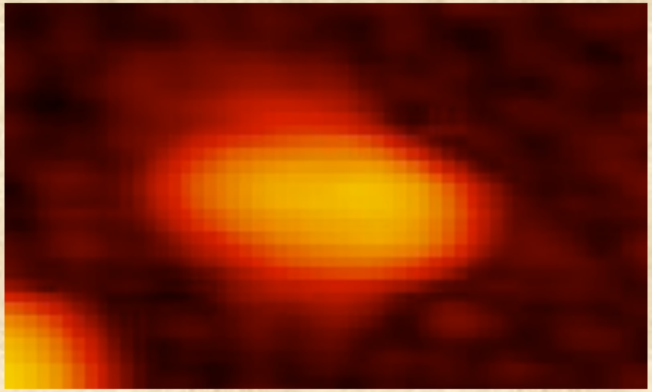
V_t~ -710mV, I_t~ -0.16nA

H-Dimers on graphite

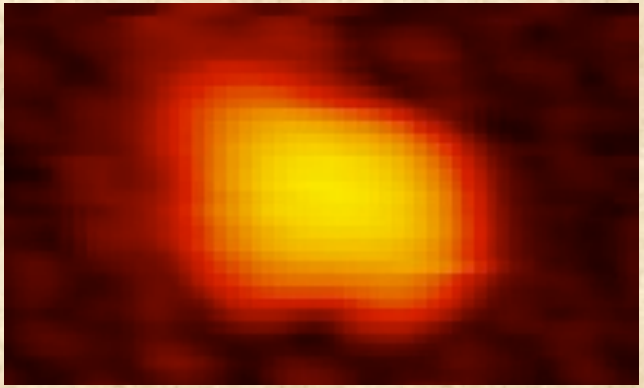
103 x 114 Å^2



Dimer A



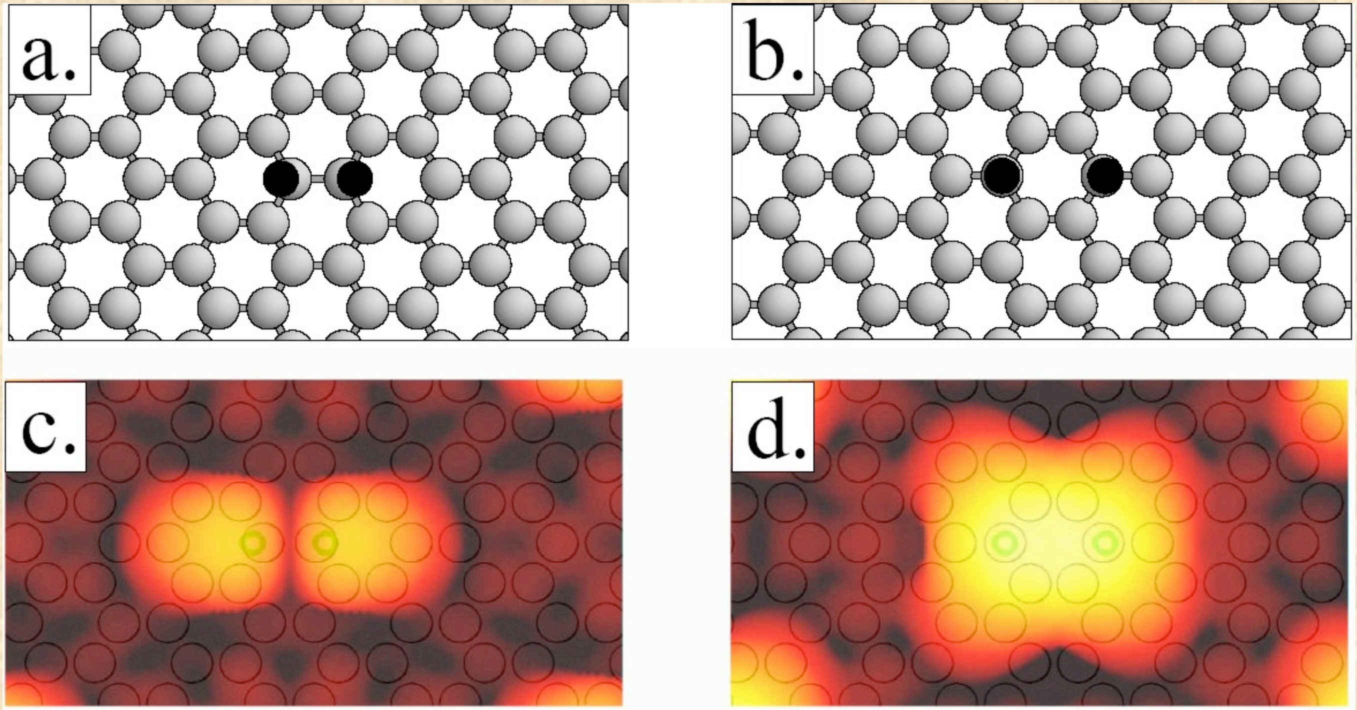
Dimer B



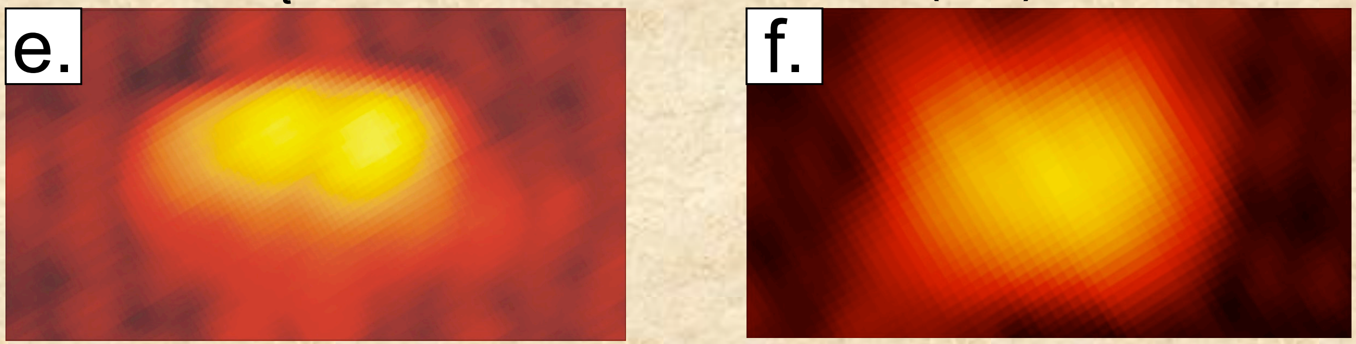
V_t = 884 mV, I_t = 0.16 nA

Dimers: Theory vs. Experiment

Ortho dimer - Dimer A   Para dimer - Dimer B



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

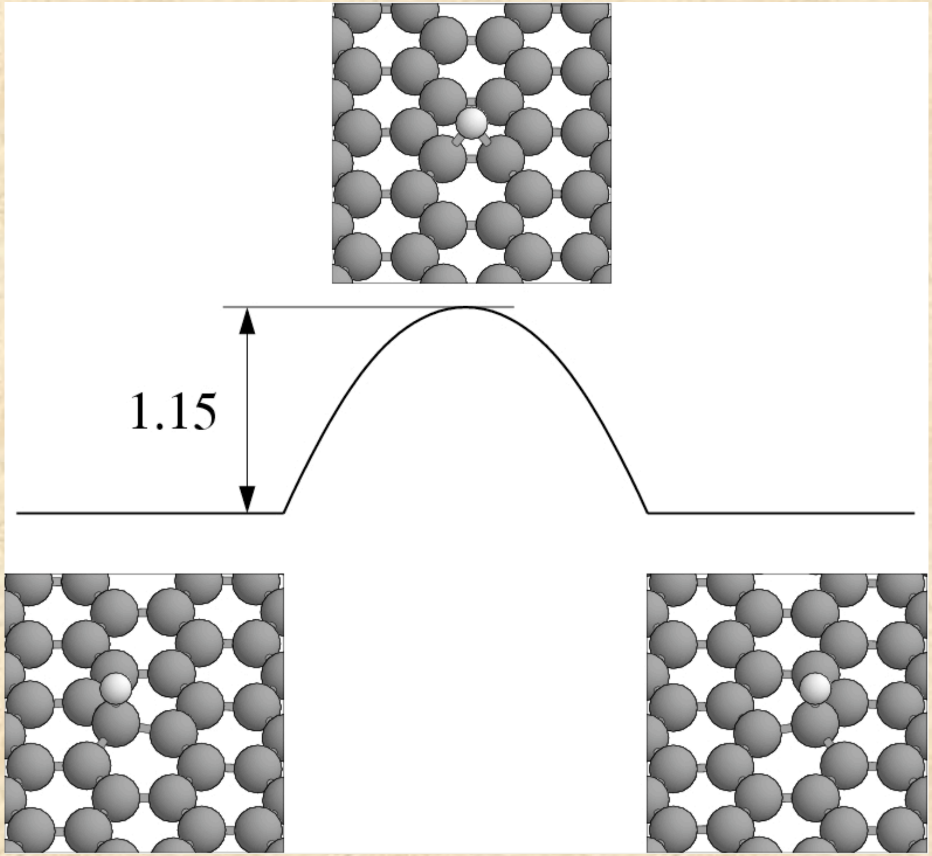


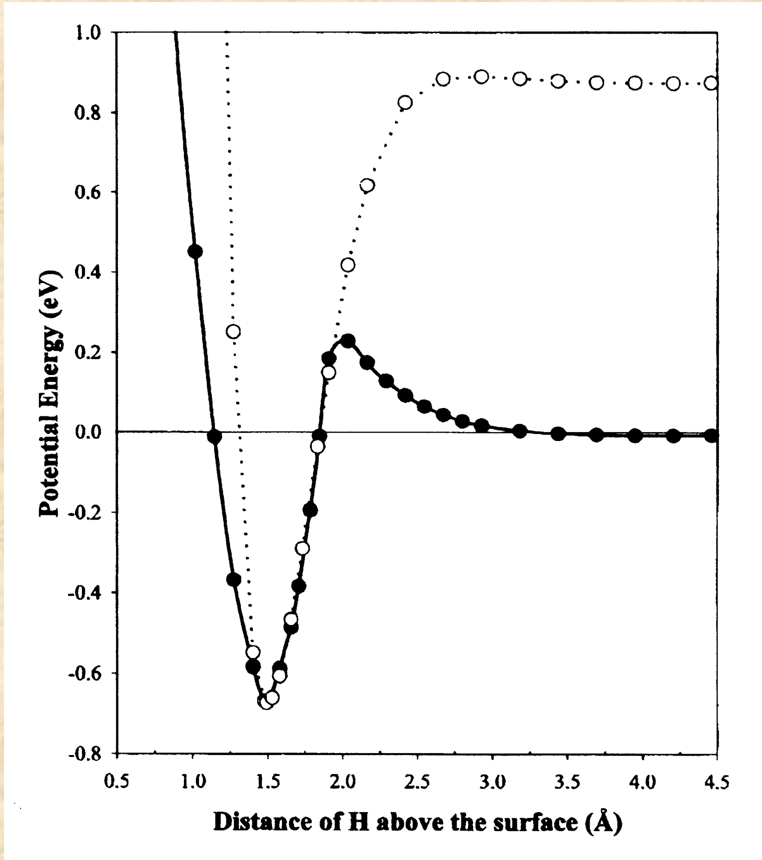
V_t = 884 mV, I_t = 0.16 nA

Diffusion

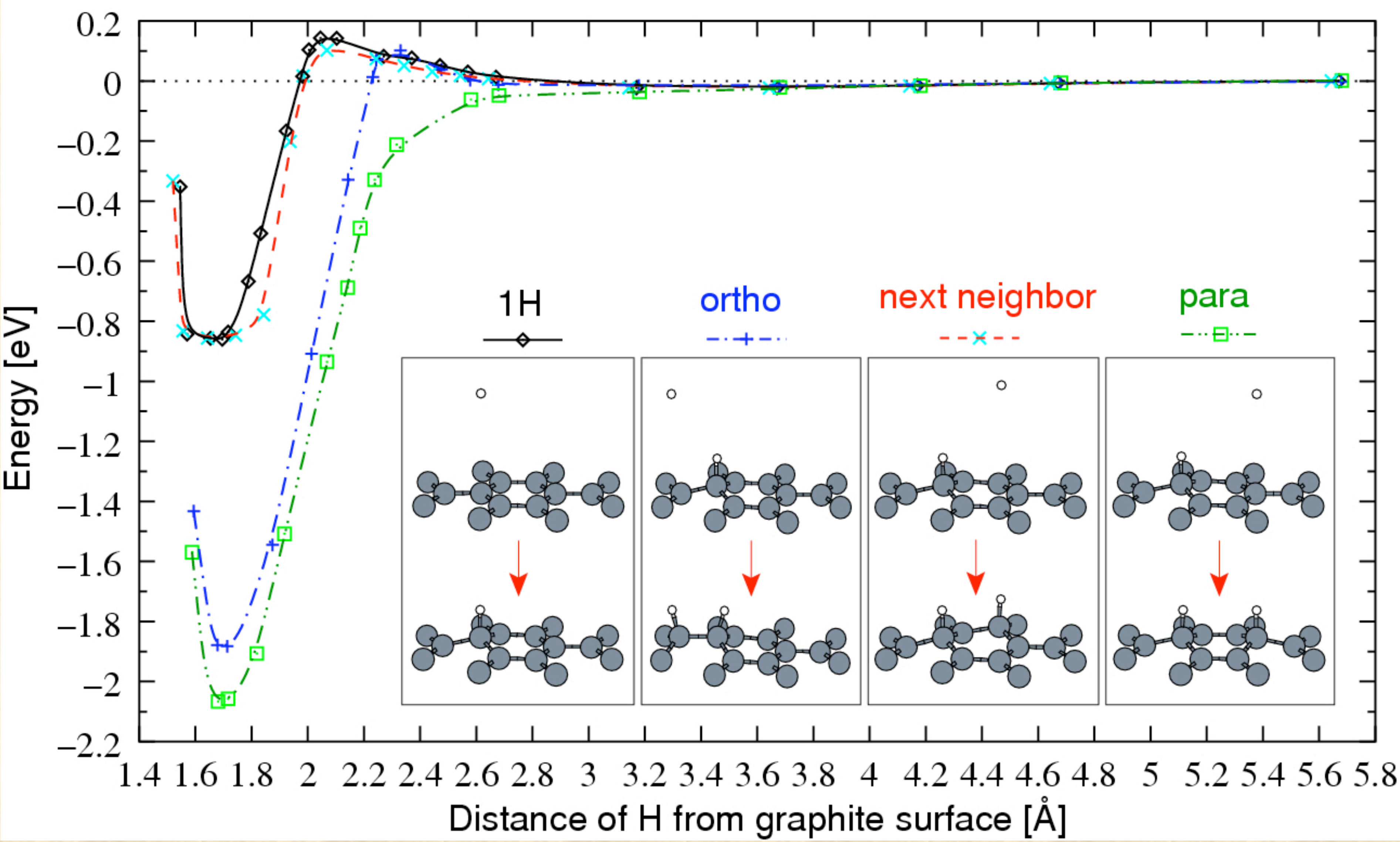
Barrier to diffusion for an isolated H atom: 1.14 eV

Barrier to desorption for an isolated H atom: 0.9 eV



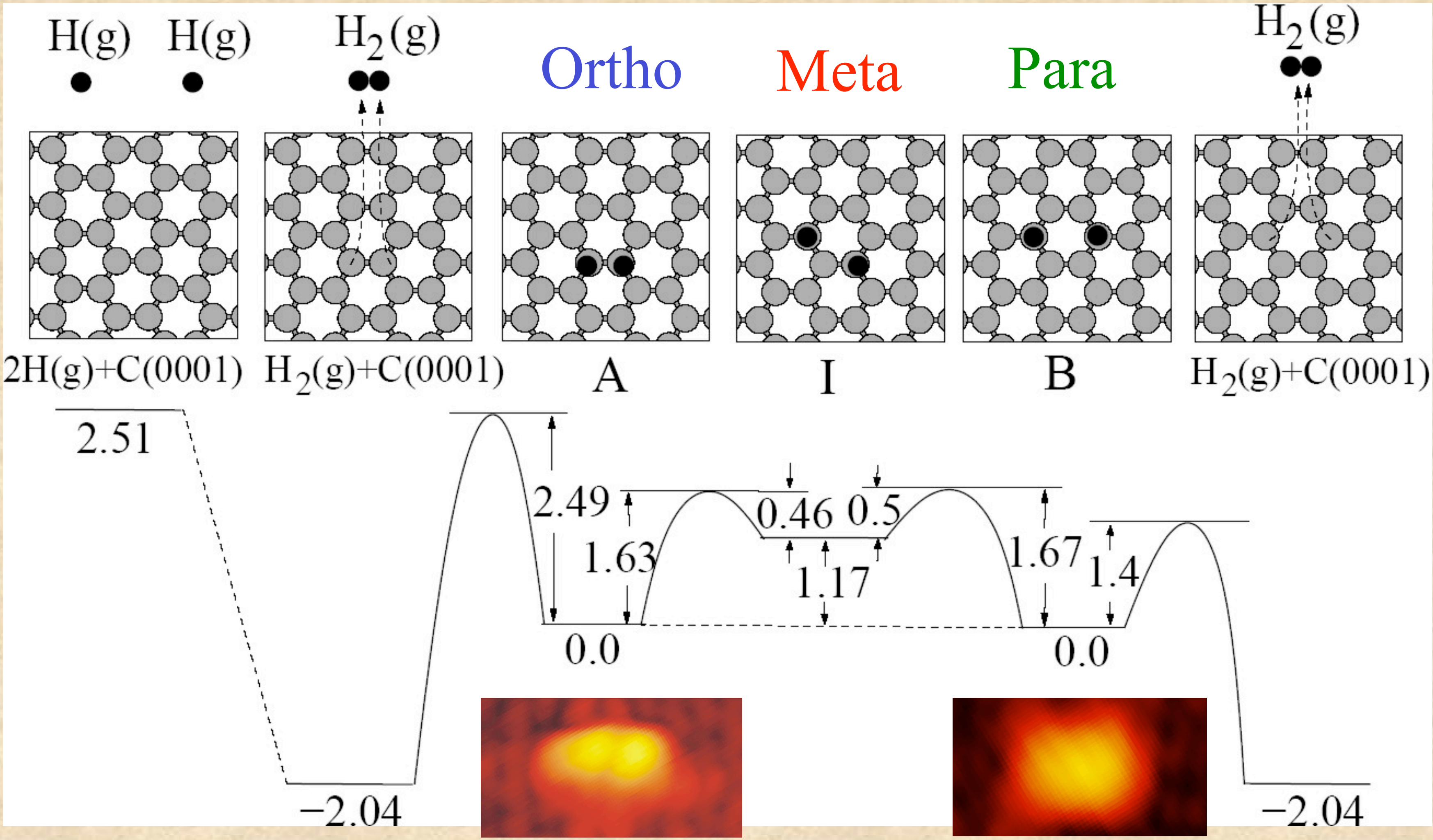


Dimer formation



Hornekær 2006

Recombination pathways



Hornekær 2006

Extrapolation to PDR and post-shock gas conditions

T_{gas} ~ 600-1000K

=> population of the chemisorbed states on graphite

Barrier to recombination: 1.4 eV

=> thermal desorption: 1000 years at 300K

Thermal spikes? Localized heating?

or high coverage of H_2

=> Eley Rideal

MC surface reaction model based on these experiments in the making – Herma Cuppen.

Status on H_2 formation under PDR and Post-shock conditions:

One system studied which offers H_2 formation routes at elevated temperatures.

Efficiency – we await Hermas model.

Needed: studies of other surfaces (silicates, amorphous Carbon) at high T.

Grain size

Grain size

Large grains: Physisorbed H not desorbed
due to thermal fluctuations.

However, if we look at chemisorbed H this is not
so critical – might even activate recombination

Small grains (or even PAHs) might contribute to or
even dominate H_2 formation under some conditions.

Conclusions

Uncertainty not only in rates - but also in reaction mechanisms

Dense clouds: Langmuir Hinshelwood (or hot atom)
Eley-Rideal ?
Rates: Better analysis models, chemical composition

Diffuse clouds: Langmuir Hinshelwood (or hot atom)
Eley-Rideal ?
Rates: surface parameters critical

PDR/Post-Shock gas: More studies needed - other surfaces
Pre-pairing on graphite
Eley-Rideal
Role of small grains and PAHs
Rates: Detailed surface models required

Fate of durface reactions in astrophysical models / reaction networks ?

Grain surfaces => reaction rates

Reaction rates => grain surfaces