Model of the molecular Hydrogen formation on carbonaceous interstellar grains

Role of the surface relaxation.

NGC 346 - Small Cloud of Magellan -

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Why are we interested in H_2 in the ISM?

Gaz (99%) → **H**, **H_2** } ~ 90%; → He ~ 10%

Dust : grains (1%)

Rovibrational state of H_2
vibrationally cold v = 0-5 *
rotationally warm j = 0-30 **

* T. Giannini et al. Astron. Astrophys. **419**, 999 (2004)
** D. Rosenthal et al. A&A **356**, 705 (2000)

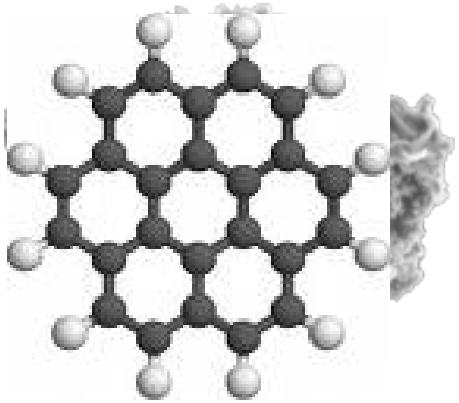
PAH *(Polycyclic Aromatic Hydrocarbon)*
Small Grains (Carbonaceaous)
Big Grains (Silicate)

Interplanetary /Comet Grains

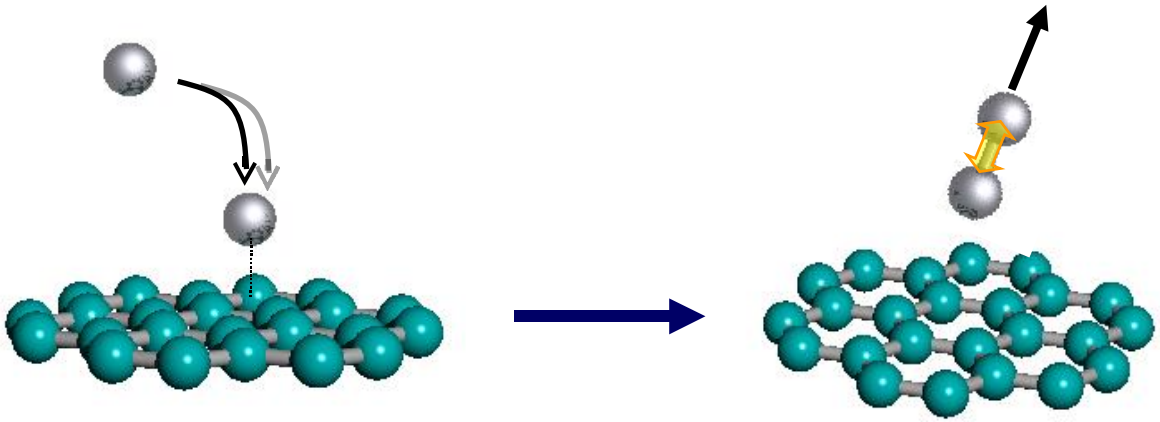
Diffuse clouds

Dissociation of H_2 very efficient (UV)
$H >> H_2$
abondance of H_2 ?

PhotoDissociation Regions

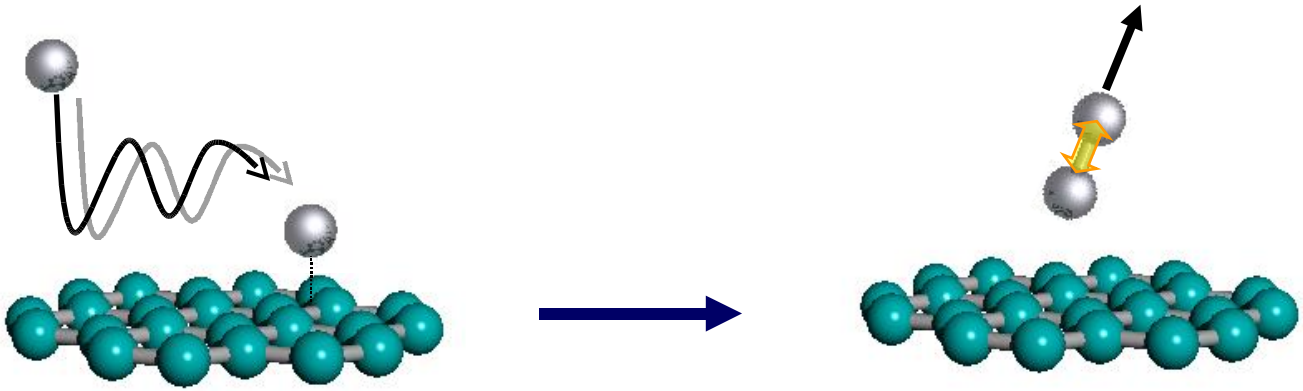


→ **Highly efficient recombination Mechanism of H atoms**

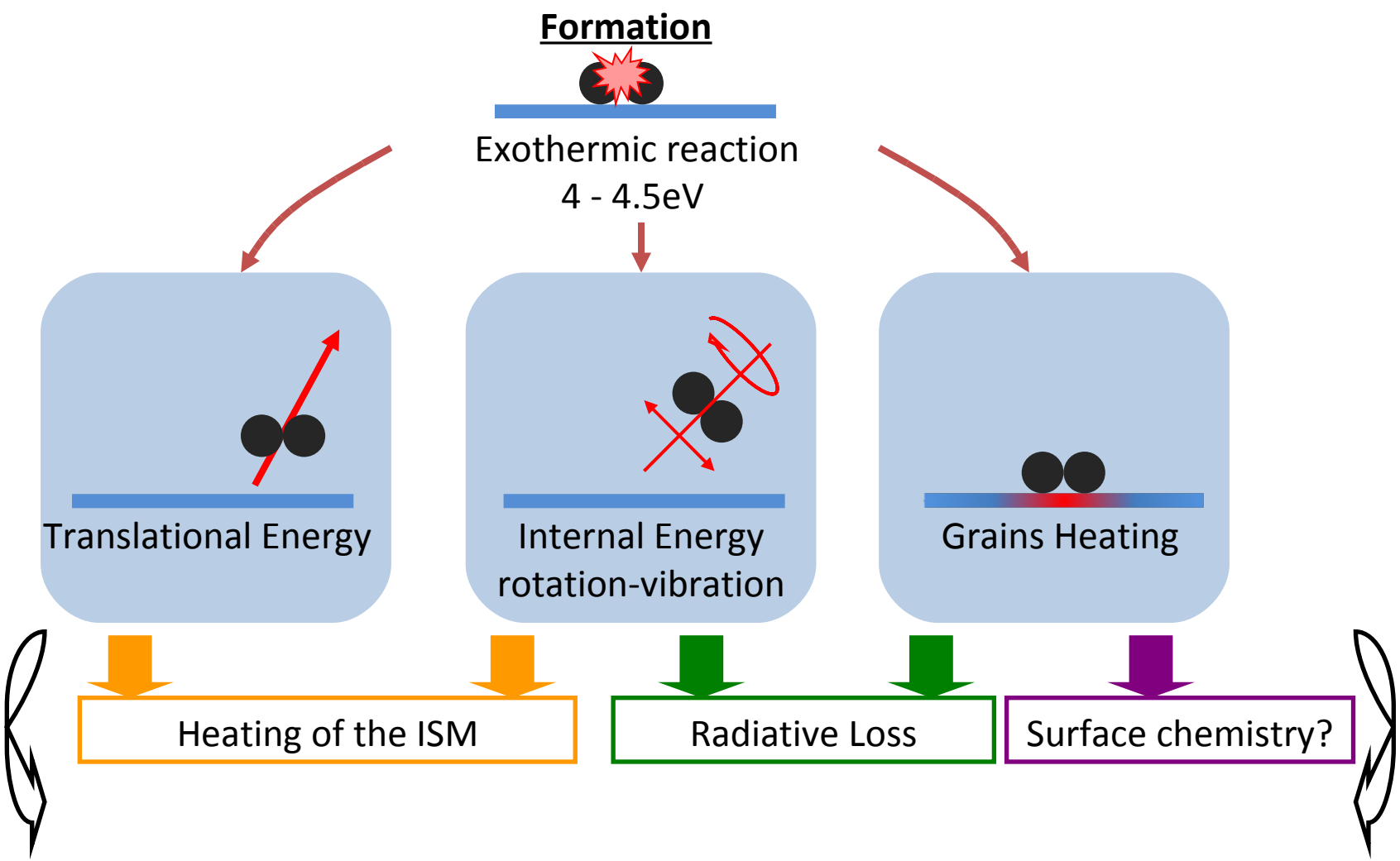


Eley-Rideal

Langmuir-Hinshelwood



« Hot-Atom »



➔ Crucial to understand the distribution of the released energy

Potential : V. Sidis, L. Jeloaica, A.G. Borisov and S.A. Deutscher *dans "Molecular hydrogen in space"*, (Cambridge University Press2000 pp.89-97.)

H_a Chemisorbed on a C sp^3

E = - 0.47 eV

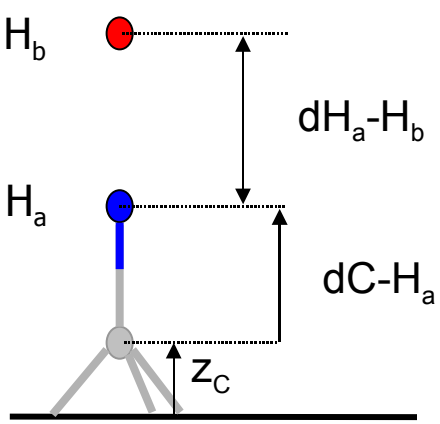
Confirmed theoretically and experimentally

Quantum Dynamics:
S. Morisset et al.

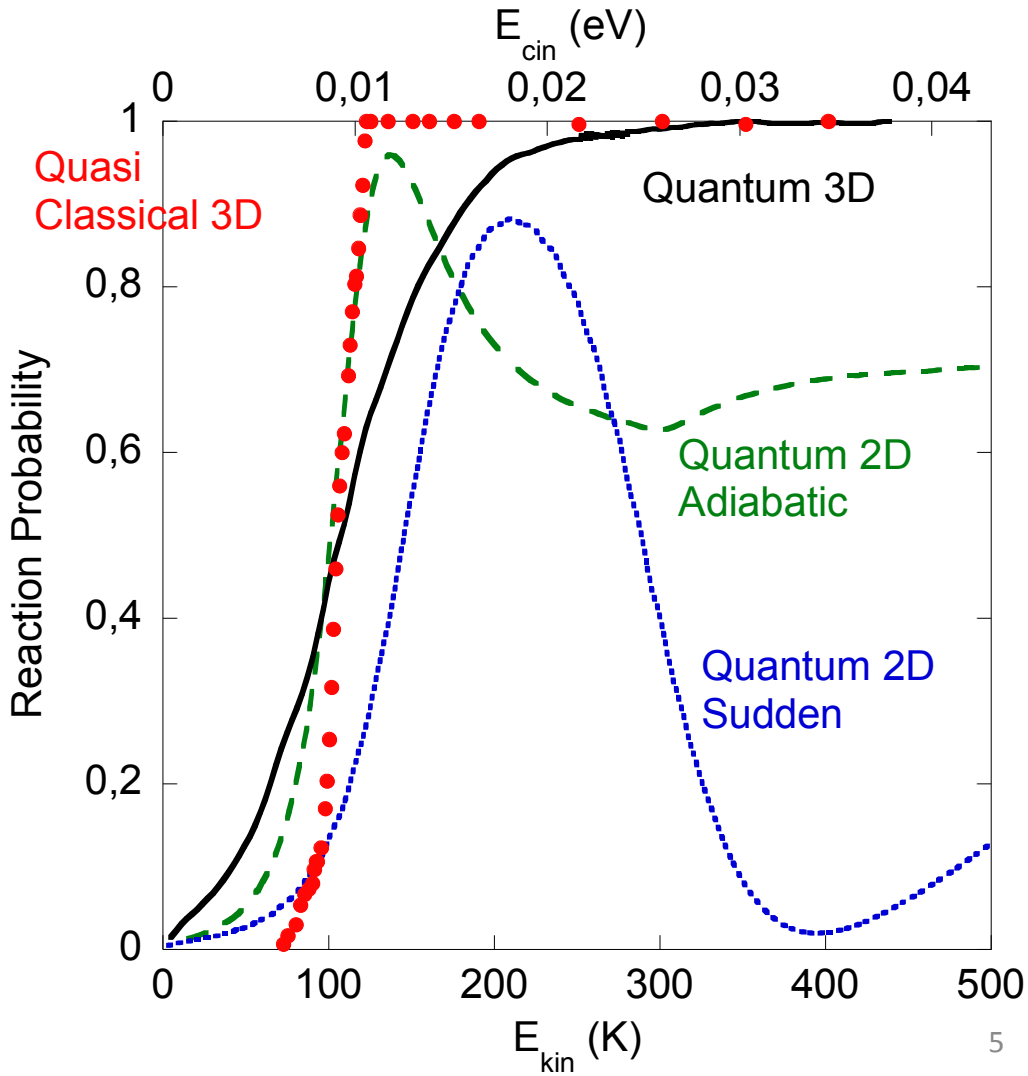
Formation of H_2

ER mechanism (1H chemisorbed)

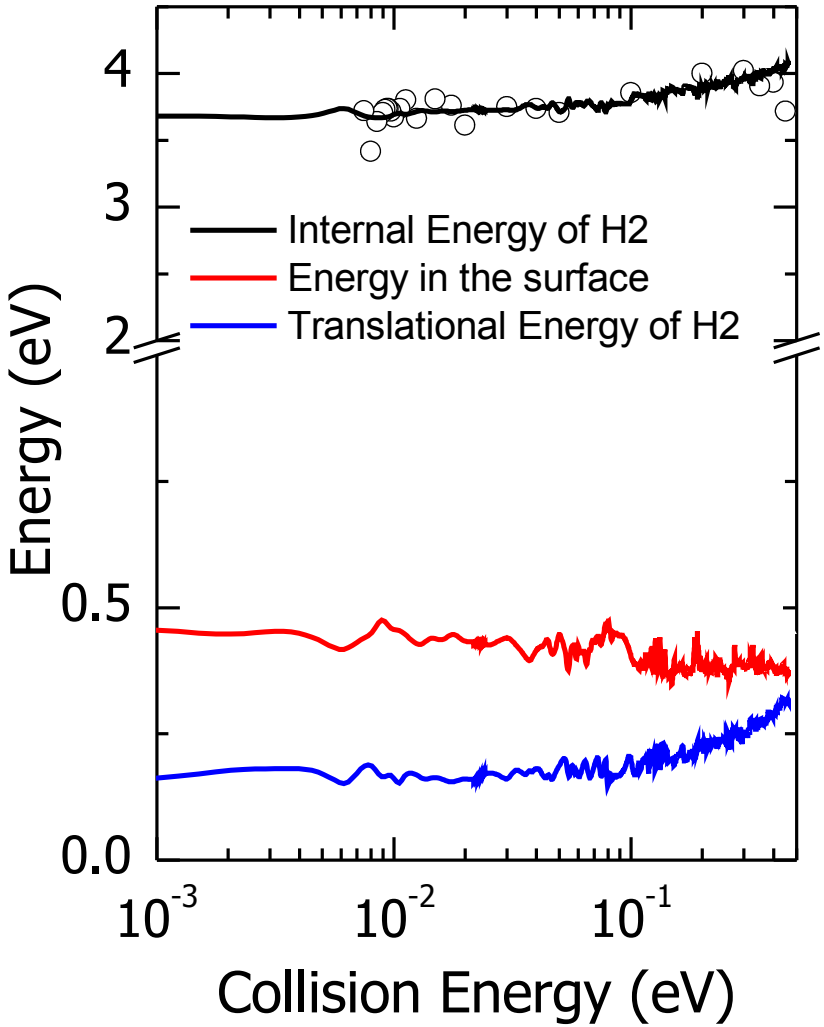
Collinear approach



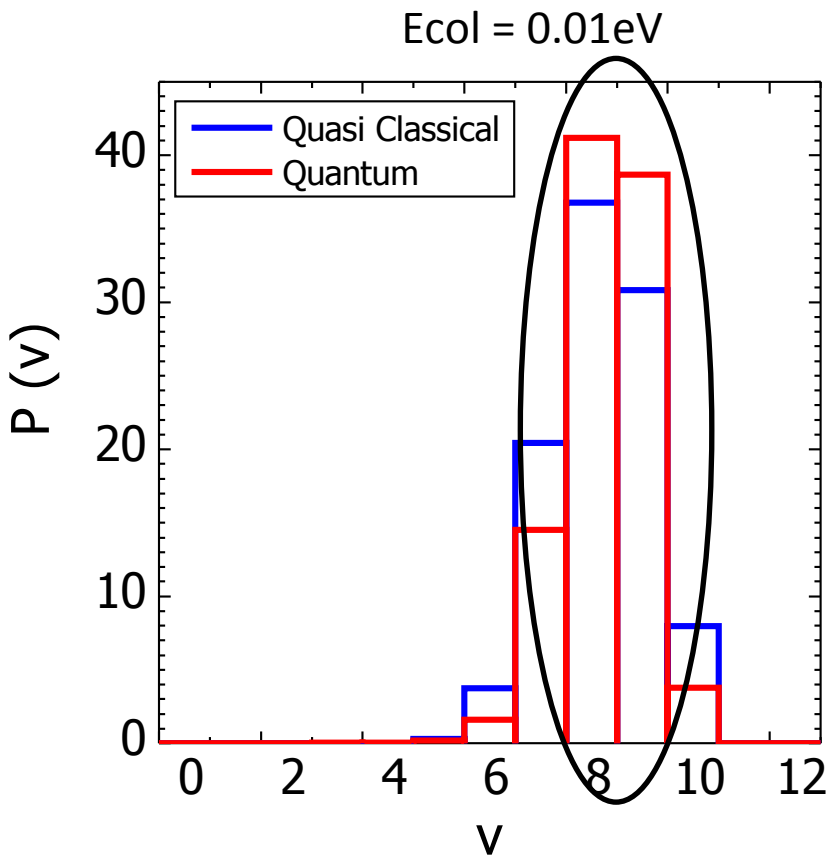
Collinear Approach : 3 degrees of freedom



Energy sharing



Vibrational distribution of H_2



Good agreement between Quantum and Quasi-classical dynamics

Form H_2 in lower rovibrational state as observed in the ISM

Take into account the full relaxation of the surface

Study of the formation of H_2 on a surface of 200 carbon atoms

606 degrees of freedom → **Classical molecular dynamics**

PES of the system?

Quantum calculation (DFT) are presently incompatible with molecular dynamics on the fly

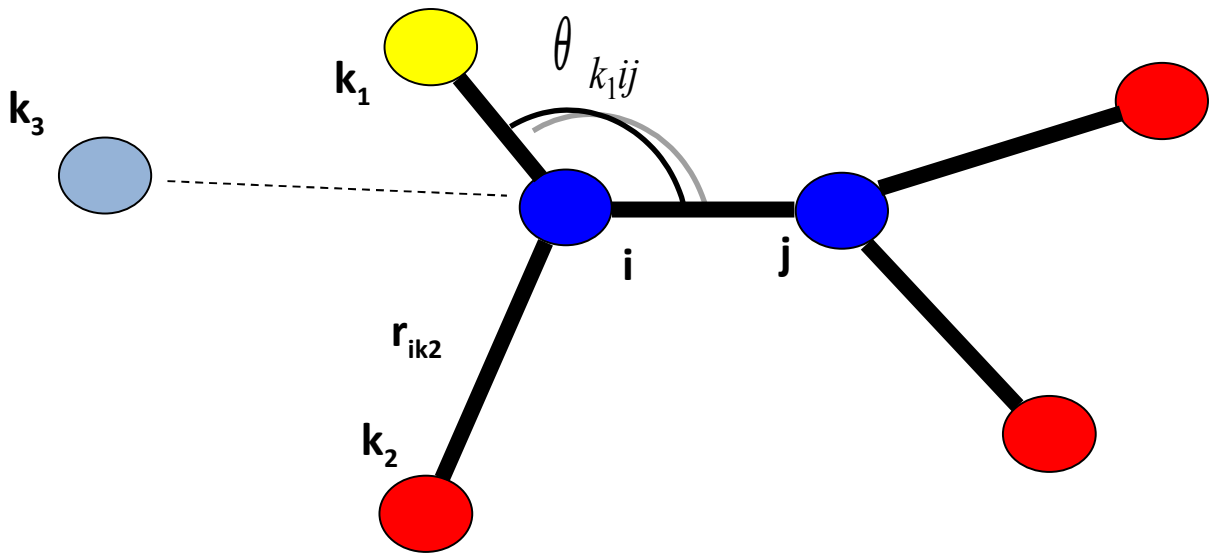
Semi-empirical potential
Bond-order potential (D.W. Brenner)

Brenner empirical potential *

Used to study small hydrocarbons

* D.W Brenner Phys.Rev.B. **42**, 9458 (1990)

$$E = \sum_{l} E_l \qquad E_{l_{(ij)}} = \left[V_R\left(r_{ij}\right) - \overline{B}_{ij} V_A\left(r_{ij}\right)\right] \qquad \overline{B}_{ij} = \frac{B_{ij} + B_{ji}}{2} + \frac{F_{ij}(xi, xj)}{2}$$



Cut-off

$r^{(2)}_{CH}$: 1.8 Å → 2.5 Å

$r^{(2)}_{HH}$: 1.7 Å → 5.0 Å

distance

$$B_{ij} = \left(1 + \sum_{k \neq i,j} f_{ik}(r_{ik}) g_{kij}(\theta_{kij}) e^{\alpha_{kij}((r_{ij} - r^e_{ij}) - (r_{ik} - r^e_{ik}))} + H_{ij}(x_H, x_C)\right)^{-\delta}$$

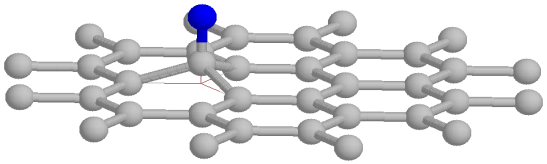
angle

Use of DFT calculations

Sidis & Jeloaica

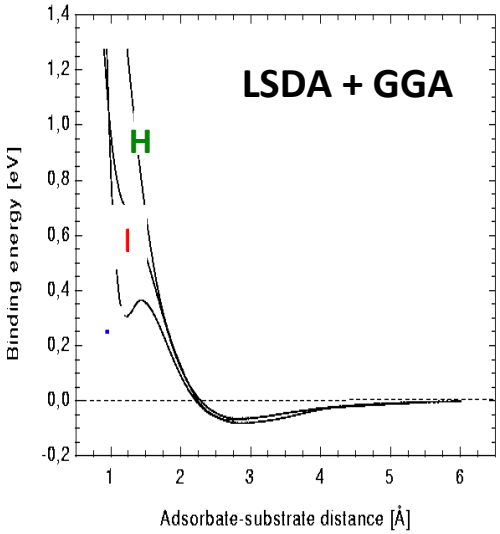
Rougeau & Teillet-Billy

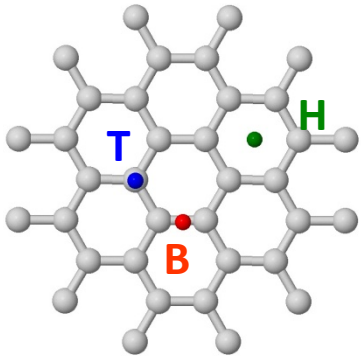
Selection of crucial points for the dynamics

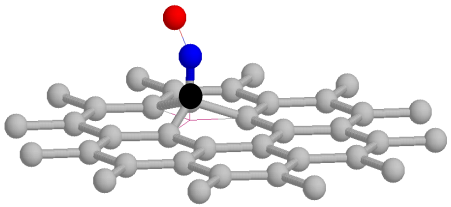


Corrugation of the surface

Jeloaica and Sidis *Chem.Phys.Letters 1999*







Chemisorption well

z_C = 0.36 Å

z_H = 1.49 Å

V = -0.47 eV

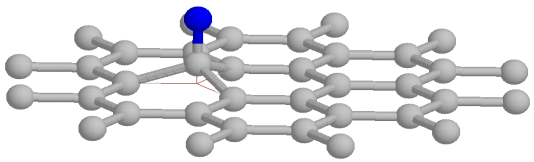
Chemisorption barrier :

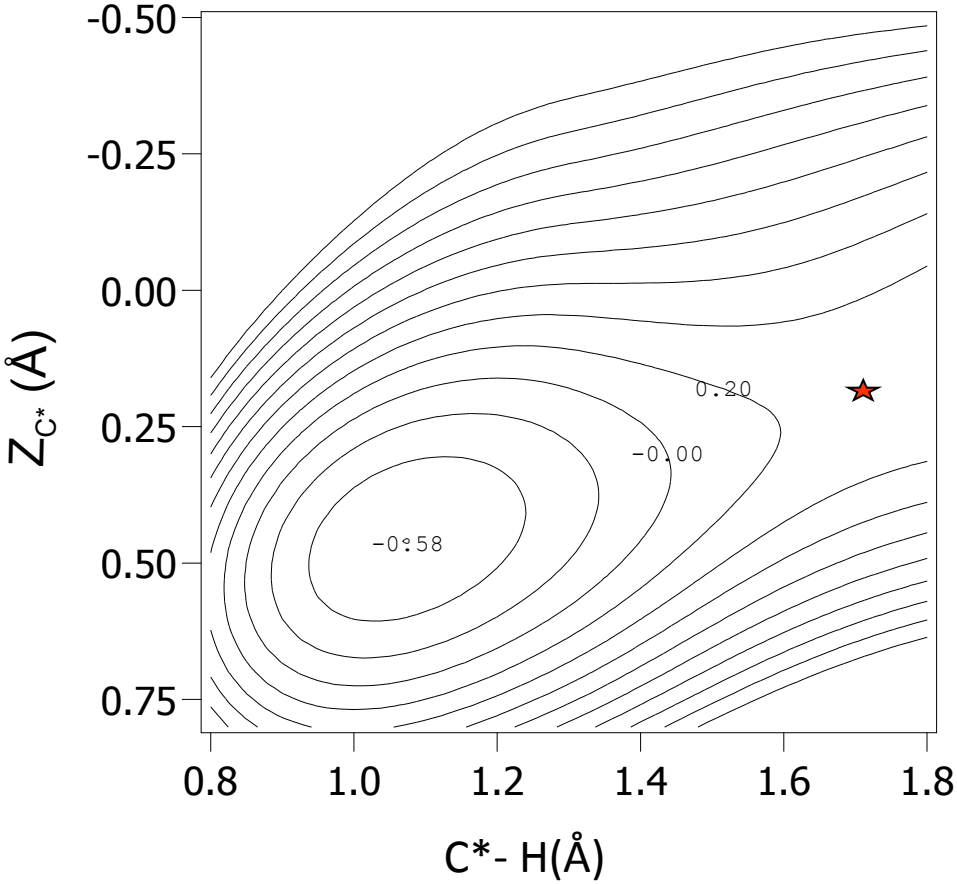
z_C = 0.13 Å

z_H = 1.86 Å

V = 0.26 eV

1H : Collinear approach of H on a C atom (TOP site)

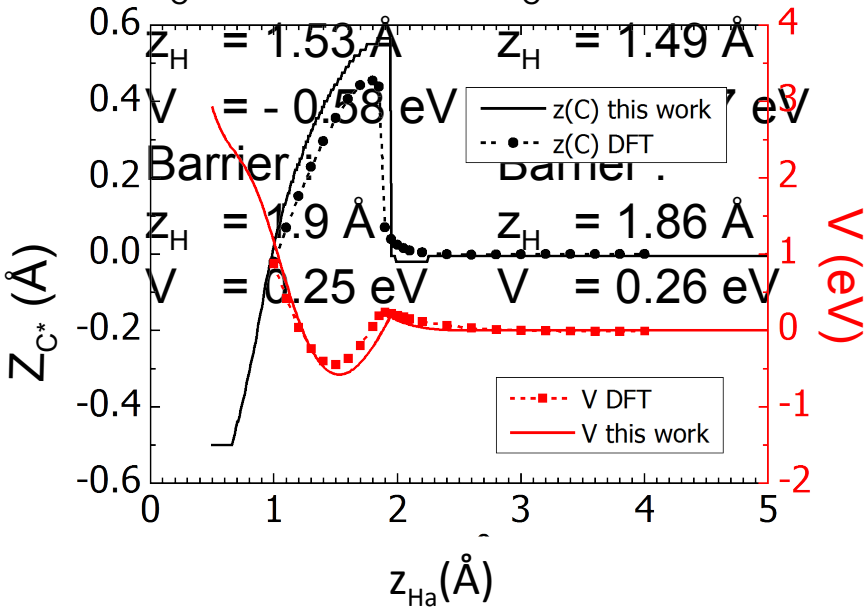




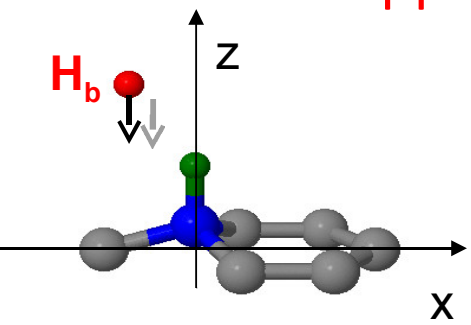
Chemisorption Well:

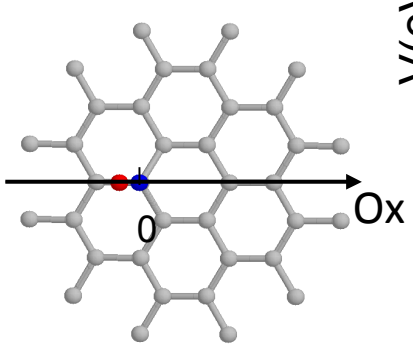
This work:
z_C = 0.46 Å
z_H = 1.53 Å
V = - 0.58 eV
Barrier :
z_H = 1.9 Å
V = 0.25 eV

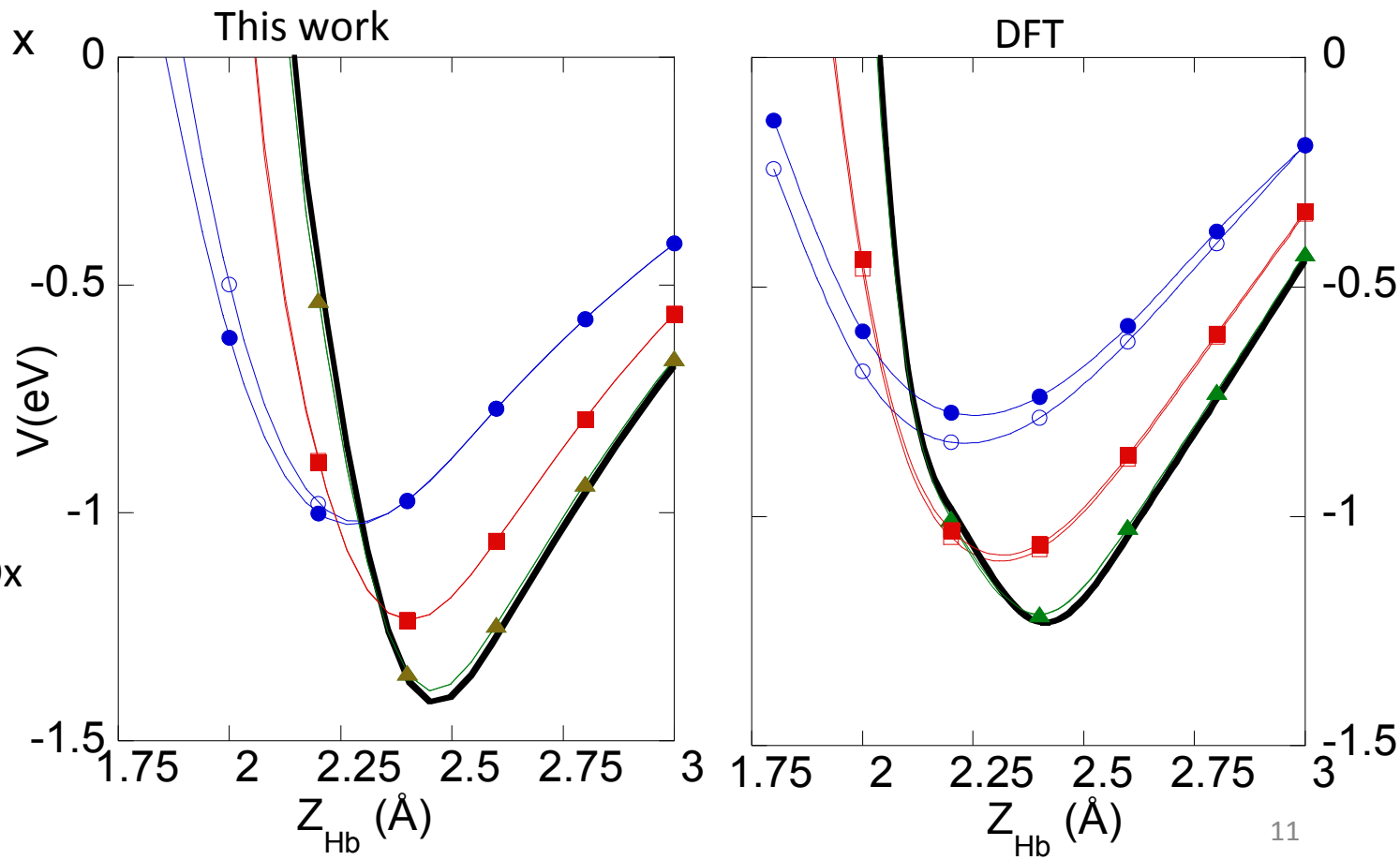
DFT :
z_C = 0.36 Å
z_H = 1.49 Å
V = - 0.7 eV
Barrier :
z_H = 1.86 Å
V = 0.26 eV



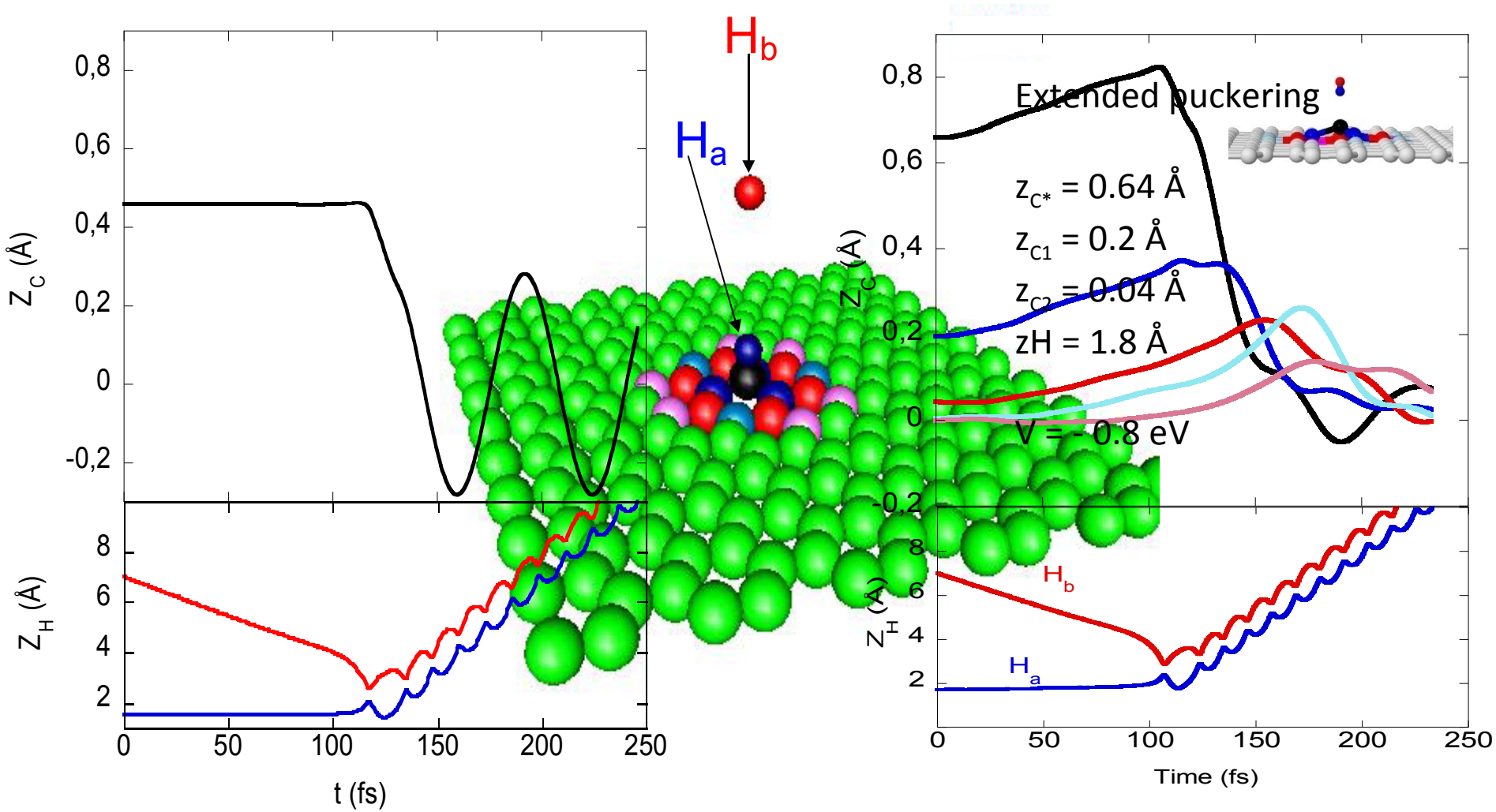
2H : Normal approach of H out of the axe of C*



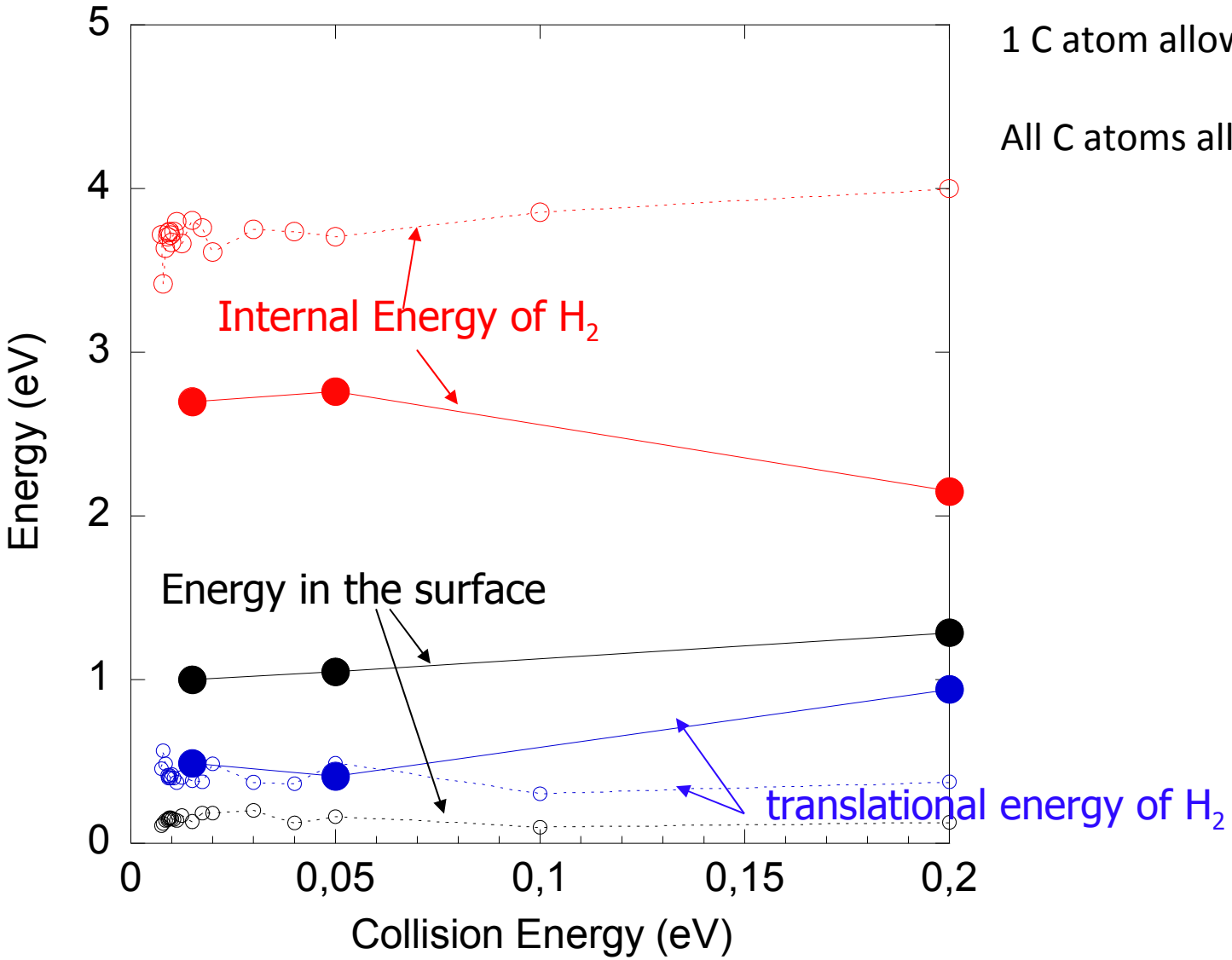




Difference between restrained relaxation and full relaxation of the surface



Energy Sharing

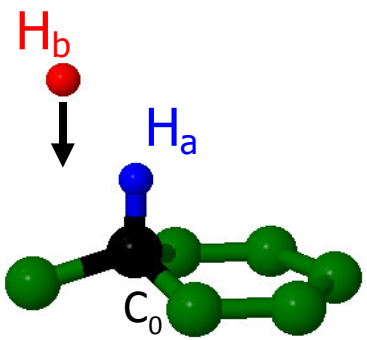


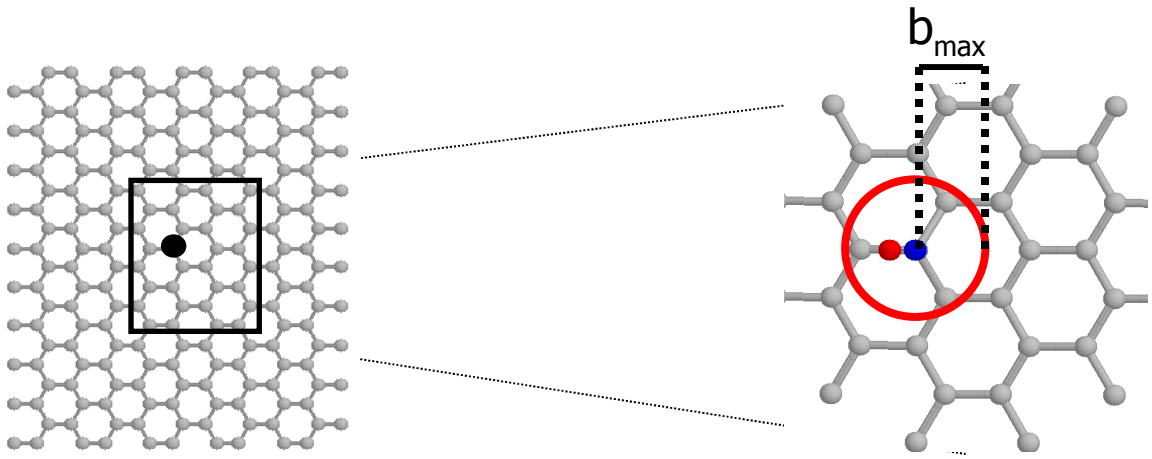
1 C atom allowed to move: ○

All C atoms allowed to move ●

Relaxation of all the surface (200 atoms)

Normal approach of H_b

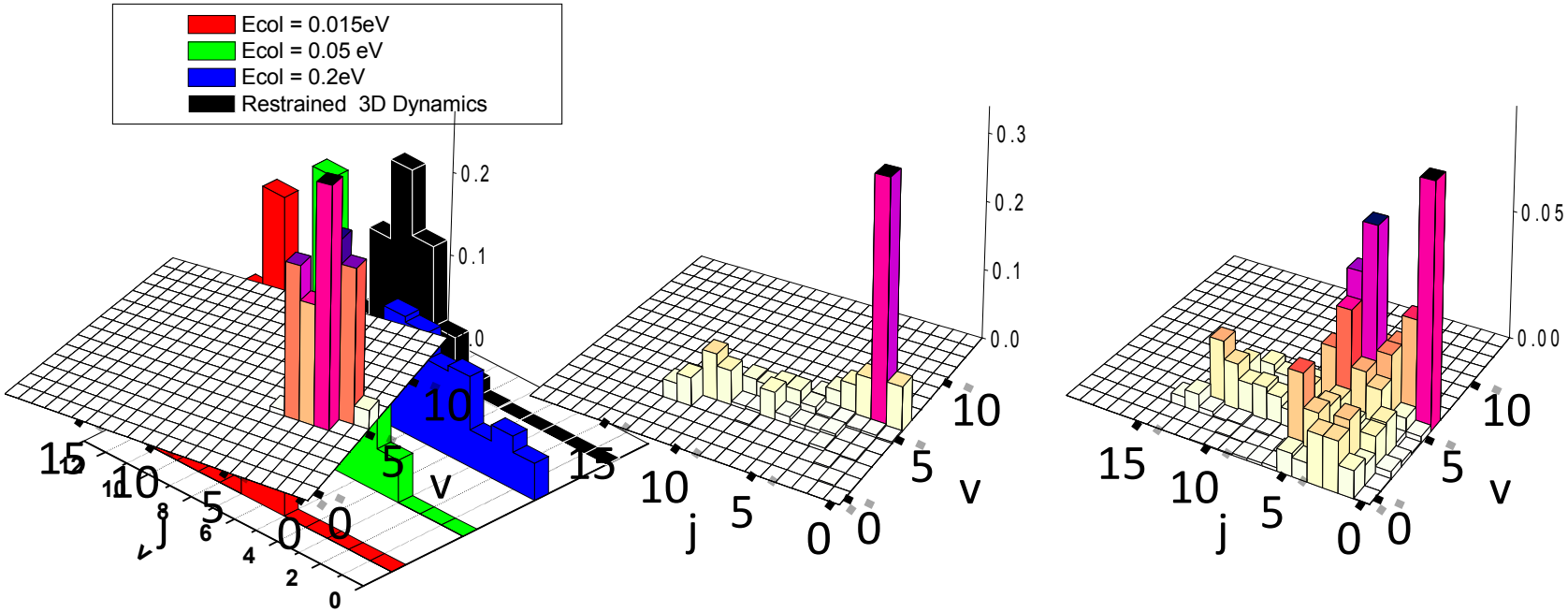




$$E_{col} \begin{cases} 0.015 \\ 0.05 \text{ eV} \\ 0.2 \end{cases}$$

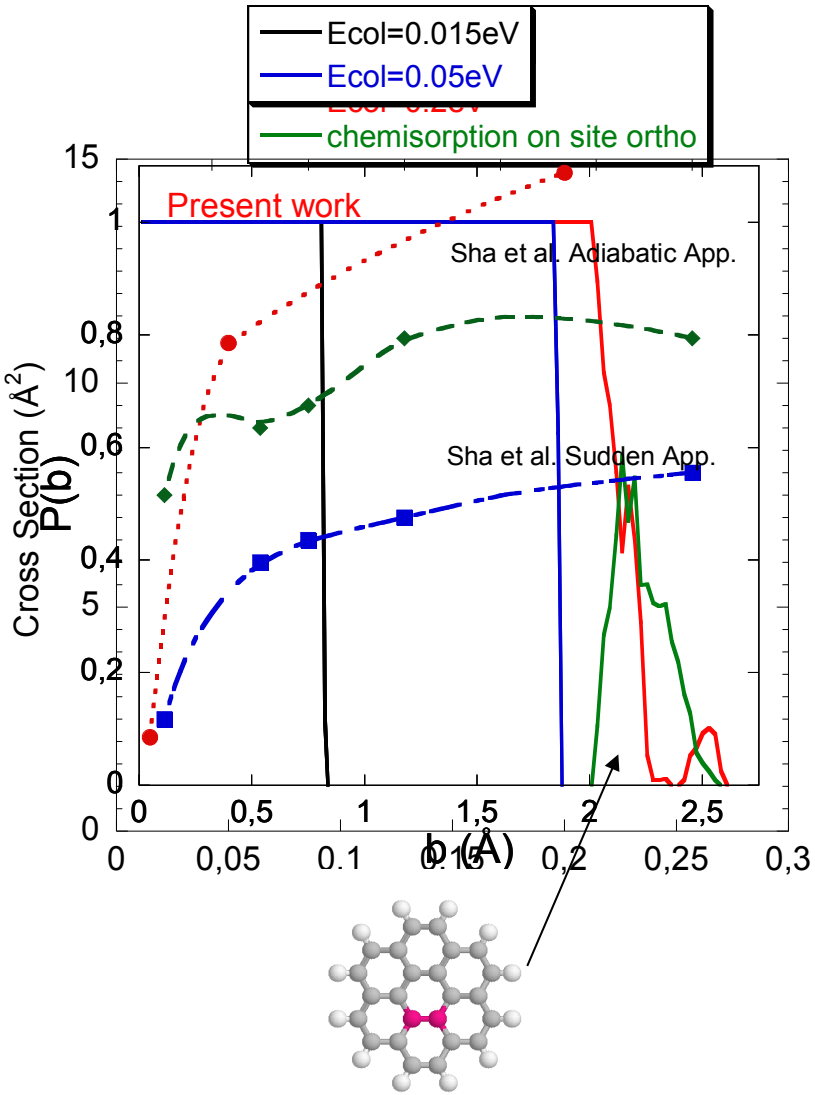
>10 000 trajectories
Velocity-Verlet algorithm

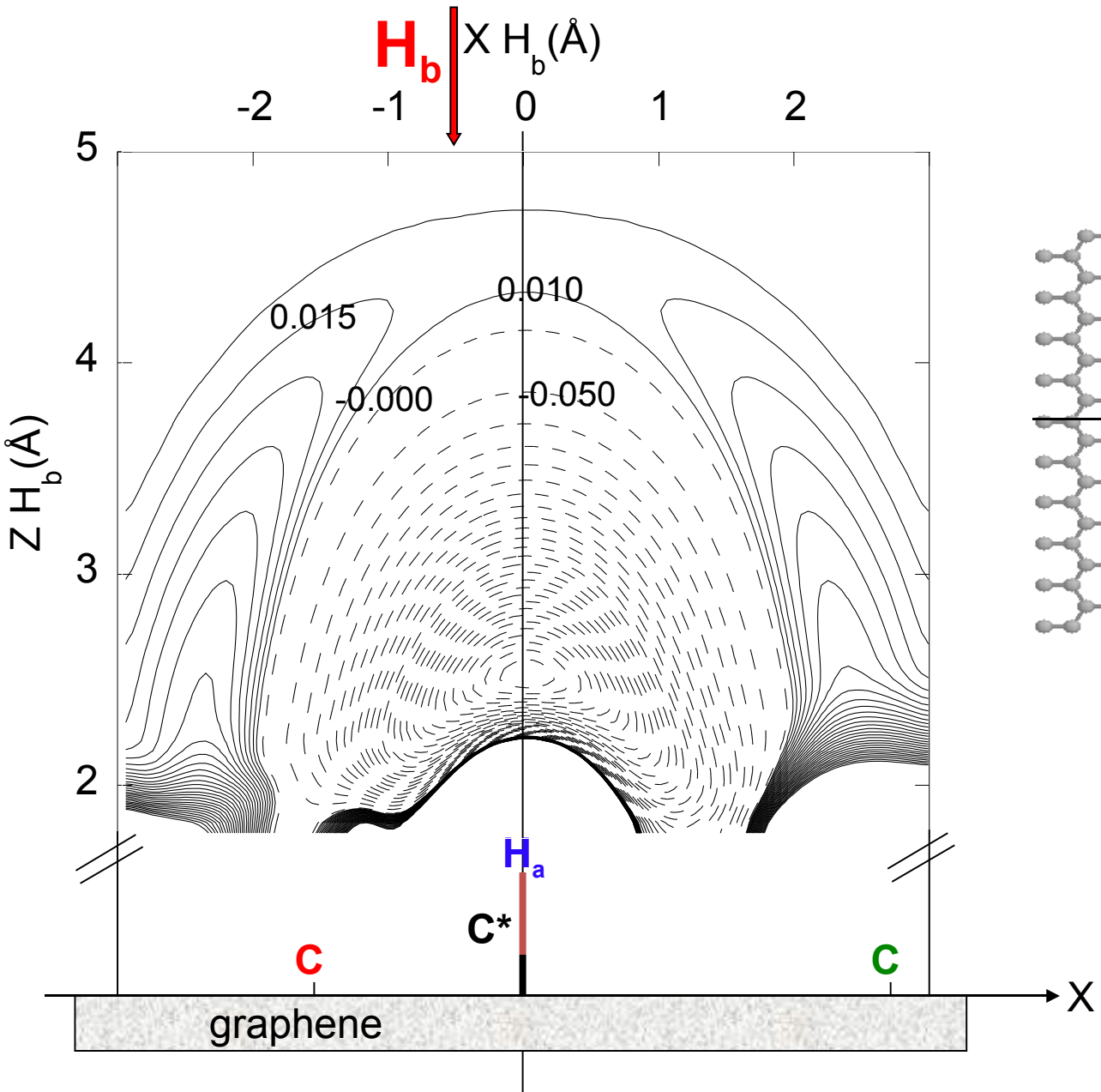
Rovibrational distribution of H_2

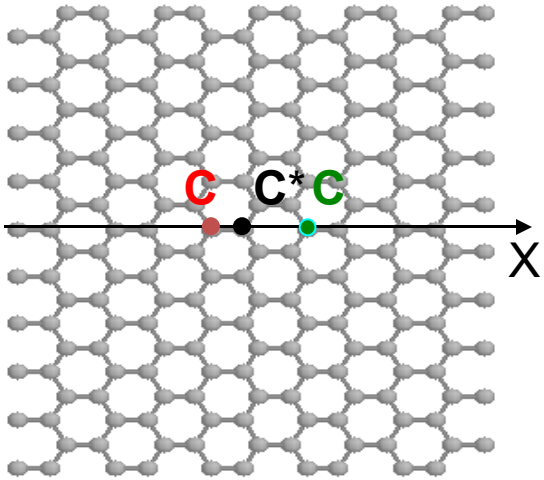


E_{col} = 0.015 eV E_{col} = 0.05 eV E_{col} = 0.2 eV

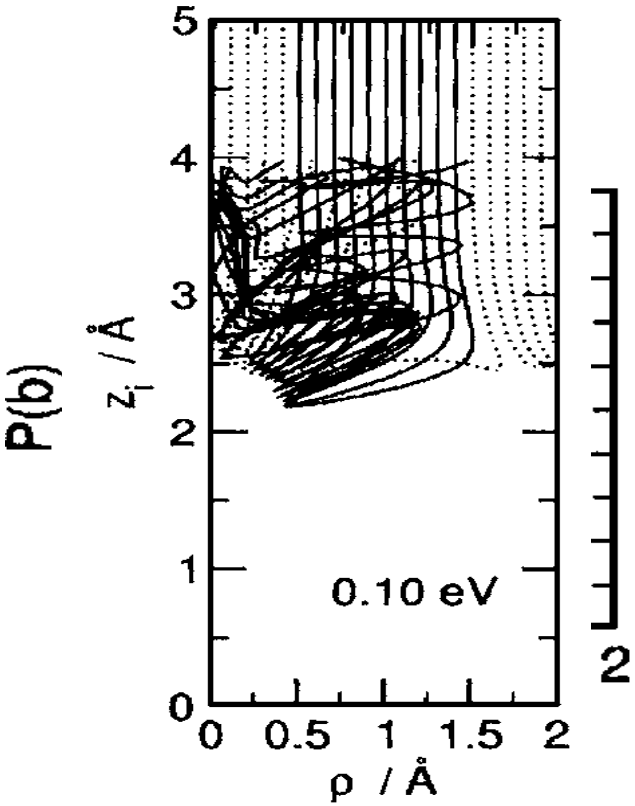
Reaction probability



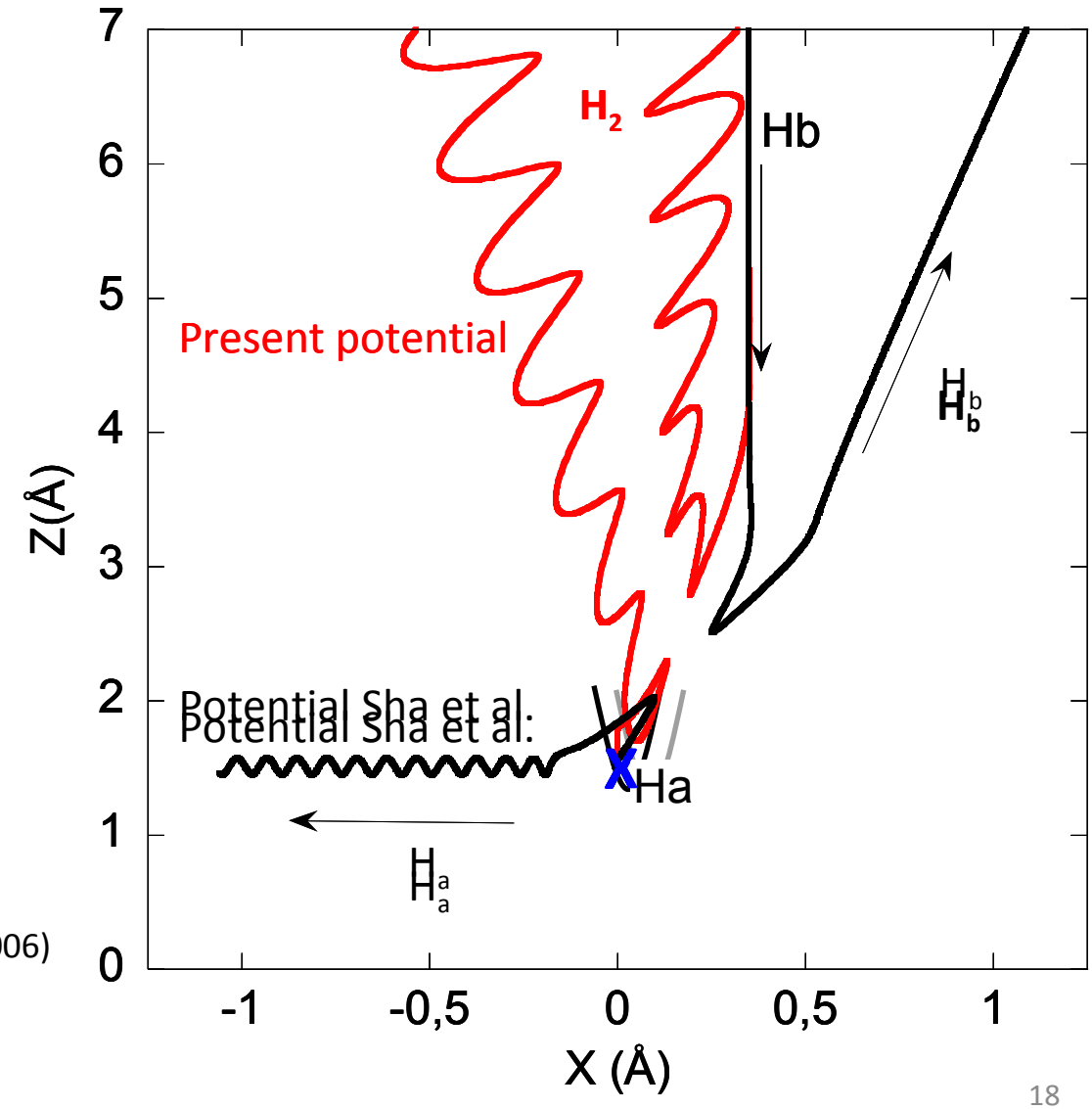

H_b
X H_b(Å)
-2
-1
0
1
2
5
4
3
2
Z H_b(Å)
0.015
0.010
-0.000
-0.050
H_a
C*
C
C
X
graphene


C
C*
C
X

Sudden approximation



Martinazzo et al. J.chem.Phys. **124** 124702 (2006)
Potential taken from Sha et al.



Conclusions

a realistic potential to study the graphene-H-H system

Potential gave rise to the extended puckering

Cross section behavior is related to the caracteristics of the potential

Significant amount of energy goes into the surface (≈25% of the released energy)

H_2 is formed in lower rovibrational states that found with the constrained relaxation

Structure et dynamique des systèmes collisionnels

Muriel Sizun
Dominique Teillet-Billy
Nathalie Rougeau
François Aguillon
Victor Sidis

ANR IRONHI
Lerma/Lamap Cergy-Pontoise University Lemaire et al.

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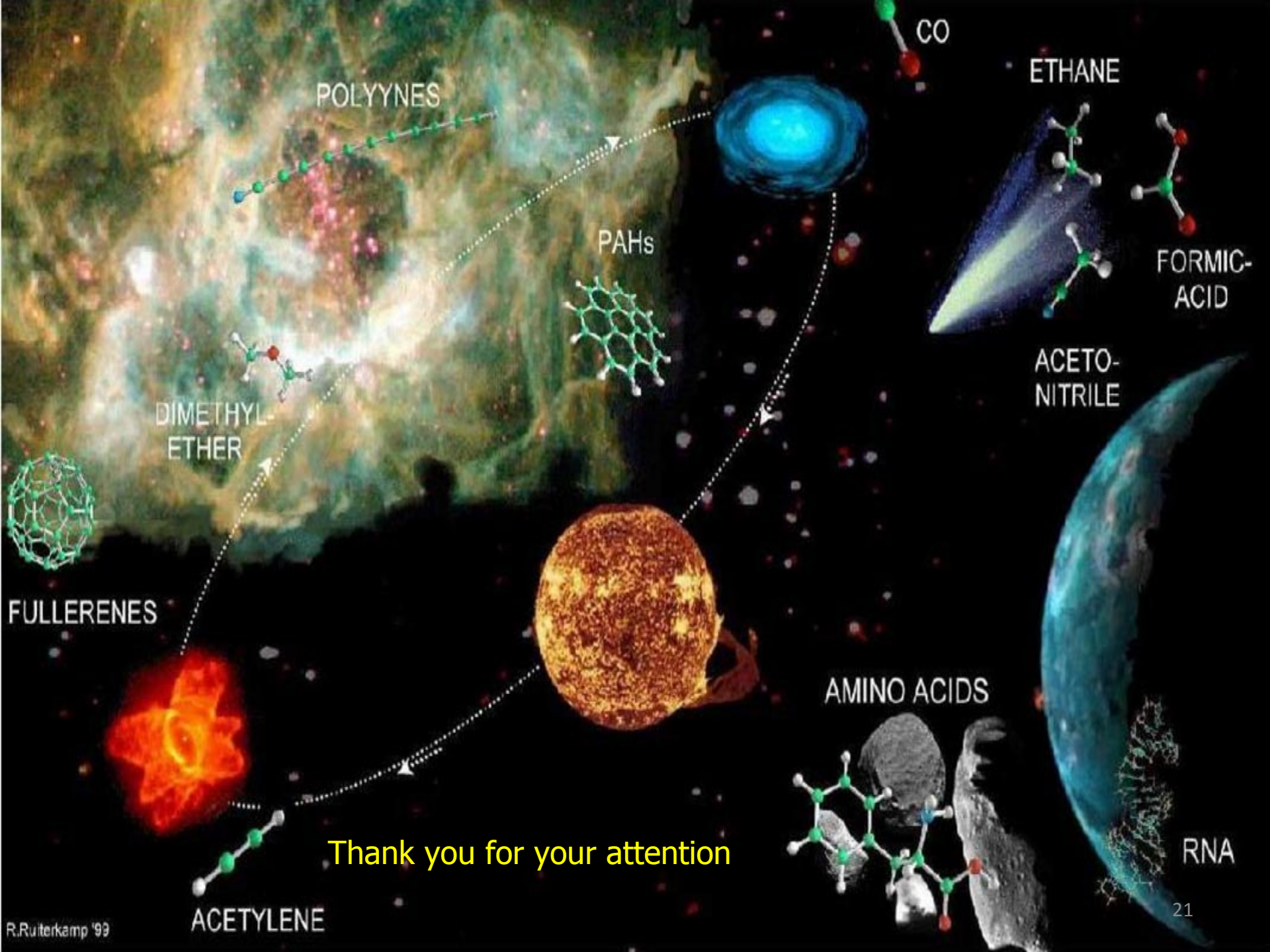

Thank you for your attention