Computational Materials Science at the crossroad among Physics, Chemistry and Biochemistry

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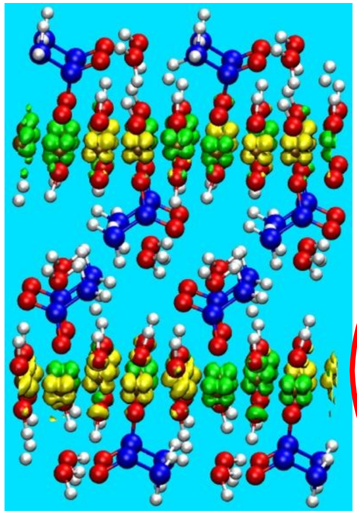
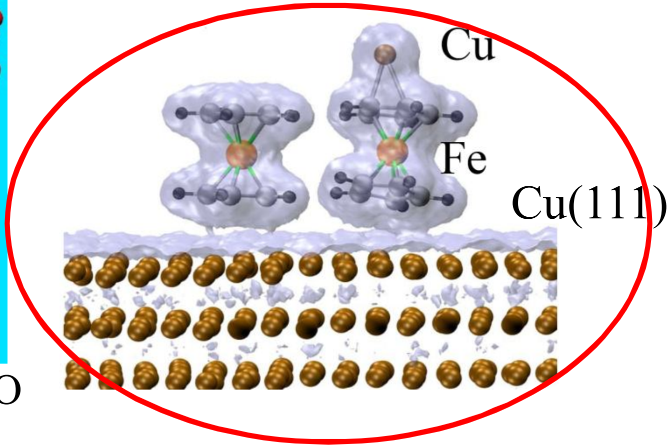
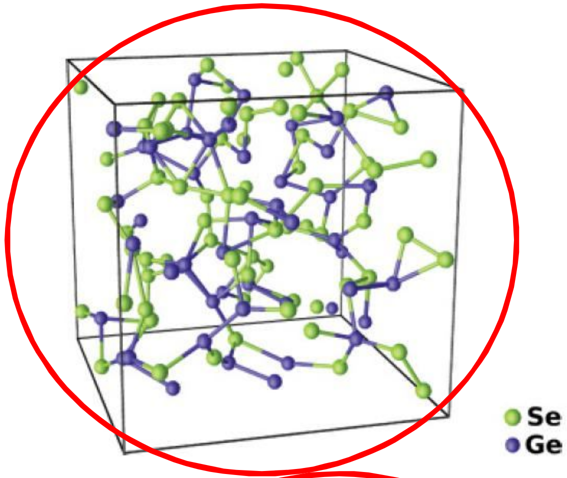
Computational Activities in a Nutshell

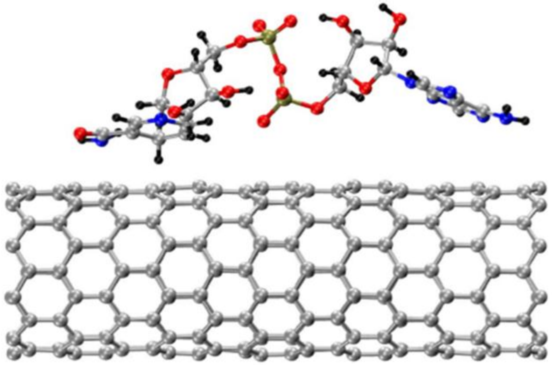
C. Massobrio, M. Boero, S. Le Roux, A. Bouzid, B. Ozdamar @ IPCMS

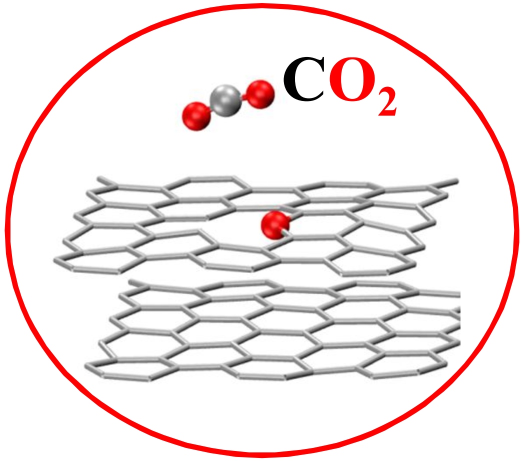


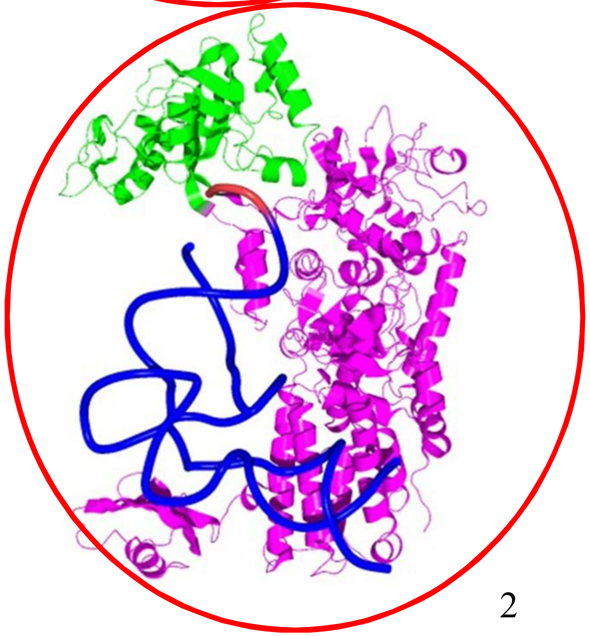
$Cu_2OH_3CH_3COO.H_2O$











Local Machines:

HPC @ IPCMS (ENIAC)

- 896 Cores network architecture with Infiniband interconnection
- Front Quad Xeon 8 GB RMA + 64 dual processor compute nodes Quad Xeon - 32 GB RAM
- Scalable network infrastructure to Gigabit Ethernet, storage > 20 TB

Equip@Meso

- Hybdrid CPU/GPU NEC HPC1812Rd-2/GPS12G4Rd-2
- 145 nodes = 2320 Computing cores (Mellanox Infiniband)

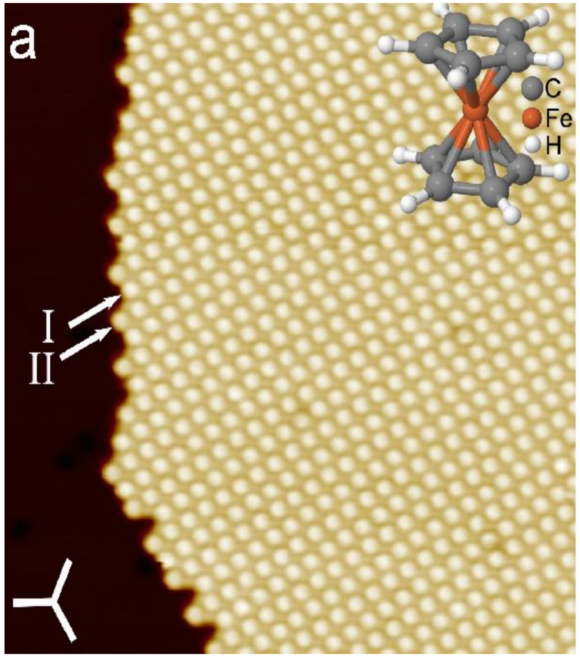
Molecules @ metal surfaces: Motivation and main target(s)

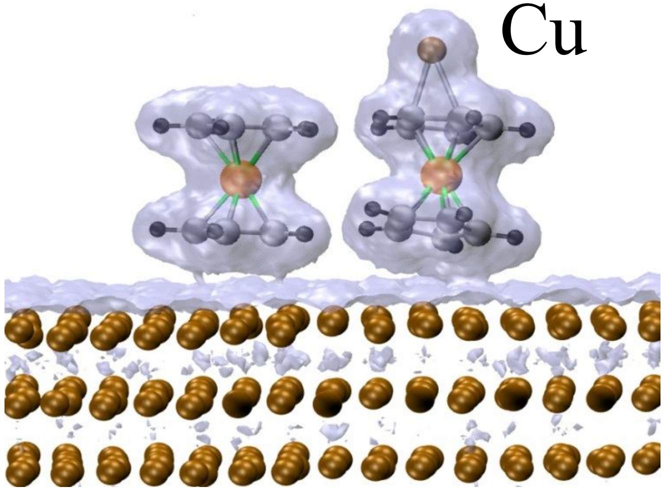
- Realization of nano-junctions for future devices relies on our ability in heterogeneous molecular objects assembly
- Understanding electronic states at the interface
- Delocalized interface states near the Fermi level are a key for tailoring charge injection [T. Komeda et al., *Nature Comm*. **2**, 217 (2011)].
- Interfacial electron delocalization depends on molecular electronic structure
- Double-decker 3D molecules are little explored despite good transport properties [T. Uehara et al., *Jap. J. App. Phys*. **45**, 3768 (2006)]

Atomic-scale simulations for nanoscience @ surfaces

Deposition of $Fe(C_5H_5)_2$ onto Cu(111) for the realization of nanojunctions metal/organic molecule/metal

[B.W.Heinrich, L.Limot, M.V. Rastei, C. Iacovita, J.P. Bucher, D.Mbongo Djimbi, C. Massobrio, M. Boero, *Phys. Rev. Lett*. **107**, 216801 (2011)]





Localized molecular states

Bidimensional state (Shockley state) at the Cu(111) surface

Simulations done within
- Free Energy Molecular Dynamics
- Born-Oppenheimer

Electrons at finite (electronic) temperature:

For a *fermionic* system, the partition function is given by

$$Z(\beta,\mu,\upsilon) = \det\left\{1 + \exp\left[-\beta(\hat{H}-\mu)\right]\right\}$$

Then, the free energy is just the logarithmic functional

$$\Omega = -\frac{1}{\beta}\log Z$$

Why is this the free energy ? Simply because of its *definition*:

$$e^{-\beta F} = \frac{1}{\upsilon}\sum_{i=0}^{N} e^{-\beta E_i} = \left\langle 1 + e^{-\beta \hat{H}} \right\rangle = \det\left(1 + e^{-\beta \hat{H}}\right)$$

including the constraint $+\mu N$ to fix the number of electrons (microcanonical ensemble)

Electrons at finite (electronic) temperature:

The ionic contribution (E_{II}) must still be added to complete the *free energy* functional of the whole system

$$F\left[\rho,\{\mathbf{R}_I\}\right]=\Omega[\rho]+\mu N_e+E_{II}$$

Now we have all the ingredients to compute:

1) The *forces* on the electrons in the DFT-like fashion

$$\frac{\delta F}{\delta\langle\psi_i|}=\frac{\delta F}{\delta\rho(\mathbf{x})}|\psi_i\rangle$$

2) The forces on the ions in a molecular dynamics fashion

$$\mathbf{f}_I=-\nabla_{\mathbf{R}_I}F$$

Electrons at finite (electronic) temperature:

- The electronic density given by KS orbitals and Fermi statstics reads

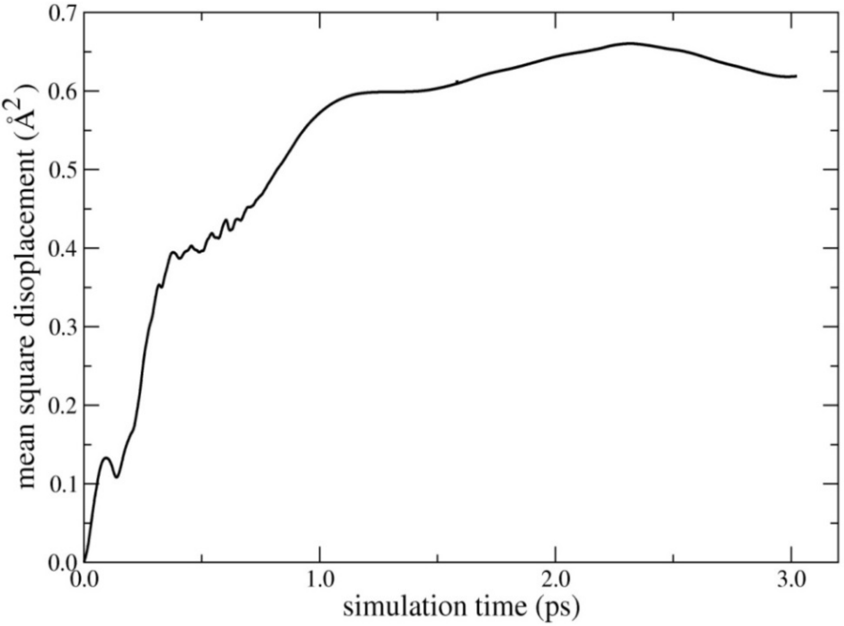
$$\rho(\mathbf{x}) = \sum_i f_i |\psi_i(\mathbf{x})|^2$$

$$f_i = 1 \Big/ \left[1 + \exp\left(\frac{E_i - \mu}{k_B T_e} \right) \right]$$

- And the fs relaxation time of e^- is << $t^{\mathrm{relx}}{}_{\mathrm{Ions}}$ so that the adiabatic theorem holds also in this case

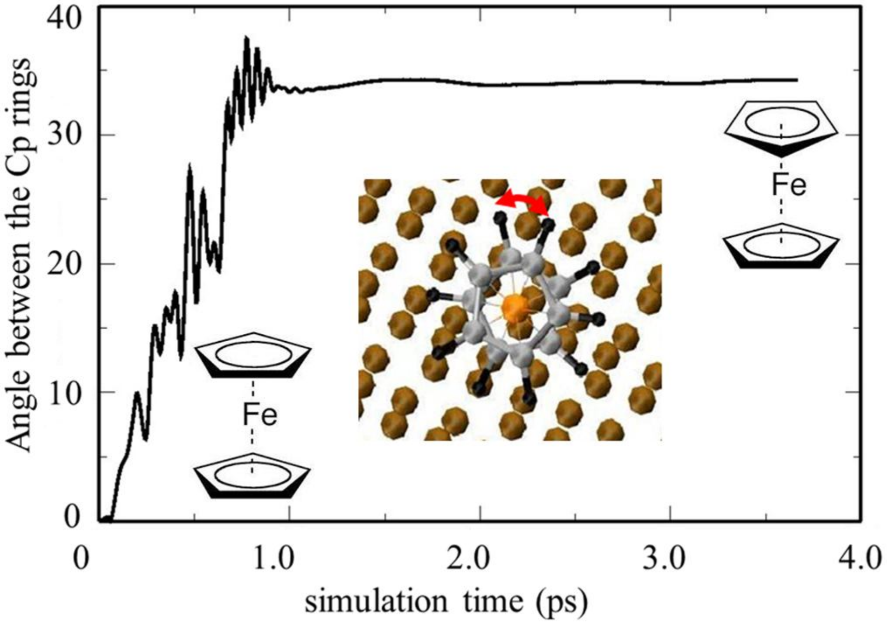
(see Phys. Rev. B **42**, 2842 (1990))

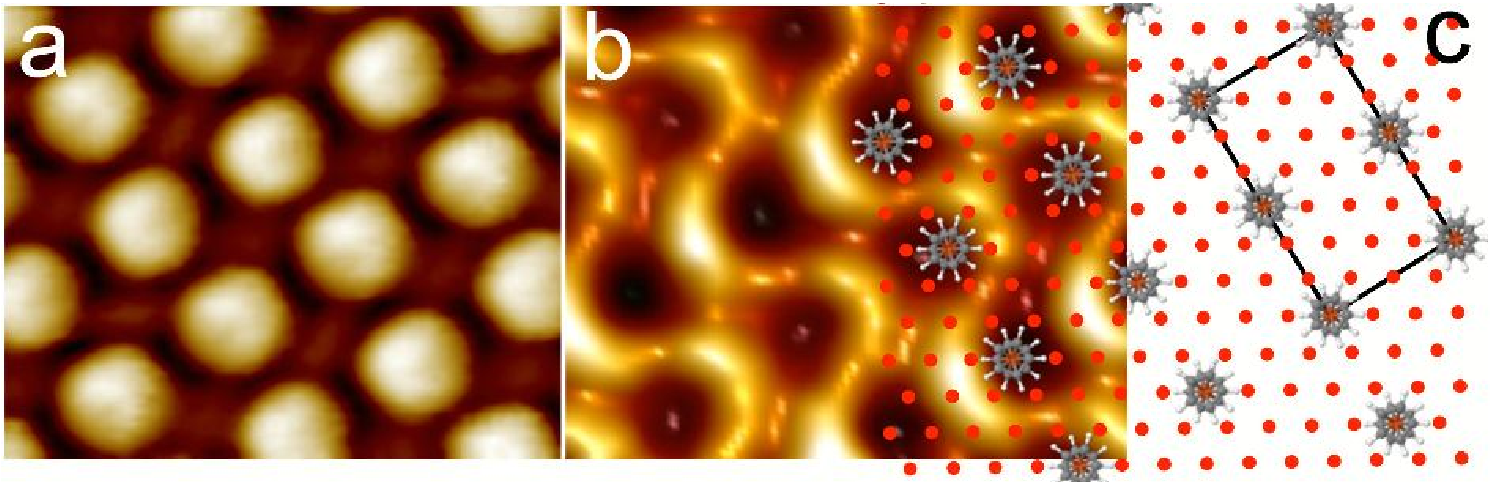
Born-Oppenheimer Dynamics at 150 K (~3 ps)



Mean square displacement $\langle|\mathbf{R}(t)-\mathbf{R}(0)|^2\rangle$ of the whole system (420 Cu atoms plus one Ferrocene molecule) during the BOMD

Evolution of the angle between the two Cp rings. Expected value on the basis of the D_5 symmetry: 36^{o} (good agreement with Experiments @ *Acta Chem. Scandinavica* **22**, 2653 (1968))

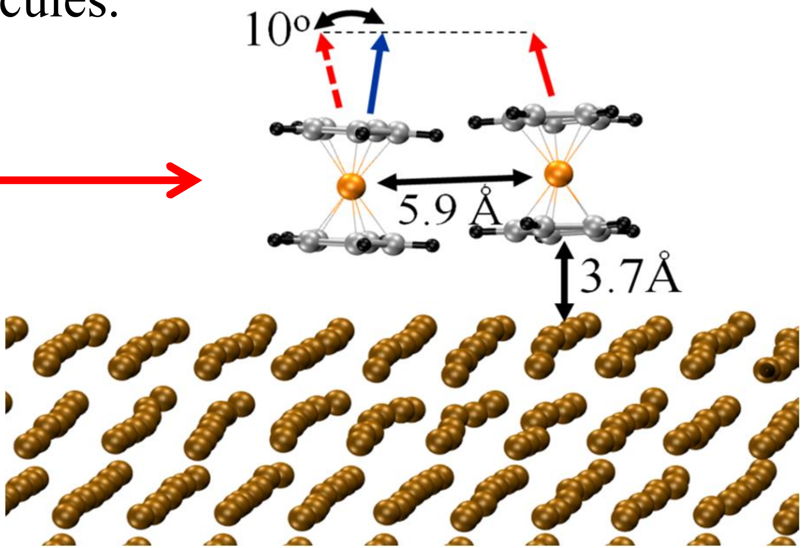




(a,b) STM images of the molecular ferrocene layer

(c) Adsorption model for the ferrocene monolayer and its unit cell, which takes into account the tilt of the molecules.

Stable configuration of two ferrocene molecules on the Cu(111) surface obtained by dynamical simulations.



Phys. Rev. Lett. **107**, 216801 (2011)

Charge redistribution around the ferrocene molecule on top of which one Cu atom has been deposited.

Electron density difference:

$$\Delta\rho(\mathbf{x}) = \rho(\mathbf{x}) - [\rho_0(\mathbf{x}) + \rho_{Cu}(\mathbf{x})]$$

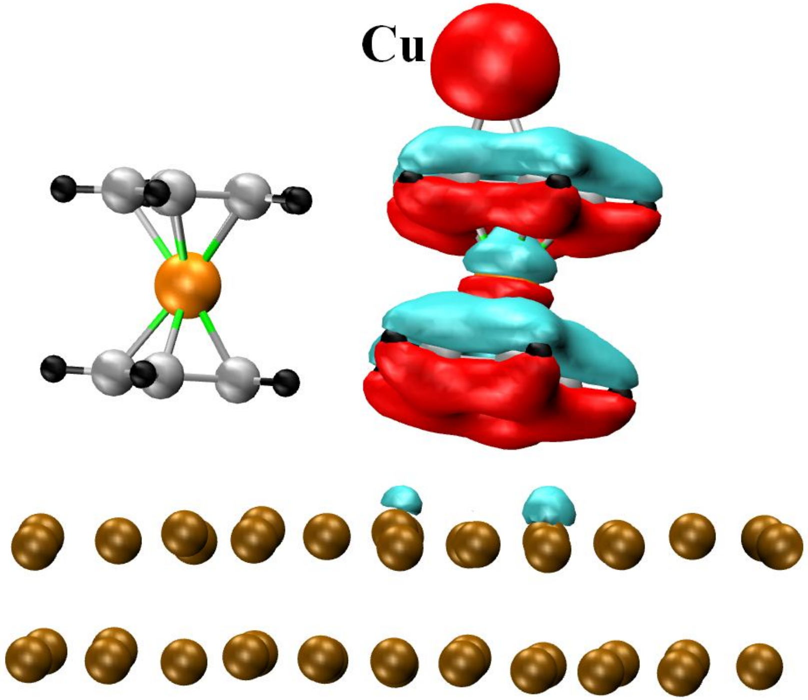
$\rho(\mathbf{x})$ = total electron density

$\rho_0(\mathbf{x})$= electron density without deposited Cu

$\rho_{Cu}(\mathbf{x})$ = electron density of an isolated Cu

Positive isosurface: $+5\text{x}10^{-2}\ e/\text{Å}^3$ indicate a leak of electronic charge

Negative isosurface: $-5\text{x}10^{-2}\ e/\text{Å}^3$ indicate an accumulation of electronic charge.



- 0.3 *e* are transferred from the deposited Cu to the ferrocene

Conclusions

- •Ferrocene molecules can be physisorbed on copper surface without giving rise to molecular dissociation with an adsorption energy of ~120 meV in agreement with experiments
- •Molecules form an alternating pattern (visible by STM) due to a tilt angle between adjacent ferrocene molecules which try to minimize their mutual steric repulsion
- •Cu metal atoms can stick on an adsorbed ferrocene molecules providing a viable way to realize nanotechnologically important metal-molecule-metal hybrid structures.

Perspectives

- •We have a tool to simulate the whole deposition process
- •We aim at inspecting the deposition of different metals (Co, Fe) on top of ferrocene to tune the junction properties

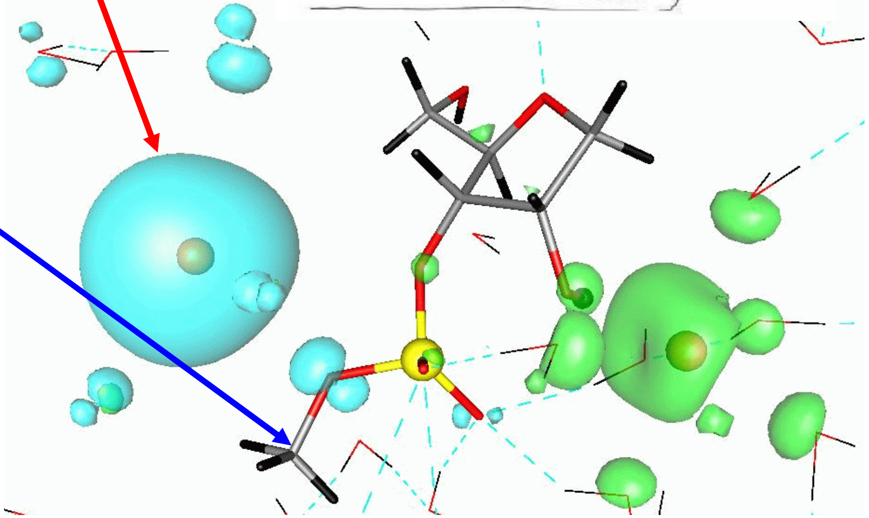
Car-Parrinello Molecular Dynamics

- Solve the related Euler-Lagrange EOM

$$\mu \ddot{\psi}_i = -\frac{\delta E^{DFT}}{\delta \psi_i^*} + \sum_j \Lambda_{ij} \psi_j$$

$$M_I \ddot{\mathbf{R}}_I = -\nabla_{\mathbf{R}_I} E^{DFT}$$

$$\mu_q \ddot{\alpha}_q = -\frac{\partial E^{DFT}}{\partial \alpha_q}$$



Temperature, pressure, etc.

A few tests used the Hybrid Functionals HSE & PBE0

Both HSE and PBE0 rely on calculation of the exact Hartree-Fock exchange functional at least at short range $E_x^{\mathrm{HF,SR}}$. Specifically, the Coulomb potential is split into short range (SR) and long range (LR) parts as

$$\frac{1}{r} = \underbrace{\frac{1-\mathrm{erf}(\omega r)}{r}}_{\mathrm{SR}} + \underbrace{\frac{\mathrm{erf}(\omega r)}{r}}_{\mathrm{LR}}$$

The mostly used HSE0 functional assumes (empirically) ω=0.2 and a mixing coefficient $a = 0.25$

$$E_{xc}^{HSE} = aE_{xc}^{HF,SR}(\omega) + (1-a)E_x^{PBE,SR}(\omega) + E_x^{PBE,LR}(\omega) + E_c^{PBE}$$

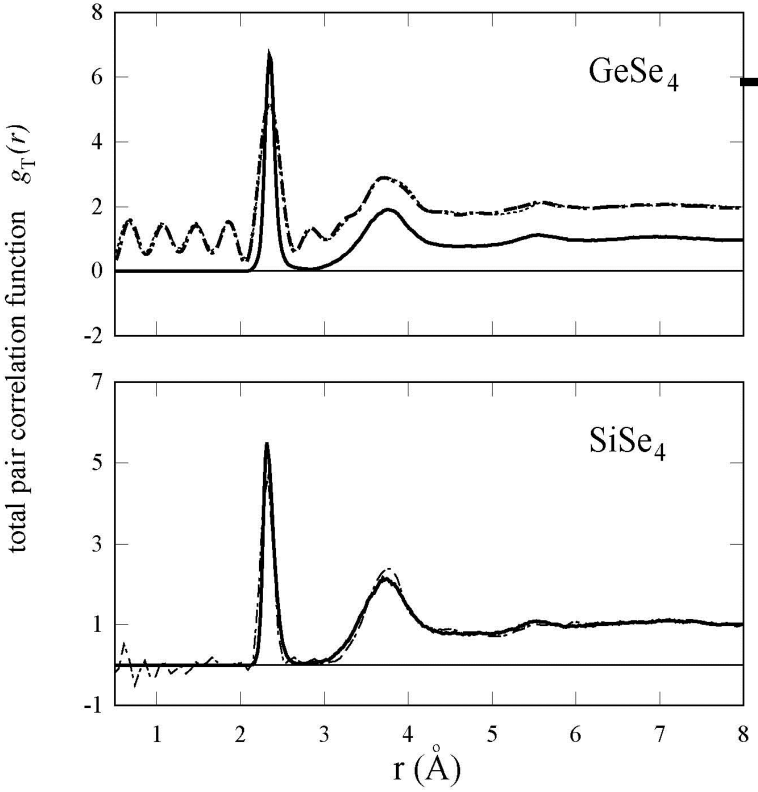
And the PBE0 is the limit ω = 0

$$E_{xc}^{PBE0} = aE_{xc}^{HF}(0) + (1-a)E_x^{PBE}(0) + E_c^{PBE}$$

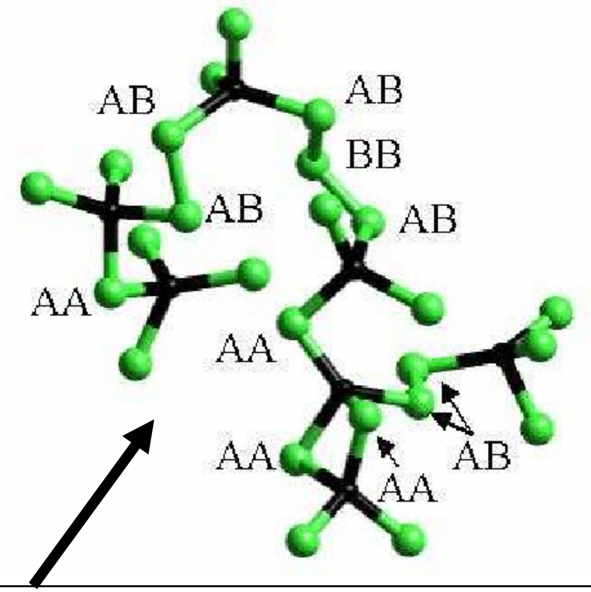
Namely only the exchange term is affected, ***not the correlation***

Amorphous materials: projet ANR Phasabinit

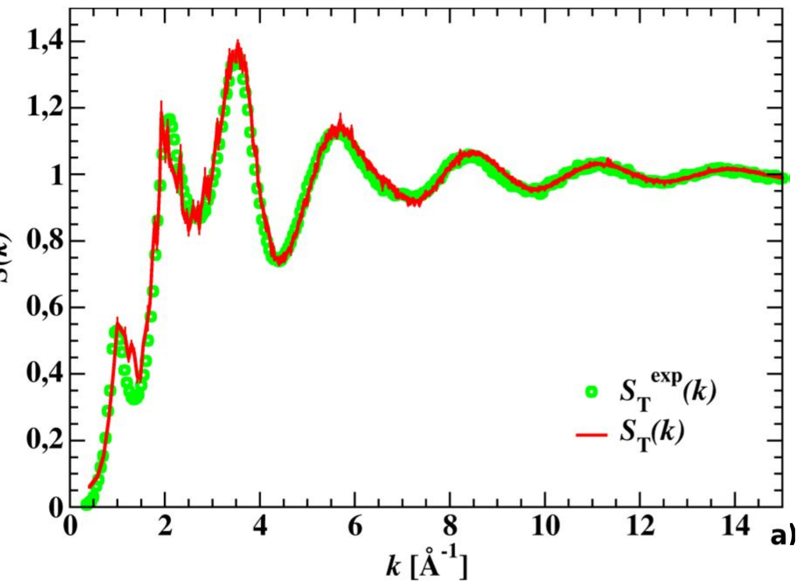
Understanding the structure of iono-covalent liquids and glasses

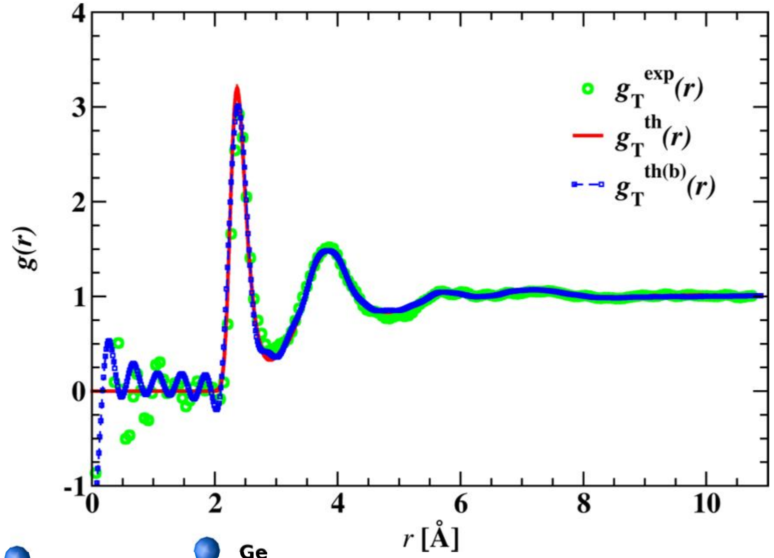


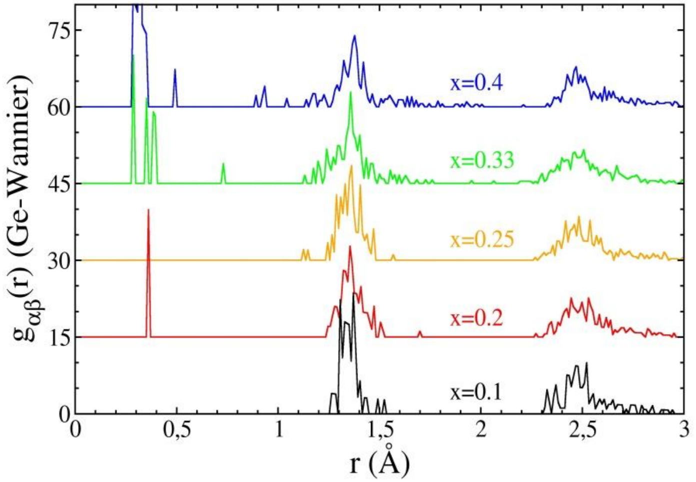
Exemple of quantitative agreement with experiments: GeSe$_4$ SiSe$_4$ glasses

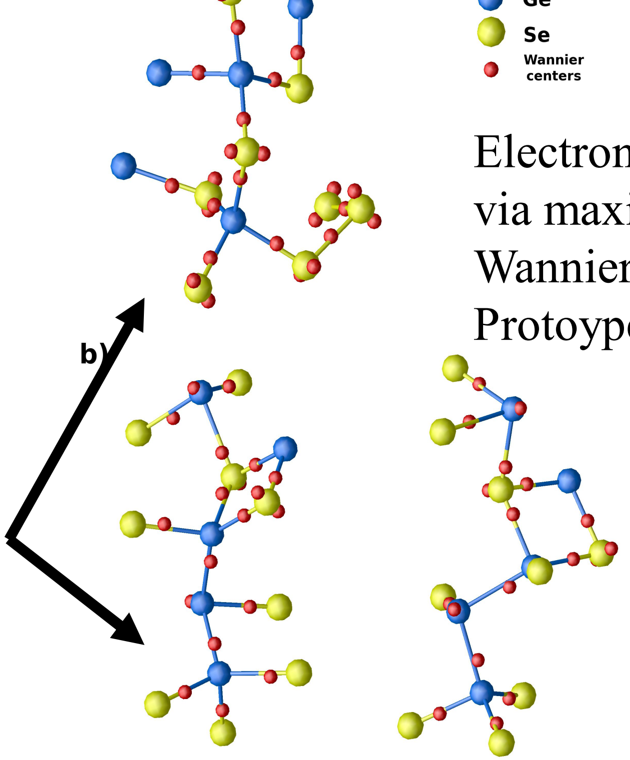


Detailed coordination local bonding of Se







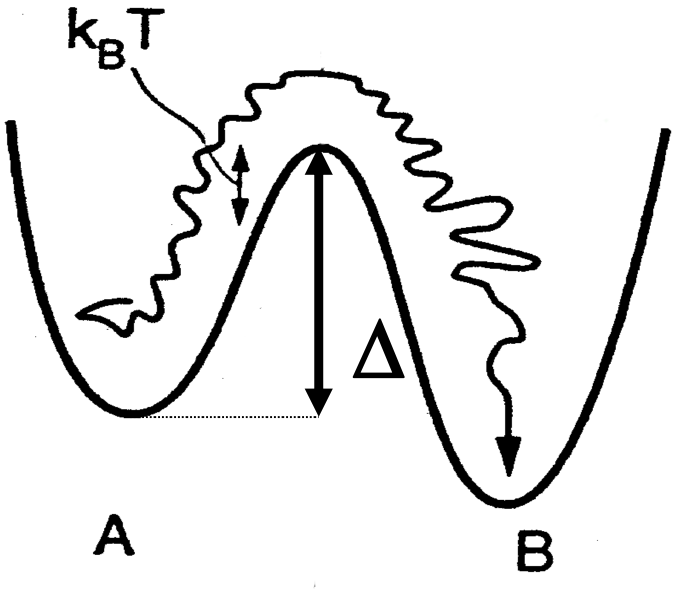


Electronic structure character via maximally localized Wannier functions centers. Protoype case: Ge_2Se_3

Simulating activated processes

From reactants A to products B: we have to climb the mountain minimizing the time

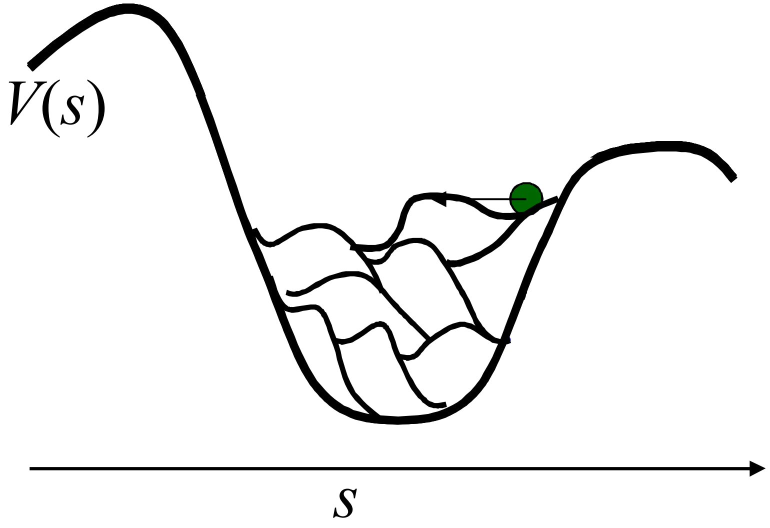
- A general chemical reaction starts from reactants A and goes into products B
- The system spends most of the time either in A and in B
- …but in between, for a short time, a barrier is overcome and **atomic** and **electronic** modifications occur
- Time scale: $\tau \sim \tau_{mol} e^{\frac{F^*}{k_B T}}$

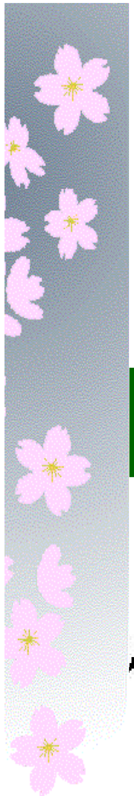


$F^* \sim \Delta$

Escaping the local minima of the FES:

In one dimension, the system freely moves in a potential well (driven by MD). Adding a penalty potential in the region that has been already explored forces the system to move out of that region, but always choosing the minimum energy path, i.e. the most natural path that brings it out of the well. Providing a properly shaped penalty potential, the dynamics is guaranteed to be smooth and therefore the systems explores the whole well, until it finds the lowest barrier to escape.





How to plug all this in CPMD ?

We simply write a (further) extended Lagrangean including the new degrees of freedom

Fictitious kinetic energy

$$\mathcal{L} = \mathcal{L}_{CP} + \sum_{\alpha} \frac{1}{2} M_{\alpha} \dot{s}_{\alpha}^{2} - \sum_{\alpha} \frac{1}{2} k_{\alpha} \left(S_{\alpha}(\mathbf{R}) - s_{\alpha} \right)^{2} - V(\mathbf{s}, t)$$

Restrain potential: coupling fast and slow variables

$\sqrt{(k_\alpha/M_\alpha)} \ll \omega_I$

$$\frac{\partial \mathcal{F}}{\partial s_{\alpha}} \simeq \langle k_{\alpha} (S_{\alpha}(\mathbf{R}) - s_{\alpha}) \rangle$$

History-dependent potential

The discrete form of $V(\mathbf{s},t)$ implemented in CPMD is

$$V(\mathbf{s},t)=\sum_{t_i<t} W_i \exp\left(-\tfrac{1}{2}\frac{(\mathbf{s}-\mathbf{s}_i)^2}{(\Delta s^{\perp})^2}\right)\exp\left[-\tfrac{1}{2}\frac{\left((\mathbf{s}_{i+1}-\mathbf{s}_i)\cdot(\mathbf{s}-\mathbf{s}_i)\right)^2}{(\Delta s_i^{\parallel})^4}\right]$$

where the Dirac δ has been expressed in the approximate Gaussian form

$$\delta(x)\approx\frac{1}{\beta\sqrt{2\pi}}\exp\left(-\frac{1}{2}\frac{x^2}{\beta^2}\right) \qquad \beta=\left|\dot{\mathbf{s}}(t)\right|\Delta t$$

and the discrete time step Δt must be such that

CPMD time step

$$\Delta t^{CPMD} << \Delta t << \omega_{\vec{s}_\alpha}^{-1}$$

Highest oscillation frequency of s_α

FES reconstruction: what $V(\mathbf{s},t)$ is used for

When the (meta)dynamics is over and the walker has explored all the portion of the $\{\mathbf{s}\}$ phase space available, we have completed our job (at large t) and filled all the local minima, then the shape of $V(\mathbf{s},\mathrm{t})$ is similar to the FES apart from a sign and an arbitrary additive constant

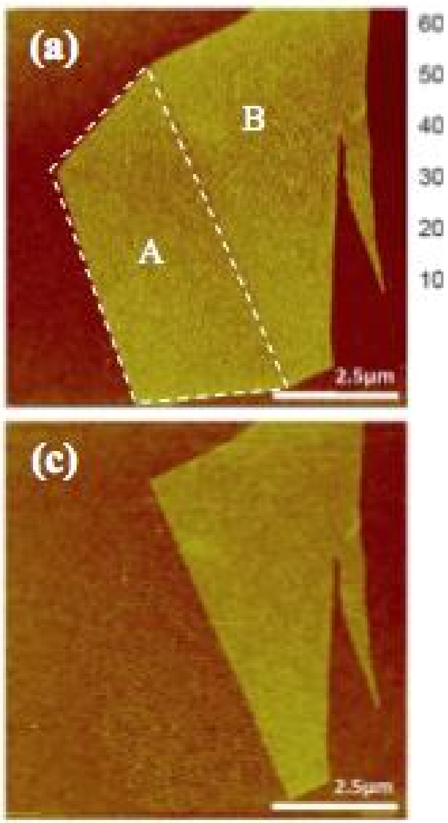
$$\lim_{t\to\infty} V(\mathbf{s},t) = -F(\mathbf{s}) + const.$$

In practice: the number of gaussians required to fill a minimum is proportional to $(1/\delta\sigma)^{\boldsymbol{n}}$ ($\boldsymbol{n}$ = dimensionality of the problem) and

$$W/\delta\sigma\, e^{-1/2} = \gamma \left\langle f_\alpha^2 \right\rangle^{1/2} \qquad \gamma \approx 0.5$$

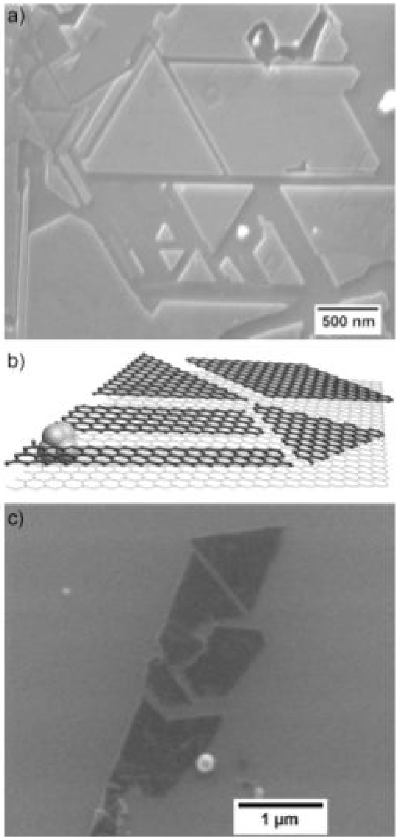
Oxygen plasma etching of graphene: A tool to fabricate nano-scale carbon devices

Oxygen plasma etching: a crucial step in the fabrication of carbon-based Nanodevices. *Nanolett*. **8**, 1965 (2008); *Science* **324**, 1530 (2009)



Layer-by-layer control

TEM images



Shape control @ atomic-scale

Etching of graphite (topics in 70's)

In mid 70's, etching of graphite surface was the target of several researchers.

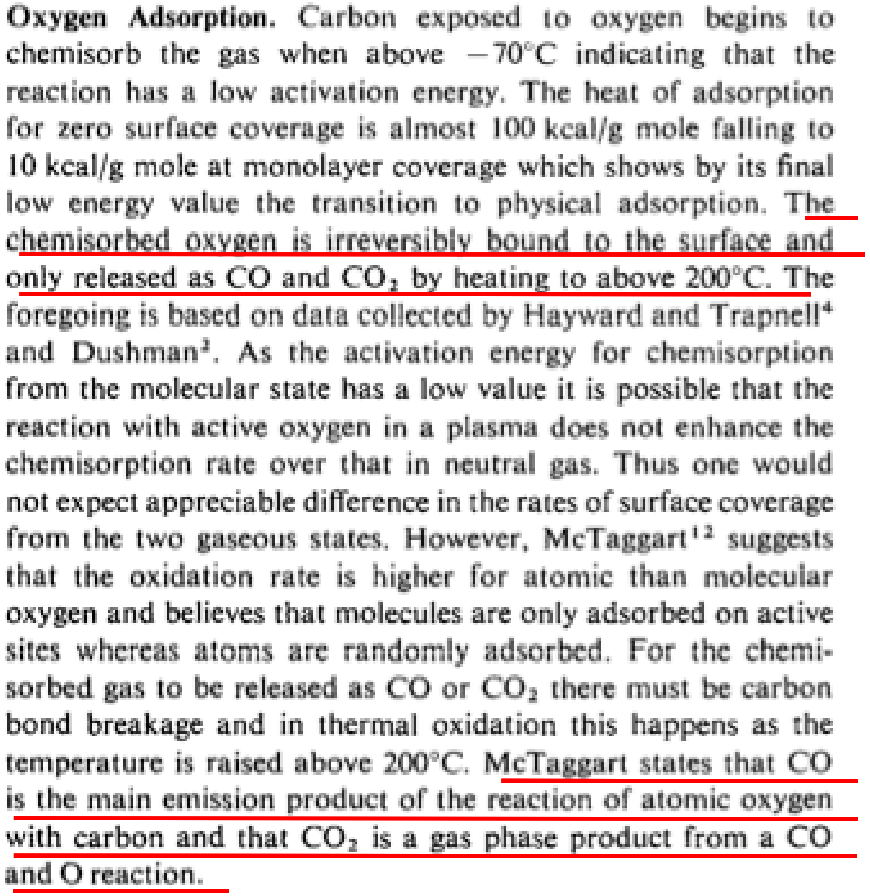
The chemical sputtering of graphite in an oxygen plasma

received 1 September 1975; in revised form 26 September 1975

L Holland* and **S M Ojha†**, *School of Mathematical and Physical Sciences, University of Sussex, Brighton, England*

Vacuum **26**, 53 (1976)

CO and CO_2 were supposed to be released

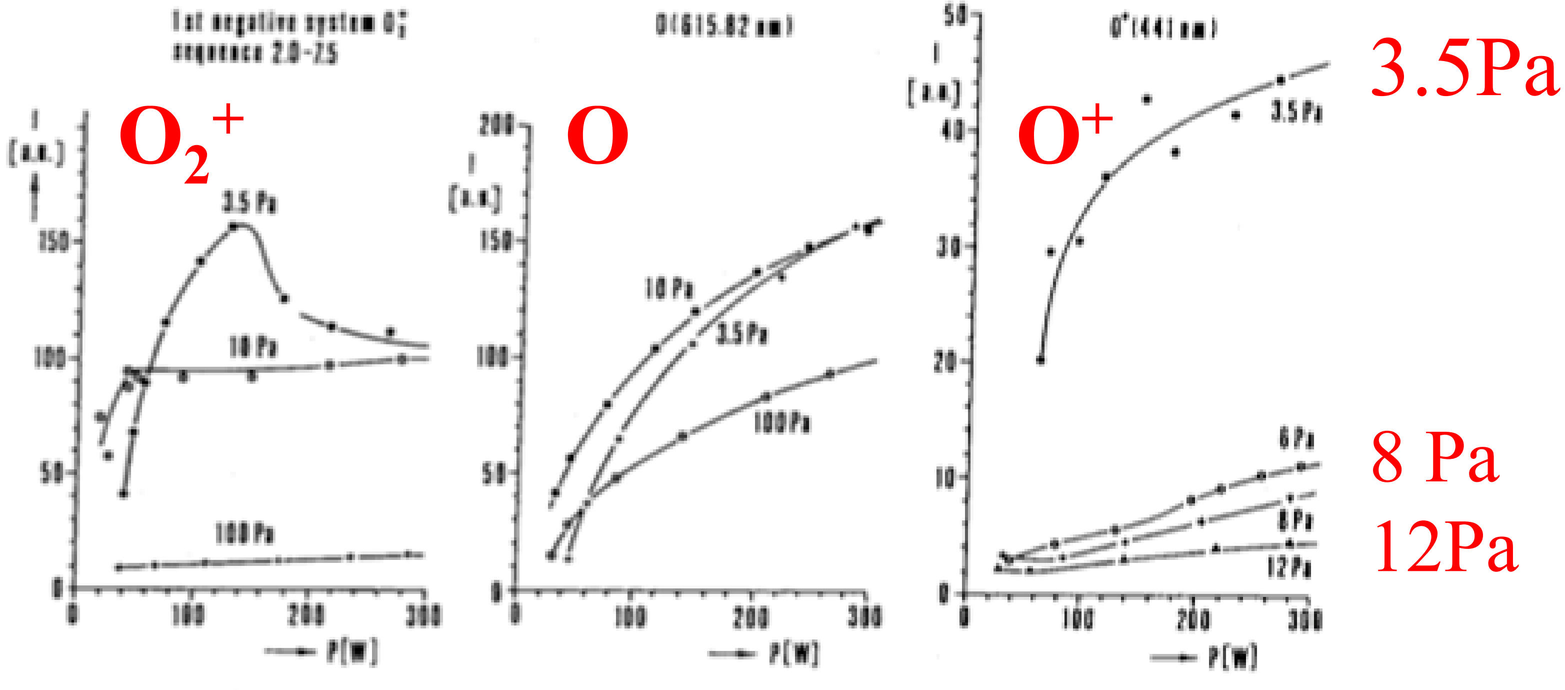


Oxygen Adsorption. Carbon exposed to oxygen begins to chemisorb the gas when above −70°C indicating that the reaction has a low activation energy. The heat of adsorption for zero surface coverage is almost 100 kcal/g mole falling to 10 kcal/g mole at monolayer coverage which shows by its final low energy value the transition to physical adsorption. The chemisorbed oxygen is irreversibly bound to the surface and only released as CO and CO_2 by heating to above 200°C. The foregoing is based on data collected by Hayward and Trapnell[4] and Dushman[2]. As the activation energy for chemisorption from the molecular state has a low value it is possible that the reaction with active oxygen in a plasma does not enhance the chemisorption rate over that in neutral gas. Thus one would not expect appreciable difference in the rates of surface coverage from the two gaseous states. However, McTaggart[12] suggests that the oxidation rate is higher for atomic than molecular oxygen and believes that molecules are only adsorbed on active sites whereas atoms are randomly adsorbed. For the chemisorbed gas to be released as CO or CO_2 there must be carbon bond breakage and in thermal oxidation this happens as the temperature is raised above 200°C. McTaggart states that CO is the main emission product of the reaction of atomic oxygen with carbon and that CO_2 is a gas phase product from a CO and O reaction.

McTaggrt guess: CO might be the main released compound.

… but CO or CO_2 ?

Optical emission spectroscopy

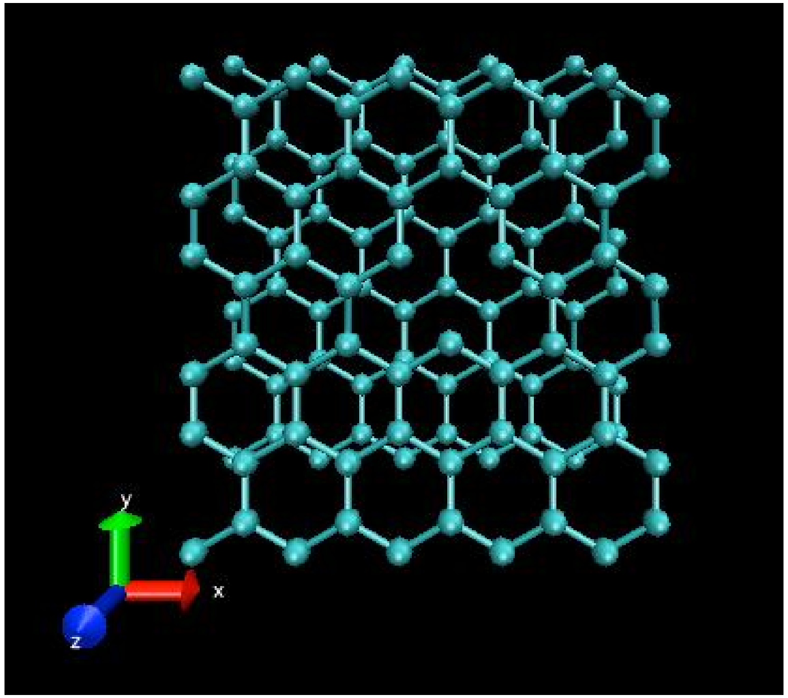


a) b) c)

Fig. 5. Intensities of emission lines from molecular oxygen ion O_2^+, atomic oxygen O and atomic ion O^+ as a function of microwave power $P = P_i - P_r$ measured at three values of oxygen pressure $p_1 = 3.5$ Pa, 10 Pa and 100 Pa.

Main components of O plasma → Atomic O and charged molecular O

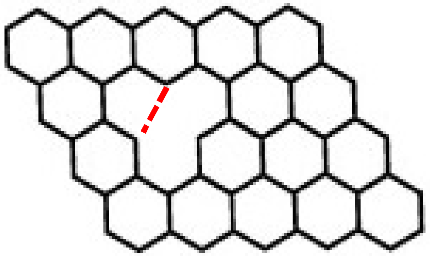
Simulated system: bilayer defect-free & vacancies



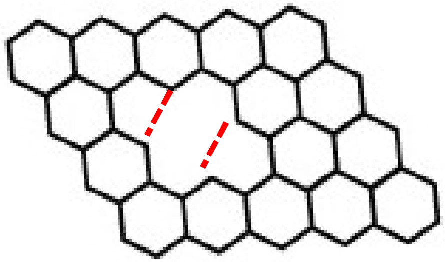
Box size: 12.3x12.75x15.0 Å^{3}

Inter-layer distance:
1.68 Å (minimum according to van der Waals corrections)

Spin-polarized PBE + Grimme's D2 or WFC vdWcorrection

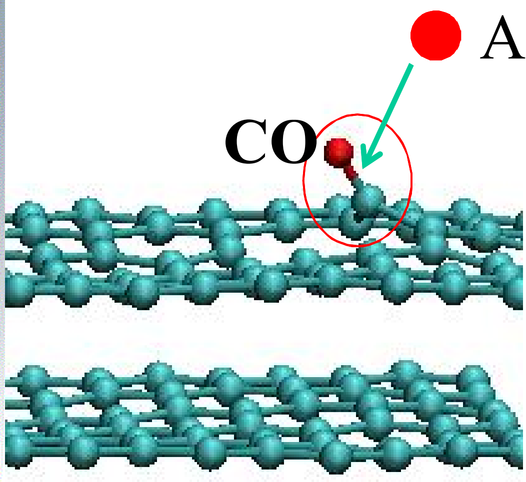


Mono-vacancy V_1
Two C rebounded
One dangling bond



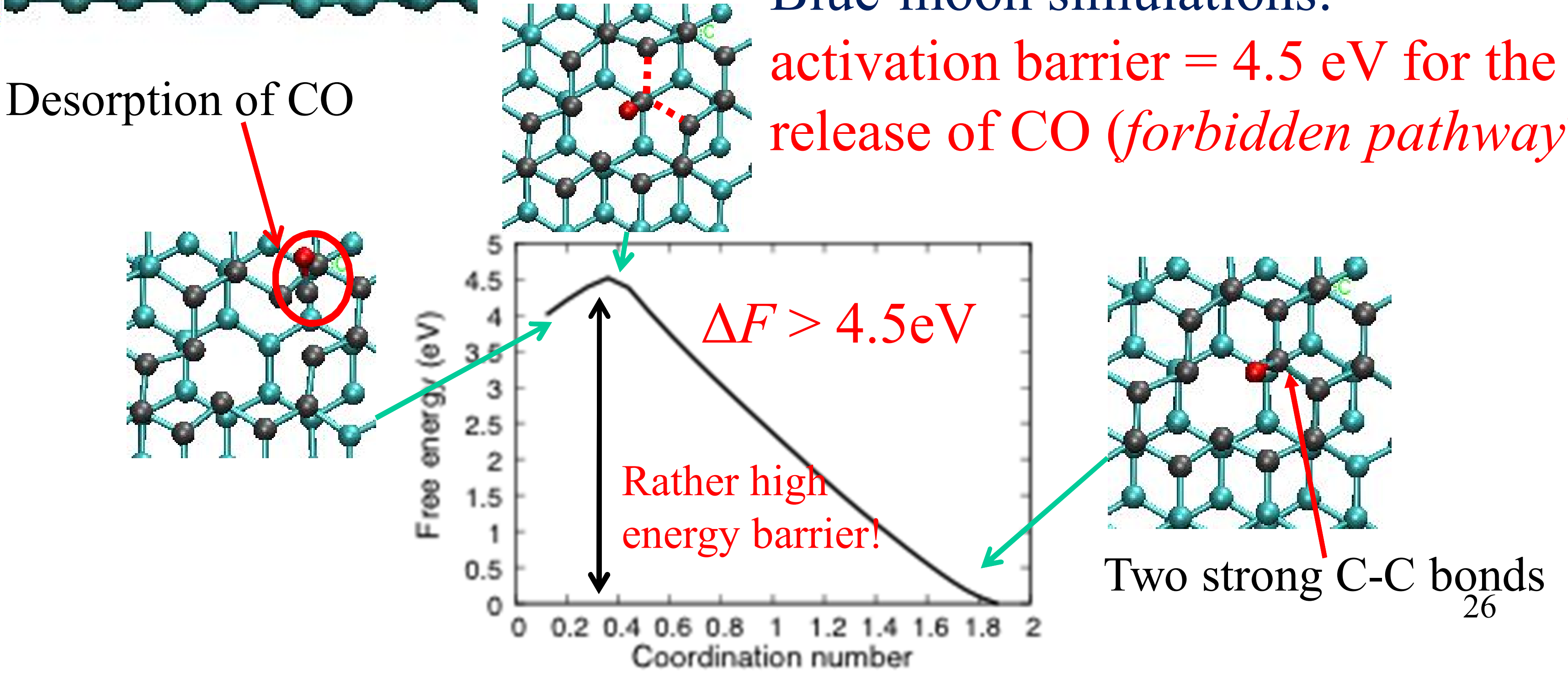
Di-vacancy V_2
Four C rebounded
No dangling bonds

Attack of atomic oxygen (O) to dangling bond and free energy barrier for CO desorption



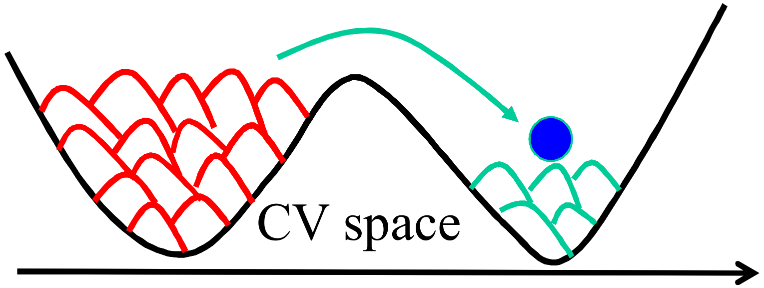
Atomic O attacks the DB @ mono-vacancy spontaneously.
This reaction generates a CO moiety

Blue-moon simulations:
activation barrier = 4.5 eV for the release of CO (*forbidden pathway*?)

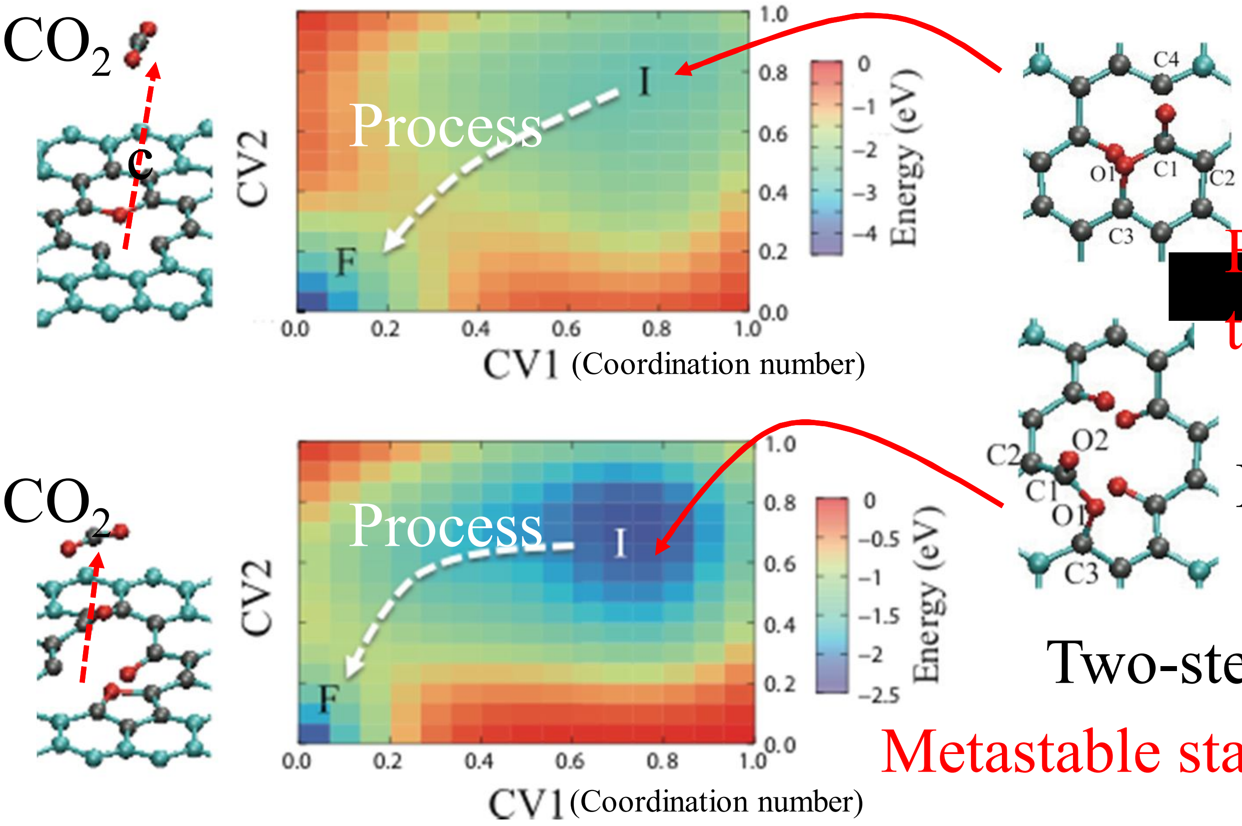


Final CO_2 desorption processes: Metadynamics free energy landscape)

Collective variables (CVs)
Coordination number of C1 to C2
Coordination number of O1 to C3



Free energy barriers for desorption of CO_2 molecules: 1.5eV



Mono-vacancy

[redacted]

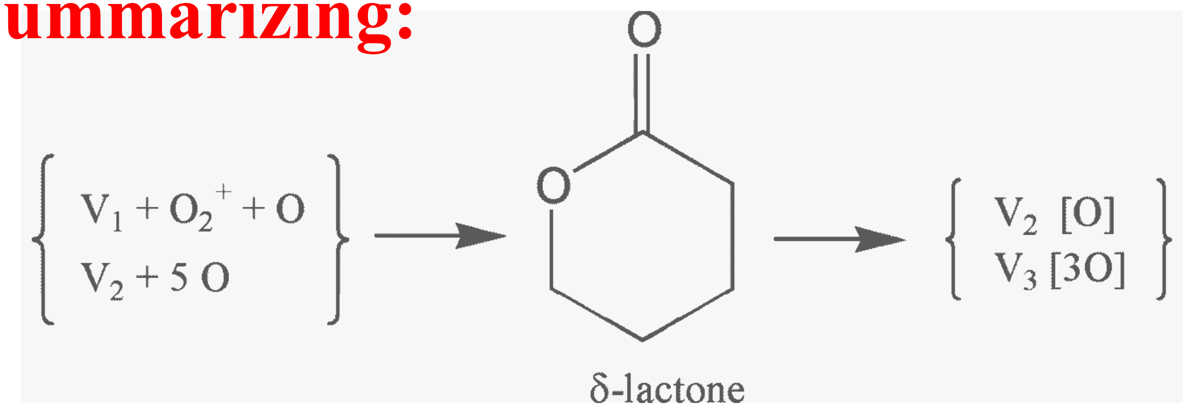
From metastable state to CO_2 desorption

Di-vacancy

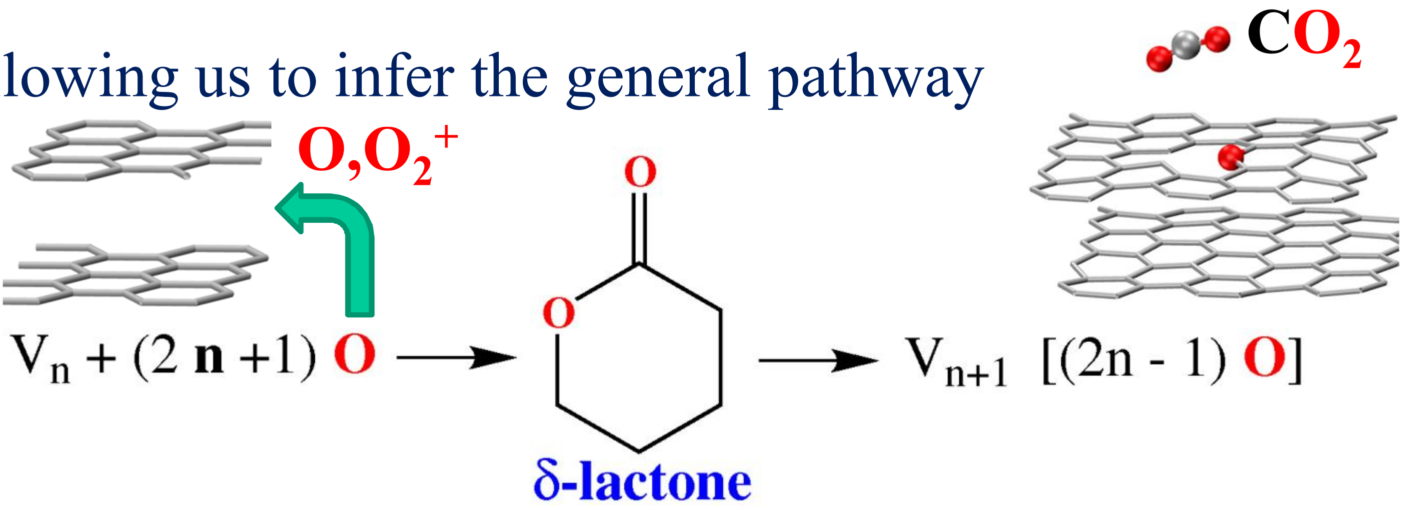
Two-step mechanism

Metastable state → CO_2desorption

Summarizing:



allowing us to infer the general pathway



for a vacancy V_n (n = number of missing C atoms)

K. Koizumi, M.B., Y. Shigeta, A. Oshiyama, *J. Phys. Chem. Lett.* **4**, 1592 (2013)

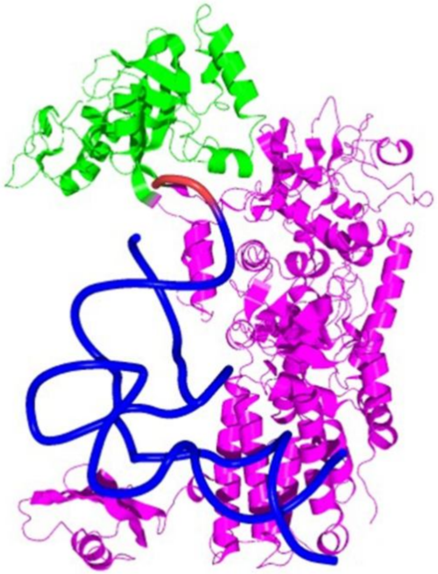
Conclusions

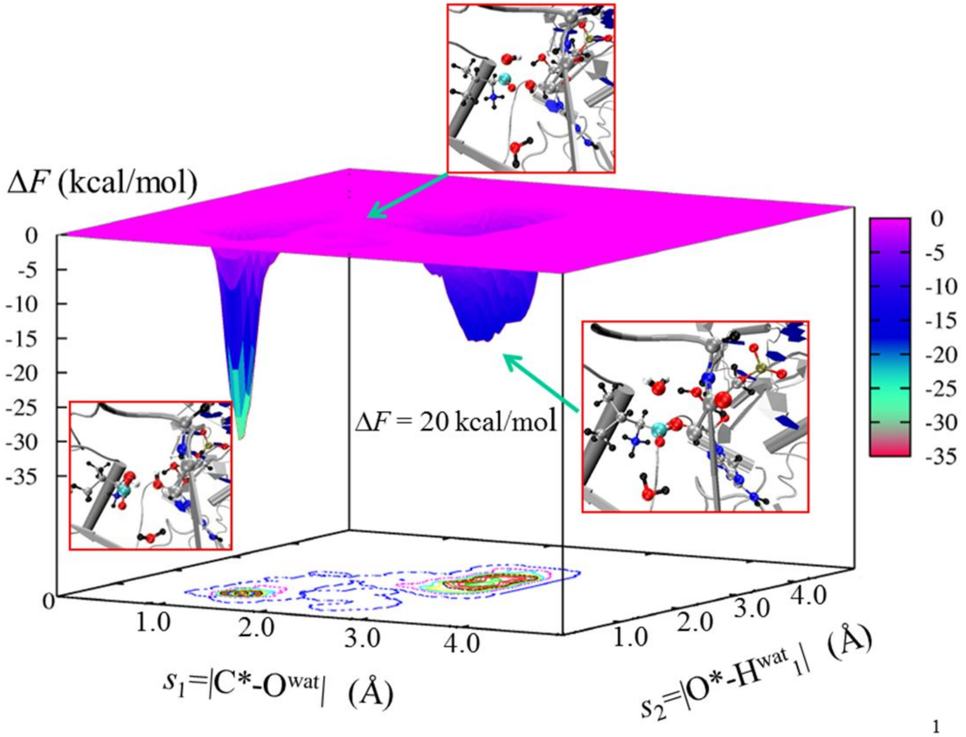
- The atom-scale mechanisms of graphene etching has been clarified by combined first principles molecular dynamics and free energy sampling methods
- Atomic O, one of the main plasma components, etches graphene from vacant sites either with or without dangling bonds.
- an efficient plasma for graphene etching is the one in which atomic O is the major component, providing a useful guideline in designing and optimizing graphene etching processes.
- The processes of graphene etching is a two-step mechanism always passing across lactone formation
- CO_2 desorption occurs, whereas CO is unlikely to desorb
- A layer-by-layer mechanism occurs: Underneath graphene layer are never attacked by O at whatever stage of the reaction

Atomic scale simulations for biomaterials

Example: editing reaction of RNA for the transmission of the genetic information (post-Genoma Project)

[M. B., *J. Chem Phys. B* **115**, 12276 (2011)]





Simulations by hybrid QM/MM molecular dynamics coupled to free energy sampling techniques (Blue Moon & Metadynamics)

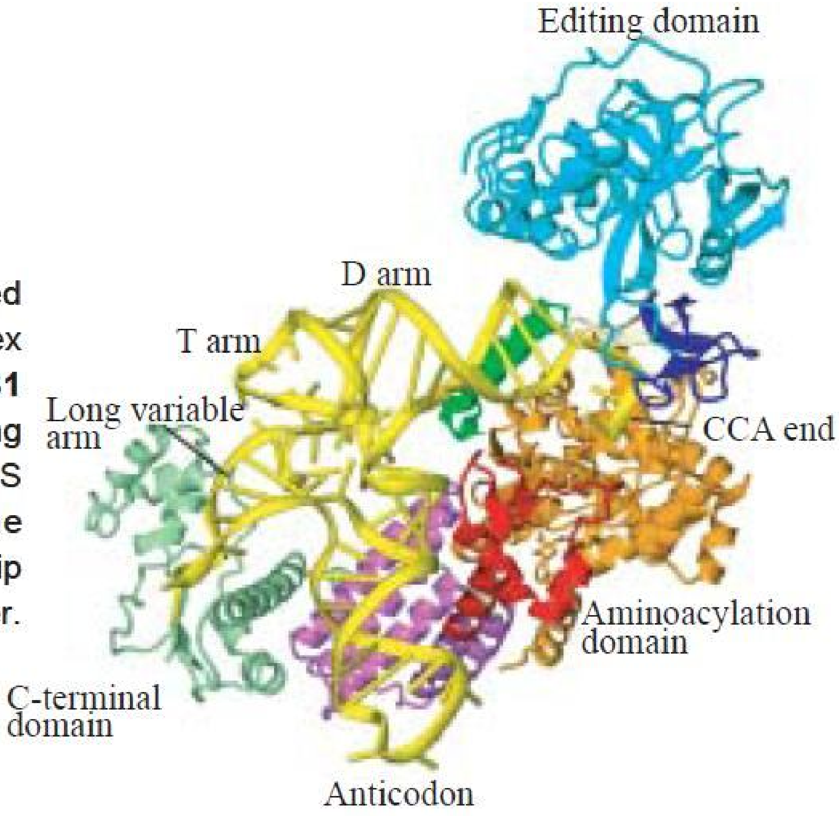
Life Science : Structural Biology

CRYSTAL STRUCTURES OF LEUCYL-tRNA SYNTHETASE COMPLEXED WITH $tRNA^{Leu}$

Ryuya Fukunaga[a,b] and Shigeyuki Yokoyama[a,b]

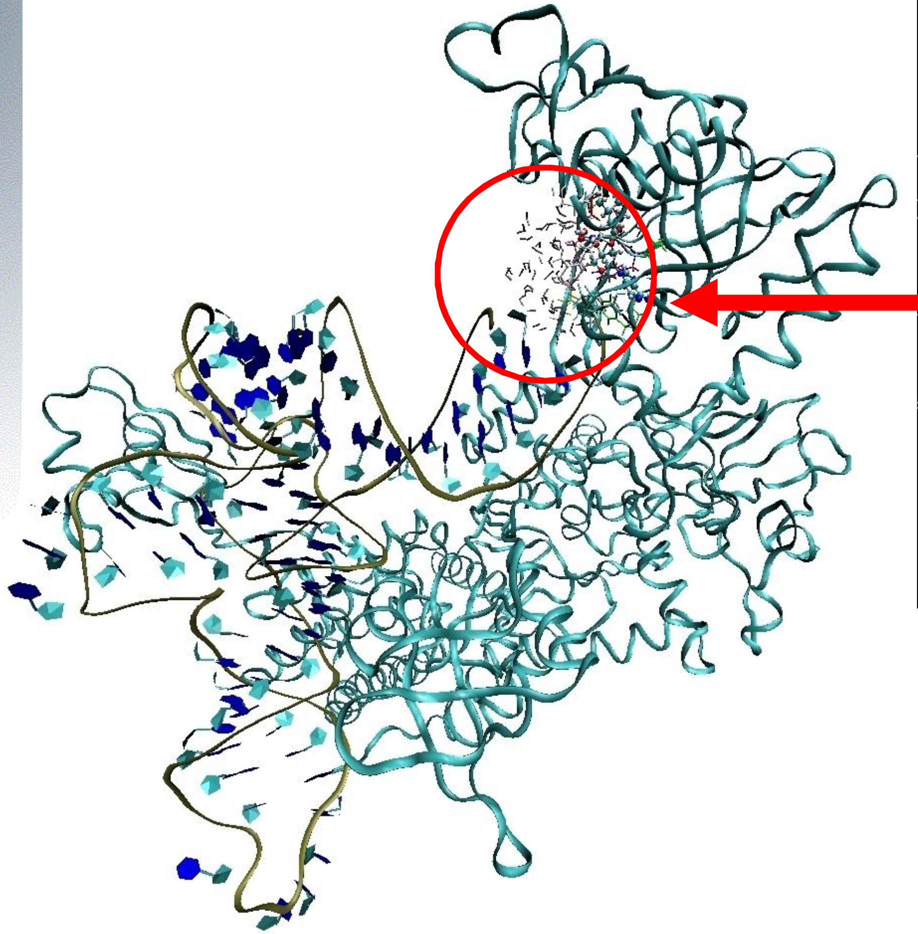
[a] Department of Biophysics and Biochemistry,
The University of Tokyo
[b] RIKEN Genomic Sciences Center
[c] SPring-8 / RIKEN

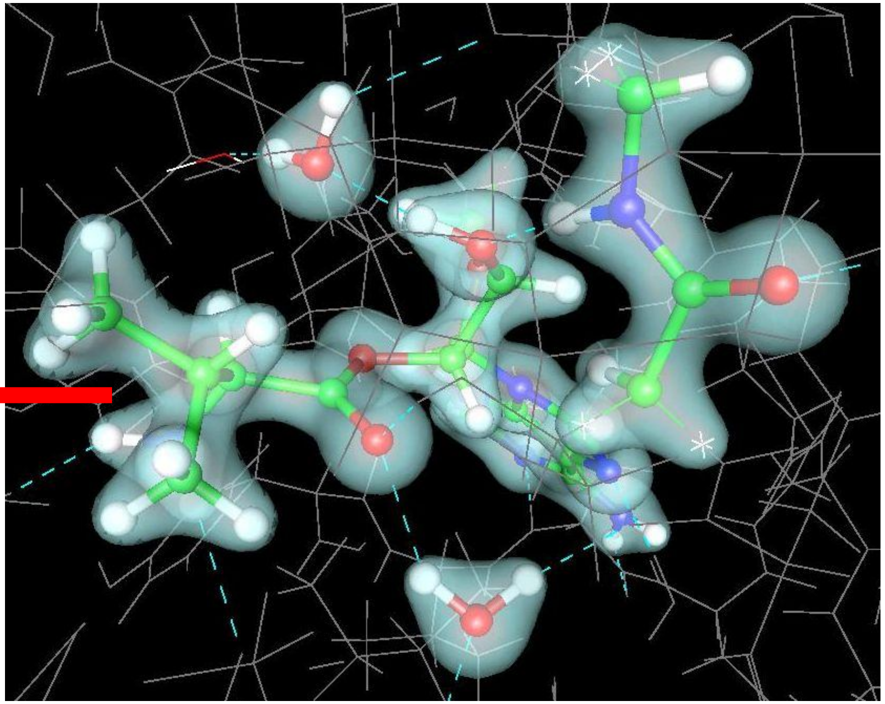
To elucidate these mechanisms, we determined the crystal structure of *P. horikoshii* LeuRS in complex with $tRNA^{Leu}$ at 3.2 Å resolution, using the **BL26B1** and **BL41XU** beamlines (Fig. 1) [2]. The protruding C-terminal domain (light green in Fig. 1) of LeuRS reaches the tip of the long variable arm. Some residues at the C-terminal extremity recognize the tip bases of the long arm in a sequence specific manner.



R. Fukunaga and S. Yokoyama, *Nature Struct. Mol. Biol.* **12,** 915 (2005)

QM/MM Simulation of the Complex of Leucine and its specific tRNA





System size:

MM: 165750 atoms

QM: 63 atoms + 5 capping H atoms

LSDA and HCTH functional

E^{cut}=70 Ry 176 e^- (Q = +1)

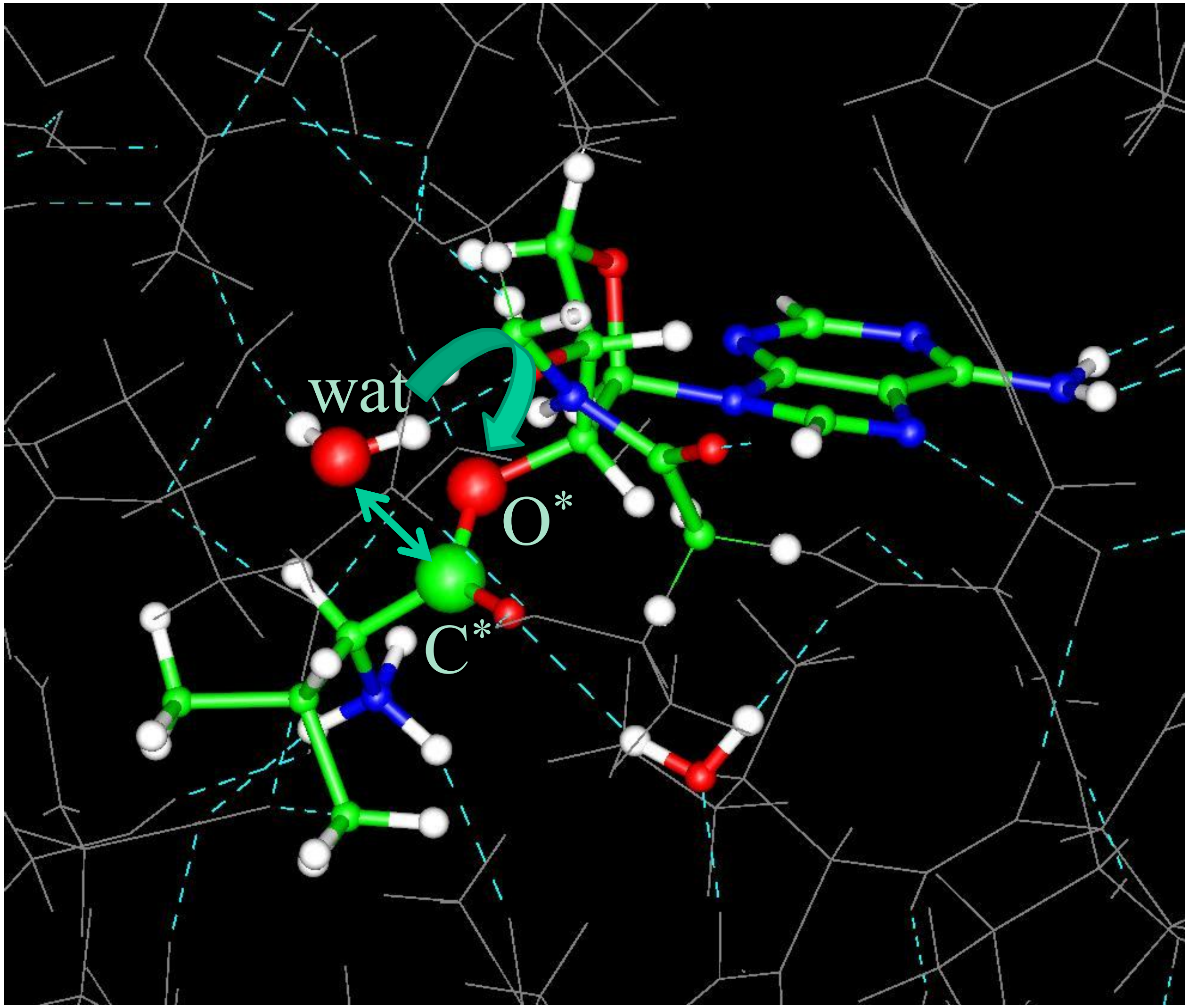
164759 PWs

QM Cell = 17x15x21 Å^3

N_xxN_yxN_z = 180x144x216

Reaction coordinates $s_\alpha(t)$ sampled via metadynamics:

- $V(s_\alpha,t)$ updated every 200 CPMD steps (0.02 ps)
- Gaussian functions with amplitudes = 0.15 kcal/mol

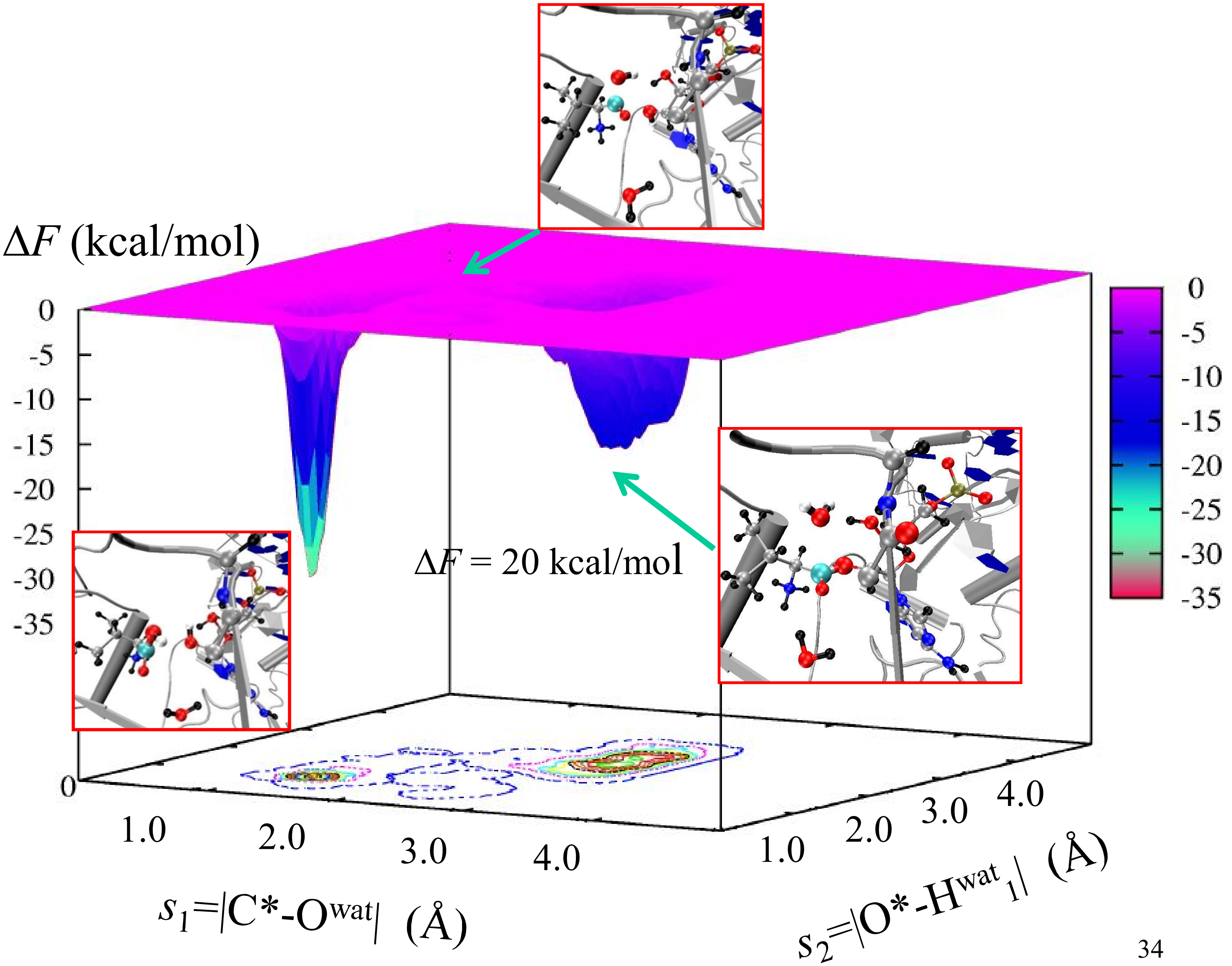


Simulation 1

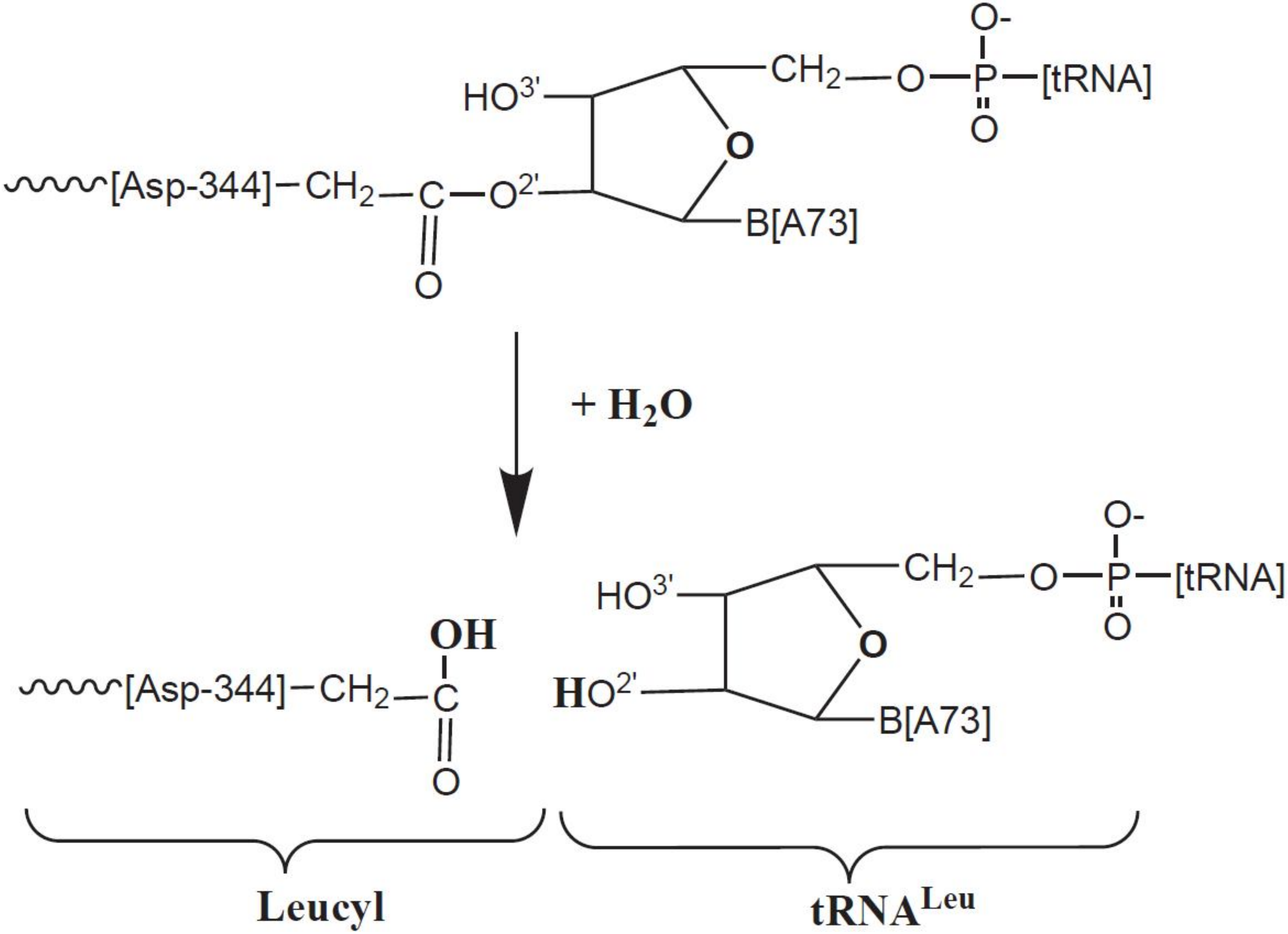
$s_1=|C^*\text{-}O^{wat}|$
$s_2=|O^*\text{-}H^{wat}_1|$

Simulation 2

$s_1=|C^*\text{-}O^{wat}|$
$s_2=|O^*\text{-}H^{wat}_2|$


ΔF (kcal/mol)
0
-5
-10
-15
-20
-25
-30
-35
0
$\Delta F = 20$ kcal/mol
1.0
2.0
3.0
4.0
$s_1 = |C^* - O^{wat}|$ (Å)
1.0
2.0
3.0
4.0
$s_2 = |O^* - H^{wat}_1|$ (Å)
0
-5
-10
-15
-20
-25
-30
-35

Summarizing:



Conclusions

- An H-bond formed between [*t*RNA]–$O^{2'}$-H and an H_2O molecule is crucial in triggering the reaction
- Two alternative (energetically equivalent) reaction pathways:

(a) the 3’-OH’group of the cognate tRNA acts as a Lewis acid

(b) the 3’-OH group of the cognate tRNA drives, via H- bond, the catalytic H_2O molecule towards the unoccupied LUMO state at the active site

Perspectives

- Applications to proteins and nucleic acids for drug and enzyme (ribozymes) design
- Provide *in silico* atomic-scale insight to complement *in vitro* and *in vivo* biochemical experiments
- Transfer of know-how to bio-inspired materials

M. Boero, *J. Phys. Chem. B* **115**, 12276 (2011)

V. Rojas, A. Ardevol, M. Boero, A. Planas, C. Rovira *Chem. Eur. J.* **19**, 14018 (2013)

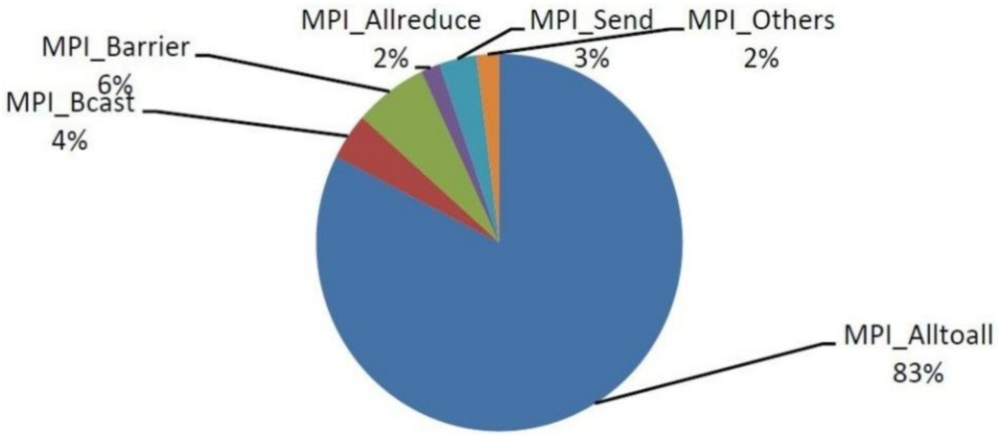
…about CPMD:

- Versions 3.* no longer developed/supported since November 2013
- **New release 4.* coming soon**
- Fortran 90/95 (c/c++ @ sysdepend.c)
- Organized in modules & structure of the code slightly changed (more rational):

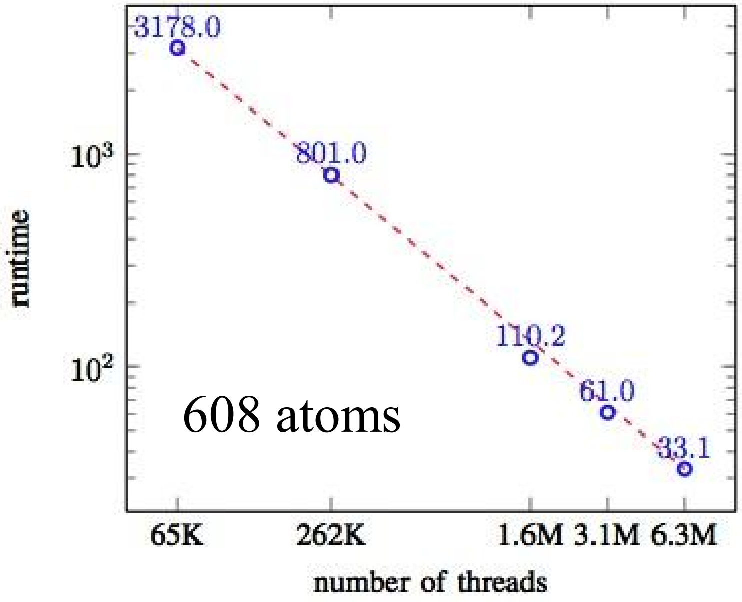
```
-|---  CPMD ---|---- src
        |      |---- configure
        |      |---- doc
        |      |---- modules -|-MM_Interface
        |      |---- src      |-Gromos/Amber
        |---- regtests
        |---- cpmd2cube
        |---- tests
```

- the code compiles in the usual way, via an adapted configure.sh script in the CPMD directory.
- ...work in progress

MPI workload distribution

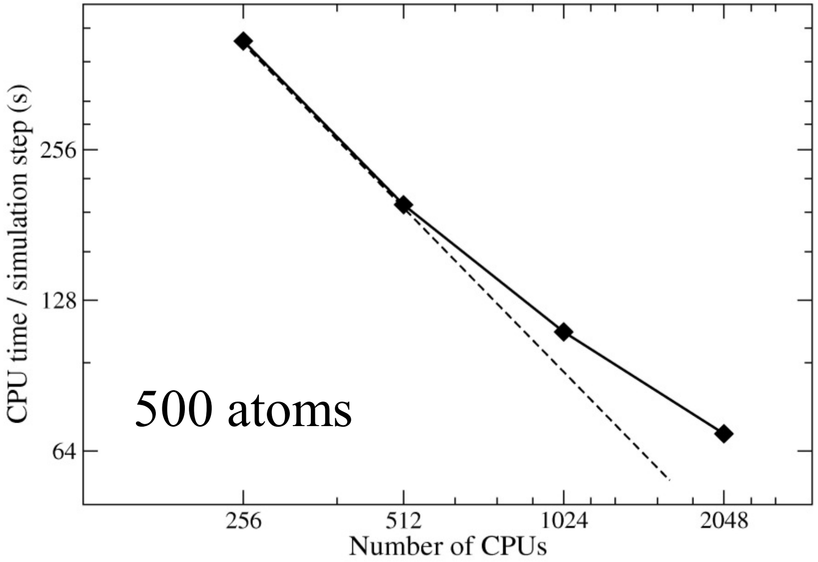


Performance of on M of threads



608 atoms

Performance on BG/Q (IDRIS)



500 atoms

Thank you for your attention
ご清聴ありがとうございます
Vielen Dank für Ihre Aufmerksamkeit
Merci de votre attention
Grazie della vostra attenzione
관심에 감사드립니다