First Principles Molecular Dynamics:
basics of the method, practical implementation and some examples of application

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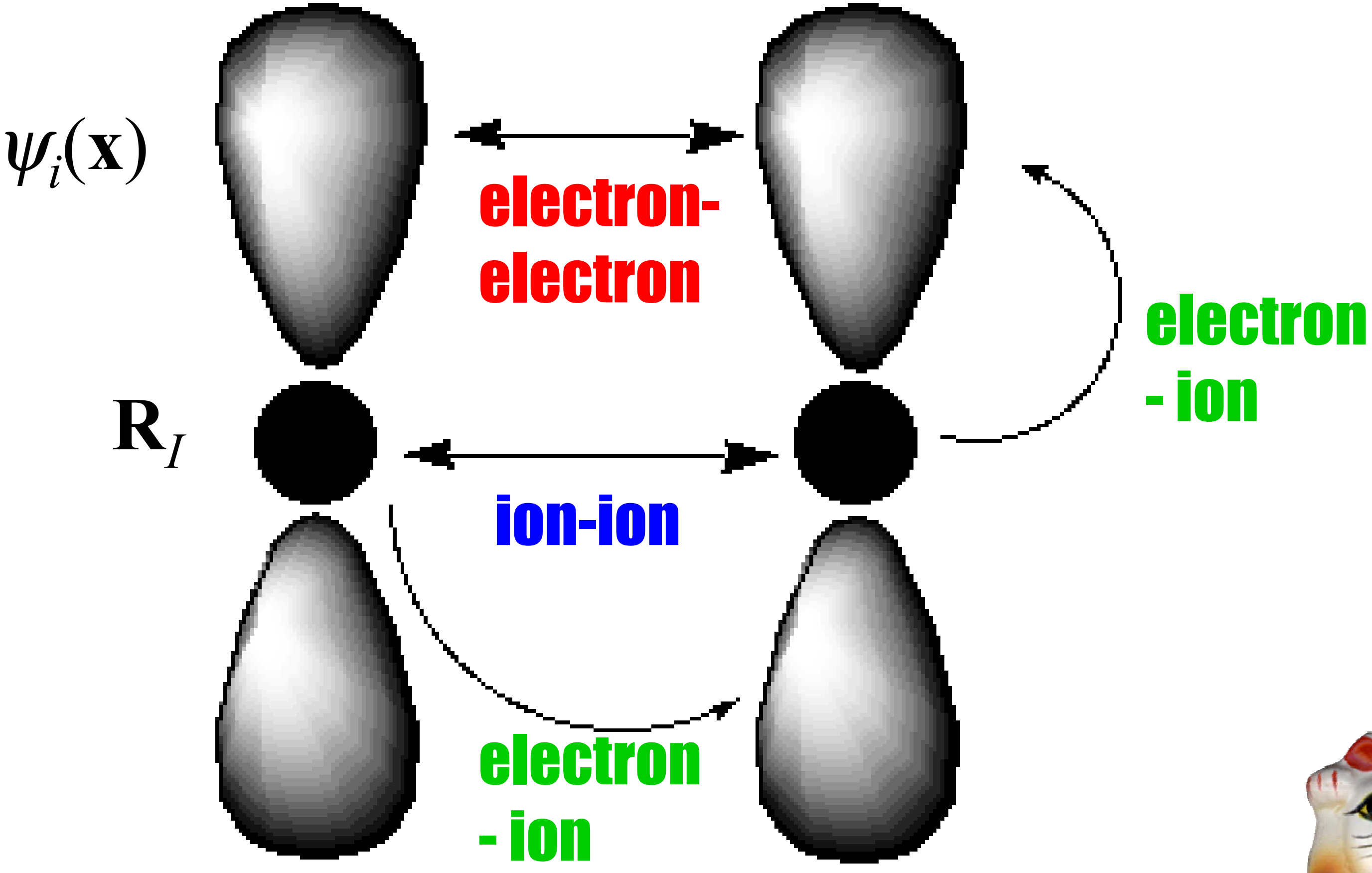
Outline

- Density Functional Theory (DFT): brief review
- Car-Parrinello (CP) method: basic formulation and algorithms
- Practical implementation: numerical scheme, basis set, direct space and Fourier transform
- Some recent applications: heterogeneous catalysis, supercritical water, RNA

(Warning: *not because they are the most important, but because they are the ones that I know directly, not from some* 物語)

What do we want to do? And which are the objects that we want to study ?



Density Functional Theory: brief review

- Define the electronic density ρ ($\mathbf{x}$) as a superposition of single particle Kohn-Sham (KS) orbitals

$$\rho(\mathrm{x}) = \sum_{i}^{occ} f_i |\psi_i(\mathrm{x})|^2$$

- Write the total energy functional as

$$E[\psi_i, \mathbf{R}_I] = E_{\mathrm{k}} + E_{\mathrm{H}} + E_{\mathrm{xc}} + E_{\mathrm{ps}} + E_{\mathrm{M}}$$

i.e. sum of electron-electron + electron-ion + ion-ion interaction

Density Functional Theory: brief review

- Electron-electron interaction:

$$E_k = -\tfrac{1}{2}\sum_i f_i \int d^3x\, \psi_i^*(\mathbf{x})\nabla^2\psi_i(\mathbf{x})$$

$$E_H = \tfrac{1}{2}\int d^3x\, d^3x'\, \frac{\rho(\mathbf{x})\rho(\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|}$$

$$E_{xc} = \int d^3x\, \epsilon_{xc}(\rho, \nabla\rho)\rho(\mathbf{x})$$

- E_k = kinetic energy, E_H = Coulomb interaction, E_{xc} = exchange-correlation interaction

Density Functional Theory: brief review

- Electron-ion interaction:

$$E_{ps} = \int d^3x \, \mathcal{V}^{ps}(\mathbf{x})\rho(\mathbf{x})$$

the core-valence interaction is described by pseudopotentials

- Ion-ion interaction:

$$E_M = \frac{1}{2}\sum_{I \neq J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}$$

Car-Parrinello Molecular Dynamics

- Generalize the classical MD lagrangean by adding the electronic degrees of freedom ψ_i and any external additional variables α_q (e.g. thermostats, stress, etc.)

$$\mathcal{L}^{CP} = \tfrac{1}{2}\sum_i \mu \int d^3x\, |\dot{\psi}_i|^2 + \tfrac{1}{2}\sum_I M_I \dot{\mathbf{R}}_I^2$$

$$+\tfrac{1}{2}\sum_q \mu_q \dot{\alpha}_q^2 - E^{DFT}[\psi_i, \mathbf{R}_I, \alpha_q]$$

$$+\sum_{ij} \Lambda_{ij} \left(\int d^3x\, \psi_i^* \psi_j - \delta_{ij} \right)$$

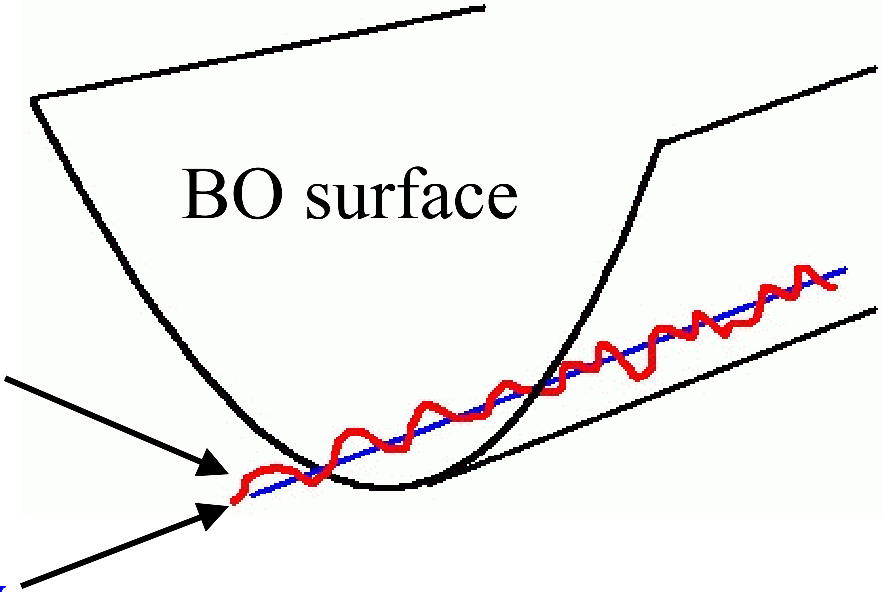
Car-Parrinello Molecular Dynamics

- Solve the related Euler-lagrange equations of motions

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

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

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



BO surface

CP trajectory

BO trajectory

The difference between the CP trajectories $\mathbf{R}_I^{\mathbf{CP}}(t)$ and the Born-Oppenheimer (BO) ones $\mathbf{R}_I^{\mathbf{BO}}(t)$ is bound by

$$| \mathbf{R}_I^{\mathbf{CP}}(t) - \mathbf{R}_I^{\mathbf{BO}}(t)| < C\, \mu^{1/2}$$

$$(C > 0) \text{ if } \quad \omega_0 = \sqrt{2 \cdot \left(\varepsilon^{LUMO} - \varepsilon^{HOMO} \right) / \mu} > 0$$

See F.A. Bornemann and C. Schuette, *Numerische Mathematik* vol.**78**, N. **3**, p. 359-376 (1998)

Practical implementation

- Verlet's algorithm on e.o.m gives

$$(\mu/\Delta t^2) \cdot [\ |\psi(t+\Delta t)> + |\psi(t-\Delta t)> - 2\ |\psi(t)>] = (\mathcal{H}^{CP}-\Lambda)\ |\psi(t)>$$

- The ionic degrees of freedom $\mathbf{R}_I(t)$ are updated at a rate (speed) **Δt** while the electronic degrees of freedom |ψ(t)> are updated at a rate $\Delta t/\mu^{1/2}$ (**Δt** ~ 5 a.u., μ ~ 500 a.u.), hence they are much slower (decoupled) with respect to the ions
- μ is the parameter that controls the adiabaticity and allows for BO-like dynamics

Practical implementation

- To implement the CP e.o.m. numerically, the KS orbitals are generally expanded in plane waves

$$\psi_i(\mathbf{x}) = \Sigma_{\mathbf{G}}\ c_i(\mathbf{G})\ e^{i\mathbf{G}\mathbf{x}}$$

- **G** are the reciprocal space vectors. The Hilbert space spanned by **PWs** is truncated to a suitable cut-off E^{cut} such that

$$\mathbf{G}^2/2 < E^{cut}$$

- PWs have so far been the most successful basis set, in particular for extended systems requiring periodic boundary conditions

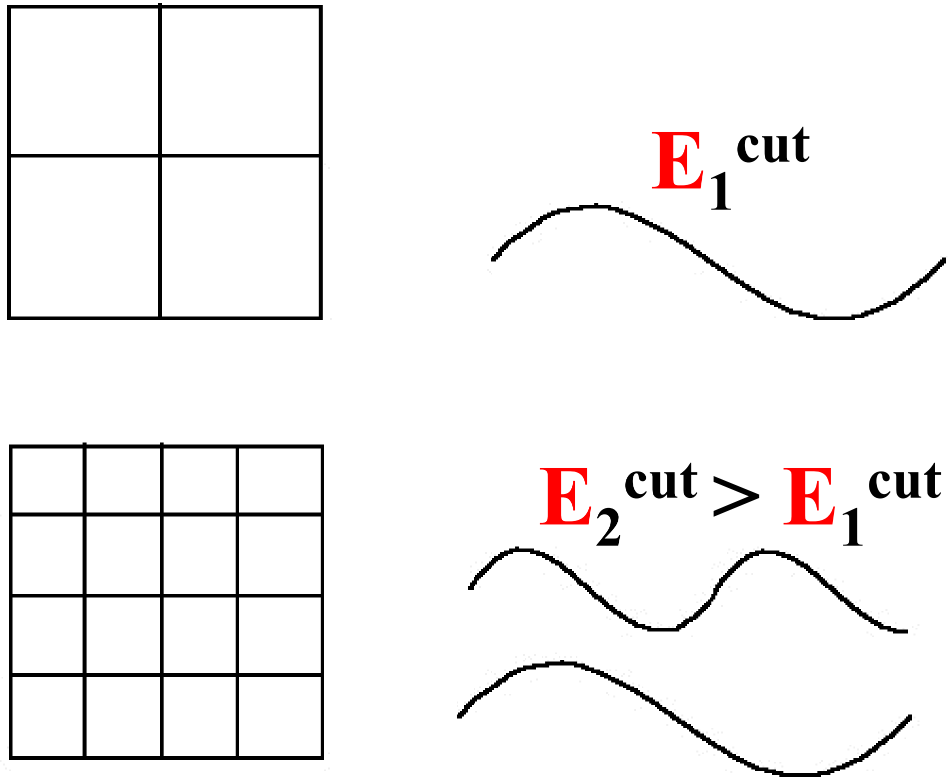
- R. Car, M. Parrinello, *Phys. Rev. Lett*. **55**, 2471 (1985)

- M. Parrinello, *Comp. in Sci. & Eng*. **2**, 22 (2000)

Plane wave expansion: $\psi_i(\mathbf{x}) = \Sigma_{\mathbf{G}}\, c_i(\mathbf{G})\, e^{i\mathbf{G}\mathbf{x}}$

For each electron $\boldsymbol{i}$**=1,…,*N*** , **G=1,…,*M*** are the reciprocal space vectors. The Hilbert space spanned by **PWs** is truncated to a cut-off $\mathbf{G}_{\mathbf{cut}}{}^{\mathbf{2}}/2 < E^{\mathrm{cut}}$

R space ↦ **G** space



$\mathbf{E_1{}^{cut}}$

$\mathbf{E_2{}^{cut} > E_1{}^{cut}}$

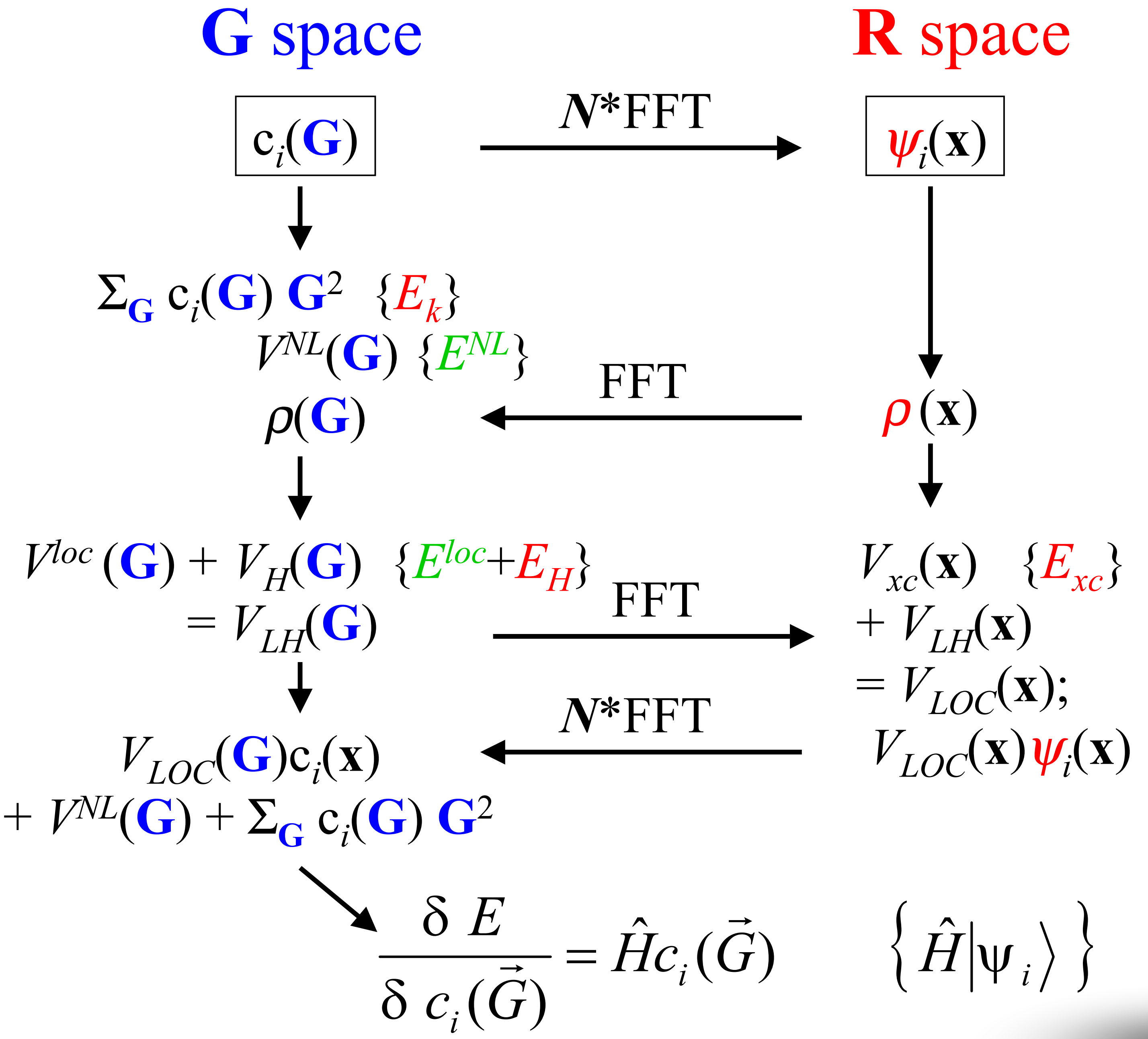
Practical implementation

- To achieve computational efficiency, pseudopotentials are written in the Kleinmann-Bylander separable form

$$V^{ps}(\mathbf{x},\mathbf{x}') = V^{loc}(\mathbf{x})\,\delta(\mathbf{x}-\mathbf{x}') + \Sigma_{lm}\,\phi_{lm}(\mathbf{x})\Delta V_{lm}\,\phi^*_{lm}(\mathbf{x}')$$

  being V^{loc} the local part and ΔV_{lm} the non-local V^{NL} angular momentum dependent part.

- Core electrons are not taken into account explicitly (unless partial core corrections or semicore states are used)



G space

R space

$\boxed{c_i(\mathbf{G})} \xrightarrow{N^*\text{FFT}} \boxed{\psi_i(\mathbf{x})}$

$\Sigma_{\mathbf{G}}\, c_i(\mathbf{G})\, \mathbf{G}^2 \quad \{E_k\}$

$V^{NL}(\mathbf{G}) \; \{E^{NL}\}$

$\rho(\mathbf{G}) \xleftarrow{\text{FFT}} \rho(\mathbf{x})$

$V^{loc}(\mathbf{G}) + V_H(\mathbf{G}) \quad \{E^{loc}+E_H\}$

$= V_{LH}(\mathbf{G}) \xrightarrow{\text{FFT}}$

$V_{xc}(\mathbf{x}) \quad \{E_{xc}\}$

$+ V_{LH}(\mathbf{x})$

$= V_{LOC}(\mathbf{x});$

$V_{LOC}(\mathbf{x})\psi_i(\mathbf{x})$

$V_{LOC}(\mathbf{G})c_i(\mathbf{x}) \xleftarrow{N^*\text{FFT}}$

$+ V^{NL}(\mathbf{G}) + \Sigma_{\mathbf{G}}\, c_i(\mathbf{G})\, \mathbf{G}^2$

$$\frac{\delta E}{\delta c_i(\vec{G})} = \hat{H} c_i(\vec{G}) \qquad \left\{ \hat{H} \middle| \psi_i \right\rangle \}$$

Practical implementation

- **G=1,…,*M*** (*loop on reciprocal vectors*) are distributed (via MPI) in a parallel processing in bunches of ***M***/(*nproc*)
- ***i*=1,…,*N*** (*loop on electrons*) is distributed (via MPI) as well
- ***I*=1,…,*K*** (*loop on atoms*) generally does not require parallelization
- The scaling of the algorithm is $O(NM)$for the kinetic term, $O(NM\log M)$ for the local potential and $O(N^2M)$ for the non-local term and orthogonalization procedure (*all other quantum chemical methods scale as* $O(MN^3)$ M=basis set)

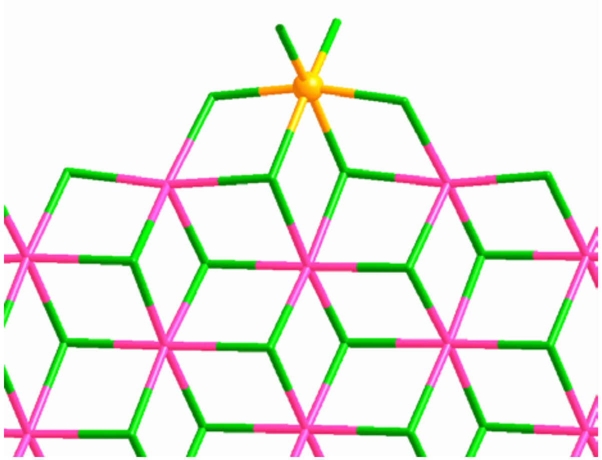
- http://www.cpmd.org
- http://www.cscs.ch/~aps/CPMD-pages/CPMD/Download

Supported platforms (LAPACK/BLAS required)

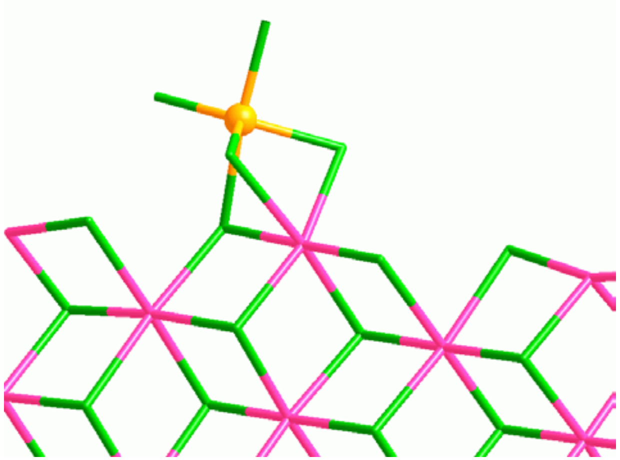
IBM-RISC
IBM-SP2
IBM-SP3
IBM-SP3-SMP
IBM-SP4
IBM-270
CRAY-YMP
CRAY-C94
CRAY-T90
CRAY-T3D
CRAY-T3E
CRAY-T3E-PACX
SGI-ORIGIN
SGI-ORIGIN-MPI
DEC-ALPHA
DEC-ALPHA-MPI
COMPAQ-SC80
SUN
NEC-SX4
NEC-SX5
NEC-SX5-MPI
HP
HP-MPI
HITACHI-SR2201
HITACHI-SR8000
HITACHI-SR8KJP
FUJITSU-VPP5000
FUJITSU-VPP
FUJITSU-VPP-MPI
FUJITSU-VPP5KJP
FUJITSU-VPP-JPN
FUJITSU-VPP-MPJP
PC-ABSOFT
PC-PGI
PC-PGI-MPI
PC-IFC
LINUX-ALPHA
LINUX-ALPHA-MPI

Example of application: Ziegler-Natta catalysis

- Ziegler-Natta catalysis is by far the most important process in the industrial production of polyolefins with high stereoselectivity
- Experimental probes fail in recovering the microscopic picture due to the very fast reaction and the low percentage of active sites

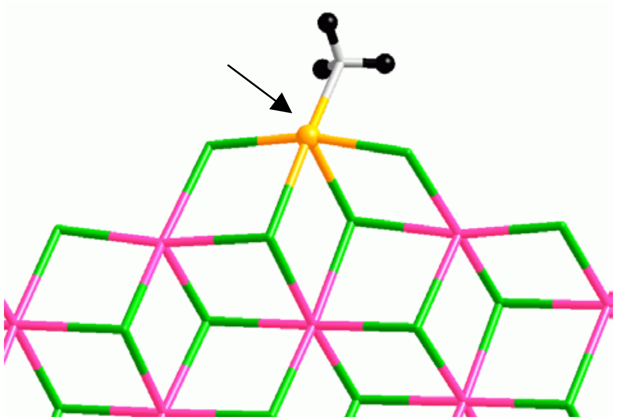


Octahedral Ti 6-fold on $MgCl_2$ (110) surface as proposed by Corradini and co-workers. E_{bind}= 40.3 kcal/mol

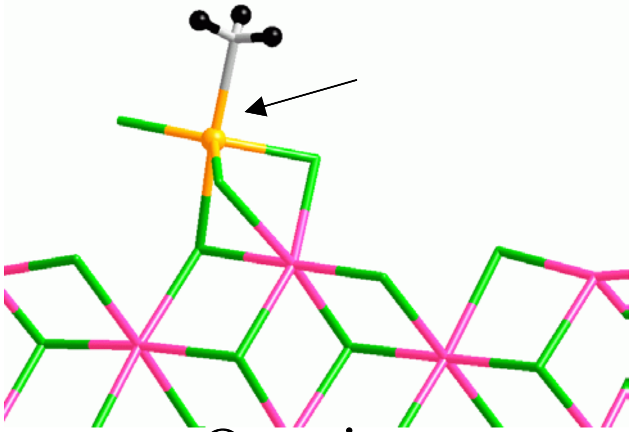


5-fold Ti site on $MgCl_2$ (110) surface obtained from CPmd. E_{bind}= 29.4 kcal/mol

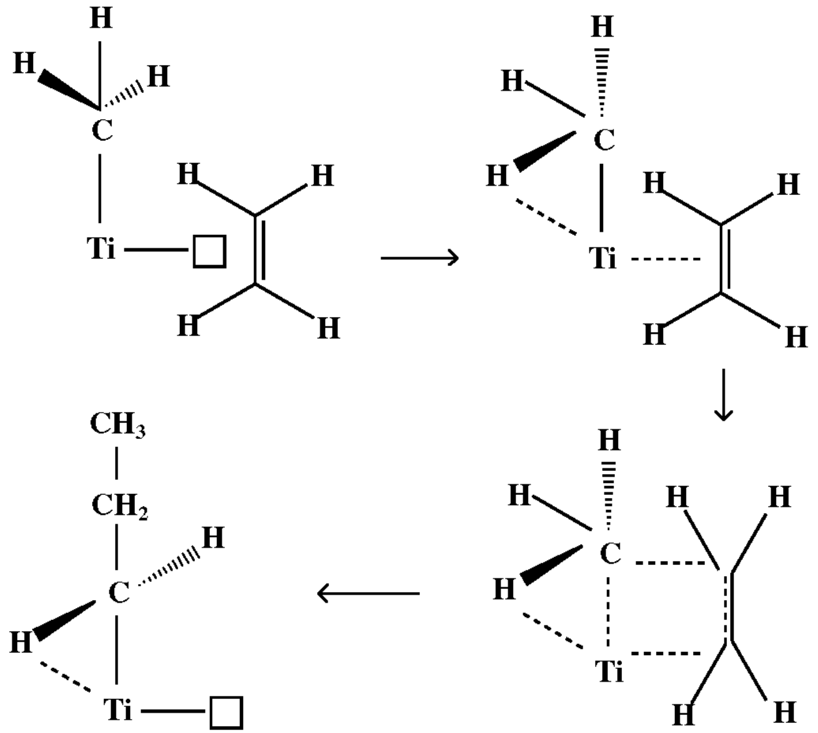
Active catalytic centers: a polymer chain initiator (CH_3) and a vacant site is required



Corradini site

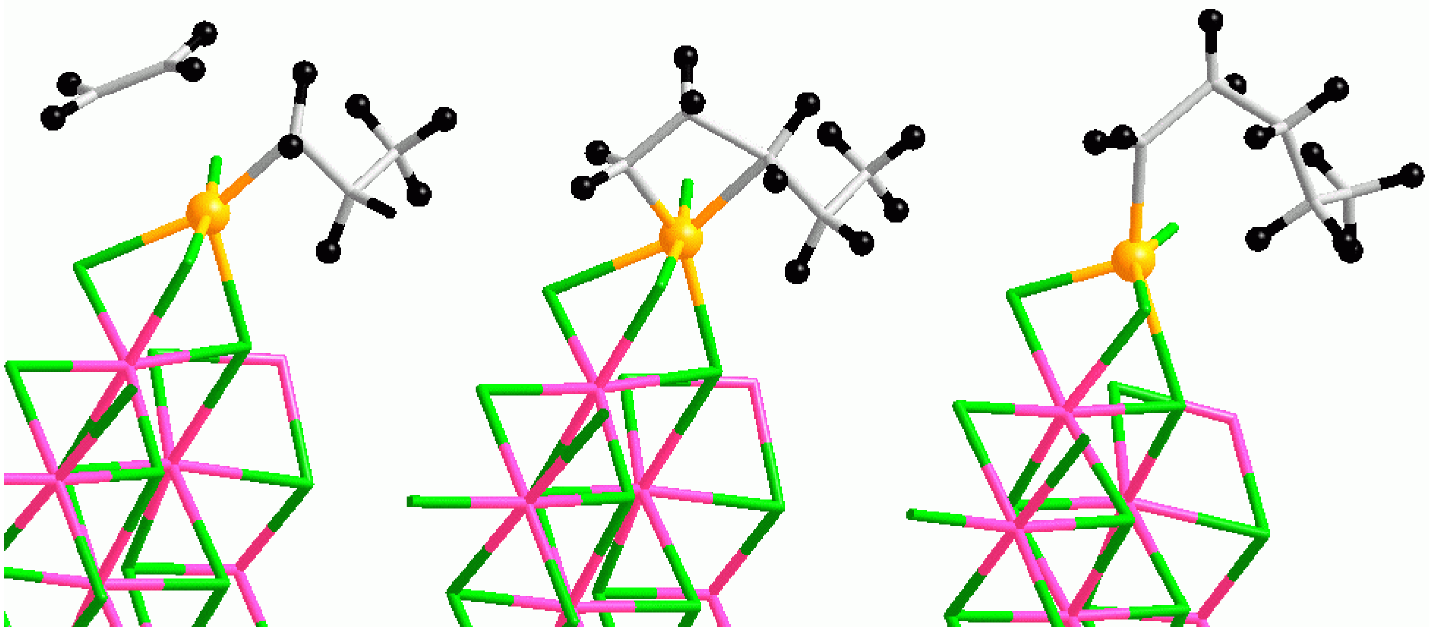


Our site



Reaction scheme

Catalysis of polyethylene: how a polymer chain is produced



Formation of a π-complex on the vacant site

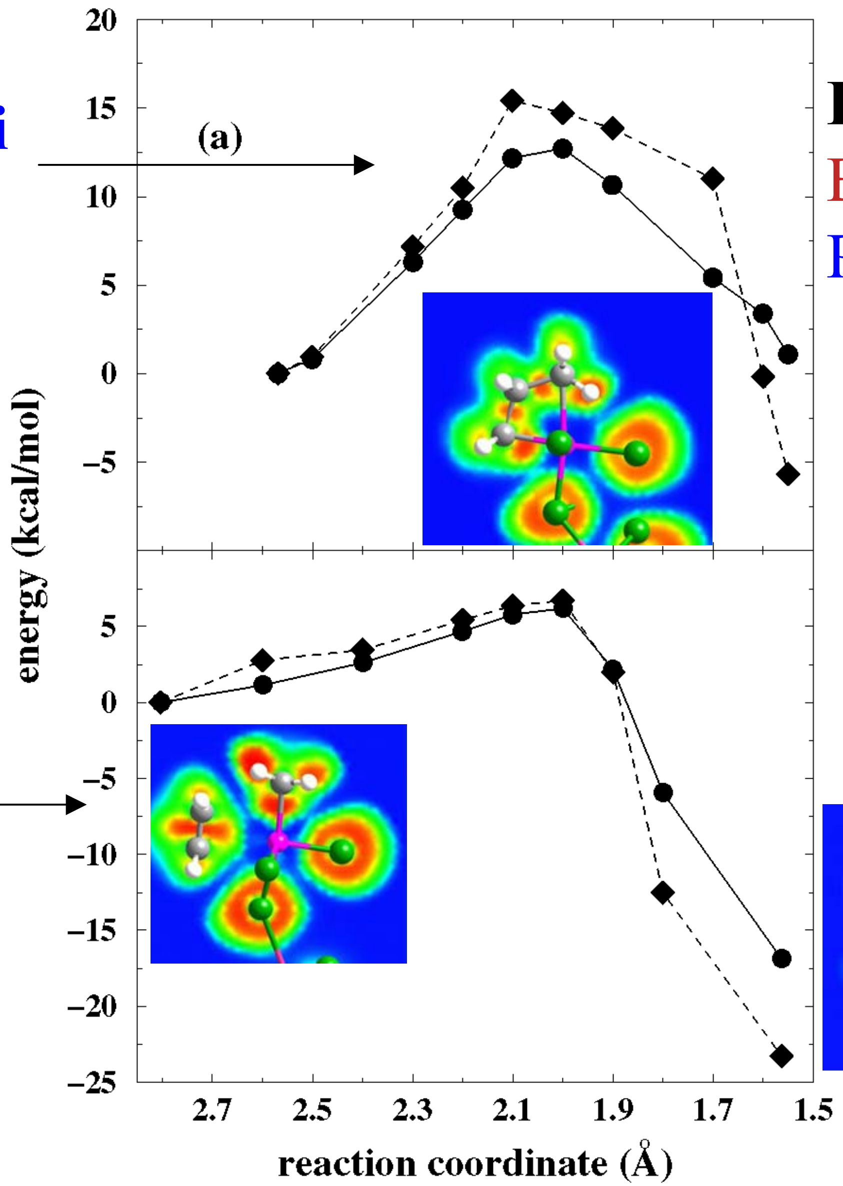
Transition state at 6-12 kcal/mol activation barrier

Final product: insertion of a new monomer

Catalysis of polyethylene: energetics

Corradini site

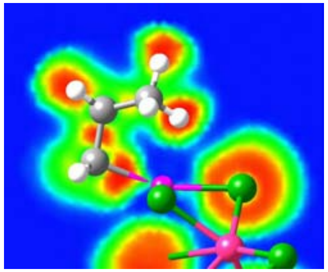
Our site



Experiment:

Barrier = 6-12 kcal/mol

Product = -22 kcal/mol



Conclusions

- The reaction pathway leading to the formation of a polyolefin in a realistic system has been simulated and understood for the first time
- A new catalytic site highly active and naturally stereoselective has been found
- The rate limiting step (insertion) of the reaction has been computed providing contact to the experimental evidence

Collaborations:

- Michele Parrinello, CSCS and ETHZ (Switzerland)
- Kiyoyuki Terakura, RICS-AIST (Japan)
- H. Weiss, BASF AG (Germany)
- S. Hueffer, BASF AG (Germany)

Related publications:

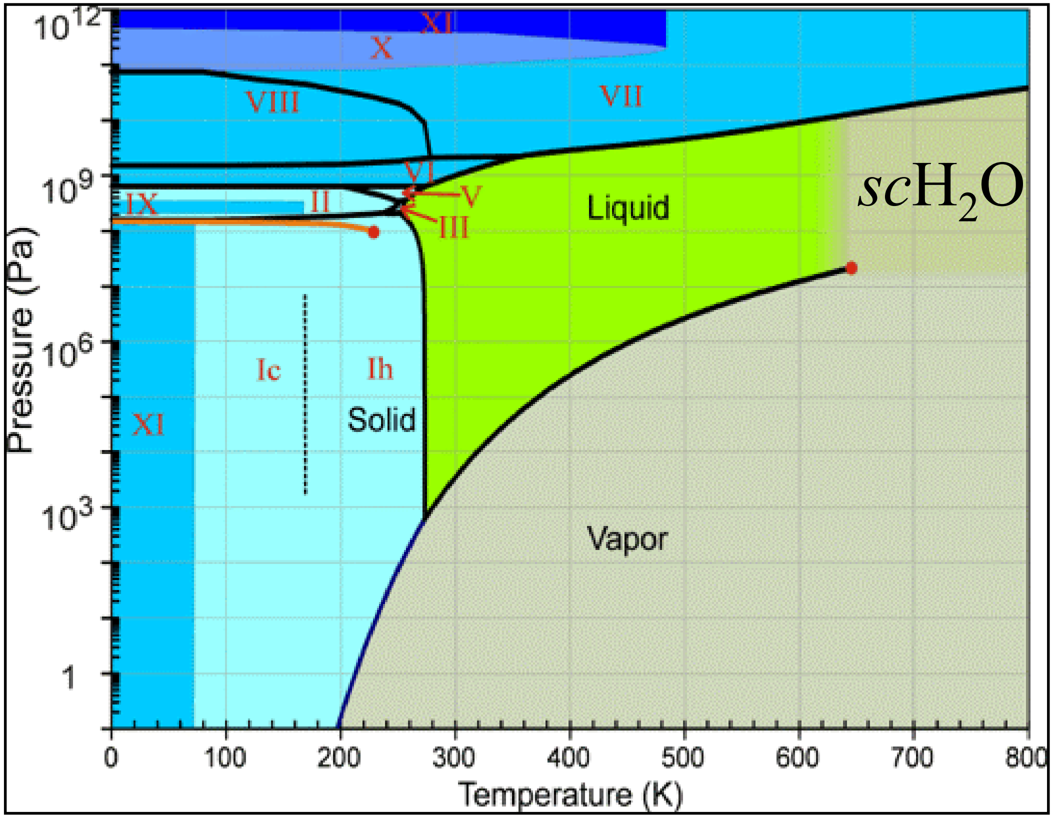
- M. Boero, M. Parrinello and K. Terakura, *J. Am. Chem. Soc.* **120**, 2746 (1998)
- M.B. et al., *Surf. Sci.* **438**, 1 (1999)
- M.B. et al., *J. Am. Chem. Soc.* **122**, 501 (2000)
- M.B. et al., *J. Phys. Chem. A* **105**, 5096 (2001)
- M.B. et al. *Int. J. Mol. Sci.* **3**, 395 (2002)
- M.B. et al. *Mol. Phys.* **100**, 2935 (2002)

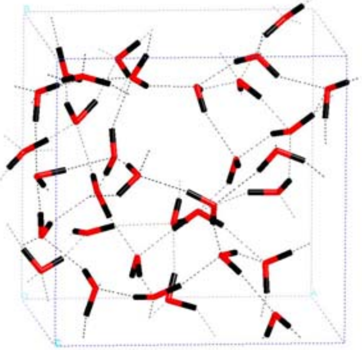
Example of application: supercritical water

◆Water above its critical point T=654 K, P=22.1 MPa, ρ=0.32 g/cm^3 has important technological applications:

i) As an advanced tool for the treatment of hazardous wastes

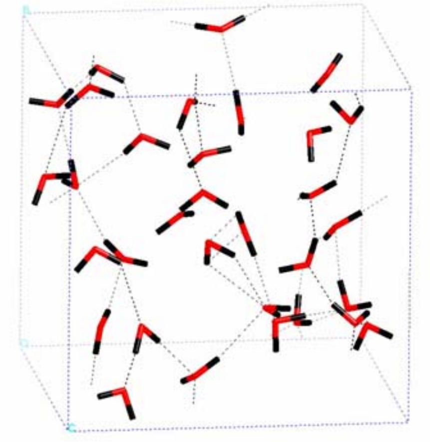
ii) As a promoter of non-catalytic chemical reactions





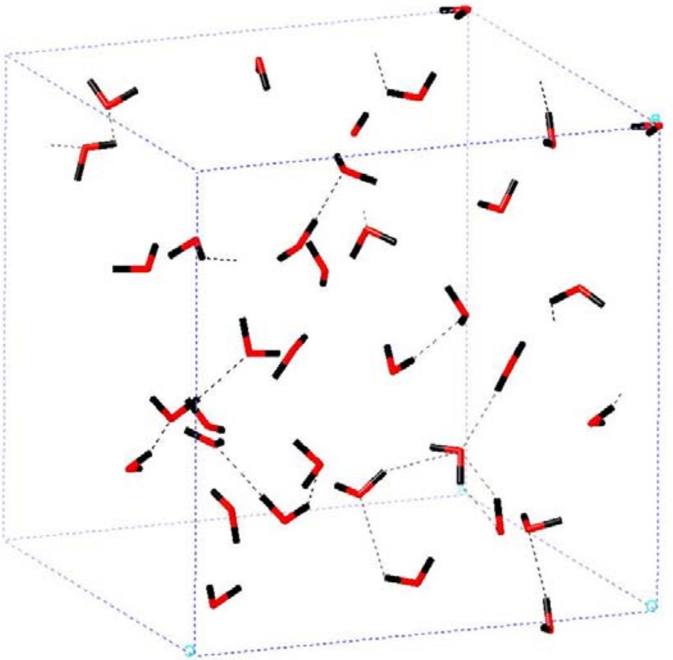
T=300 K

ρ=1.00 g/cm^3



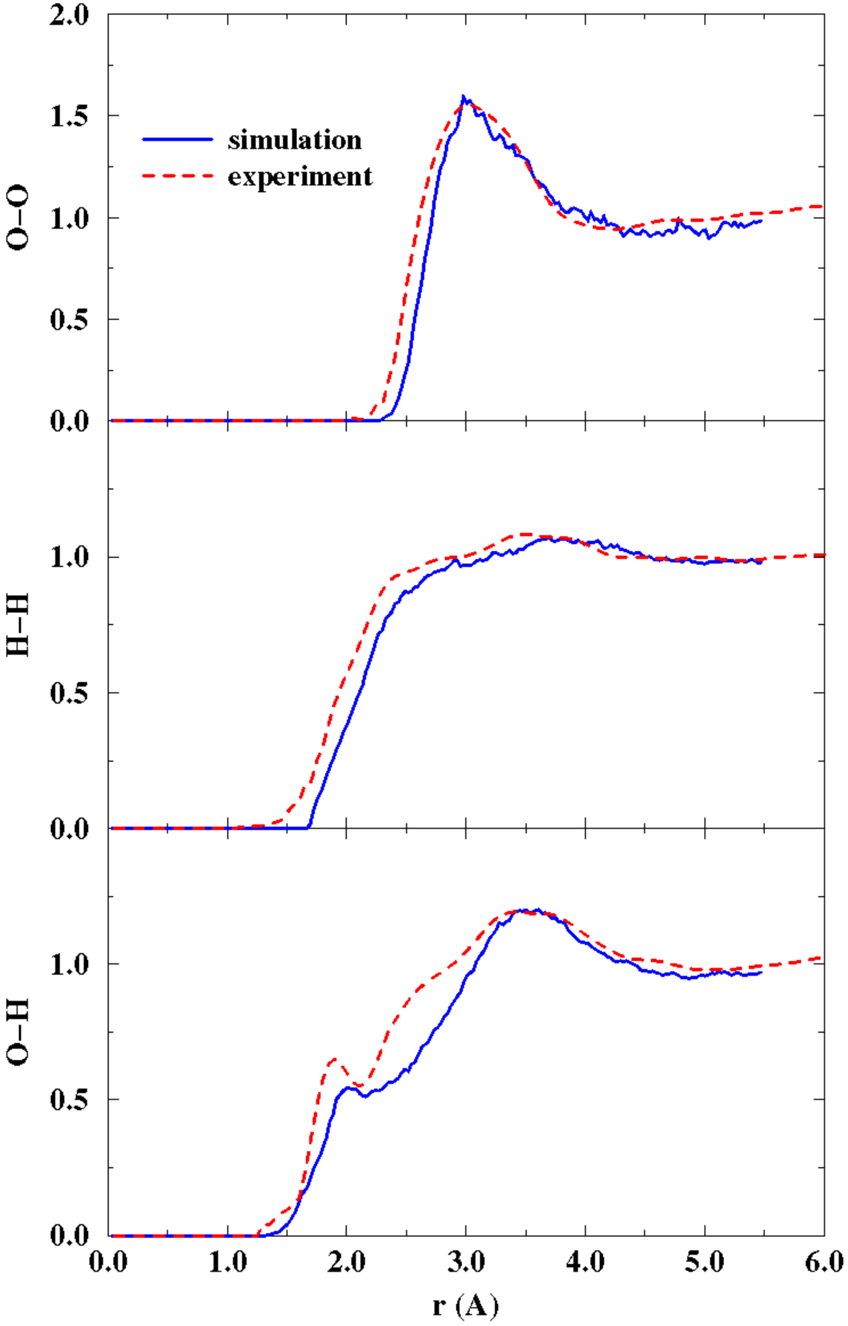
T=653 K

ρ=0.73 g/cm^3



T=647 K

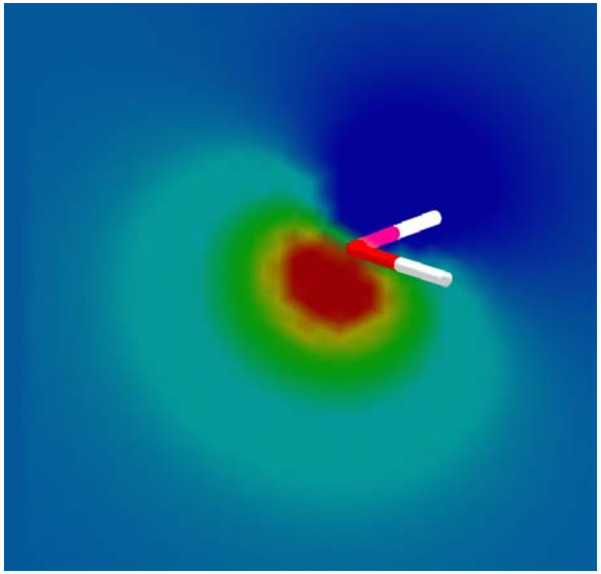
ρ=0.32 g/cm^3

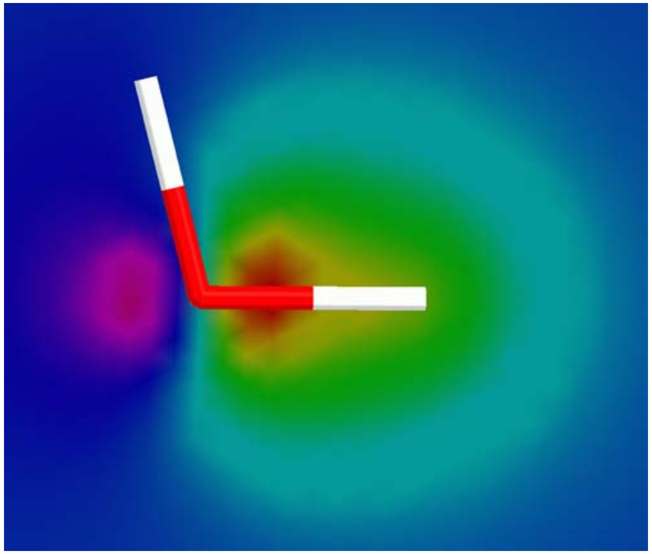


RDF of $sc\text{H}_2\text{O}$ at 0.73 g/cm^3 and 653 K

- Experiment: T. Tassaing et al., *Eur. Phys. Lett*. **42**, 265 (1998)

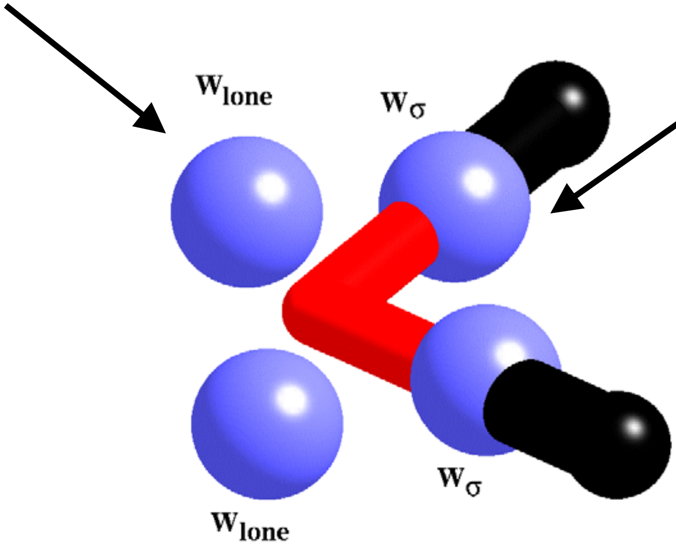
Shorthand representation of the electronic structure



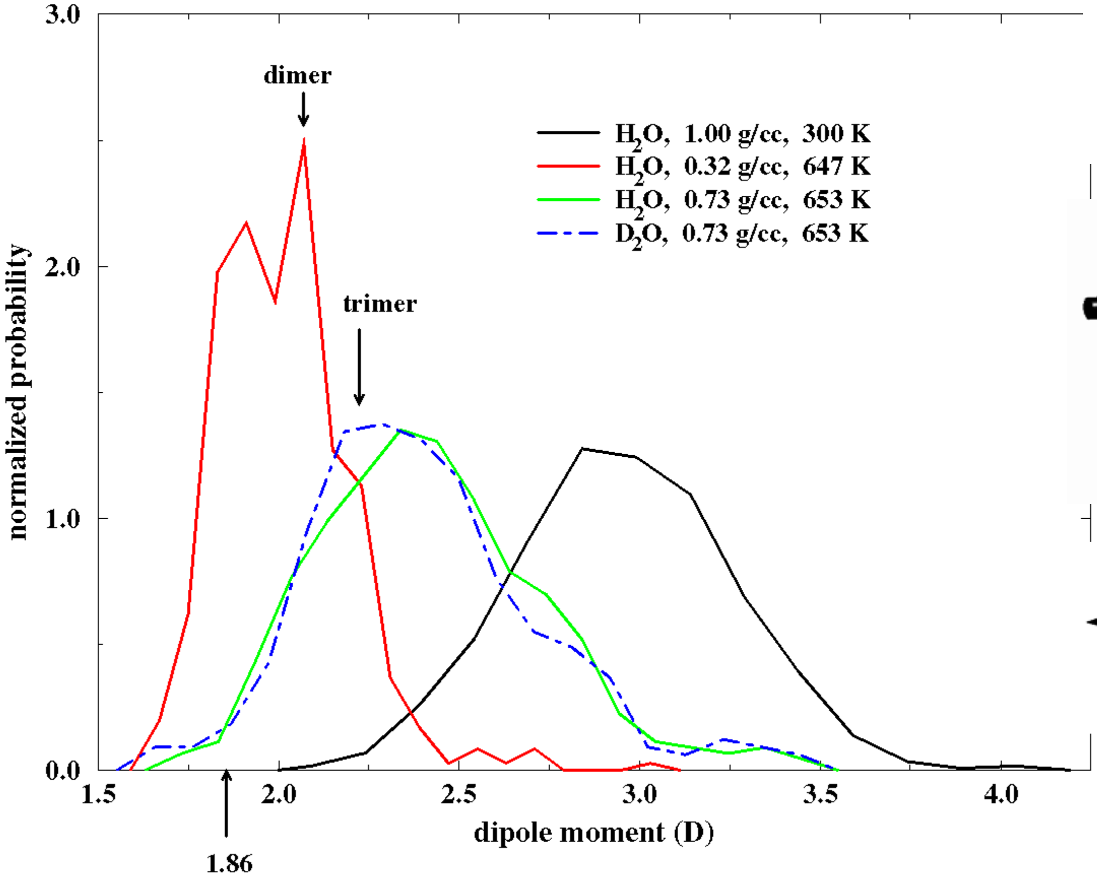


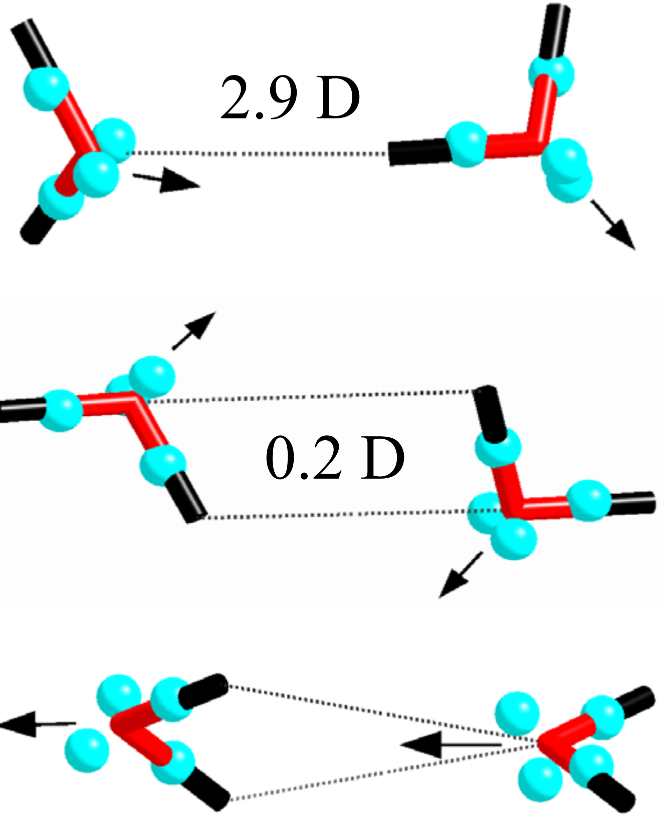
Lone pairs

σ bond



Molecular dipole moment distributions and new H-bond structures found:

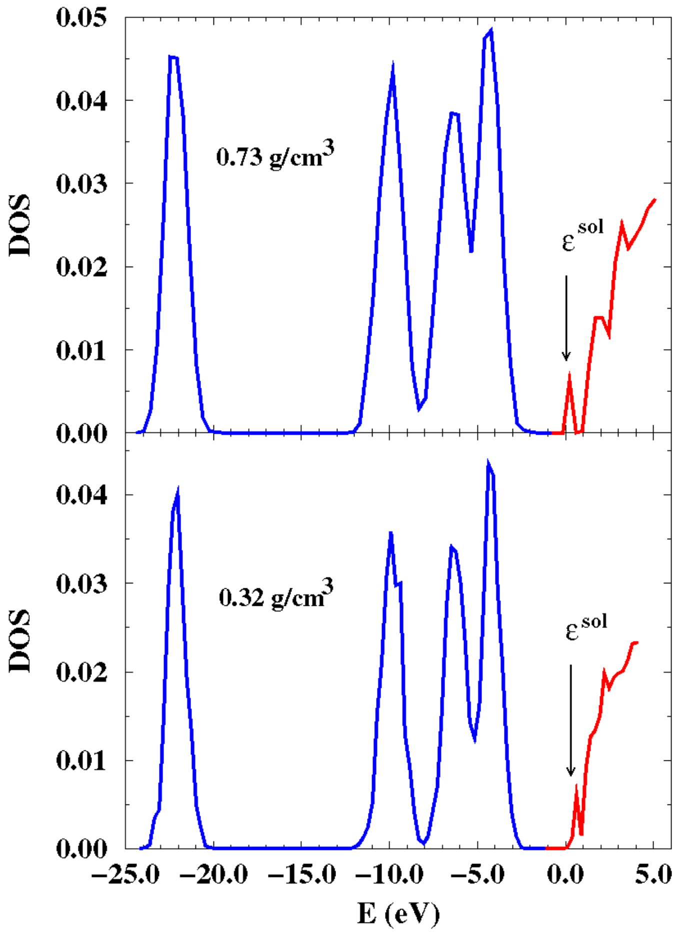


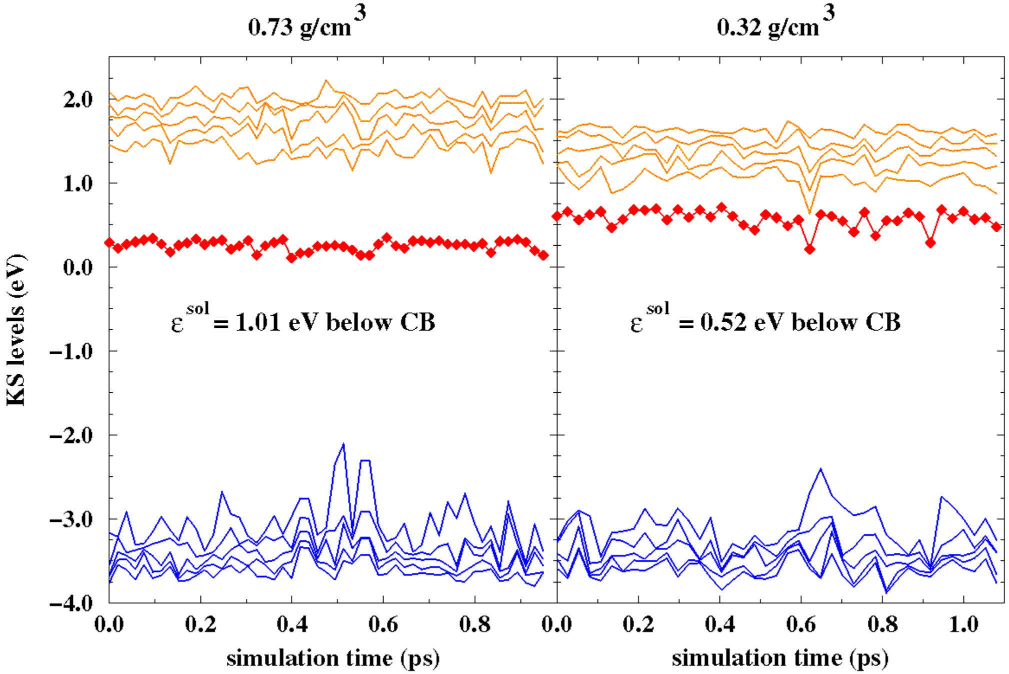


4.4 D

CHB and BHB are local minima accessible **only** to *sc*H_2O

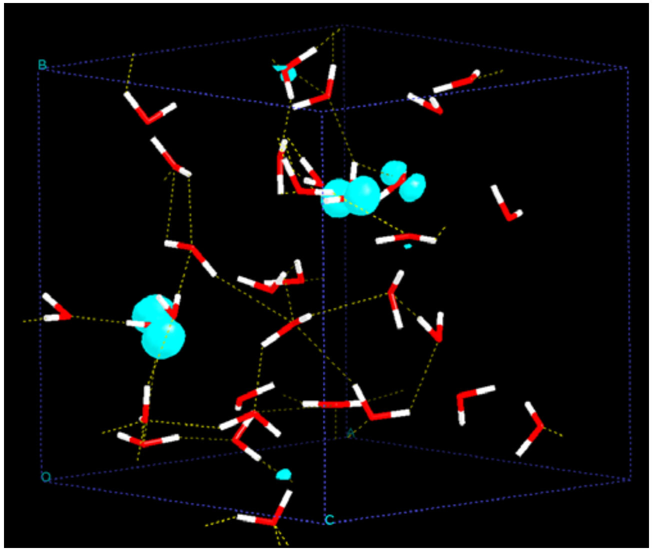
Electronic structure of *sc*H_2O: DOS and HOMO-LUMO KS levels evolution during the dynamics



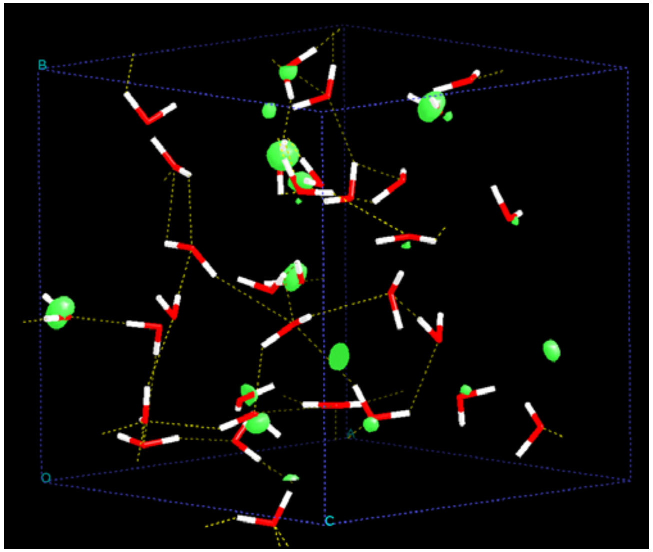


$$DOS = \left\langle \frac{1}{N} \sum_i \delta \left(E - \varepsilon_i \right) \right\rangle$$

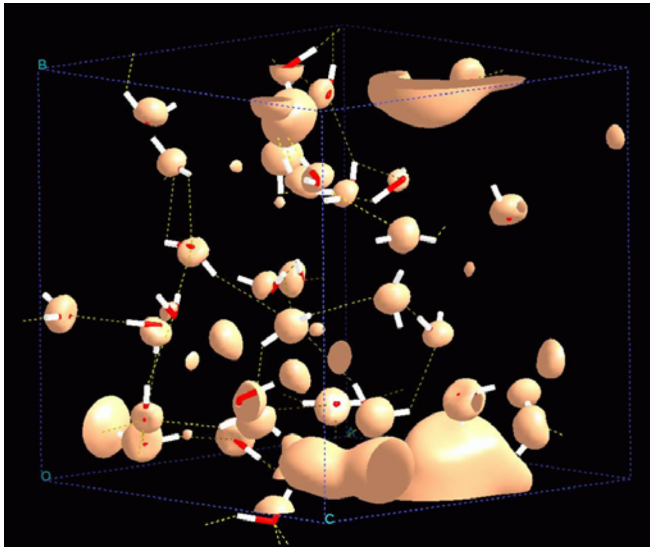
Electronic structure of *sc*H_2O in terms of KS orbitals: how do they look like ?



HOMO
HOMO-1
HOMO-2

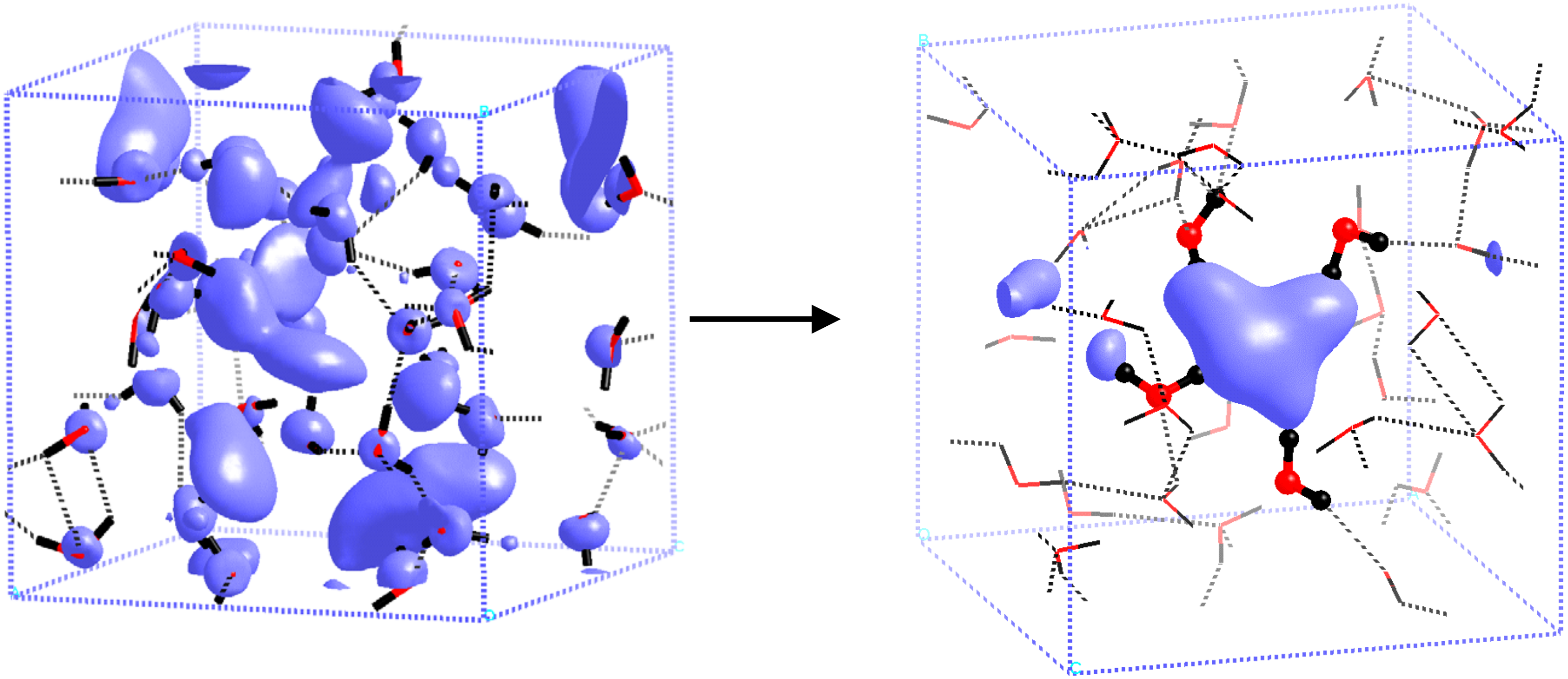


LUMO+1
LUMO+2
LUMO+3



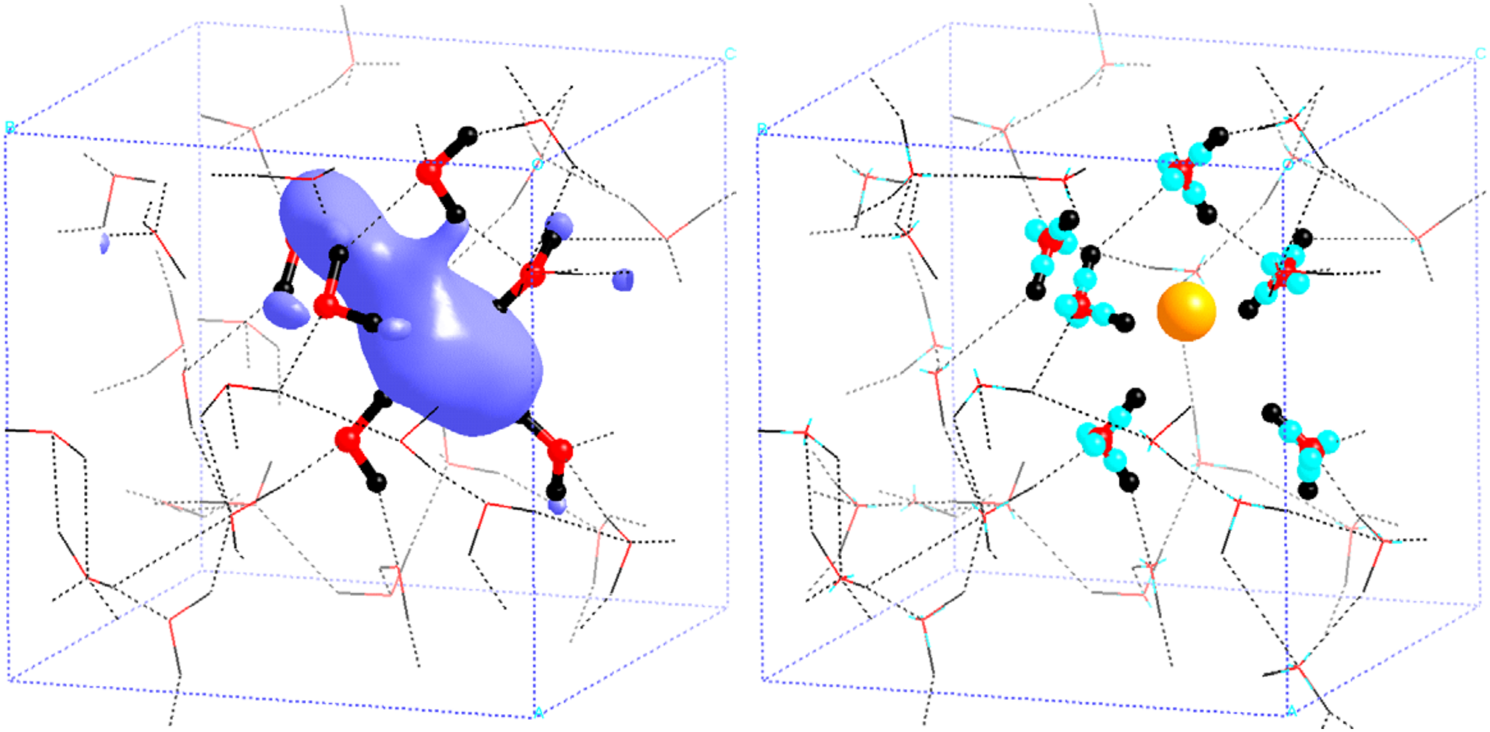
LUMO: the dispersed level spreads in the cavities in between the molecules where no H-bonds are present

…and if an electron is added to the system



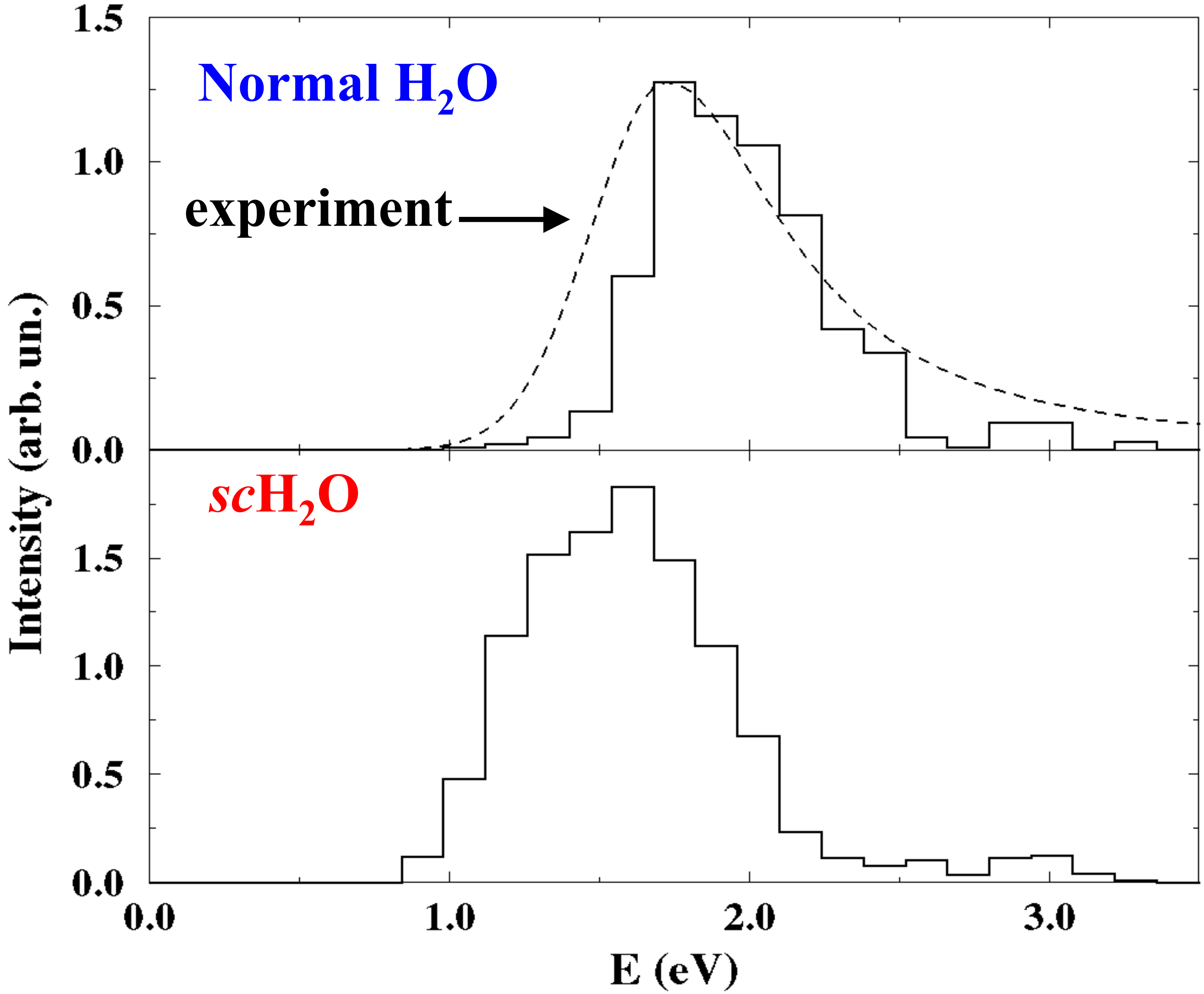
- The electron fills the dispersed LUMO level
- It creates (in about than 0.7 ps) a single cloud where H_2O molecules form a solvation shell around it

And in normal liquid water (after ~1.6 ps)



- Wannier function as isosurface (left) and WFC of the solvated electron (right). In normal water 6 water molecules form the solvation shell

Optical absorption spectra. Experiment from Jou and Freeman (*J. Phys. Chem*. **83**, 2383 (1979))



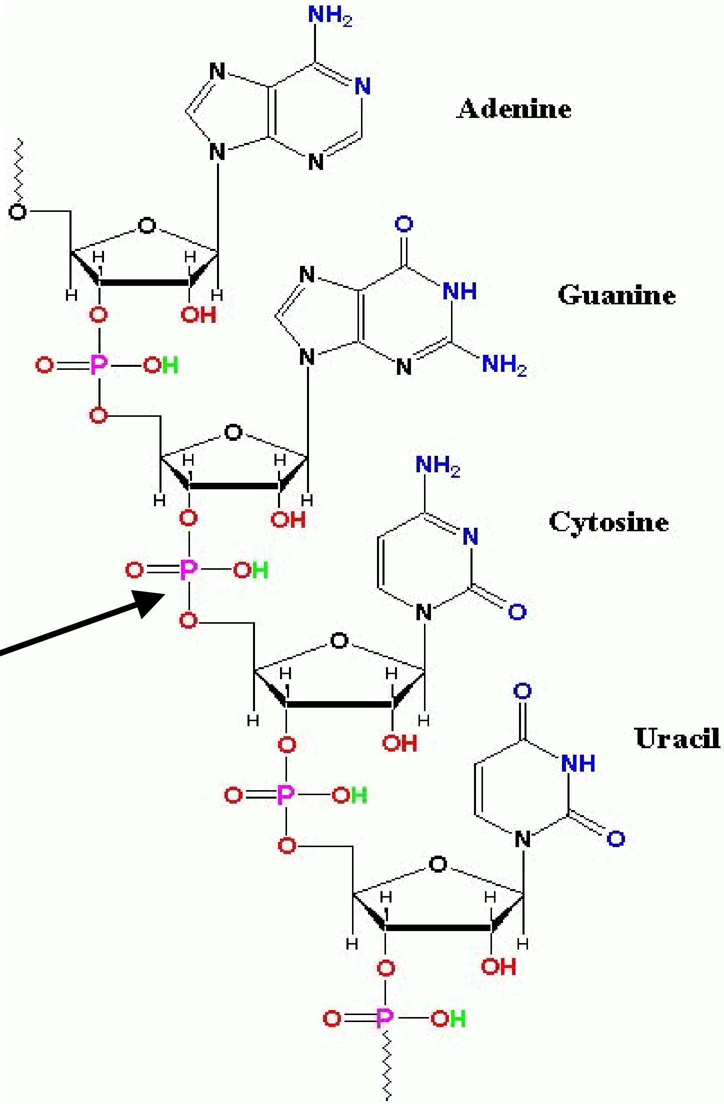
Collaborations:

- Kiyoyuki Terakura, RICS-AIST (Japan)
- T. Ikeshoji, RICS-AIST (Japan)
- C. C. Liew, RICS-AIST (Japan)
- Michele Parrinello, CSCS and ETHZ (Switzerland)

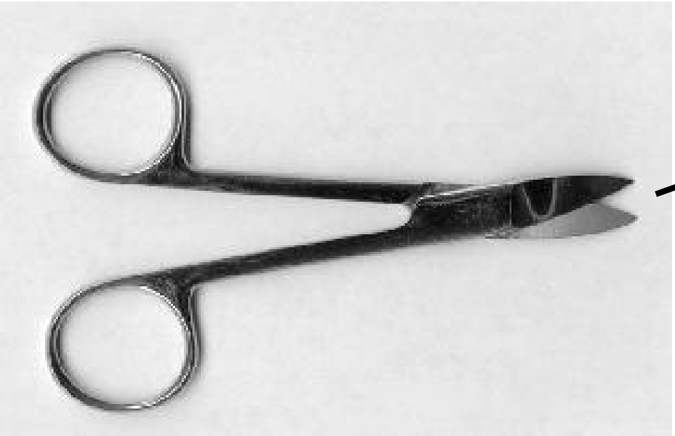
Related publications:

- M. Boero, K. Terakura, T. Ikeshoji, C. C. Liew and M. Parrinello *Phys. Rev. Lett.* **85**, 3245 (2000)
- M.B. et al., *Prog. Theor. Phys. Suppl.* **138**, 259 (2000)
- M.B. et al, *J. Chem. Phys.* **115**, 2219 (2001)

RiboNucleic Acid (RNA) molecules can be engineered to cleave other RNA molecules, are able to inhibit gene expression and can be used in gene therapy of cancer (see D. Zhou and K. Taira, *Chem. Rev.* **98**, 991 (1998))

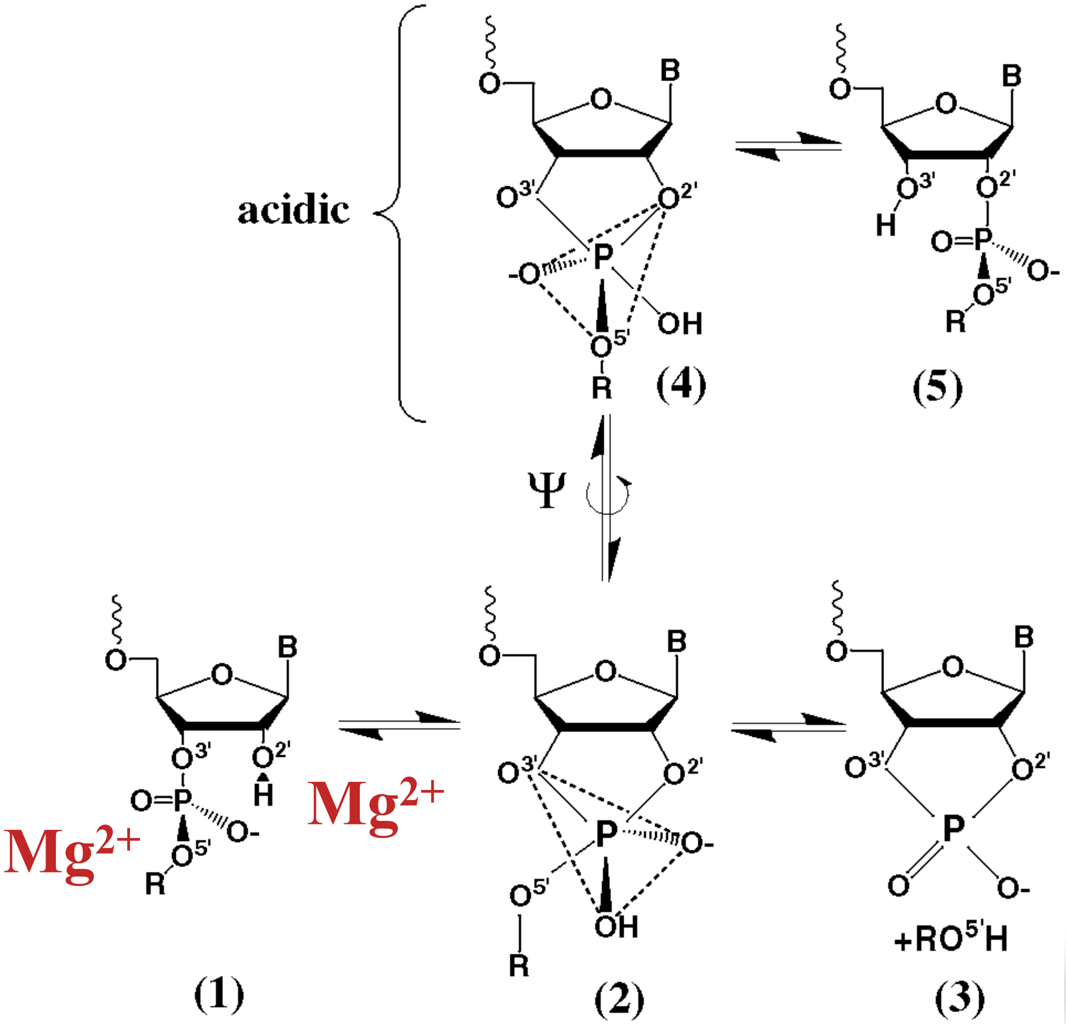


cut the RNA at a target site when a genetic defect occurs…

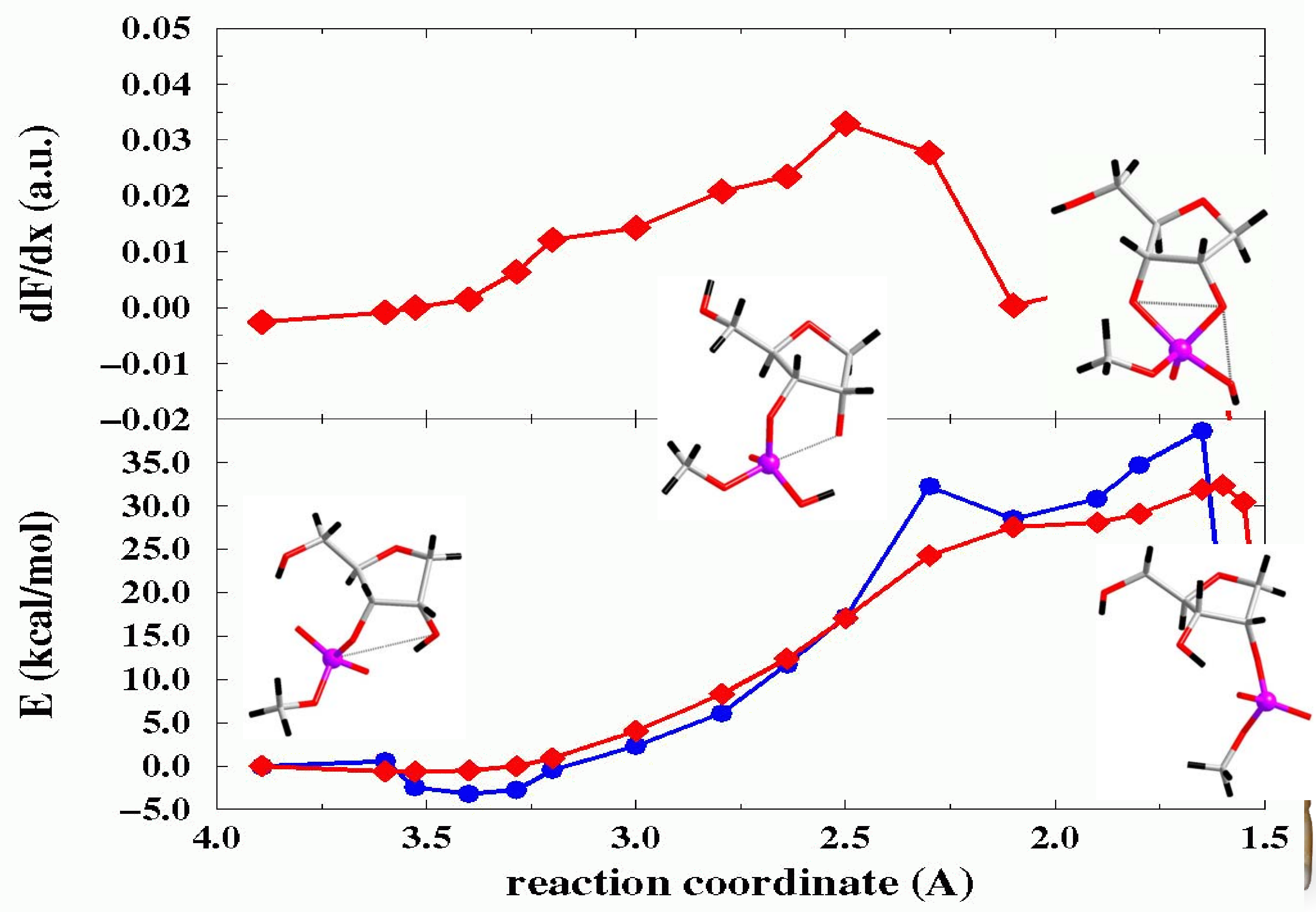


(molecular) scissors =
chemical (**catalytic**) reaction

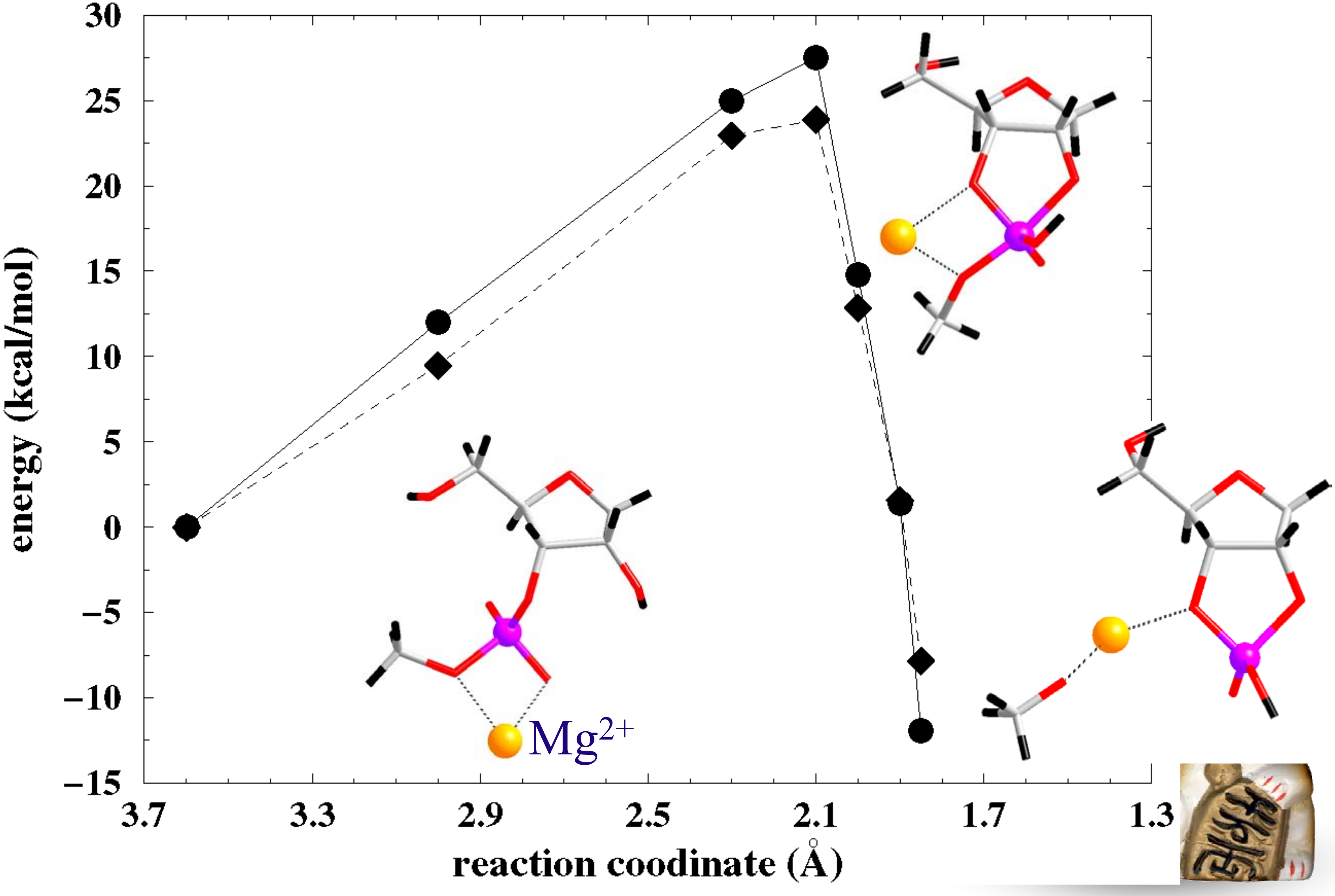
General reaction mechanism: a divalent metal ion is known to be the catalyst (how does it act ?)

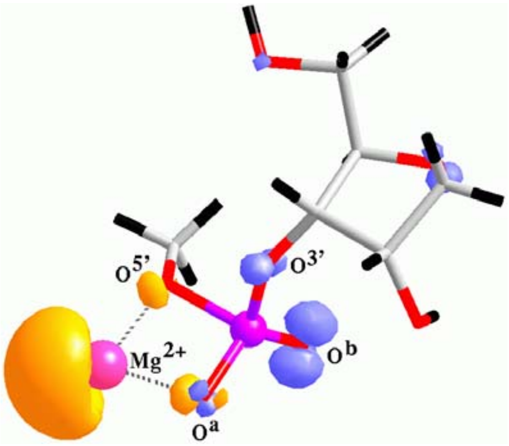


Reaction of the anionic species in vacuum

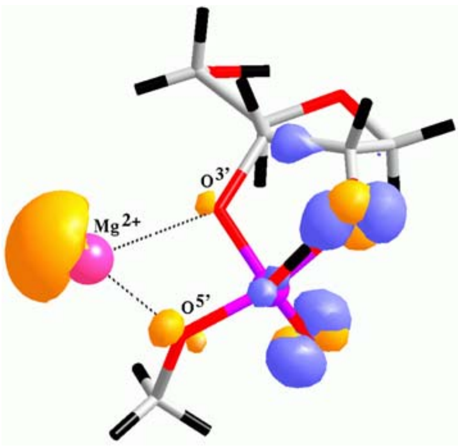


Effect of Mg^{2+} lowering of the activation barrier and selection of the right path

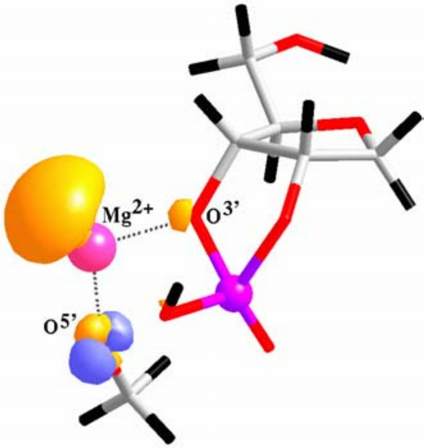




Initial state



transition state

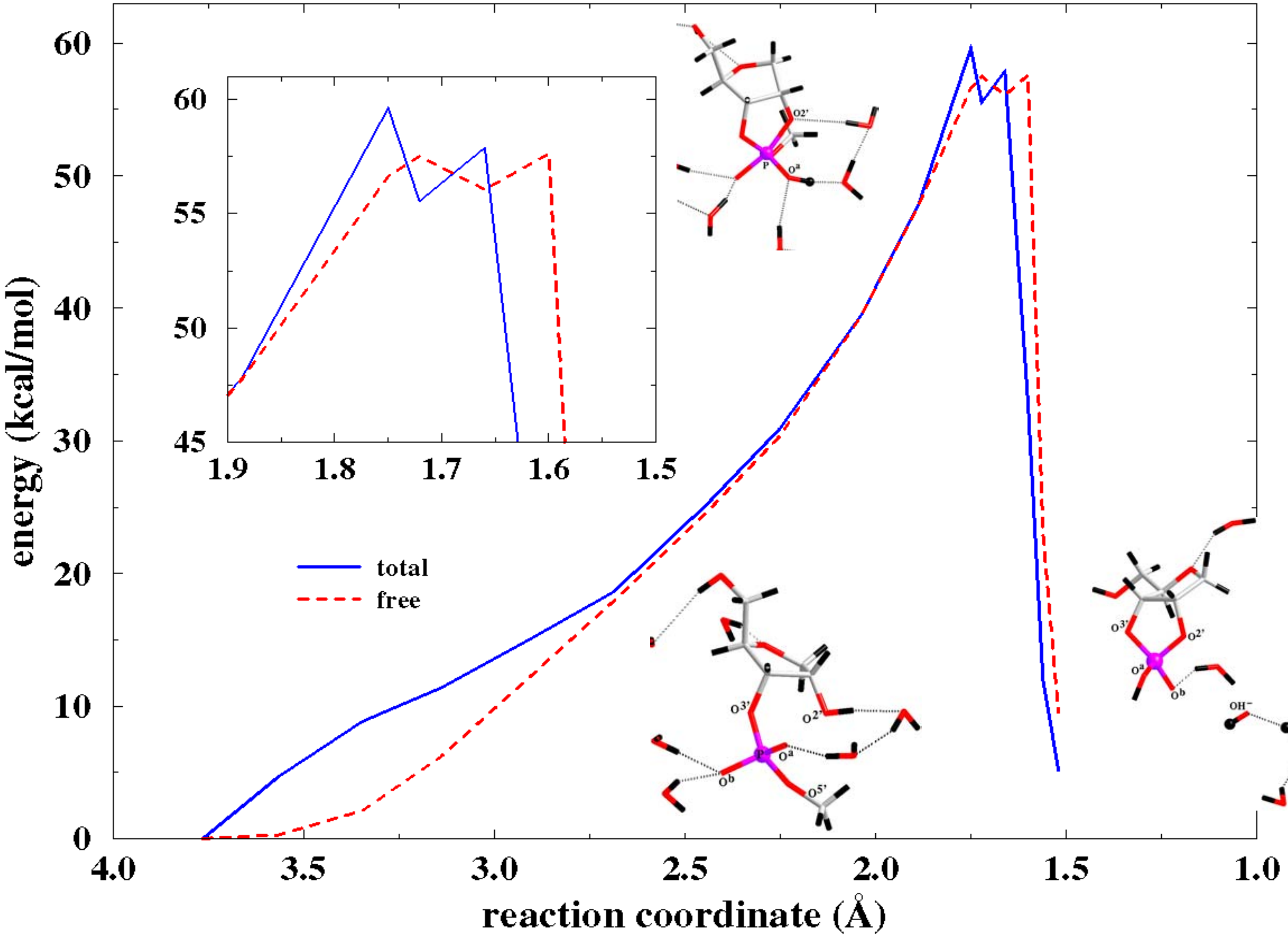


final product

Energy barrier: 40 kcal/mol without Mg^{2+} (and wrong path)
24 kcal/mol with Mg^{2+}

Open questions: which is the effect of a second metal ion close to
$O^{2'}$ in solution ?
Are there better catalysts ?
Is the size important ?
…and DNA ?

Free and total energy profiles of the reaction in solution without the divalent metal ion



Collaborations:

- Kiyoyuki Terakura, RICS-AIST (Japan)
- M. Tateno, RICS-AIST (Japan)

Related publications:

•M. Boero, K. Terakura and M. Tateno *J. Am. Chem. Soc.* **124**, 8949 (2002)

(Press Release)

-日本工業新聞　2面　2002年8月9日
-常陽新聞　1面　2002年8月9日
-日経産業新聞　6面　2002年8月9日
-日刊工業新聞　5面　2002年8月9日
-日本経済新聞　13面　2002年8月16日
-化学工業日報新聞　7面　2002年8月19日

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…and many others !