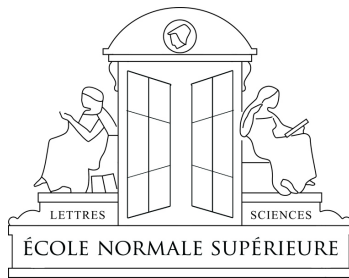# Simulation of molecular processes in radiation chemistry
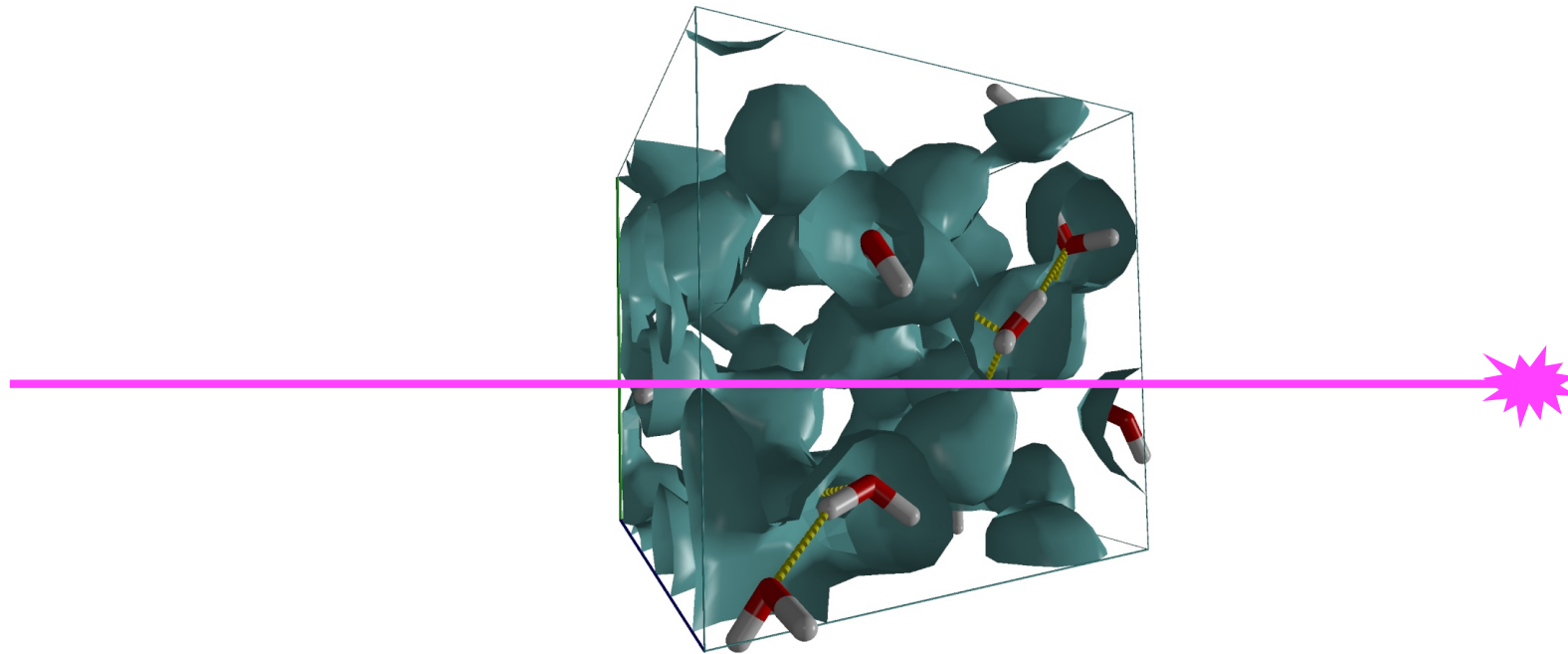
Anne Boutin & Rodolphe Vuilleumier

Département de Chimie

Ecole Normale Supérieure
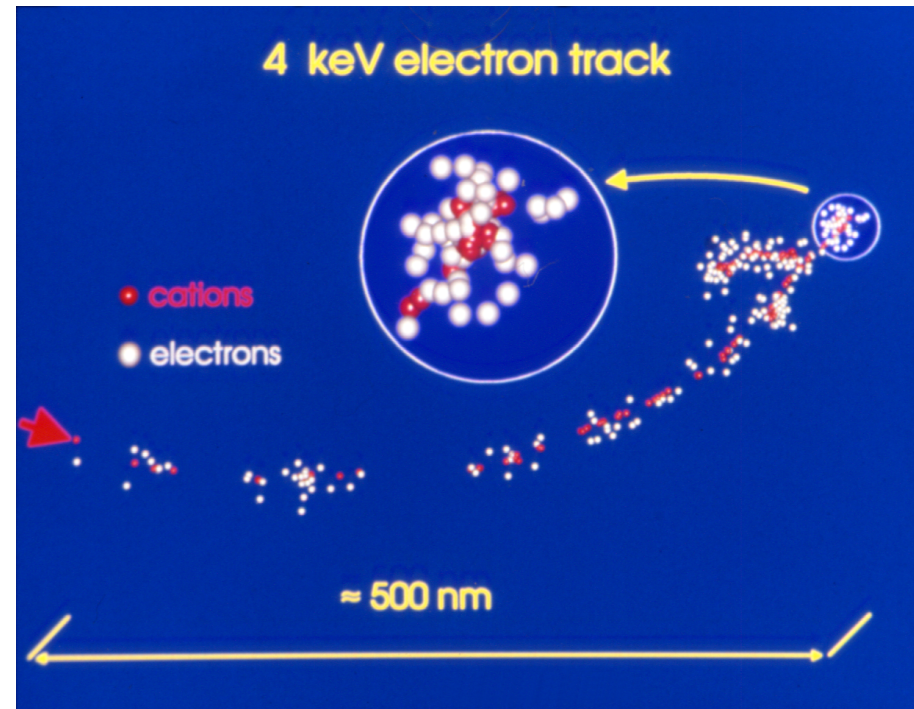
Radiation induced processes at the atomic scale

- How is matter transformed under energy deposition?

- Physical properties and chemical reactions?

Energy deposition

- Energy deposition is highly inhomogenehous

- Transient species

- Hierarchy of events

Three stages description

1. **Physical stage**

   $t < 10^{-15}$ s

   collision of swift ions with molecules in the path

   transport and interaction of secondary e^-, Auger effect

2. **Chemical-physics stage**

   $t \sim 10^{-15}\text{-}10^{-12}$ s

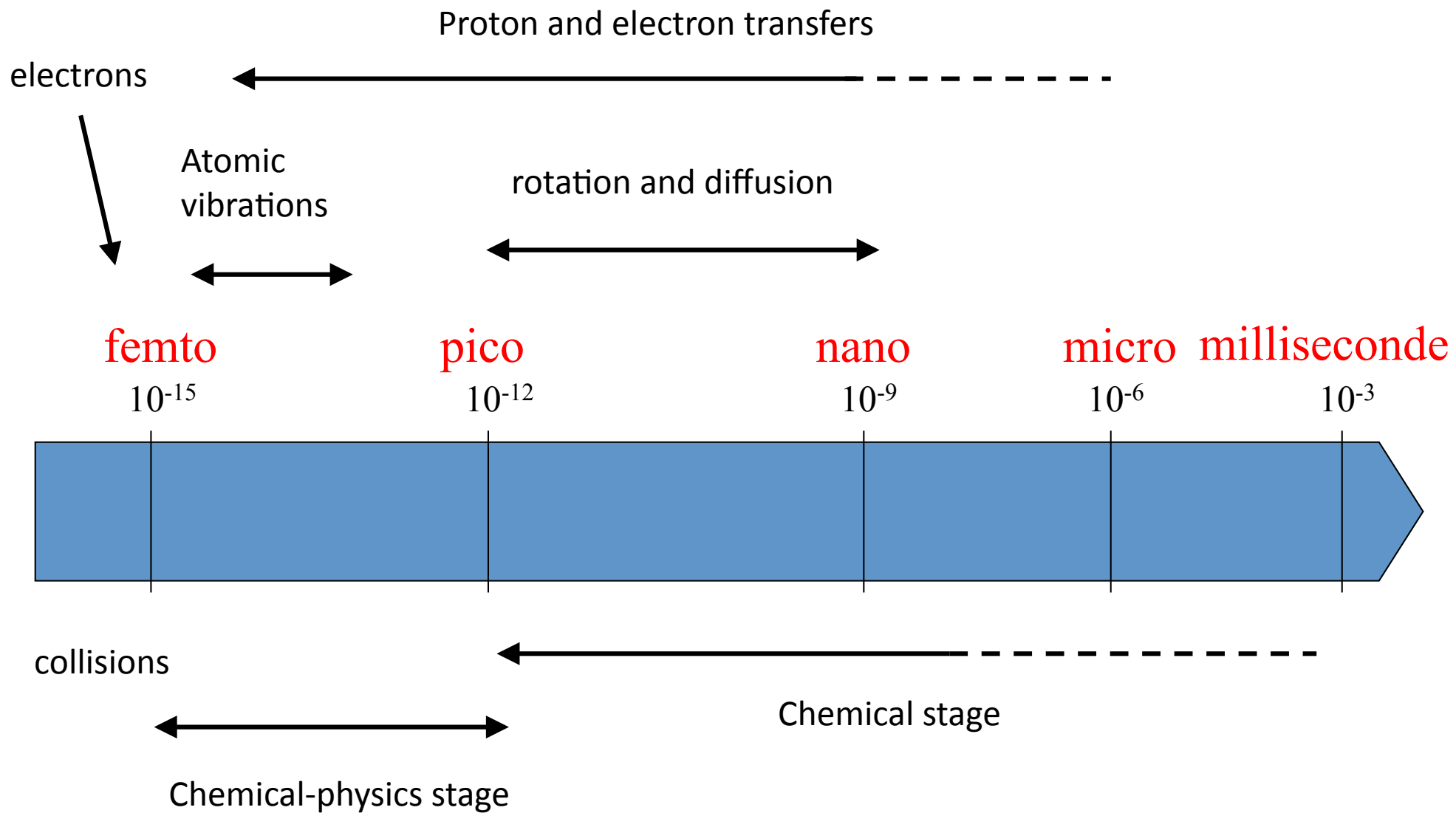   fragmentation, recombination with close partners

3. **Chemical stage**

   $t \gg 10^{-12}$ s

   diffusion of radicals, chemical reactions

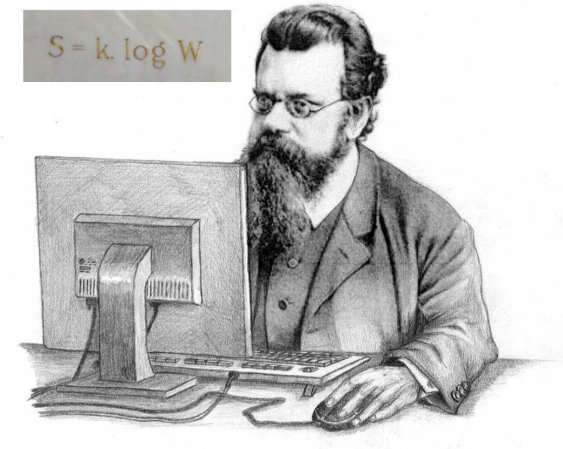And further: biological events…

Time scales involved

Molecular dynamics simulations

Numerical statistical mechanics

- Link macroscopic properties to structure and dynamics at the atomic scale

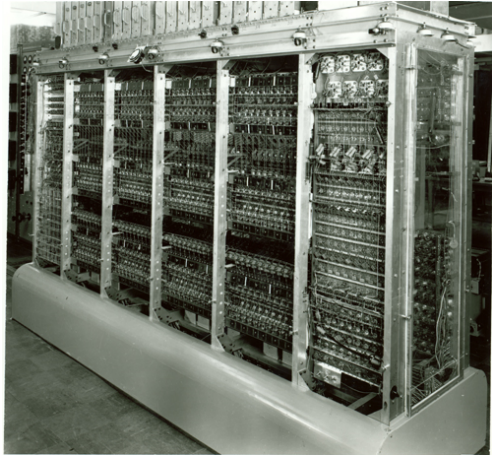- Computation and interpretation of experimental data

- Experiments « in silico »

Principle

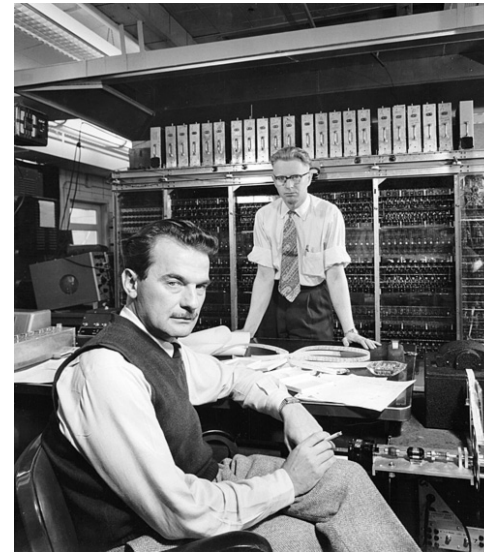Numerical integration of Newton's equation of motion for an assembly of particles

$$\sum \vec{F} = m\vec{a}$$

See: A. Boutin and R. Vuilleumier, Actu. Chimique 353-54, 61-65 (2011)

Early simulations

MANIAC 1 computer

Metropolis

Monte-Carlo Simulation

Metropolis Rosenbluth Rosenbluth Teller Teller (1953) Equation of state of 224 hard disks

Molecular Dynamics

- Fermi Pasta Ulam (1955) 64 coupled oscillators – Study of energy transfer

- Alder and Wainwright (1957) Equation of state of hard spheres

- Gibbons et al. (1960) Dynamics of radiation damage

First simulation of a realistic material: simulation of radiation induced damages in metallic Cu

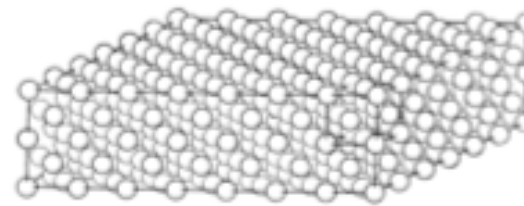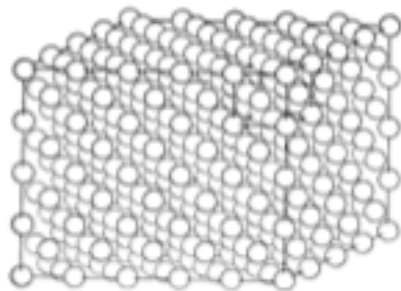## Dynamics of Radiation Damage*

J. B. GIBSON, A. N. GOLAND,† M. MILGRAM, AND G. H. VINEYARD
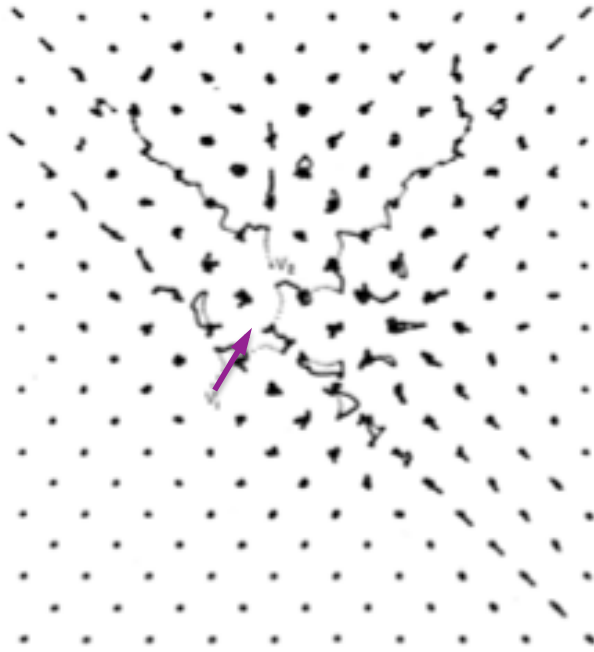Brookhaven National Laboratory, Upton, New York
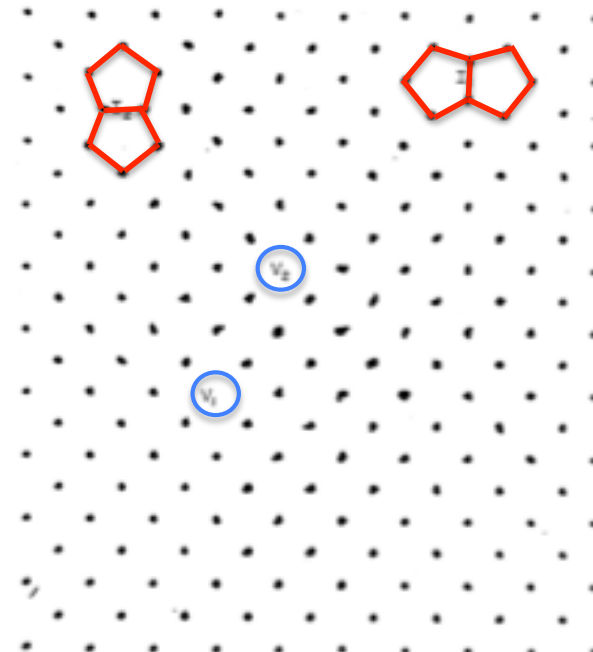
$$u(r) = Ae^{-Br}$$

About a hundred trajectories, each a few 100's femtosecond long, on an IBM 704

Initial momentum transfered to a specific Cu atom
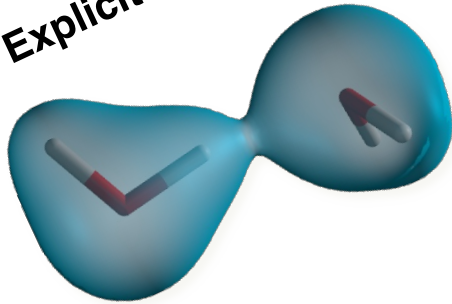
100 *e*V collision

Collision chains

Vacancies and interstitials

Threshold for creating permanent defects: 25-30 *e*V
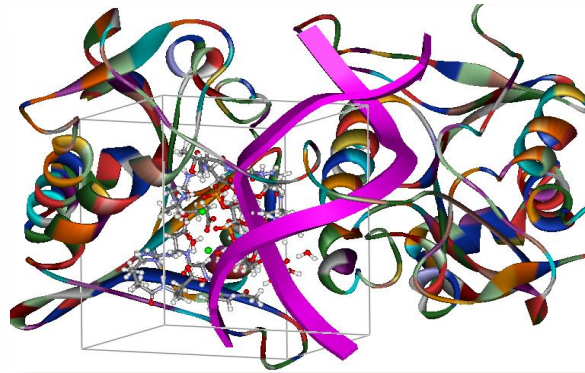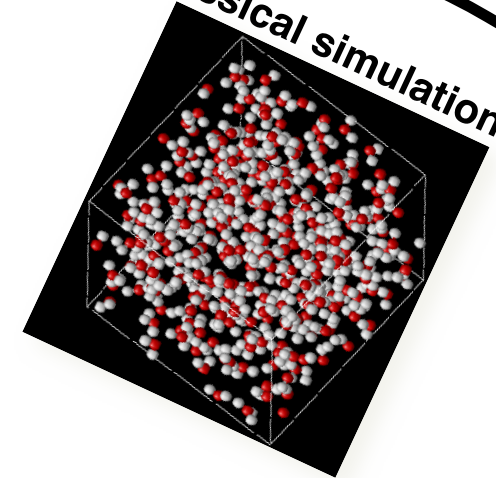
System description

Level of details

Quantum-classical simulations

Explicit electrons

Classical simulations
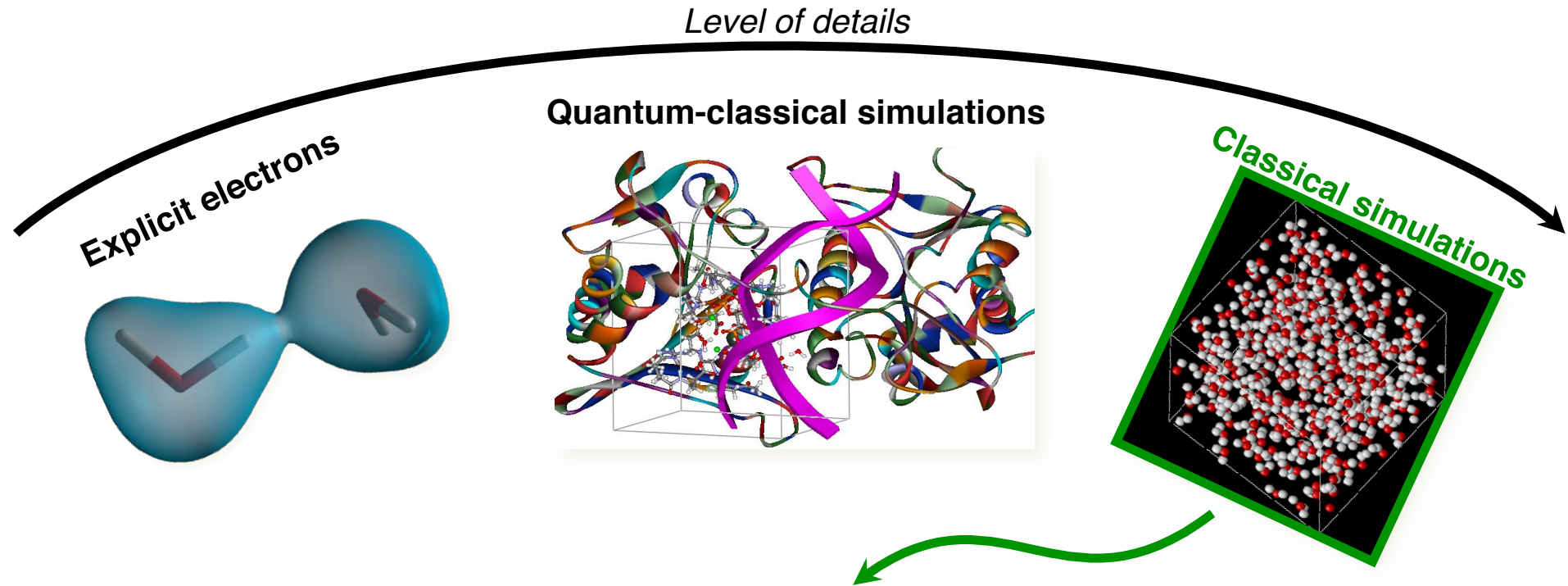
System description

Level of details

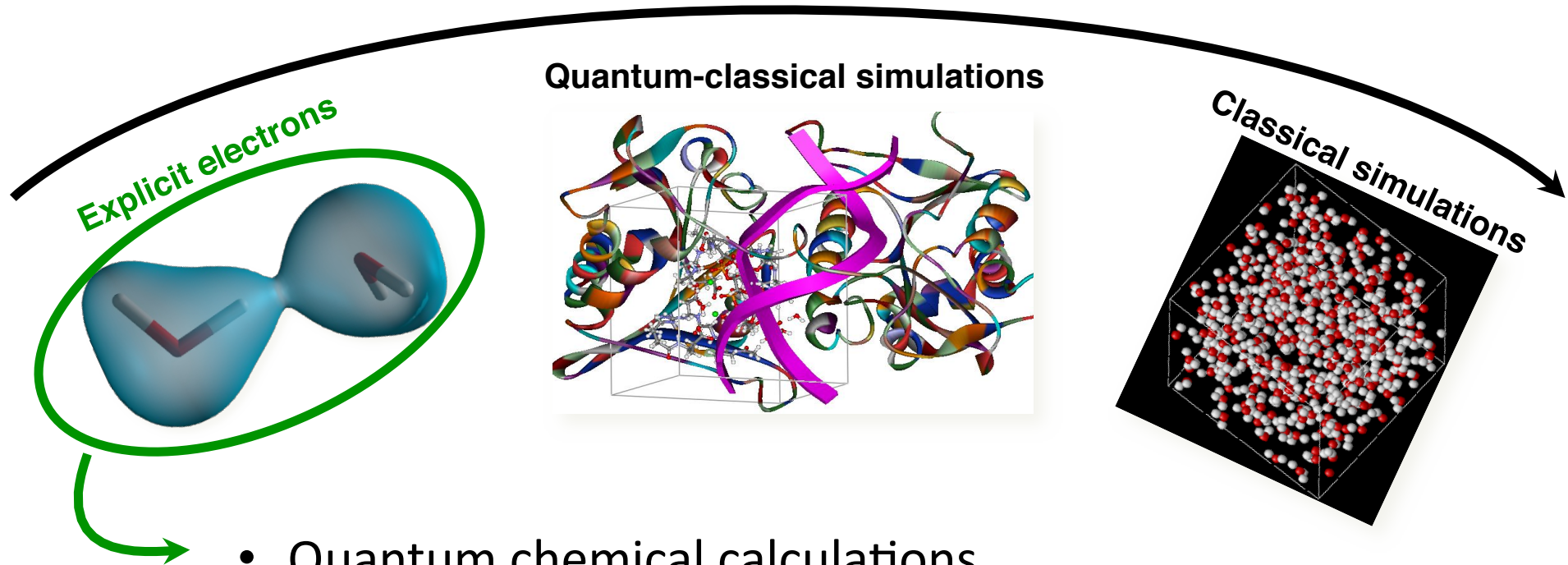**Quantum-classical simulations**

Explicit electrons

Classical simulations

- Analytical modeling of forces
- Large scale simulations (up to 1 000 000's atoms)
- No or limited chemistry

System description

Level of details

Quantum-classical simulations

Explicit electrons

Classical simulations

- Quantum chemical calculations

- Ab initio Molecular Dynamics (forces from quantum calculation)

- Very high computational cost

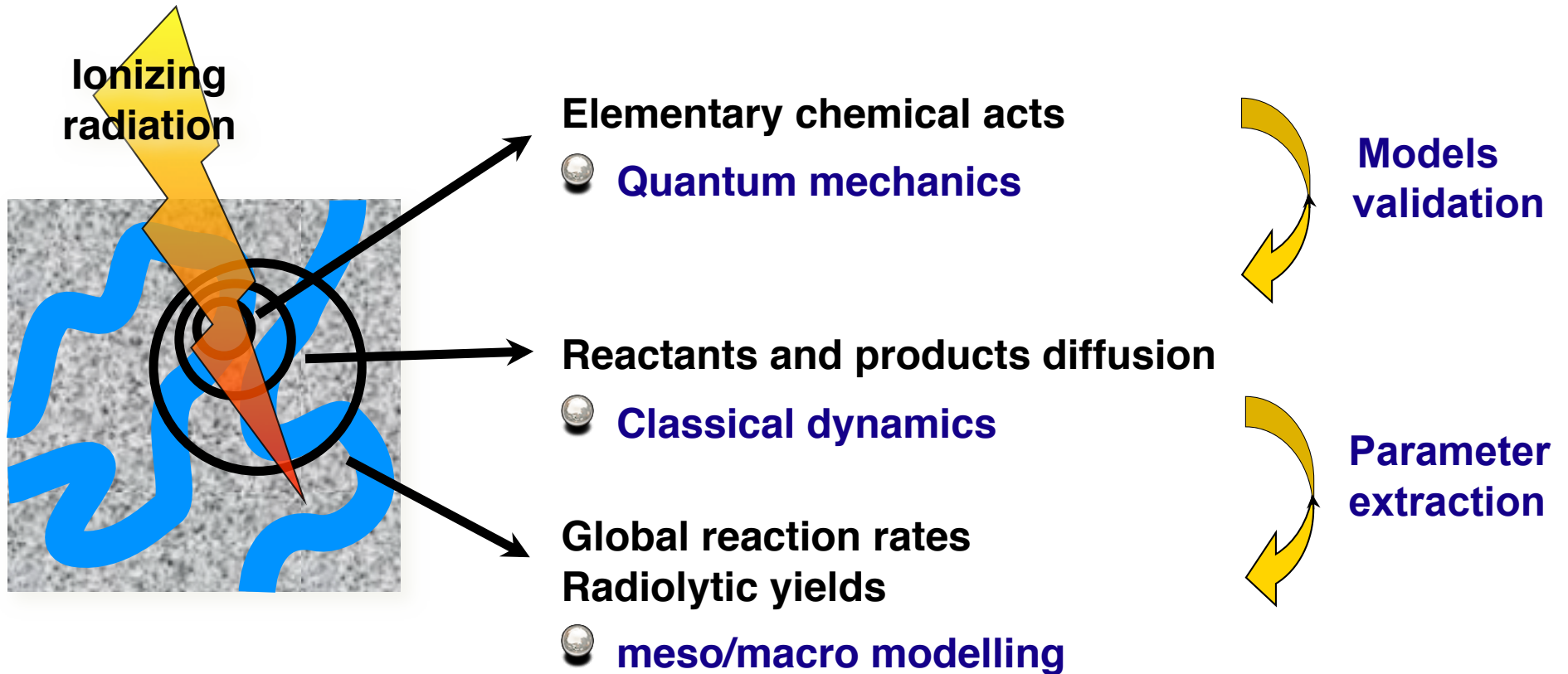- Allow bond breaking and bond formation

System description

Level of details

Explicit electrons

Quantum-classical simulations

Classical simulations
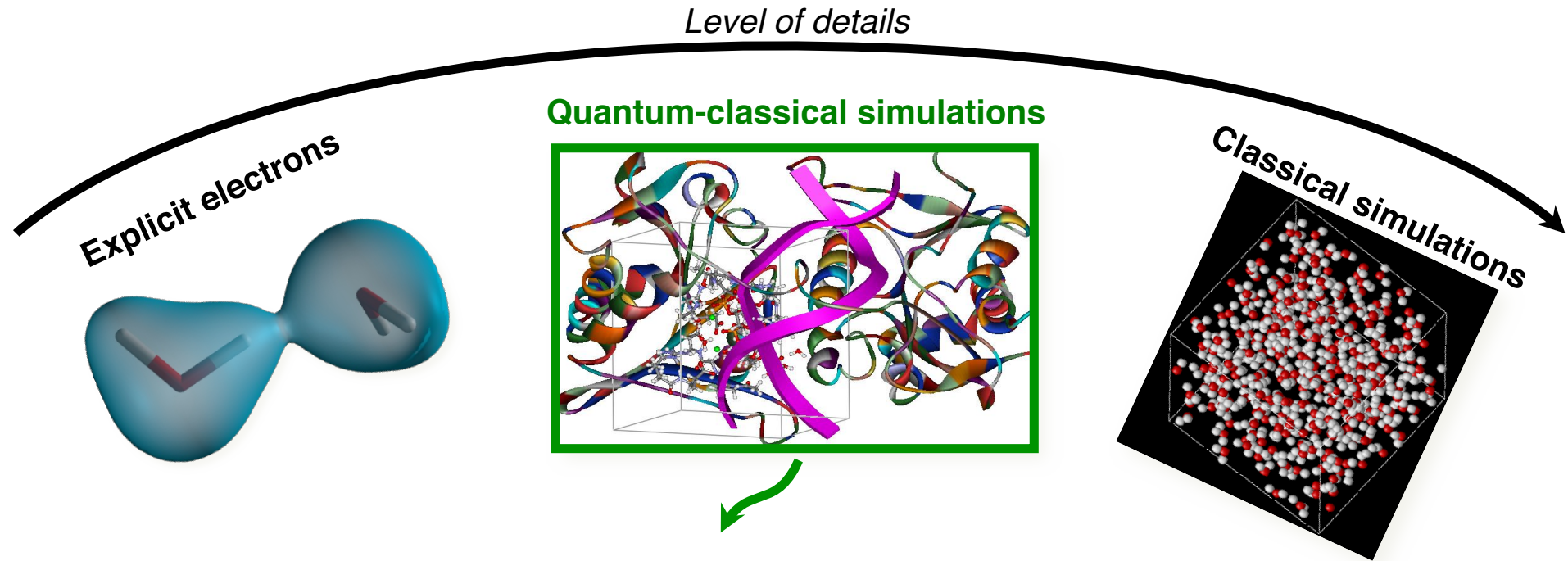
- Advantages from both quantum and classical simulations
- Difficulty of combining two levels of description
- Choice of the « quantum » region

Simulation of radiolysis

from micro (femtochemistry) to macro (primary and final species)

Ionizing radiation

Elementary chemical acts

- **Quantum mechanics**

Models validation

Reactants and products diffusion

- **Classical dynamics**

Parameter extraction

Global reaction rates
Radiolytic yields

- **meso/macro modelling**

Two examples

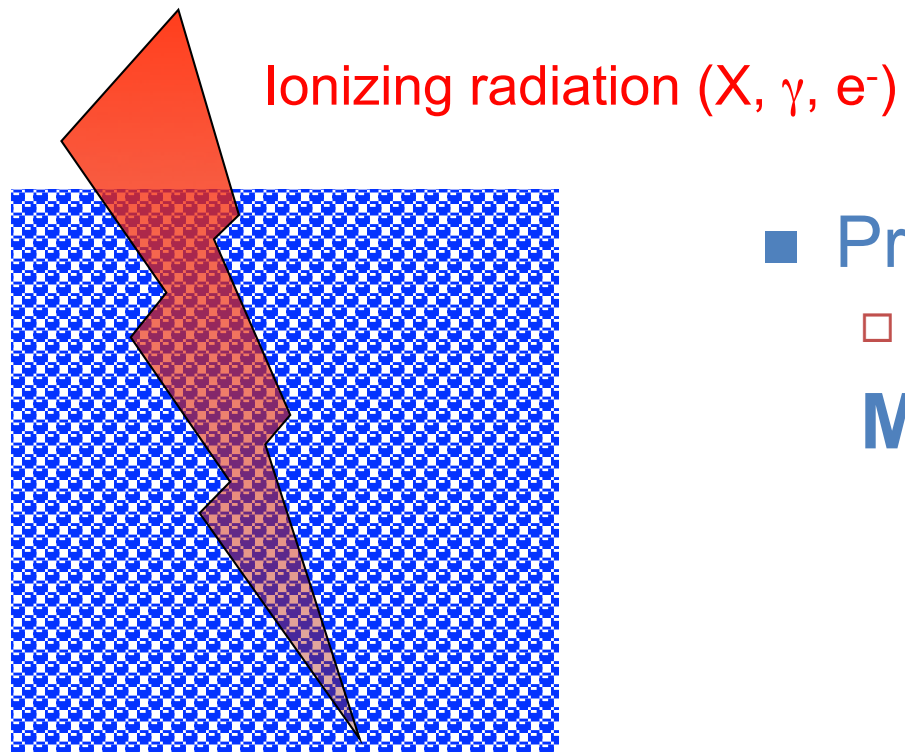
Solvated electron and its reactivity

Ultrafast dissociation of ionized molecules
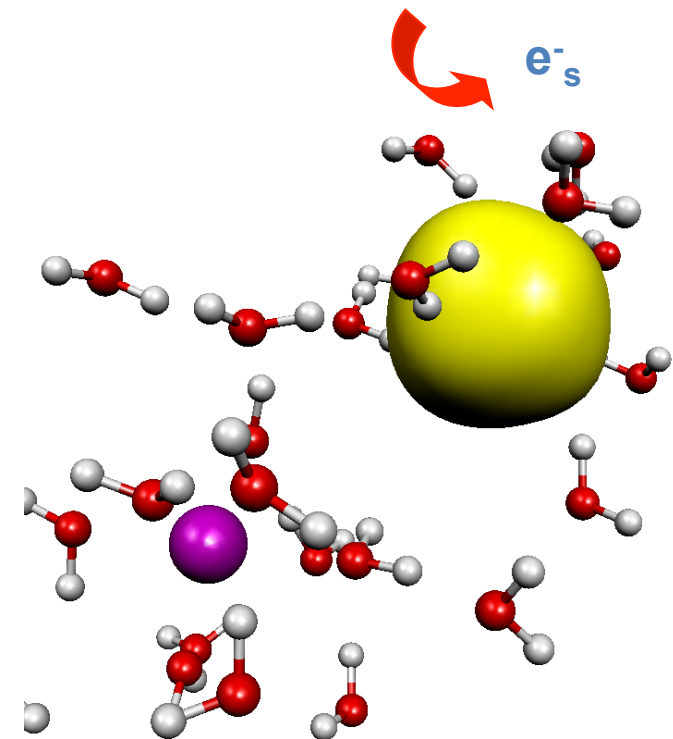
Two examples

Solvated electron and its reactivity

Ultrafast dissociation of ionized molecules

Solvated electron

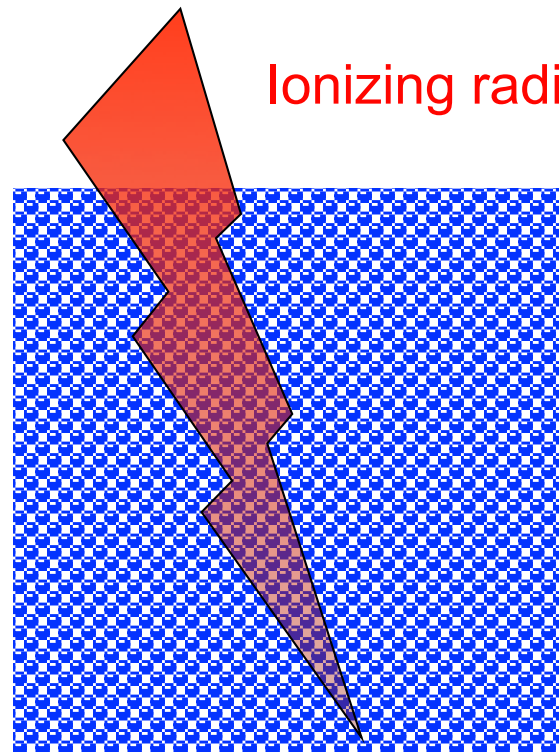Ionizing radiation (X, γ, e⁻)

- ■ Primary phenomena
  - □ Ionisation

$$M \rightsquigarrow M^+ + e^-$$

e^-_s

- – Properties of solvated electron
  - • Strong reductant : $E° = -2,8 \ V_{ENH}$ in water
    - – Oxydoreduction reaction
    - – Electron transfer
    - – Interaction with cations
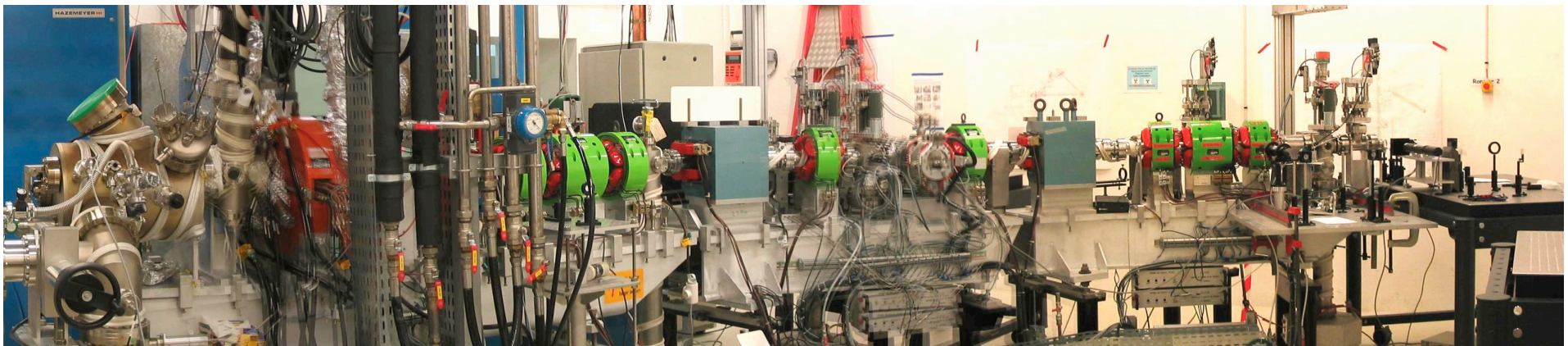
Experiments

Ionizing radiation (X, γ, e⁻)

- Picoseconde pulsed radiolysis
- ELYSE: Centre de cinétique rapide, Orsay

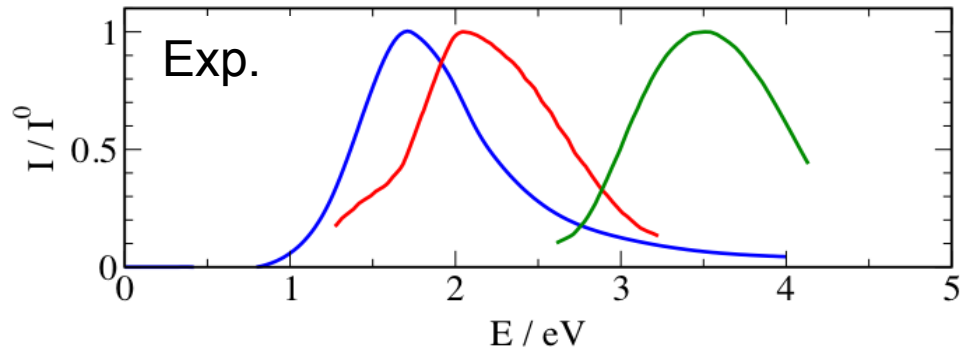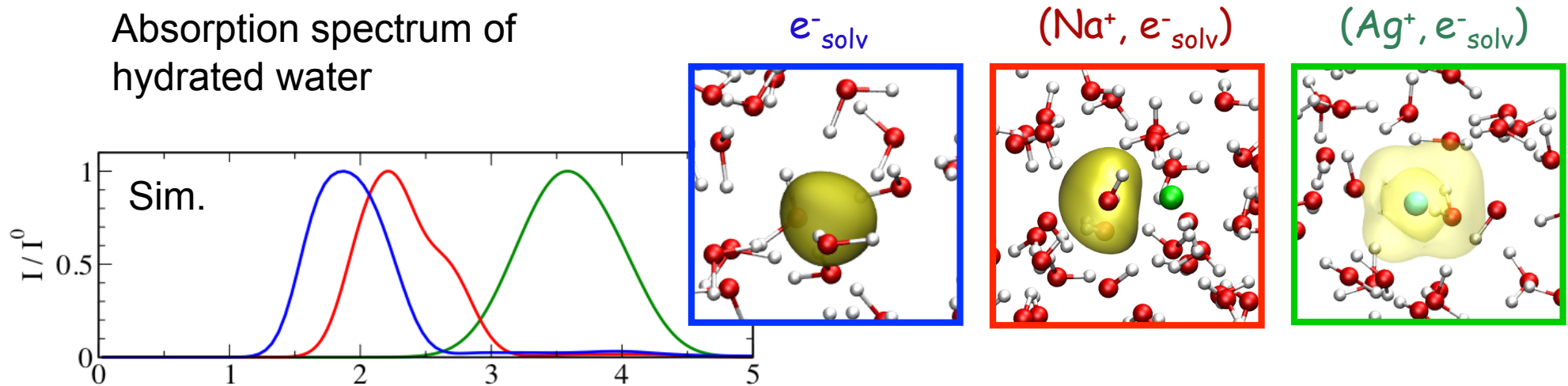*Picosecond electron beam*   synchronisation   *Femtosecond laser*
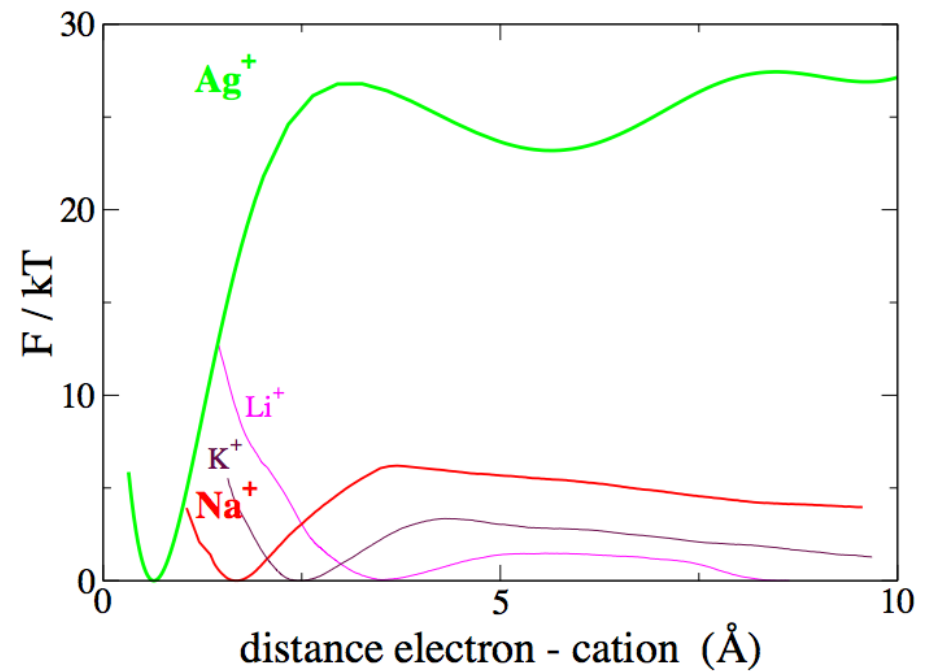
Solvated electron in water – electron in a cavity

Absorption spectrum of hydrated water

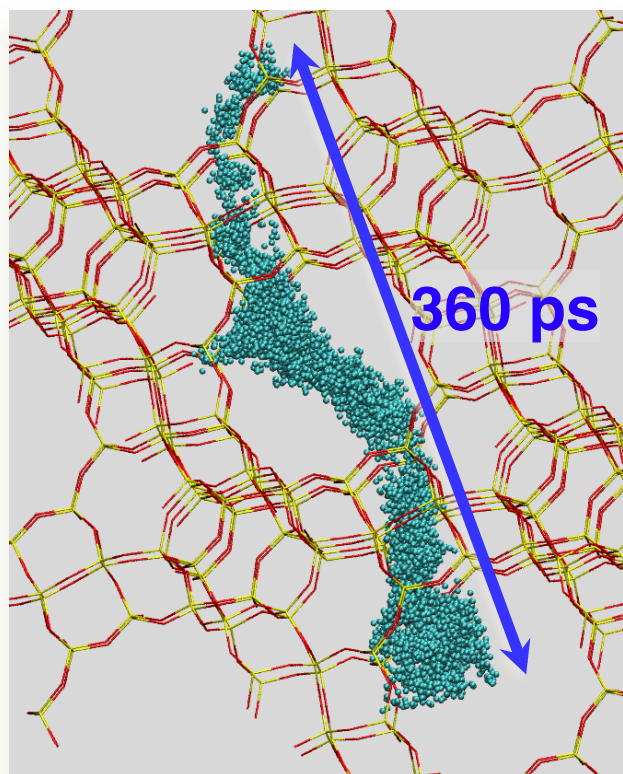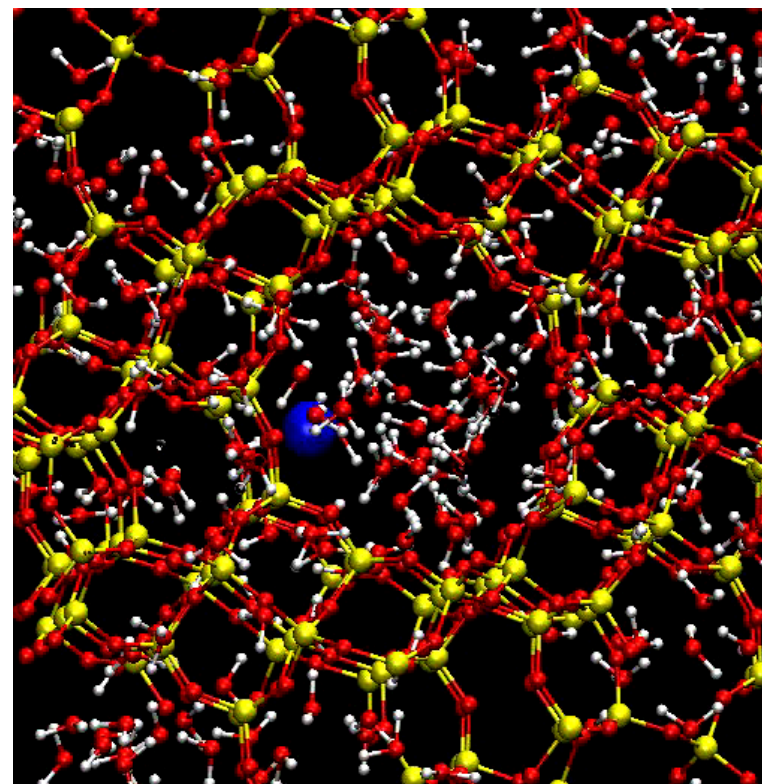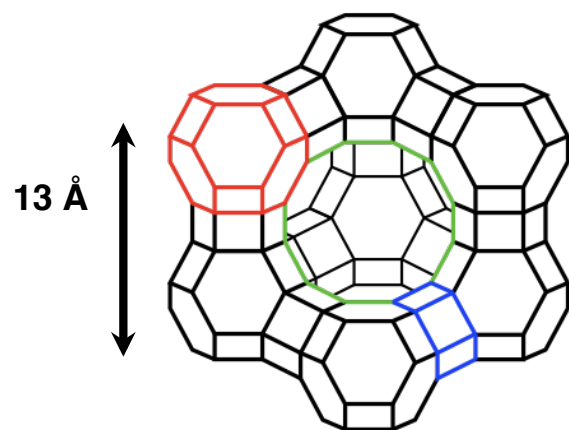e^-_{solv}

(Na^+, e^-_{solv})

(Ag^+, e^-_{solv})

Sim.

Exp.

Ag⁰
Excitonic state

QCMD	2.4D
CPMD	1.9D
Théorie	2.0D

$$E_0(Ag^+/Ag^0) = -1.9V_{NHE}$$
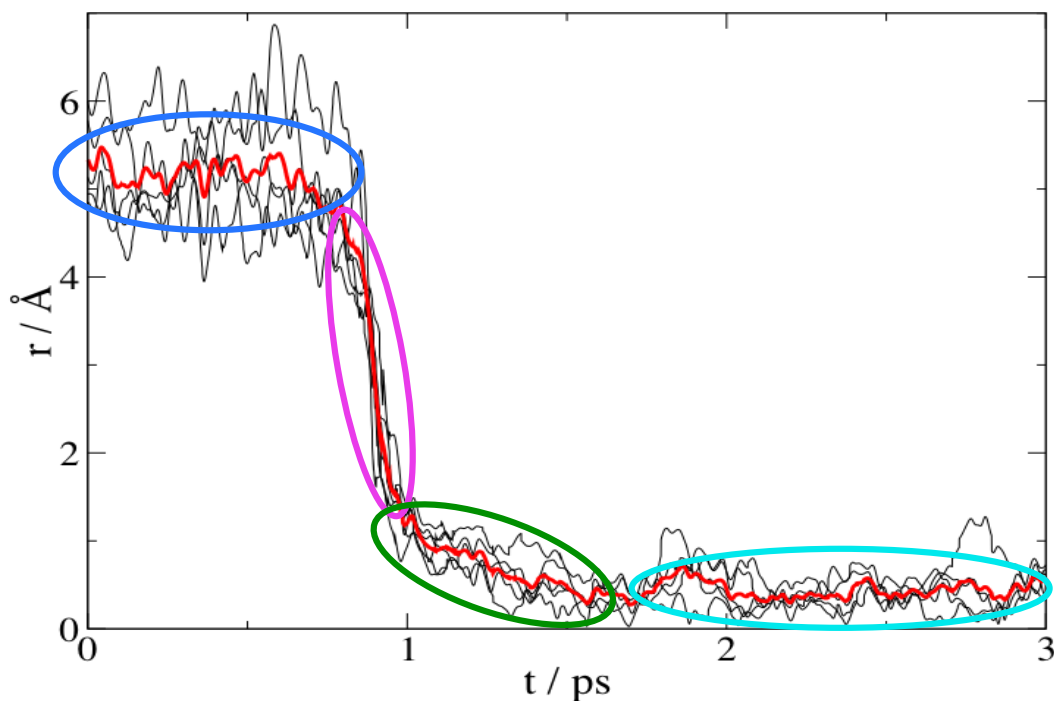
Diffusion of solvated electron

13 Å

360 ps

D_e (bulk) ~D_{H20} (bulk)

D_e (zeo) ~D_{H20} (zeo)
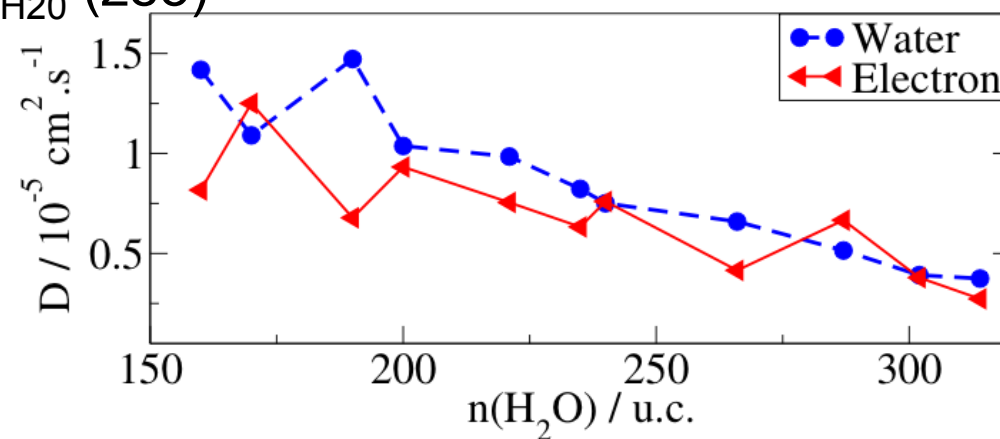
Elementary chemical acts with solvated electron

Ag⁺ Reduction in confined media

$(Ag^+)_{solvated}$ → Hopping → End of solvant reorganization → $(Ag^0)_{solvaté}$

~150 fs   ~0.8 ps (exp: k_{ET} < 1 ps)
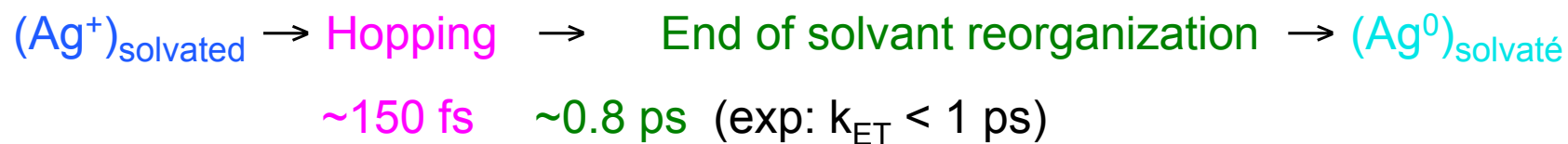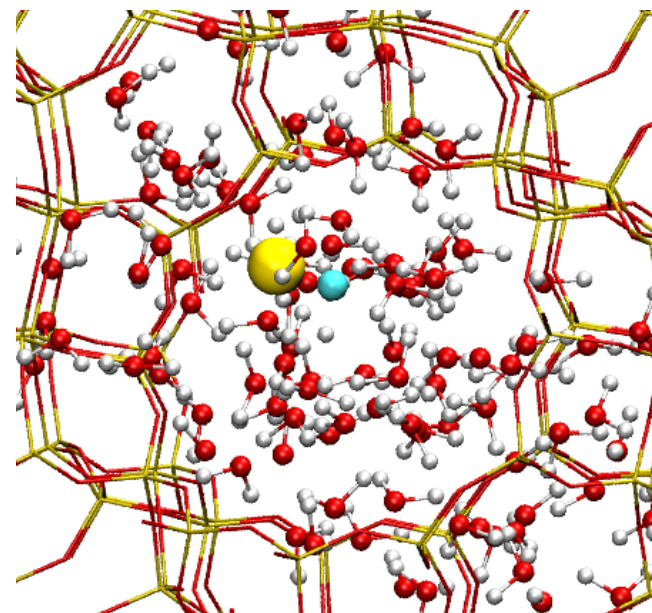
Confinement -> slowing down of solvent reorganization

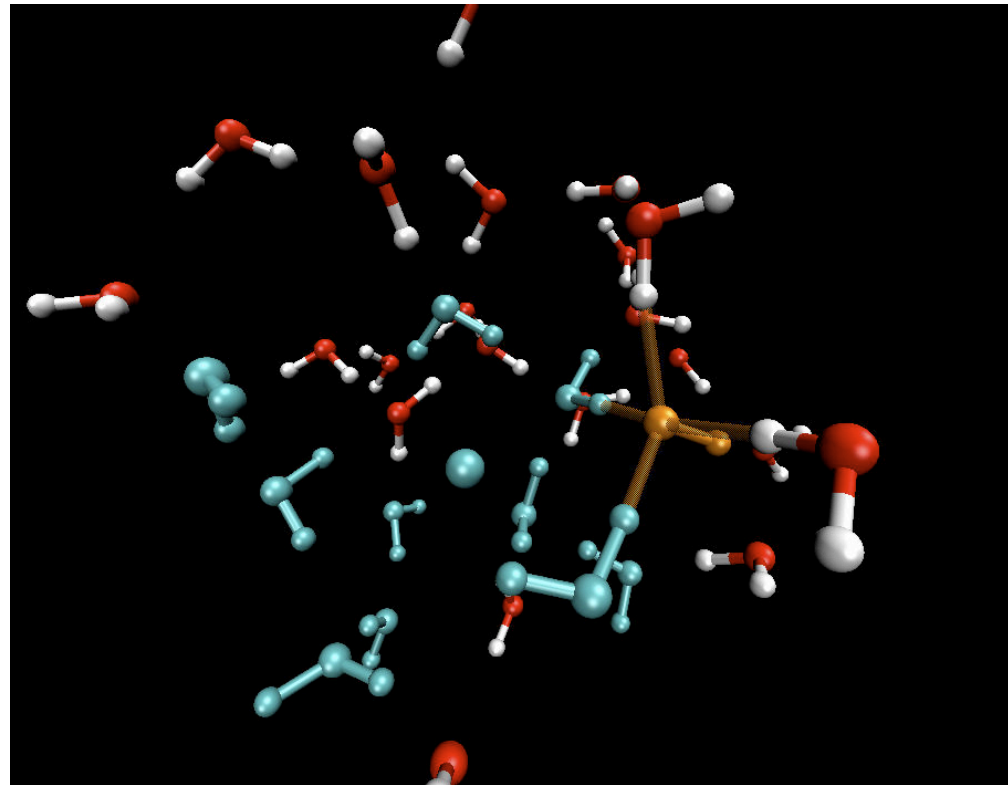# Reaction of hydrogen atom with OH⁻

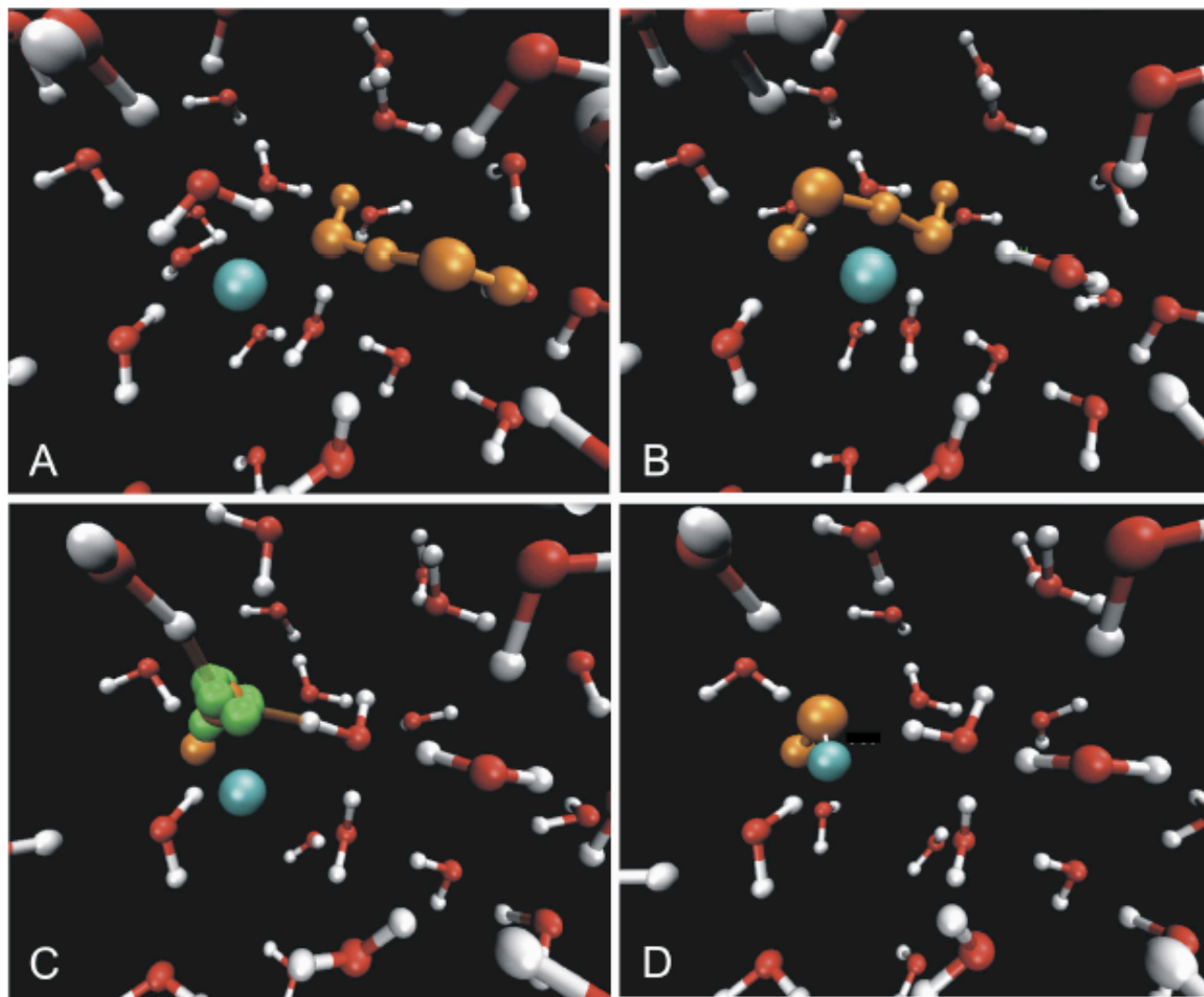$$H^{\cdot} + OH^{-} \rightarrow e^{-} + H_2O$$
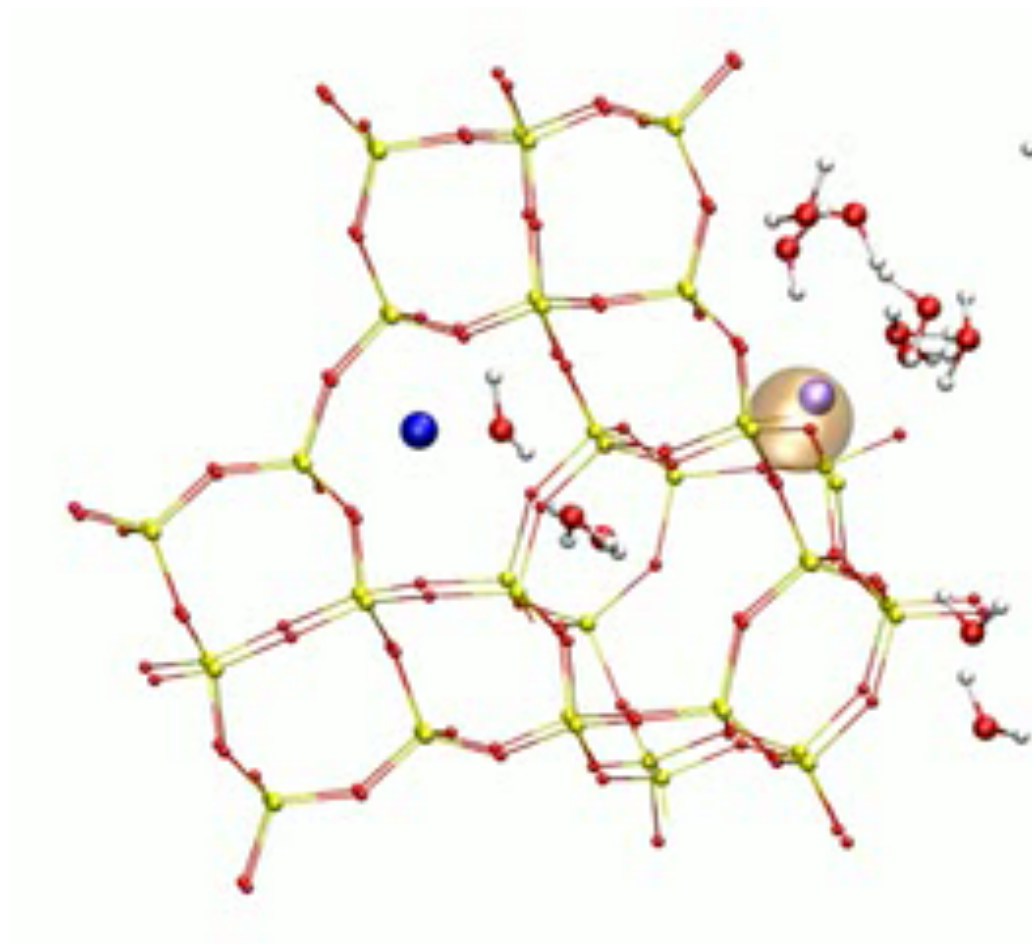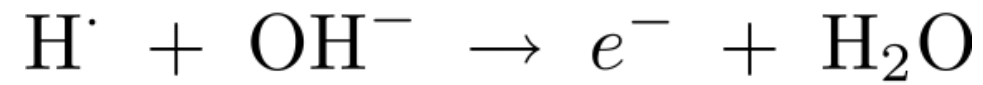
Studied with ab initio Molecular Dynamics

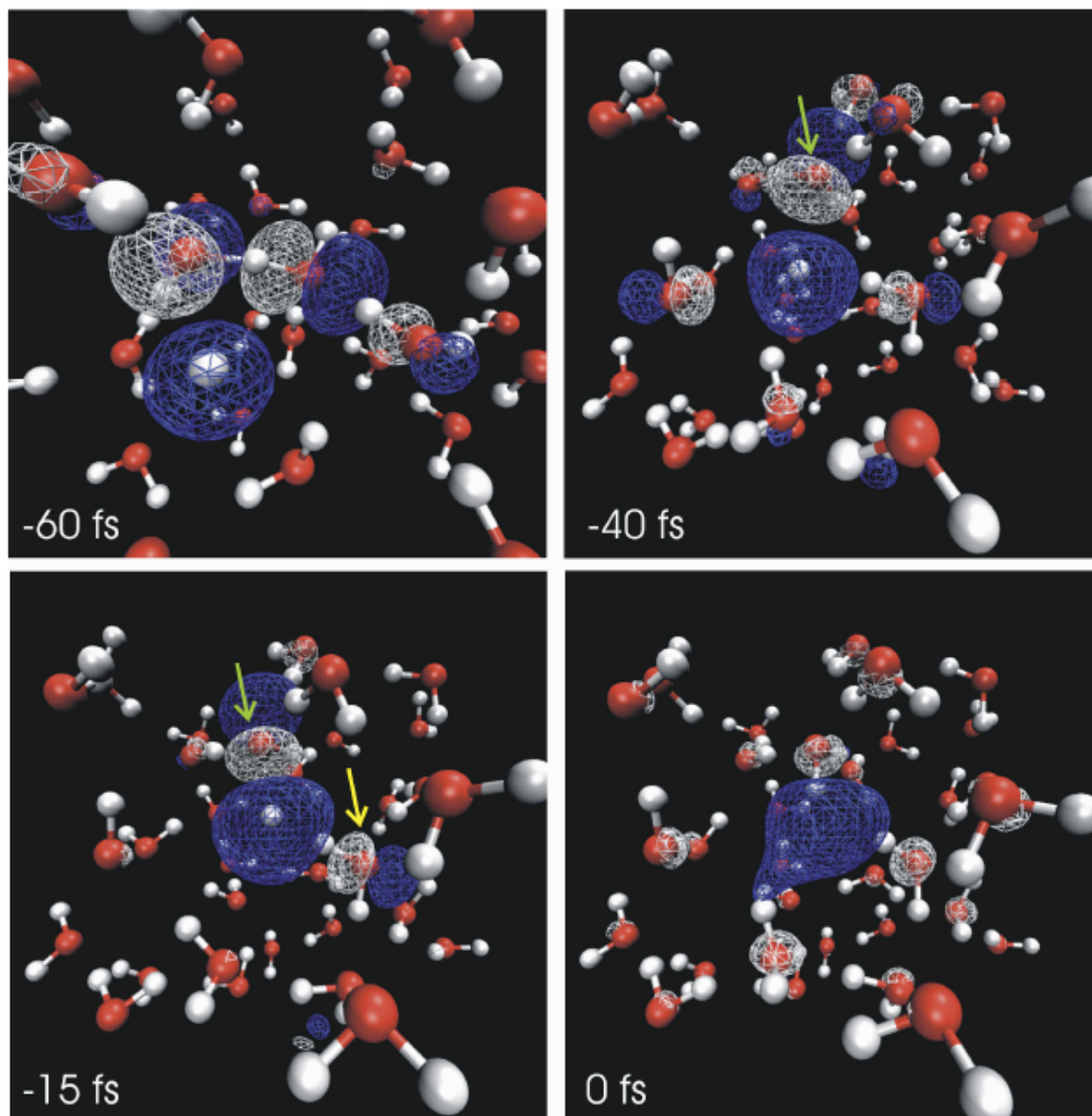Proton transfer reaction

Metastable configuration

Reaction of hydrogen atom with OH⁻: mechanism

J.-P. Renault et al., JPC A **112**, 7027 (2008)

Reaction of hydrogen atom with OH⁻: e^- orbital

# Two examples

Solvated electron and its reactivity

Ultrafast dissociation of ionized molecules

Ultrafast dissociation of ionized biomolecules

- High ionization density in swift heavy ion tracks (Ar^{18+}, C^{6+} ; v=1/3c)

- K-shell ionization

- Multiple ionization (M^{2+}, M^{3+}, …) represent about 10% of collision events but most lethal events

- Primary species formed?

- Liquid water : Important amount of HO_2 / O_2^- radicals & O_2 molecules (very harmful for the cell)

- Direct or indirect mechanisms: are damages caused by water ionization that produces oxydative stress or by direct ionization of DNA?

Modelling of the chemical-physics stage: double ionisations

- Multiple ionization are not negligeable at high LET (Linear Energy Transfer)
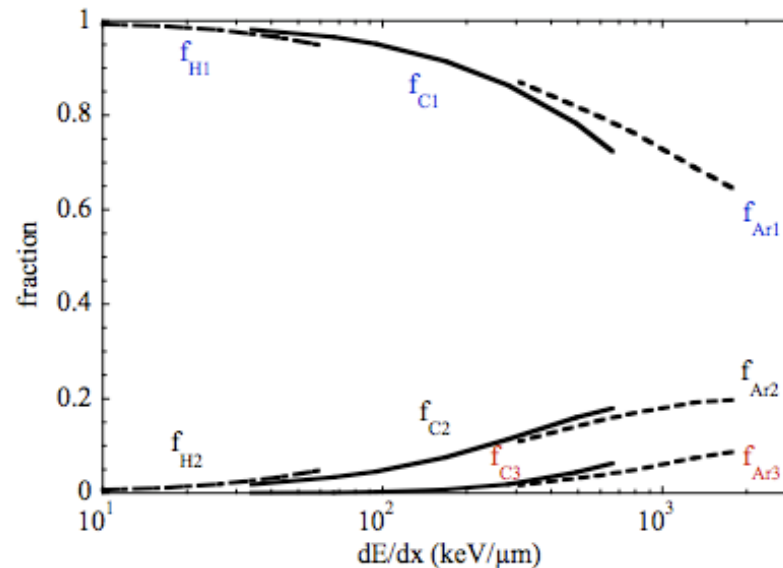
(B. Gervais et al.)

- Very damaging

- It was shown (A. Chetioui et al.) that cell death is correlated with K-shell ionization

  double ionisation after Auger effect

Simulation of the fragmentation induced by double ionization or core hole of water and biomolecules

Propagation of electron density by Time-Dependent Schrödinger equation

- Electrons are out of equilibrium

- Explicit treatment of electron dynamics by time-dependent Schrödinger equation:

$$i\hbar \frac{\partial \phi_i}{\partial t} = -\frac{1}{2}\nabla^2 \phi_i + v_s(\vec{r}, t)\phi_i$$

- Mean field (Ehrenfest) coupling with atomic motion

where the orbitals depend on positions and time

Time-dependent density functional theory framework

The time-dependent potential is a functional of the time-dependent density

H_2O^{2+} coulomb explosion in liquid : TD-DFT in liquid water
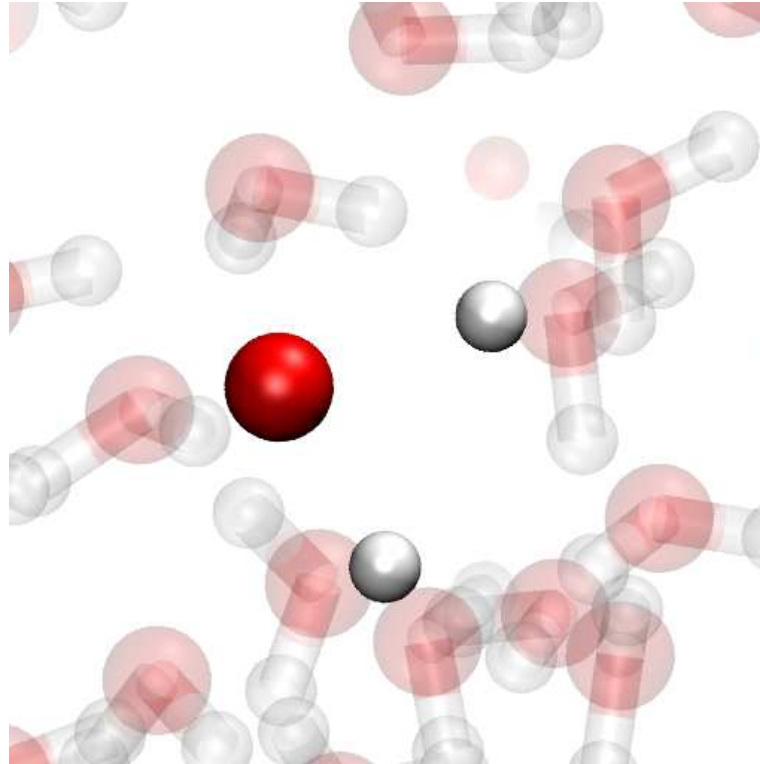
Evolution with time of the two O-H distances of the ionized H_2O^{2+} water molecule
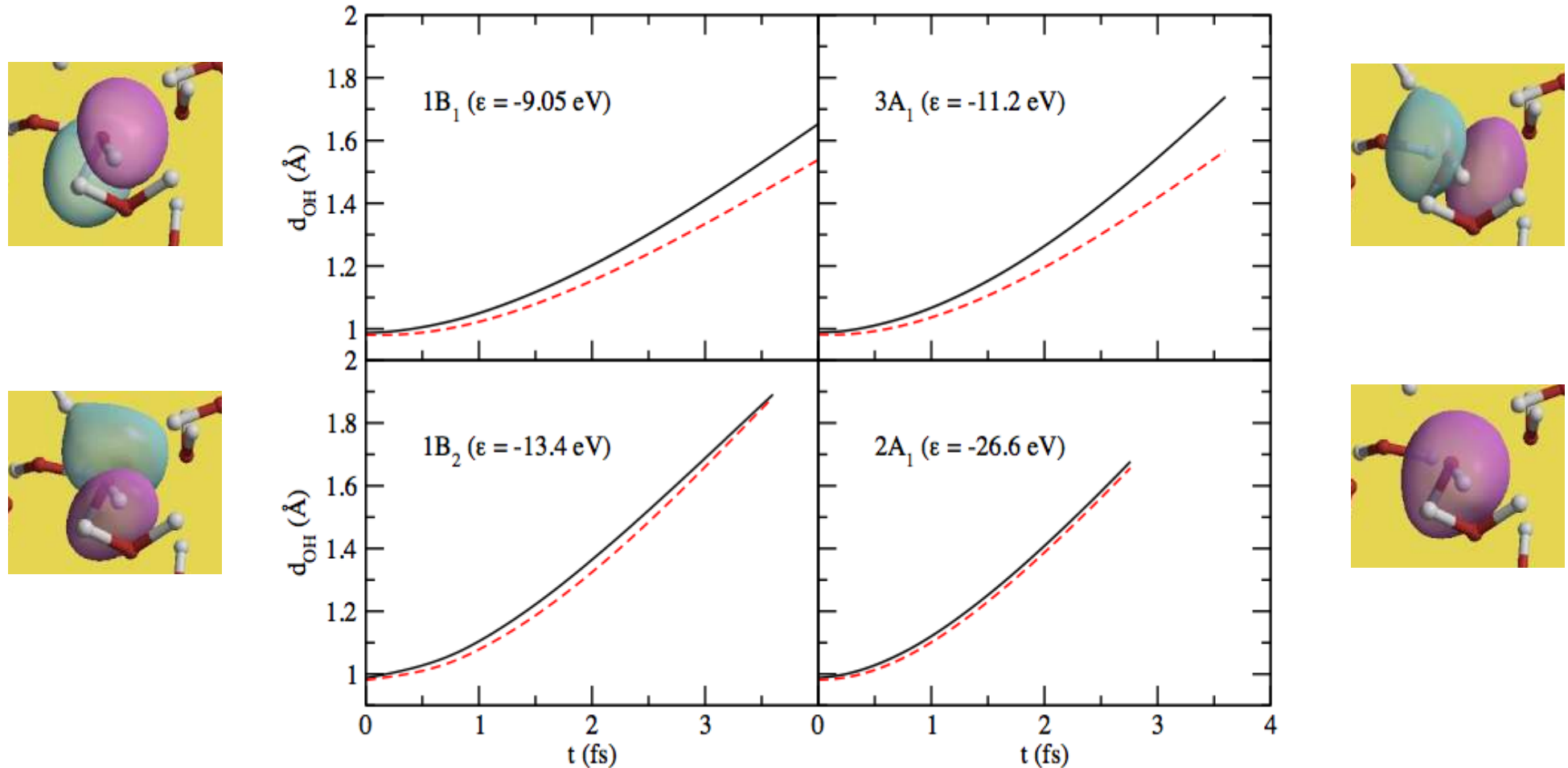
Fragmentation leads to one O and two H^+ atoms & recombination
with the surrounding solvent : $H_2O^{2+} \rightarrow 2H_3O^+ + O$

Ionization from inner-shells : faster time-scale

Formation of atomic oxygen

- Highly reactive

- Born-Oppenheimer MD leads quickly to the formation of H_2O_2

- In presence of OH radical leads to the superoxyde HO_2
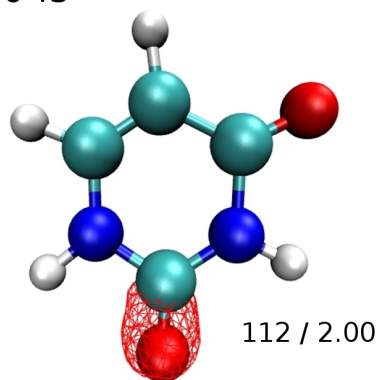
Direct effects of ionization : gas phase Uracil^{2+}

Hypothesis : remove 2 electrons from the inner shell
molecular orbitals of neutral Uracil (most violent events)

$E_3 = -24.18$ eV

$E_2 = -25.82$ eV

$E_1 = -26.85$ eV
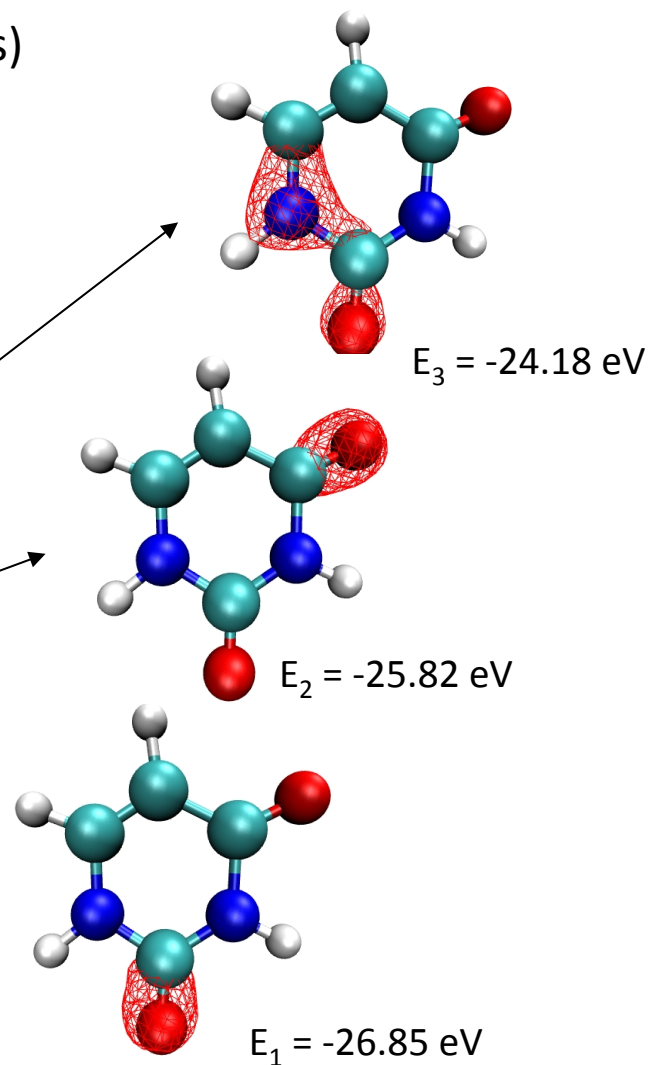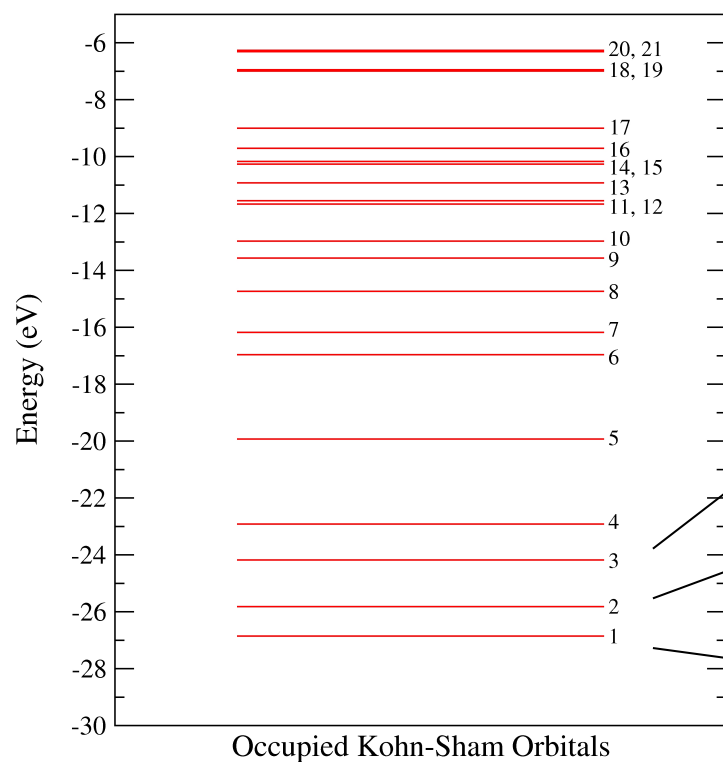
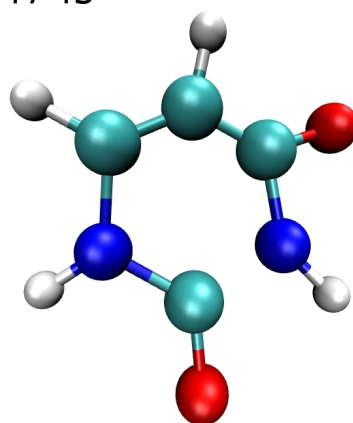Initial ionisation is either
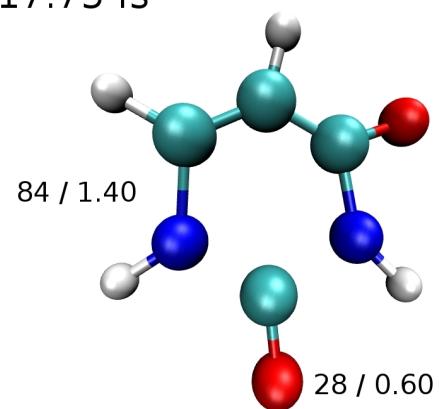localised on C=O groups or partially delocalised on the ring

Ionisation from C=O

0.00 fs   112 / 2.00

16.47 fs
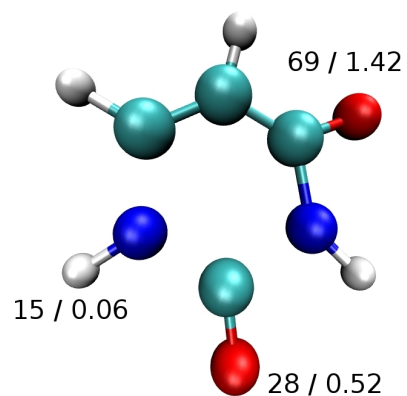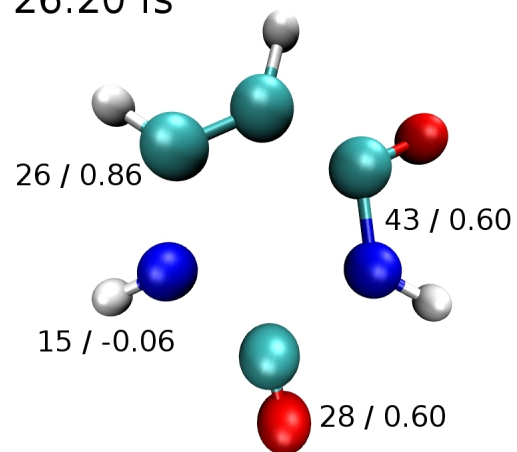
17.75 fs   84 / 1.40   28 / 0.60

18.71 fs   69 / 1.42   15 / 0.06   28 / 0.52

26.20 fs   26 / 0.86   43 / 0.60   15 / -0.06   28 / 0.60

38.96 fs   26 / 0.69   43 / 0.63   15 / 0.29   28 / 0.36
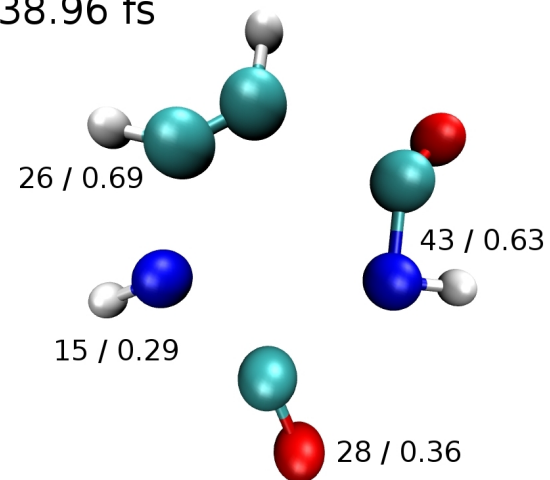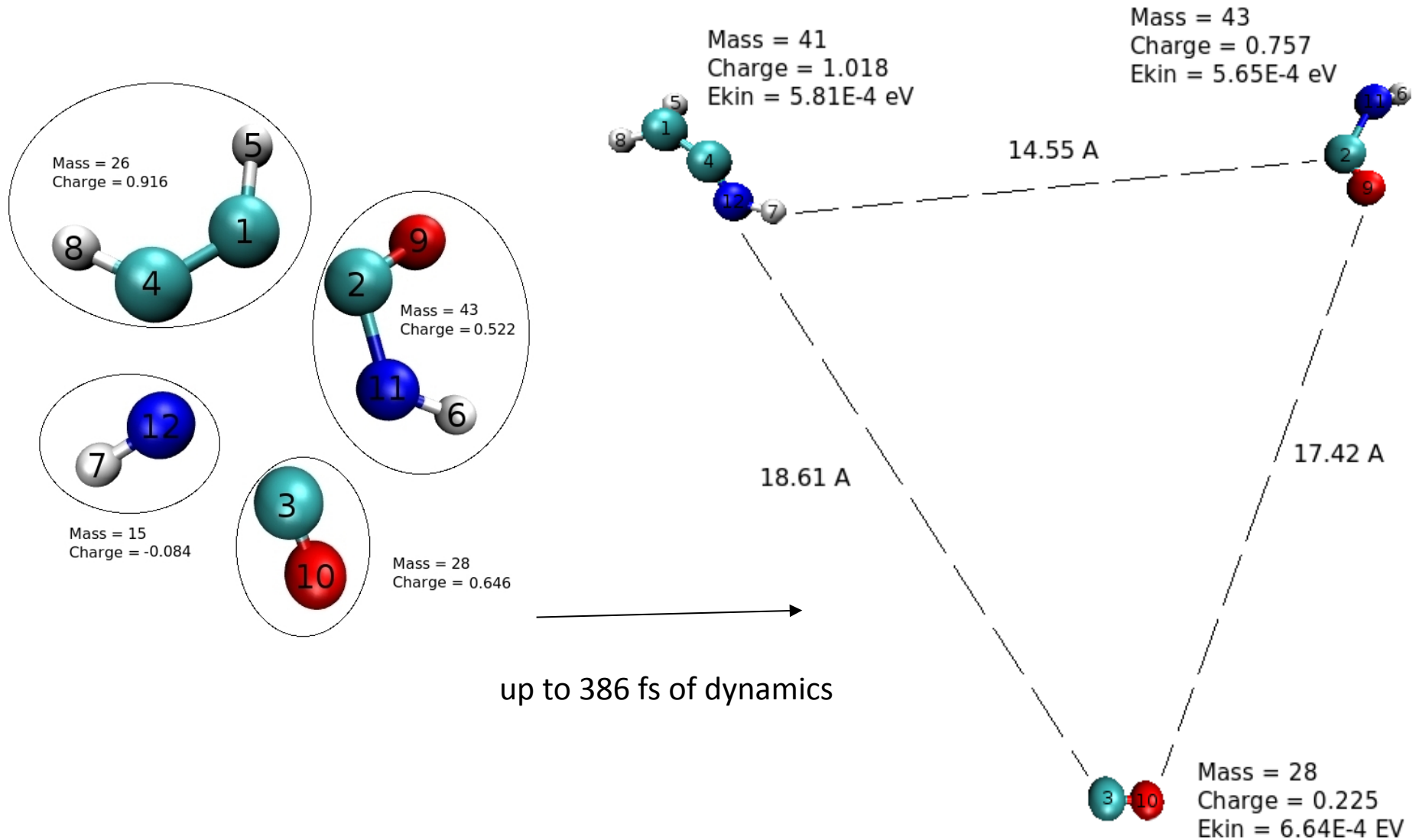
Follow-up with adiabiatic dynamics

Later along the trajectory: electrons are assumed to be back at equilibrium with the atomic positions (ground state)


Mass = 26
Charge = 0.916

Mass = 43
Charge = 0.522

Mass = 15
Charge = -0.084

Mass = 28
Charge = 0.646

Mass = 41
Charge = 1.018
Ekin = 5.81E-4 eV

Mass = 43
Charge = 0.757
Ekin = 5.65E-4 eV

14.55 A

18.61 A

17.42 A

Mass = 28
Charge = 0.225
Ekin = 6.64E-4 EV

up to 386 fs of dynamics

Comparison with experiment

Uracil in gas phase collision with protons in the 25 keV– 100 keV energy range
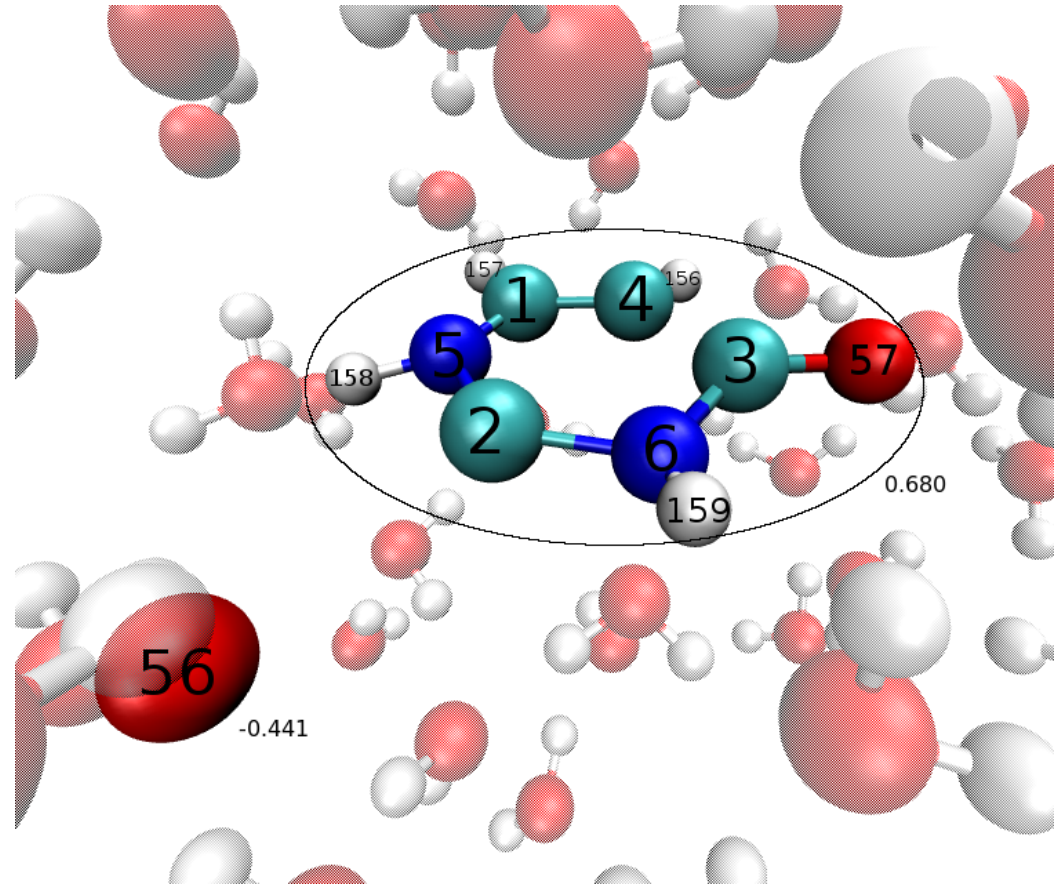
Coincidence diagram of charged fragments:

P Moretto-Cappelle's Group - Toulouse, France
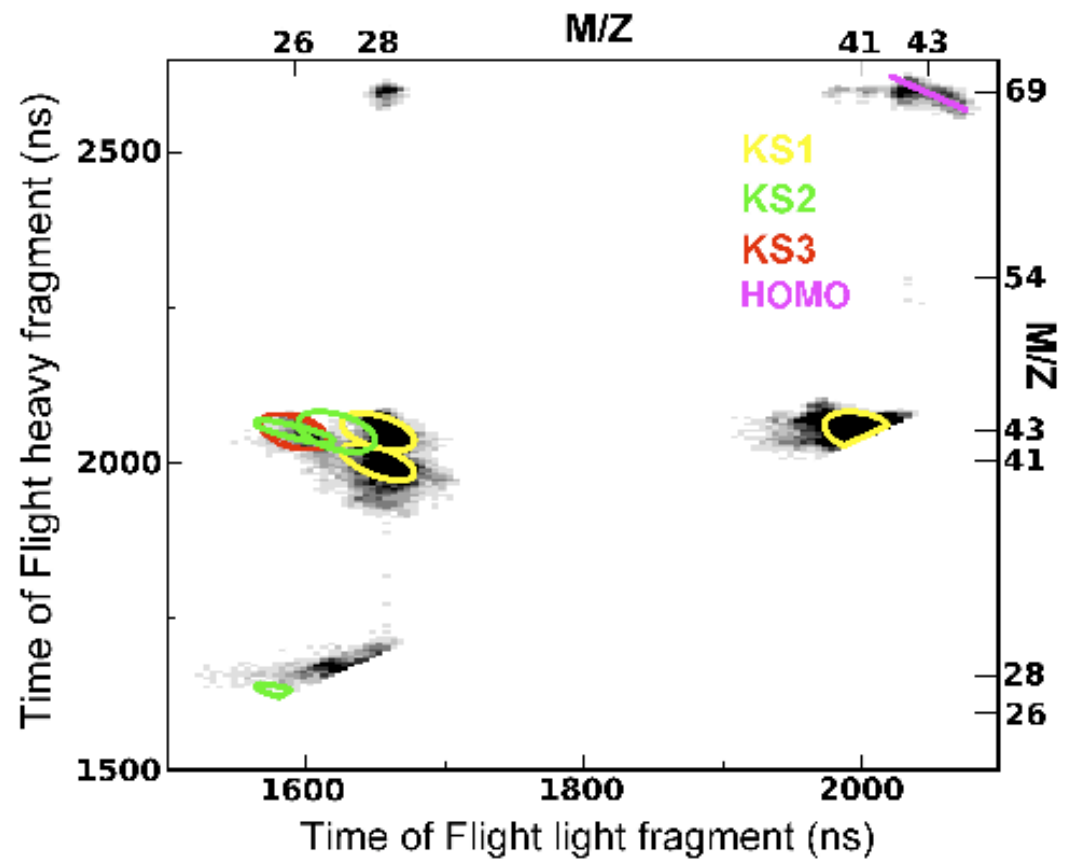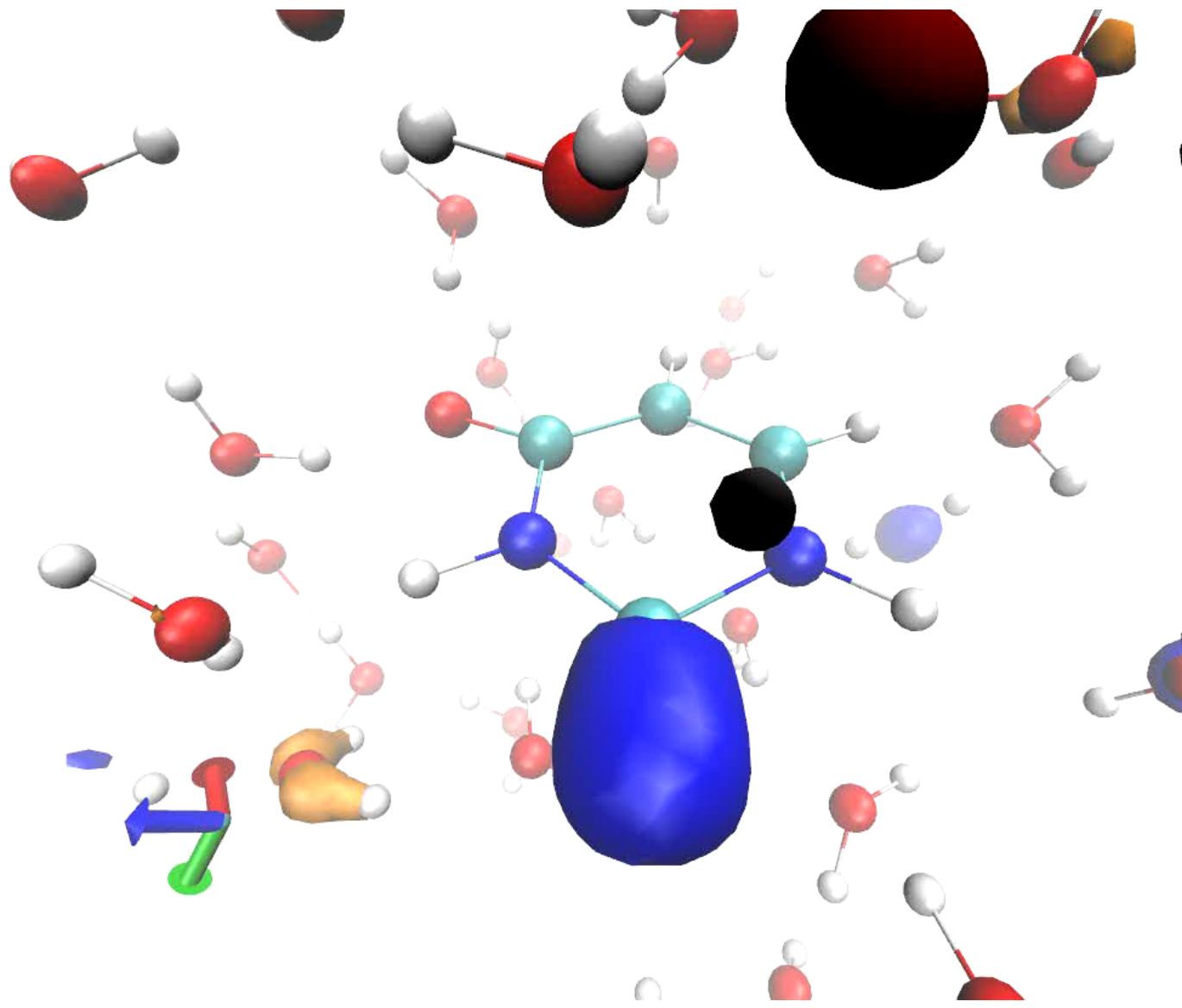
Ionisation from C=O

- After 31.20 fs of TD-DFT dynamics

- Loss of an oxygen atom in the liquid

- Oxygen negatively charged, just like after the Coulomb explosion of H_2O^{2+} in pure liquid water

Conclusions

- Computer experiments: different media (water, porous materials), different conditions…

- Radiation induced chemistry has always been attractive to molecular simulations

- Primary species and their reactivity

- Radiation chemistry is a stringent test of models and level of description

- Challenge for molecular simulations: multiple levels of description

- Molecular simulations are one part of the modelling of radiation chemistry

Acknowledgements