AQUEOUS HYDRATION OF CYANIN DYE MOLECULE: AN ATOMISTIC INSIGHT

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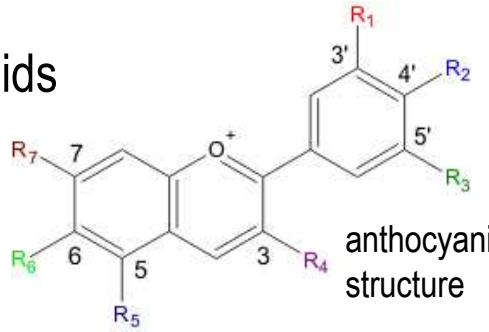
introduction

- **ANTHOCYANINS** are natural **water-soluble** flavonoids (polyphenolic derivative), positively **charged** in the ground state configuration (**flavylium cations**)



anthocyanin structure

- anthocyanins are the main **natural dyes** - from **red** to **blue**– in plants, flowers and fruits

- further properties
  - absorption of UV radiation
  - antioxydant activity in cells

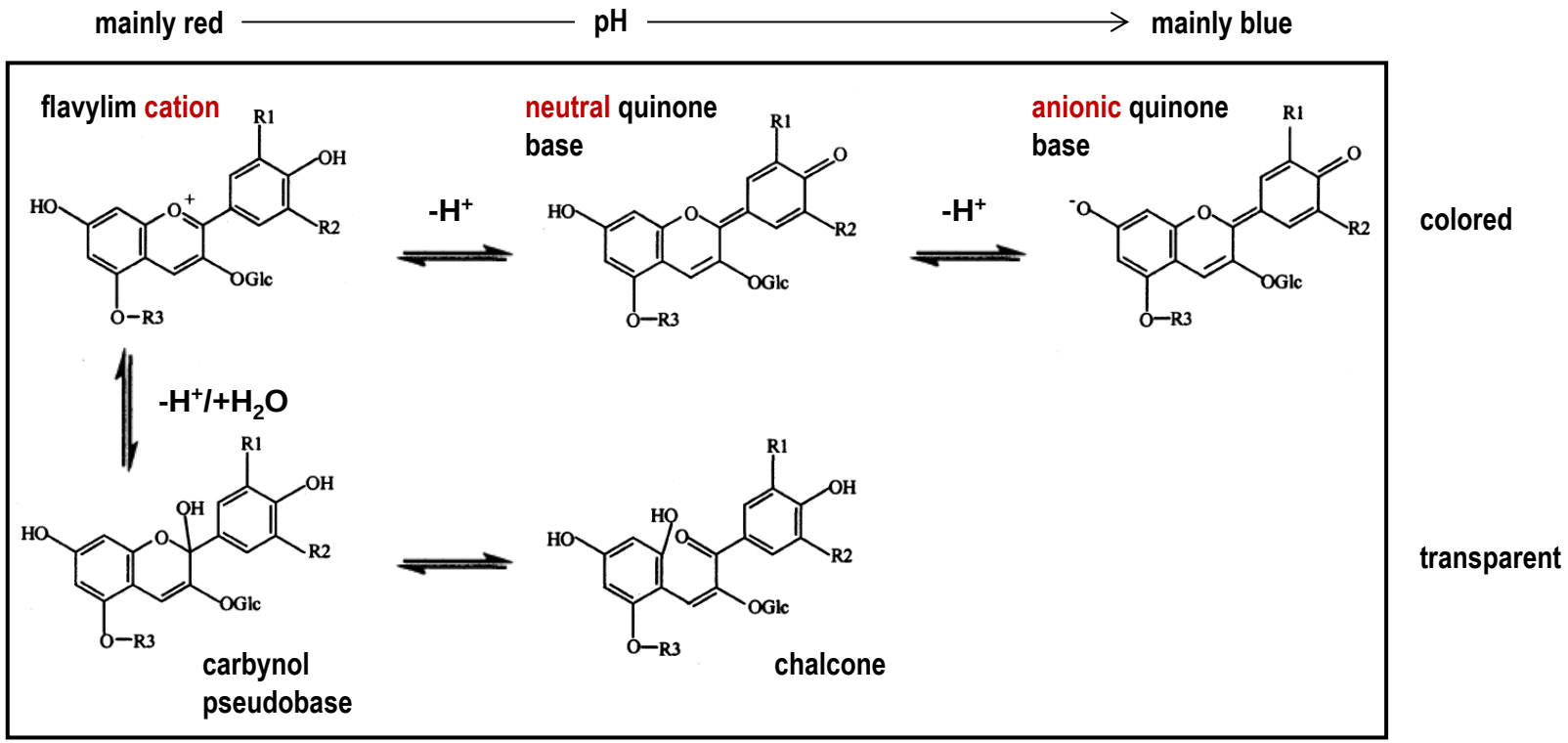
  } medical and farmaceutical applications

  - absorption of visible radiation
  - metal ions **chelators** (e.g. Al, Zn)
  - **self-assembly** and **stacking** configurations

  } **solar cells and nanoscale applications** (e.g. artificial eyes, sensors, etc)

what we know from biology

- in natural systems anthocyanins are in **aqueous solution**
- in solution anthocyanins undergo **structural transformations** as a function of pH
  → **modulation of the electronic and optical properties**
  → **change of color from red to blue and transition to transparent phase**



motivations

open questions

- **what are the intrinsic properties of anthocyanins?**
- **what are the effects induced by the solvent?**

main goal

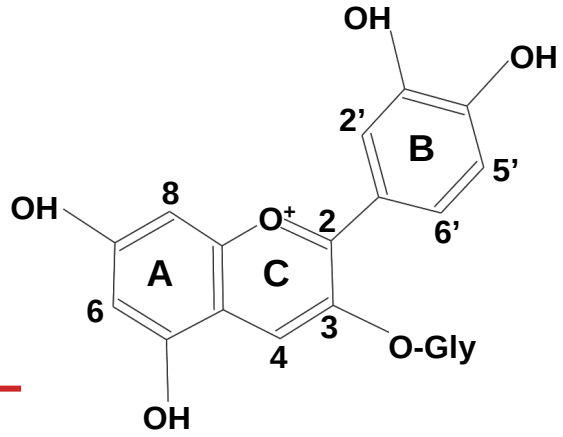
exploitation of these molecules for biomedical and nanoscale applications requires the fine characterization of anthocyanins and their interactions with water from an atomistic point of view

selected anthocyanin molecule →

CYANIN molecule (flavylium cation phase)

- very frequent in colored vegetables

- red dye



multiscale methods

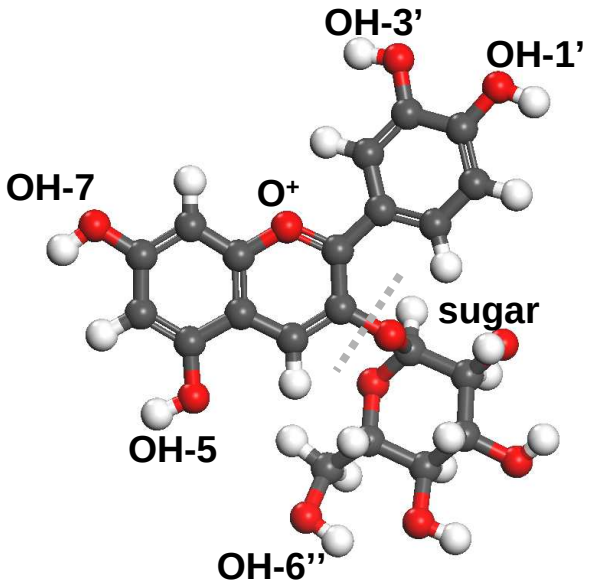
- **ground state properties of isolated cyanin molecule (charged system)**
  - total-energy and forces optimization (PWscf code)
  - **density functional theory** (DFT) – PBE-GGA included
  - *ab initio* ultrasoft pseudopotentials
  - plane-wave basis set

- **dynamical properties of cyanin molecule in solution (water+counterions) at room temperature**

  - interaction properties at the interface
    - *ab initio* molecular dynamic simulation (**Car-Parrinello** code)
    - **density functional theory** (DFT)
    - plane-wave basis set, *ab initio* ultrasoft pseudopotentials

  - hydration effects
    - classical **force field** molecular dynamic simulation (AMBER code)
    - solvent molecules described by the TIP3P water model
    - partial charges from 6-31G* Hartree-Fock calculations in the equilibrium geometries, RESP procedure

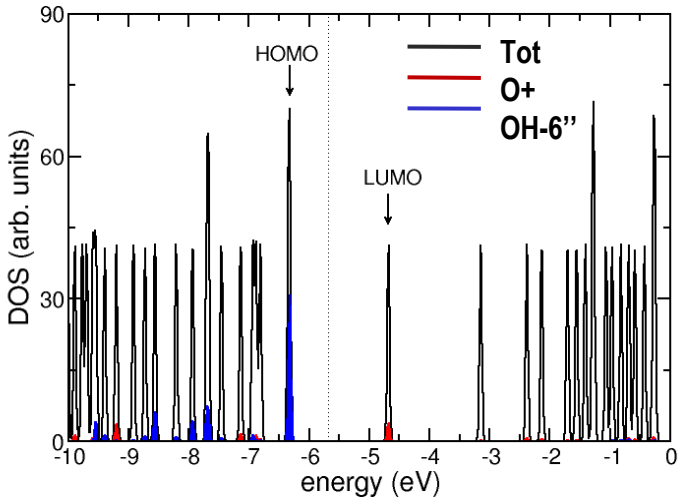
cyanin single molecule

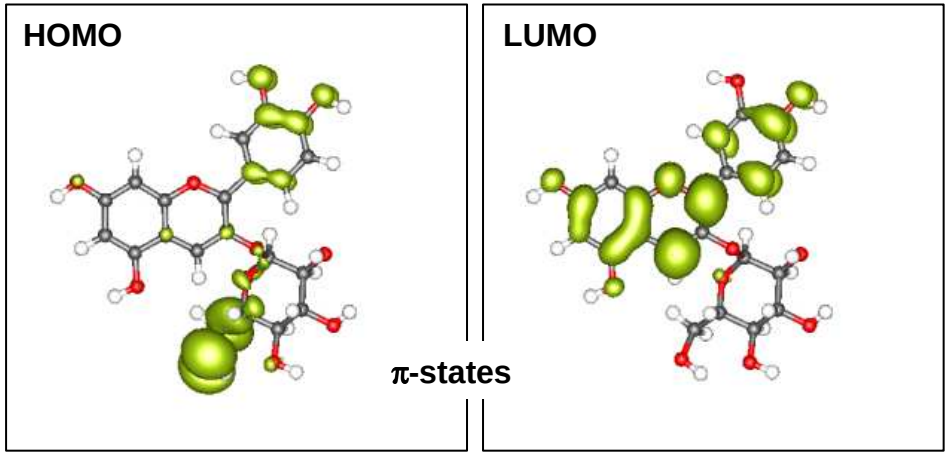


Ground state characteristics

- charged system **but** even number of electrons
  → **no partially occupied electronic states**

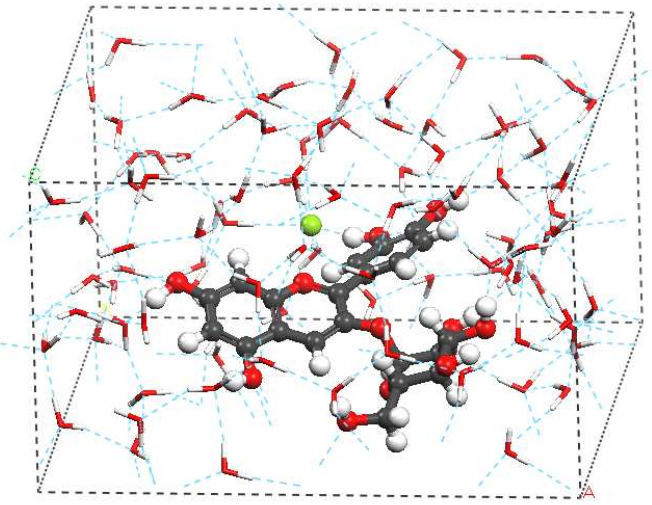
- non-uniform charge distribution
  → **high intrinsic dipole moment**
  → **important polarization effect of the solvent**

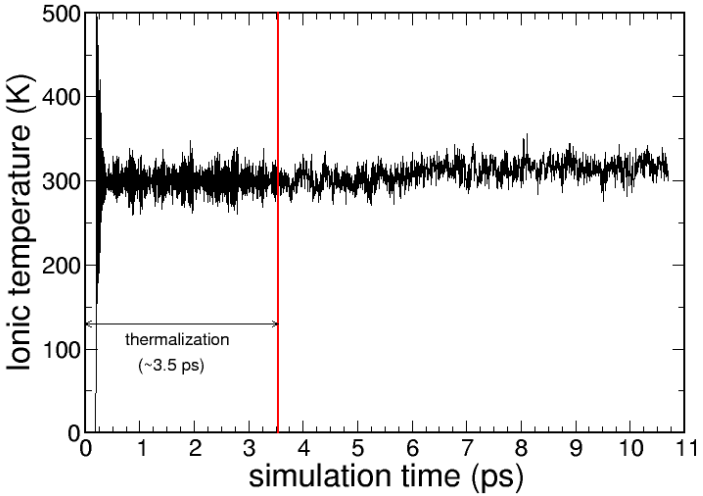




ΔE [HOMO-LUMO] = 1.638 eV

car-parrinello simulation (I)





globally neutral system

→ 1 cyanin (cation)

→ 1 Cl^- (counter ion)

→ solvent (95 H_2O molecules)

technical details

μ=340 au, δt=0.075 fs, Γ-only

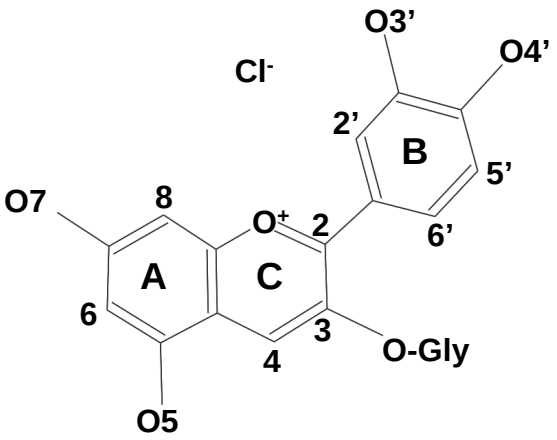
288 atoms (939 valence electrons) → **large system for *ab initio* simulations**

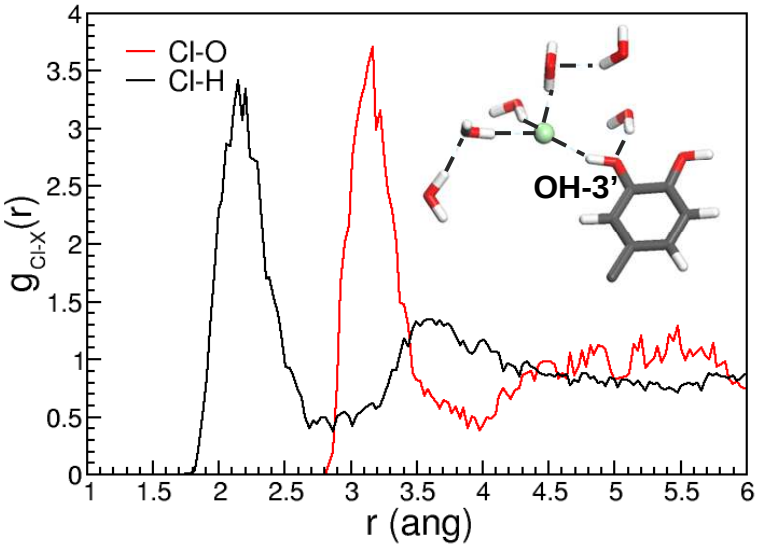
*****work in progress*****

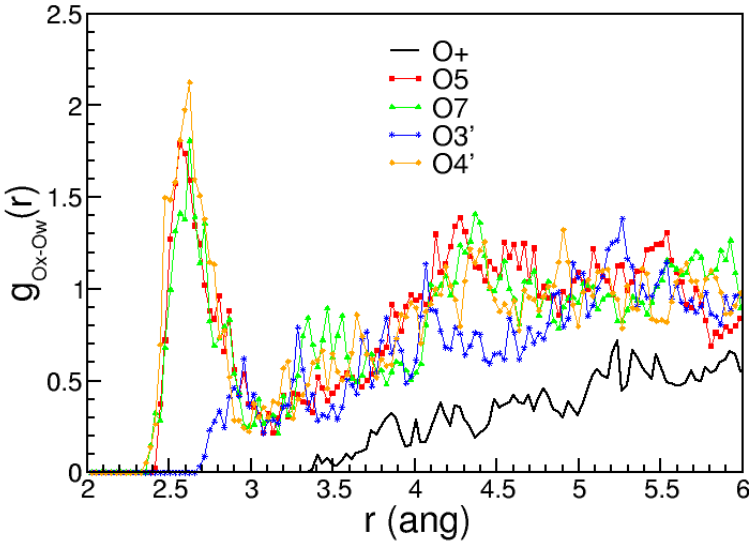
3.5 ps of thermal equilibration at T=300K

+ 8 ps of production time (microcanonical ensemble)

car-parrinello simulation (II)



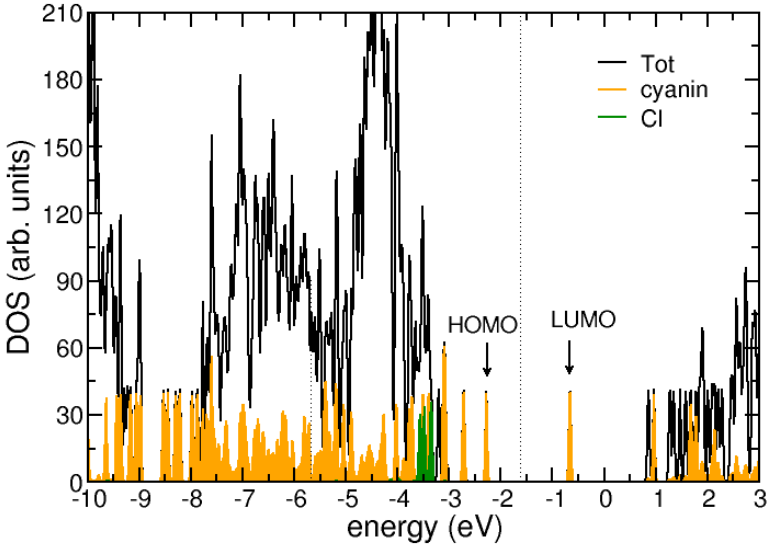


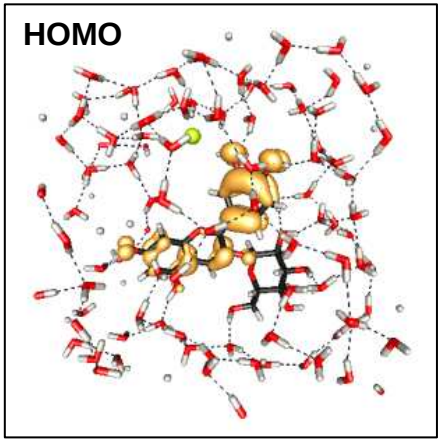


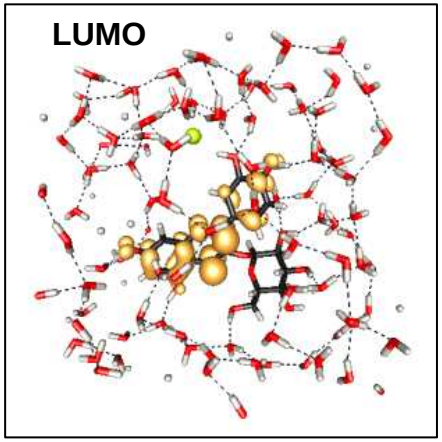
radial distribution functions g(r)

- water properties in agreement with previous theoretical data
- both water and cyanin -OH contribute to counter ion solvation shell
- water –molecule interaction depends on the oxygen polarity

car-parrinello simulation (III)







ΔE [HOMO-LUMO] = 1.6197 eV

electronic properties (on average structure)

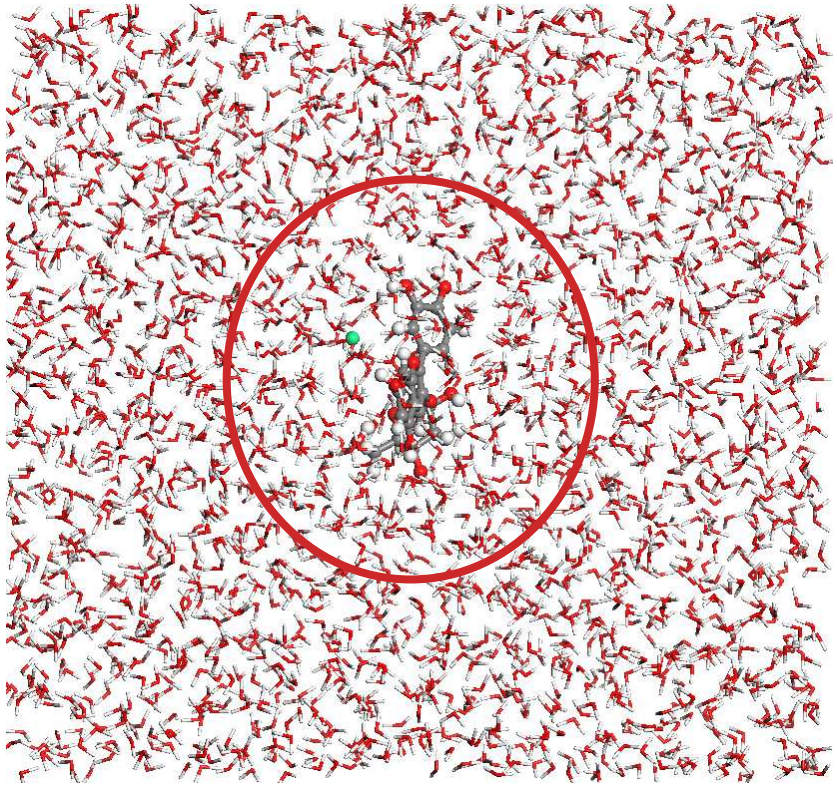
- no significant HOMO-LUMO gap modification
- no Cl and /or water states in the cyanin HOMO-LUMO gap

  → **Cl ion fully screened (solvated) by water**
- solvent-molecule-counterion electrostatic interactions

  → **modification of molecular electronic states**

  → **possible modification of optical properties (ongoing work)**

force field simulation (I)



globally neutral system

→1 cyanin (cation)

→ 1 Cl^- (counter ion)

→ solvent (2400 H_2O molecules)

large scale system

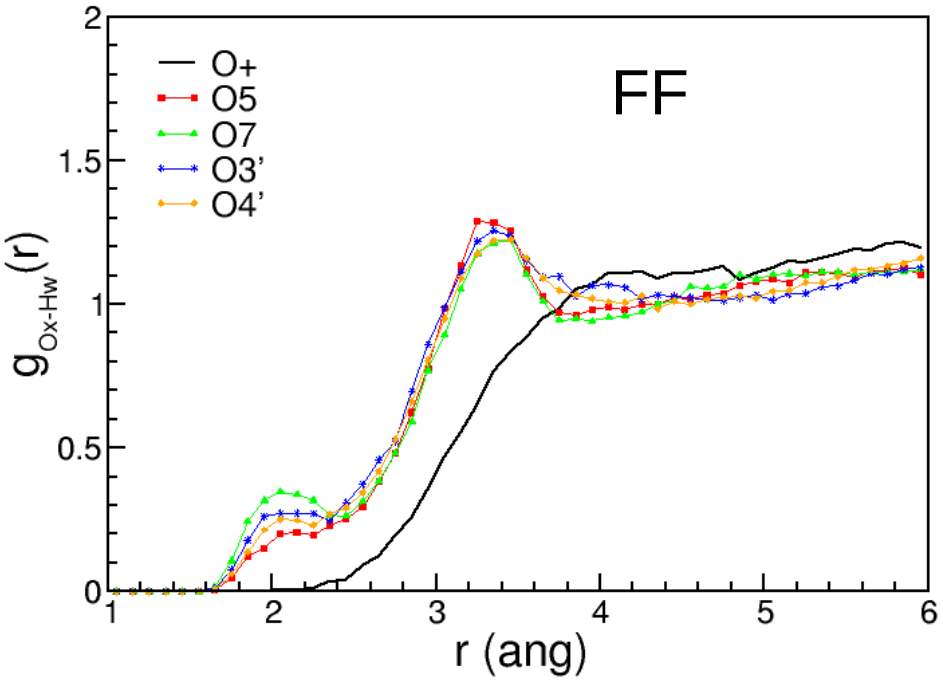
technical details

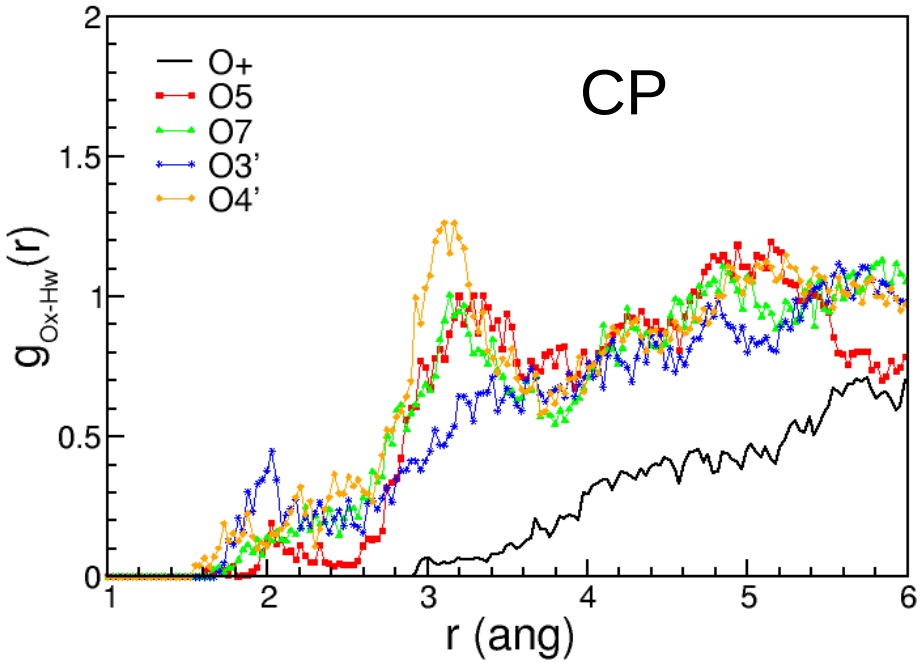
→ constant pressure (1 bar)

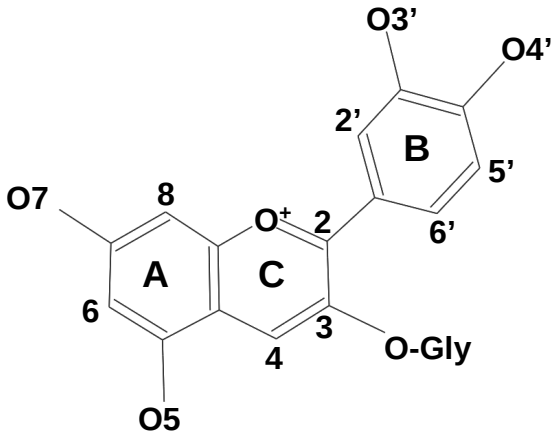
→ δt = 2fs

→ 200 ps of thermal equilibration at T=300K + 5 ns of production time (microcanonical ensemble)

force field simulation (II)







radial distribution functions g(r)

- except O^+ hydroxyl oxygens have similar solvation properties
- **first solvation** shell estimation < 2.5 Å
- mean water molecules in the first shell ~ 20

very good agreement with ab initio results → generalization to other charge-state configurations

conclusions & perspectives

- atomistic characterization of the structural, electronic and hydration properties of CYANIN DEY molecule
- **multiscale approach** from gas phase to fully hydrated system
- important electrostatic **effect of water** on highly polar cyanin molecule → hydrophilic interactions

What's next

- study of the effect of the solvent on the **optical properties** (e.g absorption spectra) → TDDFT calculation (ongoing work)
- extension to other charge state configurations (ongoing work)

outline

- **introduction & motivations**
  - **anthocyanin** in biological, medical and nanoscale systems
  - **cyanin as representative anthocyanin dye**
- **methods → multiscale approach**
  - **single molecule**
    - → *ab initio* (DFT) total energy and force characterization
  - **hydrated molecule**
    - →*ab initio* molecular dynamics (Car-Parrinello)
    - →classical molecular dynamics (force field)
- **results & discussion**
- **conclusions & perspectives**