First principle molecular dynamics of a key reaction of water radiolysis: $OH^-+H^\bullet \rightarrow e^-_{aq}+H_2O$.

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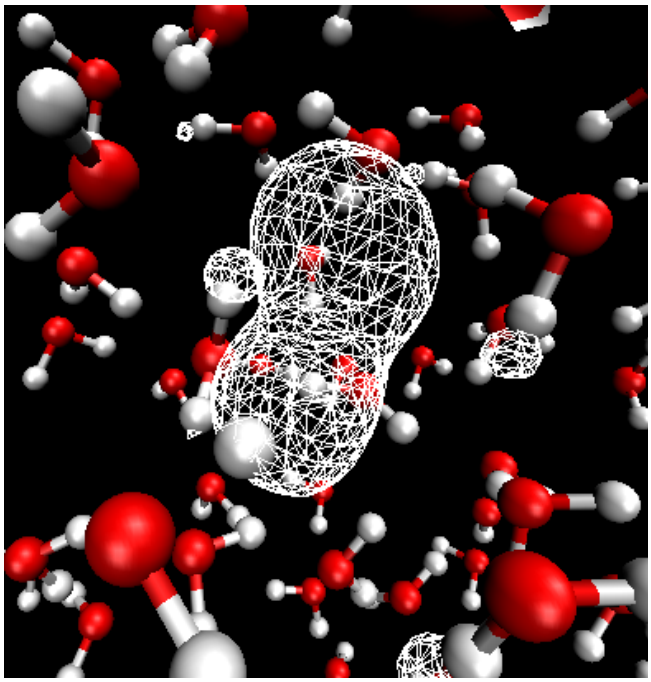
As water is both solvant and reactant in reaction involving radiolytic species, these reactions are highly sensitive to water structure and dynamics. We have tested Car-Parrinello Molecular dynamics as a way to understand radiolysis reactions in water. Ab initio molecular dynamics can take explicitly into account the solvatation effects on the electronic properties, stability and reactivity of radiolytic species. Furthermore most reactions of radiolytic species are rapid enough to be observed spontaneously during simulation. Such calculations have allowed us to decipher the prototype reaction $OH^-+H^\bullet \rightarrow e^-_{aq}+H_2O$.
These simulations share three main features :

- All trajectories have conducted to a reactive event occuring between 1 and 15 ps after equilibration.
- The hydroxyde anion enters the cavity around the $H^\bullet$ atom following a proton transfer allong the H bond network. The “new” hydroxyl anion has lost one of its coordination water. In this configuration, there is now a lone pair available for reaction.
- During the creation of the H-OH bond, the excess electron stays in the anti-bonding orbital that points toward the empty space left by the $H^\bullet$ atom. The water reorganisation leads to a delocalisation of this orbital on the whole cavity.



Wannier orbital of the solvated electron in water at room temperature issued from the reaction $OH^-+H^\circ \rightarrow e^-_{aq}+H_2O$ (t= +35 fs).