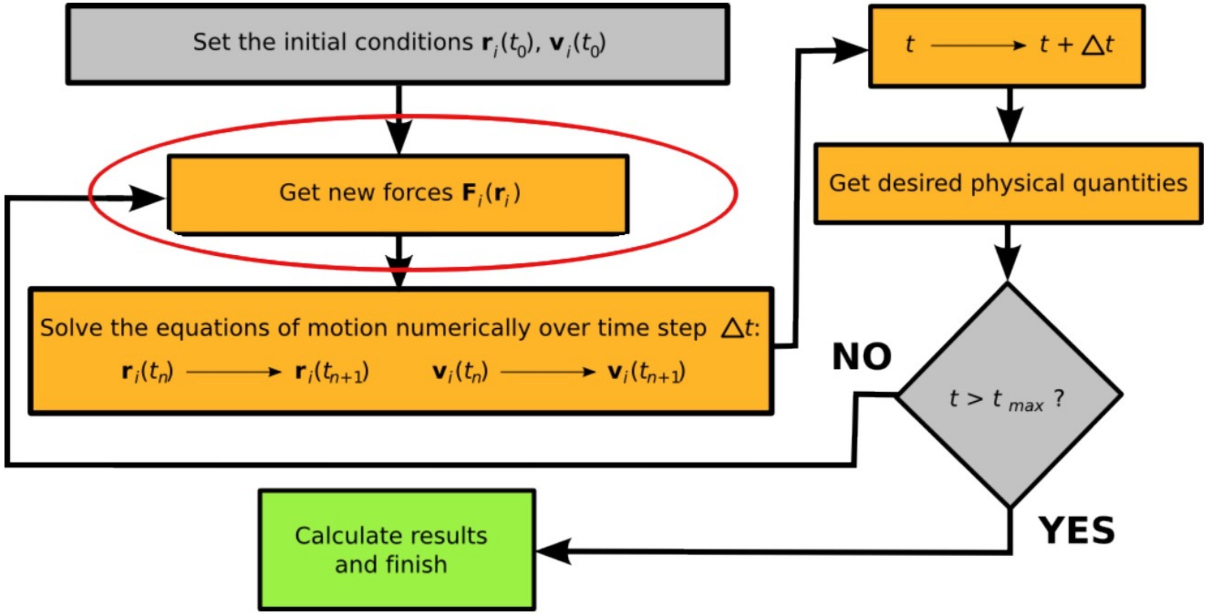
Ab initio molecular dynamics

Why *ab initio* methods in MD?



Set the initial conditions $\mathbf{r}_i(t_0)$, $\mathbf{v}_i(t_0)$

Get new forces $\mathbf{F}_i(\mathbf{r}_i)$

Solve the equations of motion numerically over time step Δt:

$\mathbf{r}_i(t_n) \longrightarrow \mathbf{r}_i(t_{n+1}) \qquad \mathbf{v}_i(t_n) \longrightarrow \mathbf{v}_i(t_{n+1})$

$t \longrightarrow t + \Delta t$

Get desired physical quantities

$t > t_{max}$?

NO

YES

Calculate results and finish

This can be done in two ways

- Fitting an empirical potential
- Generating forces directly from electronic structure calculations as MD trajectory evolves

Ab initio molecular dynamics

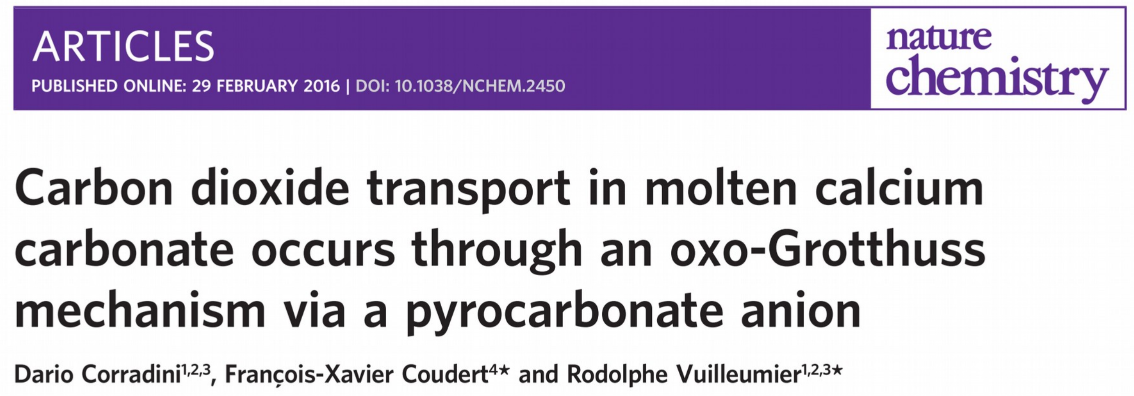
- Parameter-free molecular dynamics: the potential energy surface is obtained from density functional theory

- The price to pay is that the Kohn-Sham equations need to be solved at all the nuclear configurations in a trajectory

- The problem is greatly simplified (conceptually and in practice) by calculating the electronic structure on the fly during nuclear dynamics

- The task is achieved with a generalized molecular dynamics scheme in the extended space of nuclear $\{R\}$ and electronic $\{\psi\}$ coordinates

Example



ARTICLES
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nature chemistry

Carbon dioxide transport in molten calcium carbonate occurs through an oxo-Grotthuss mechanism via a pyrocarbonate anion

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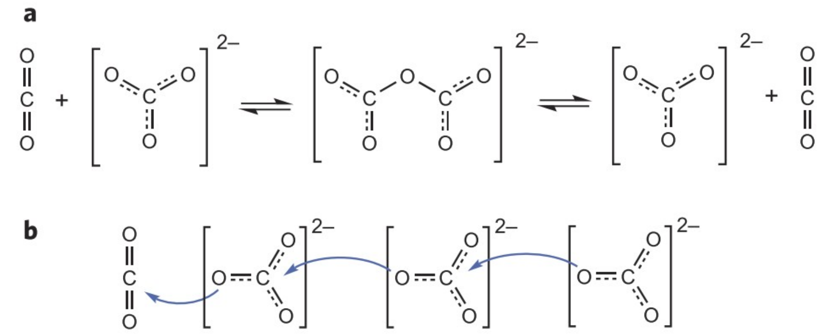
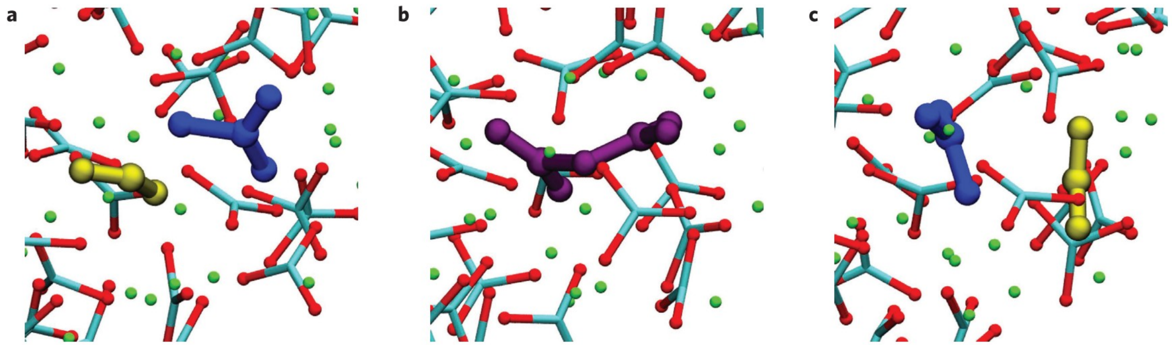


Figure 1 | Oxo-Grotthus mechanism via a pyrocarbonate anion.
a, Formation of the pyrocarbonate ion $C_2O_5^{2-}$ from the reaction of CO_2 with carbonate anion CO_3^{2-}. **b**, A cascading mechanism, with rapid sequence of pyrocarbonate formation and dissociation events.



QM/MM

Combined quantum-mechanics/molecular-mechanics (QM/MM) approaches have become the method of choice for modeling reactions in biomolecular systems.

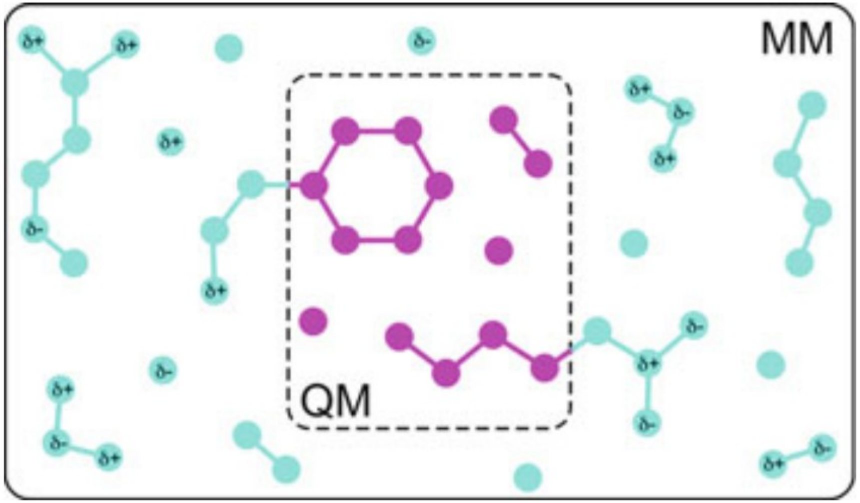


Fig. 1. Illustration of the QM/MM concept. A small region, in which a chemical reaction occurs and therefore cannot be described with a force field, is treated at a sufficiently high level of QM theory. The remainder of the system is modelled at the MM level.

Example: QM/MM

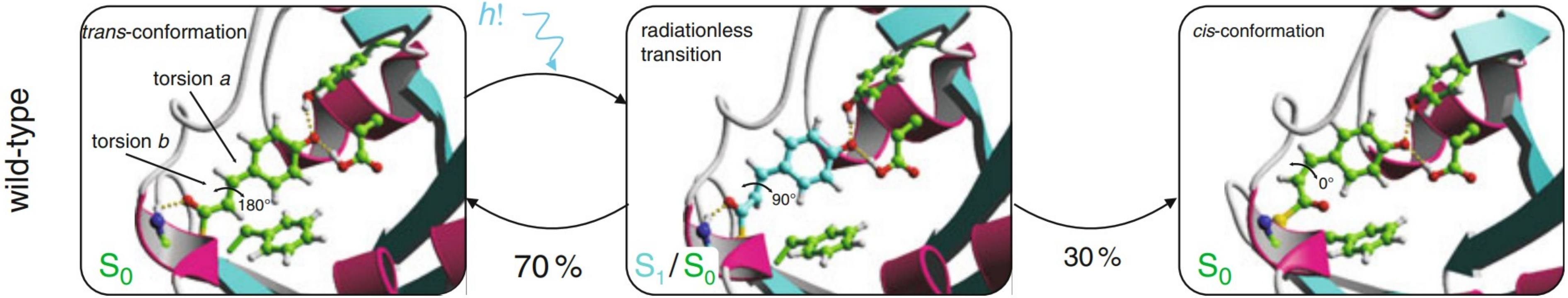


Fig. 7. Snapshots from excited-state trajectories of wild-type PYP, showing the chromophore (pca) in the active site pocket. The first snapshot is at the excitation. The second shows the configuration at the radiationless transition from S_1 to S_0. The third snapshot shows the photoproduct, in which the carbonyl oxygen of the thioester linkage has flipped and is no longer hydrogen bonded to the backbone of Cys69.

Example: QM/MM

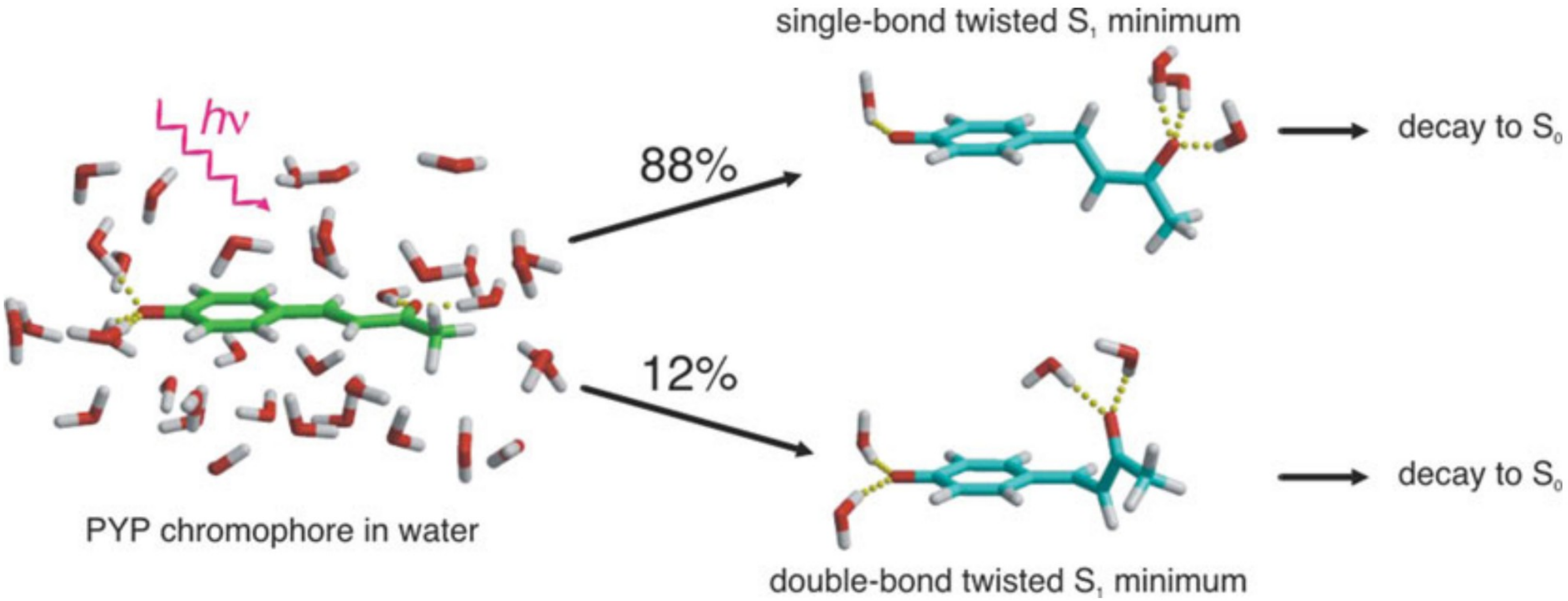


Fig. 10. In water the chromophore undergoes both single-and double-bond isomerization. Excited-state decay from these minima is very efficient due to stabilization of the chromophore's S_1 charge distribution by specific hydrogen bond interactions.