The Effect of a Mobile Solvent Environment on Quantum Control of Chemical Reactions

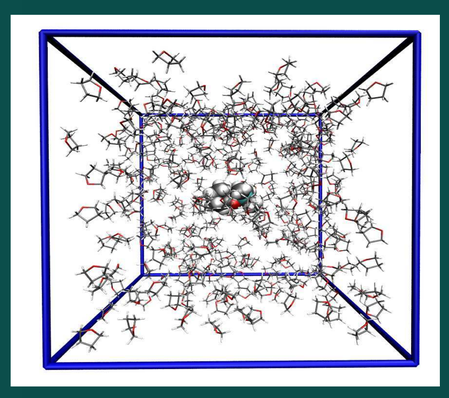
LMU LUDWIG-MAXIMILIANS-UNIVERSITÄT MÜNCHEN

Daniel Keefer and Regina de Vivie-Riedle

Question:
What is the influence of solvent environments on the **controllability** of chemical reactions? Is it possible to overcome the arising complexities?

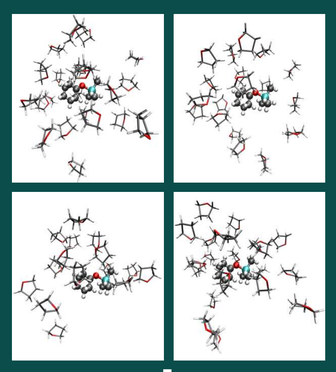
Aspect 1: Quantum Control in Static solvent Cages

Methodology



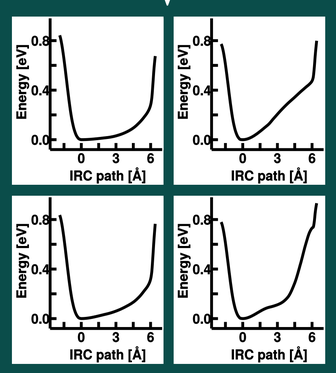
MD simulation
GROMACS/FFOPLSAA

extract snapshots randomly



freeze solvent molecules

compute PES
M062X/6-31G*



define target

Optimal Control Theory

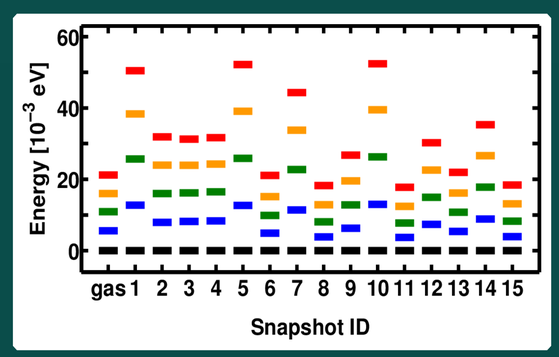
Multi-target Hamiltonian:

$$\mathcal{H}_{mt} = \begin{pmatrix} \ddots & \vdots & \\ \cdots & 0 & \cdots \\ & \vdots & \ddots \end{pmatrix} + \mu\varepsilon$$

optimize laser pulses

Findings

Vibrational energy levels



Control challenge #1: highly imhomogeneous properties

Even highly complex and inhomogeneous targets are controllable!
J. Phys. B **48** (2015), 234003

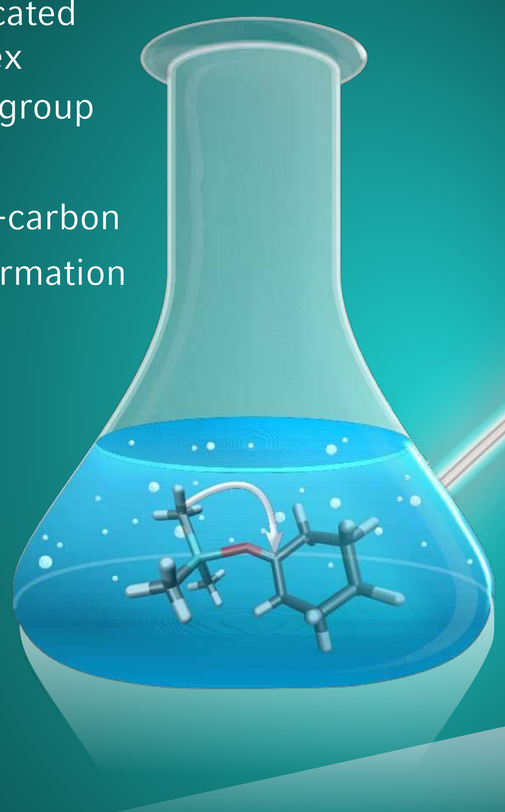
Background references:

QD/MD Procedure:
J. Chem. Theory Comput. **11** (2015), 1987

Multi-target OCT
Phys. Rev. Lett. **89** (2002), 157901

Review on the current stage of quantum control simulations:
J. Phys. B **50** (2017), 082001

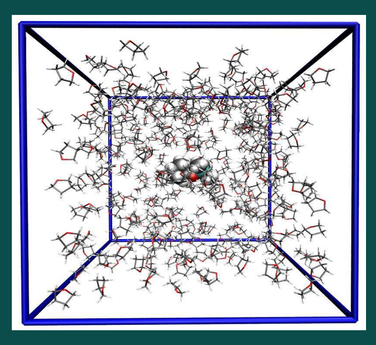
The reaction:
Trimethylaluminium + Cyclohexanone
→ preallocated complex
→ methyl group transfer
→ Carbon-carbon bond formation

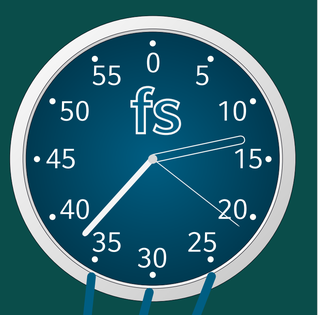


Aspect 2: Is the Reaction Still Controllable if the Environment Changes Over the Pulse Duration?

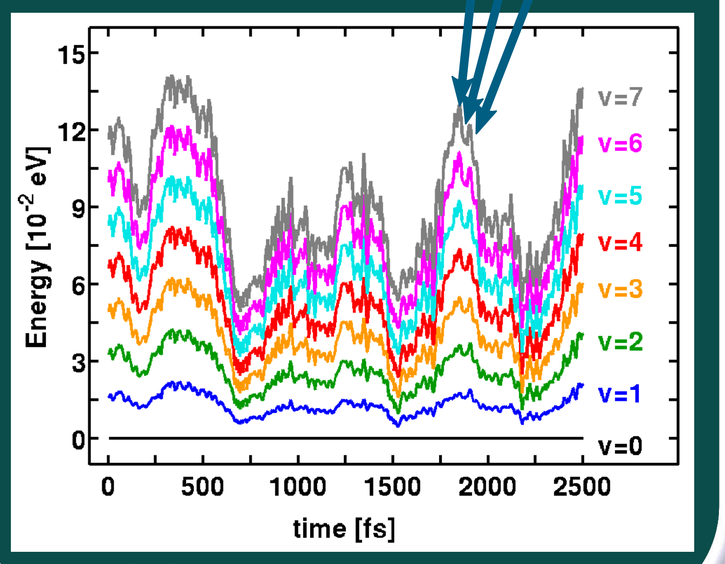
A Question of Timescales

On which timescale does the solvent influence change?





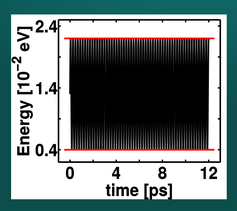
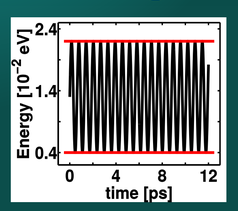
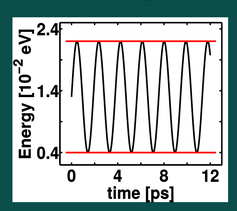
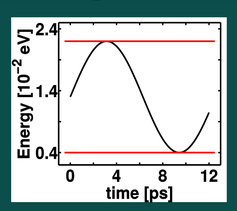
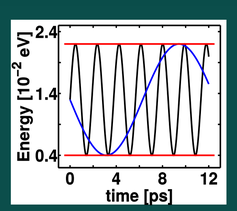
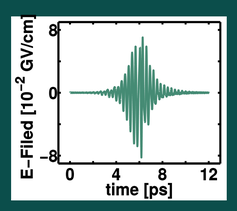
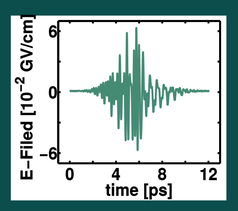
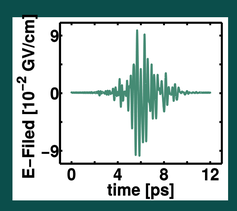
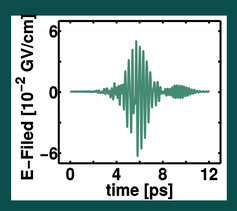
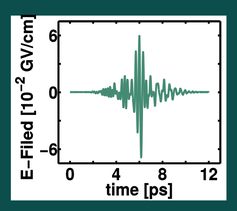
→ single MD trajectory
→ extract snapshot every 5 femtoseconds
→ evaluate level structure



≈ 300 fs between extreme cases

Time dependent Control Targets

Control challenge #2: time-dependent target

control problem					
optimized pulse					
is control possible?	yes	yes	yes	yes	yes

... even for many more cases and more complex multi-target control aims!

Answer(s):
Chemical reactions in solution seem to be controllable ***despite***:
→ highly inhomogeneous line broadening
→ fluctuations of the environment
... at least theoretically

Next steps:
→ improve theoretical description: include feedback from solute to solvent (**PO2-15**)
→ go beyond one-dimensional coordinates