Controlling Chemical Reactions in Their Inhomogeneous Solvent Environment: A Multi Target Approach

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Abstract

What we are interested in:
- Quantum control of molecular processes in condensed phase
- Exploring the limits of optimal control theory (OCT) [1] as the algorithm to design controlling laser fields

Where the main challenges are:
- Solvent environment makes a theoretical description more challenging
- The vast manifoldness of solvent arrangements around the reactant necessitates an elaborate approach for an appropriate theoretical description

What we present:
- Optimization of laser fields for multiple solvent arrangements simultaneously by means of multi target OCT (MTOCT) [2]
- Investigations on how the algorithm deals with increasing control task complexity and on how well the system remains controllable
- A way to statistically estimate how efficient the optimized laser fields are expected to work in the complete thermodynamical ensemble
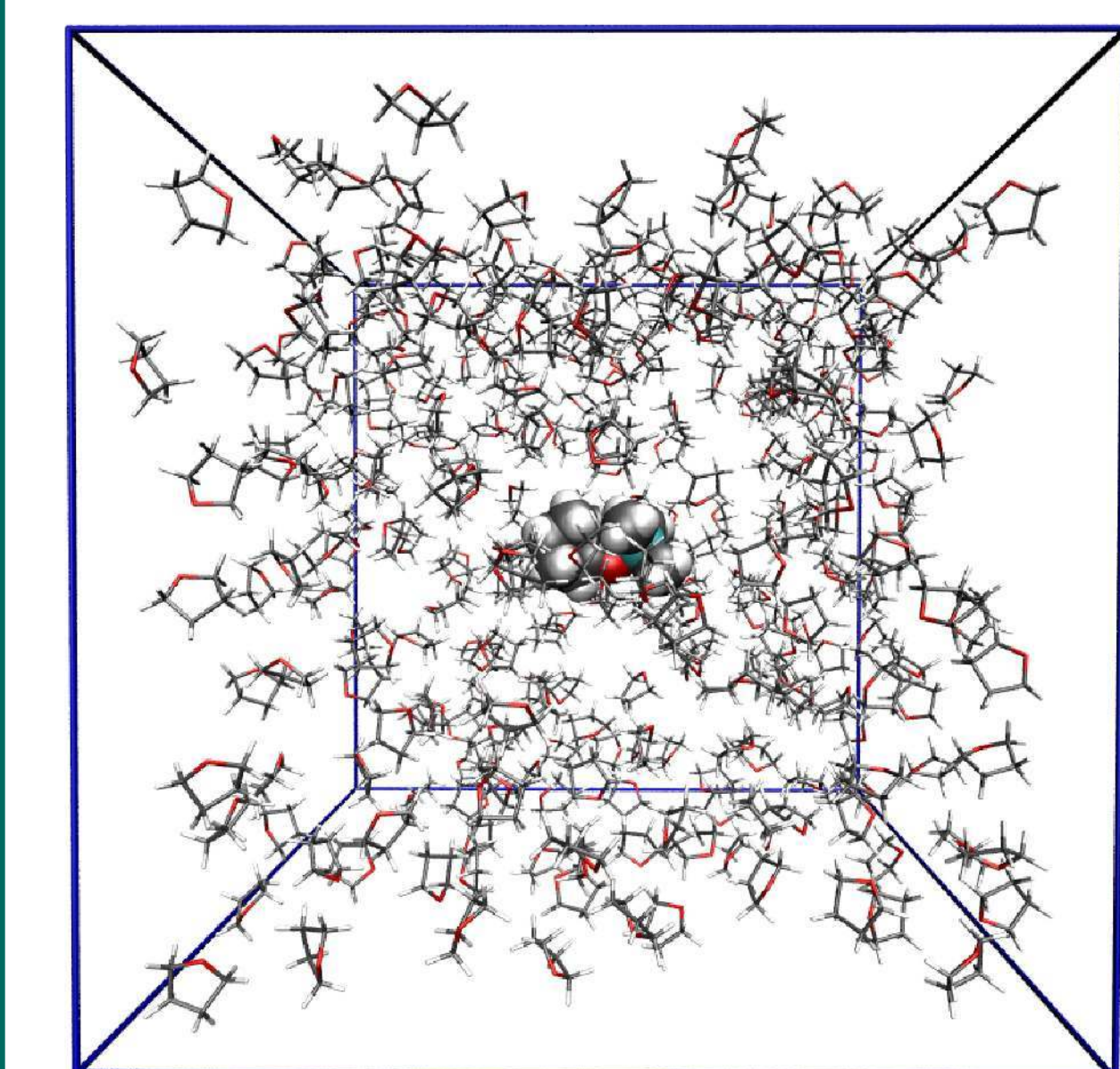
The reaction we want to steer:
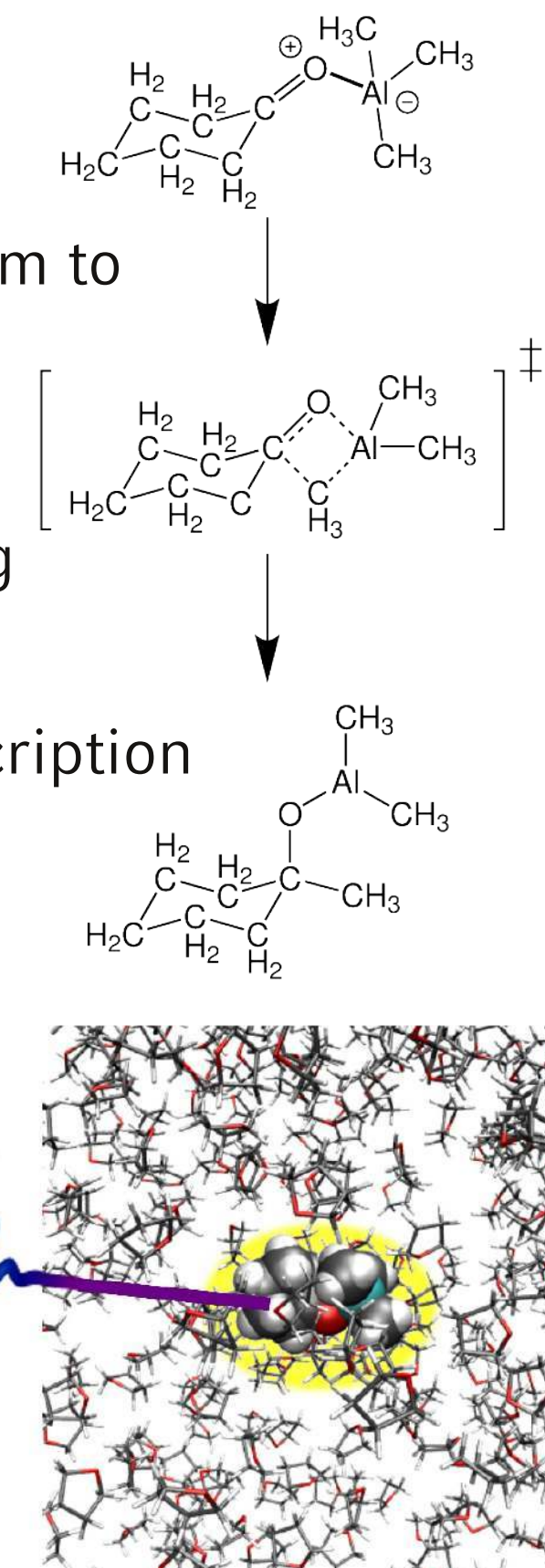
Molecular system and MD simulations
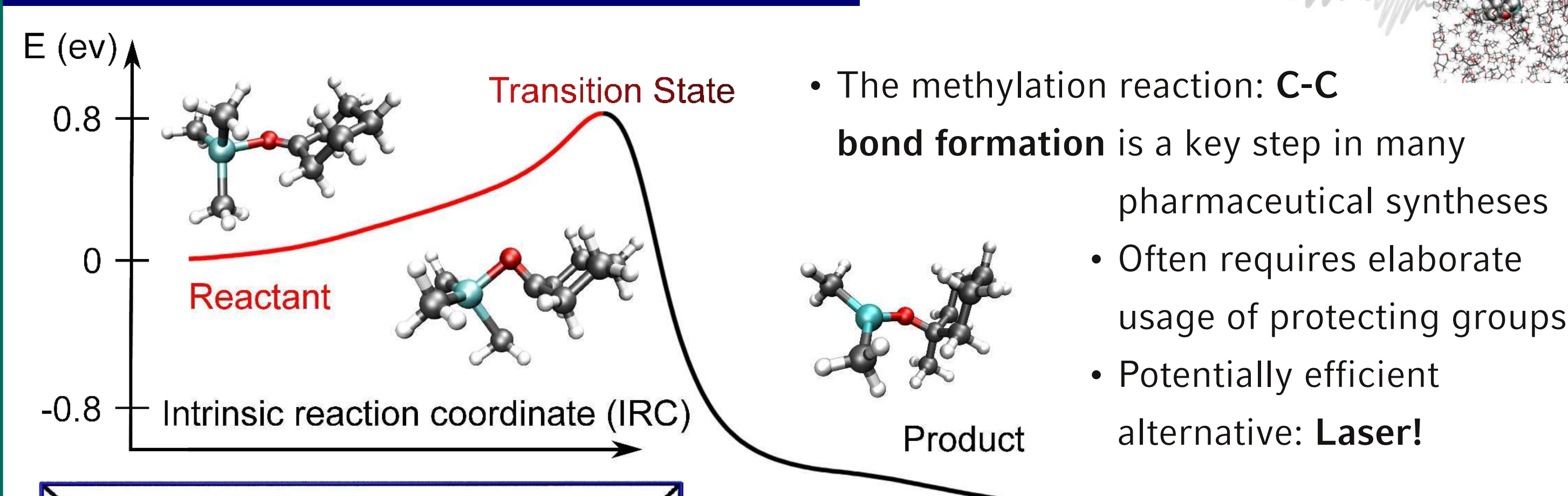
- The methylation reaction: **C-C bond formation** is a key step in many pharmaceutical syntheses
- Often requires elaborate usage of protecting groups
- Potentially efficient alternative: **Laser!**

- **MD simulation** of solvent molecules around the reactant
- Force field: OPLS-AA
- **Extraction of solvent configurations** from MD trajectories at random times [2]

- **Reduction to first solvation shell**
- Insertion of reactant structures along the gas phase IRC into the solvent cage
- **Recomputation of the IRC** potential energy surface (PES) within the frozen solvent cages
- Quantum chemical method: M06-2X/6-31G(d)

Setup for multi target OCT

- Time dependent Schrödinger equation in our approach:

$$ih\frac{\partial}{\partial t}\psi(r_{IRC},t) = \left(-\frac{\hbar^2}{2}m^{-1}\nabla_{r_{IRC}} + V(r_{IRC};R)\right)\psi(r_{IRC},t)$$

- $V(r_{IRC};R)$ depends parametrically on the solvent coordinates R of one particular snapshot

- Influence of the solvent cage on the **PES**... ...and on the **vibrational energy levels**
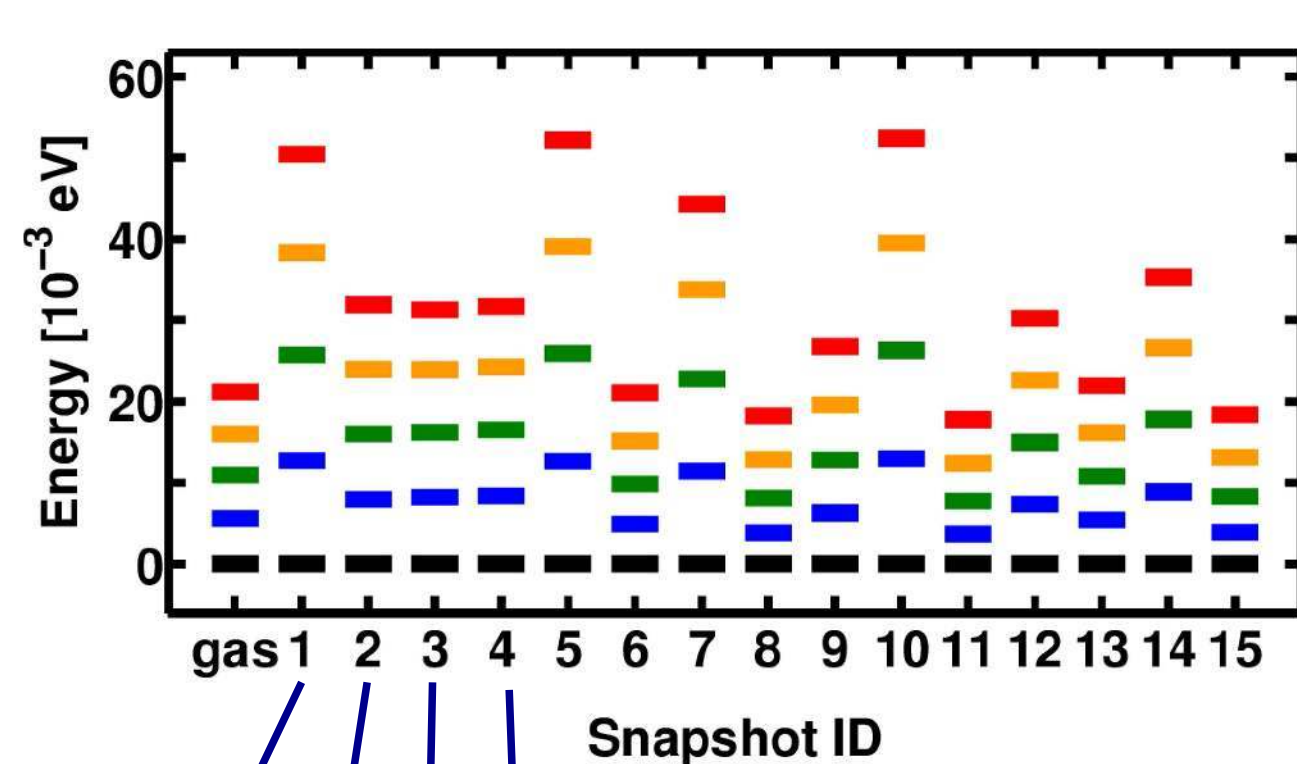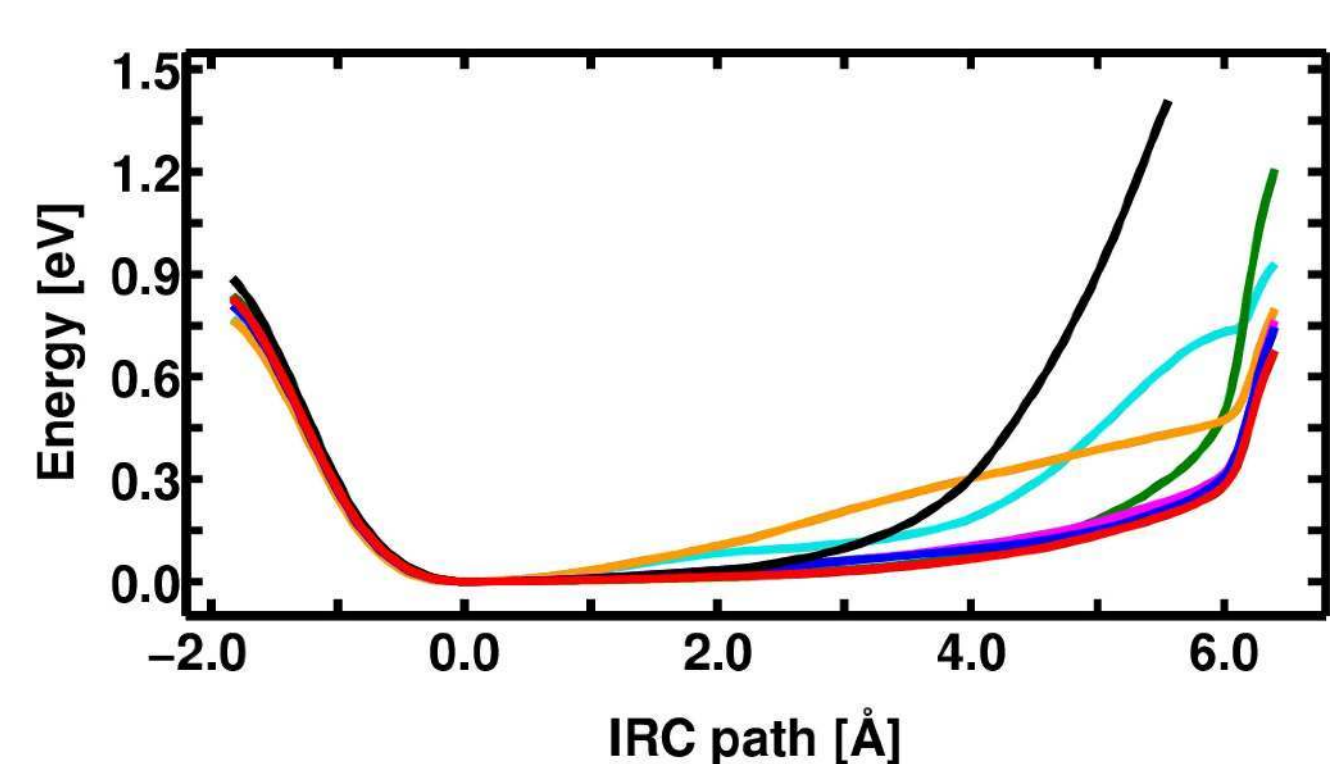
- Multiple snapshots are combined within the **multi target Hamiltonian**:
- Q: Vibrational energy levels
- M: Transition dipole matrix

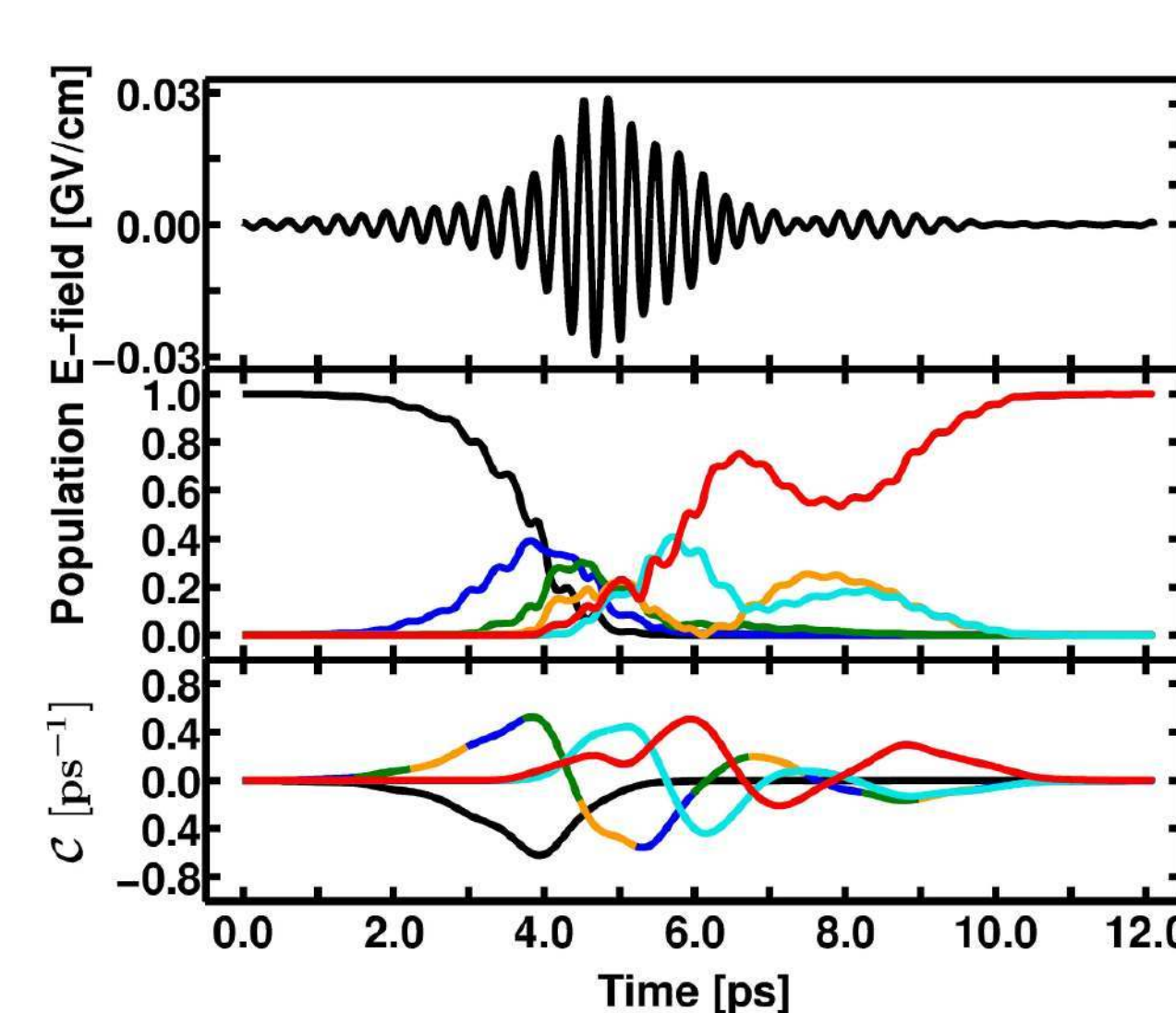$$\mathscr{H}_r(r_{IRC};R) = \begin{pmatrix} \underline{Q_1} & 0 & \cdots \\ 0 & \underline{Q_2} & \\ \vdots & & \underline{Q_3} \\ & & & \underline{Q_4} \end{pmatrix} - \varepsilon(t)\begin{pmatrix} \underline{M_1} & 0 & \cdots \\ 0 & \underline{M_2} & \\ \vdots & & \underline{M_3} \\ & & & \underline{M_4} \end{pmatrix}$$

- general OCT functional: $J[\psi_i(t),\psi_f(t),\varepsilon(t)] = F[\psi_i(t)] - \int_0^T s(t)|\varepsilon(t)|^2 dt - \int_0^T \psi_f(t)G[\psi_i(t),\varepsilon(t)]dt$

- Multi target control aim: $F[\psi_{i1}(t),\psi_{i2}(t),...,\psi_{iN}(t)] = \sum_{k=1}^{N}|\langle\psi_{ik}(t)|\phi_{fk}(T)\rangle|^2$

- In our case: maximum population in v = 4 in every snapshot
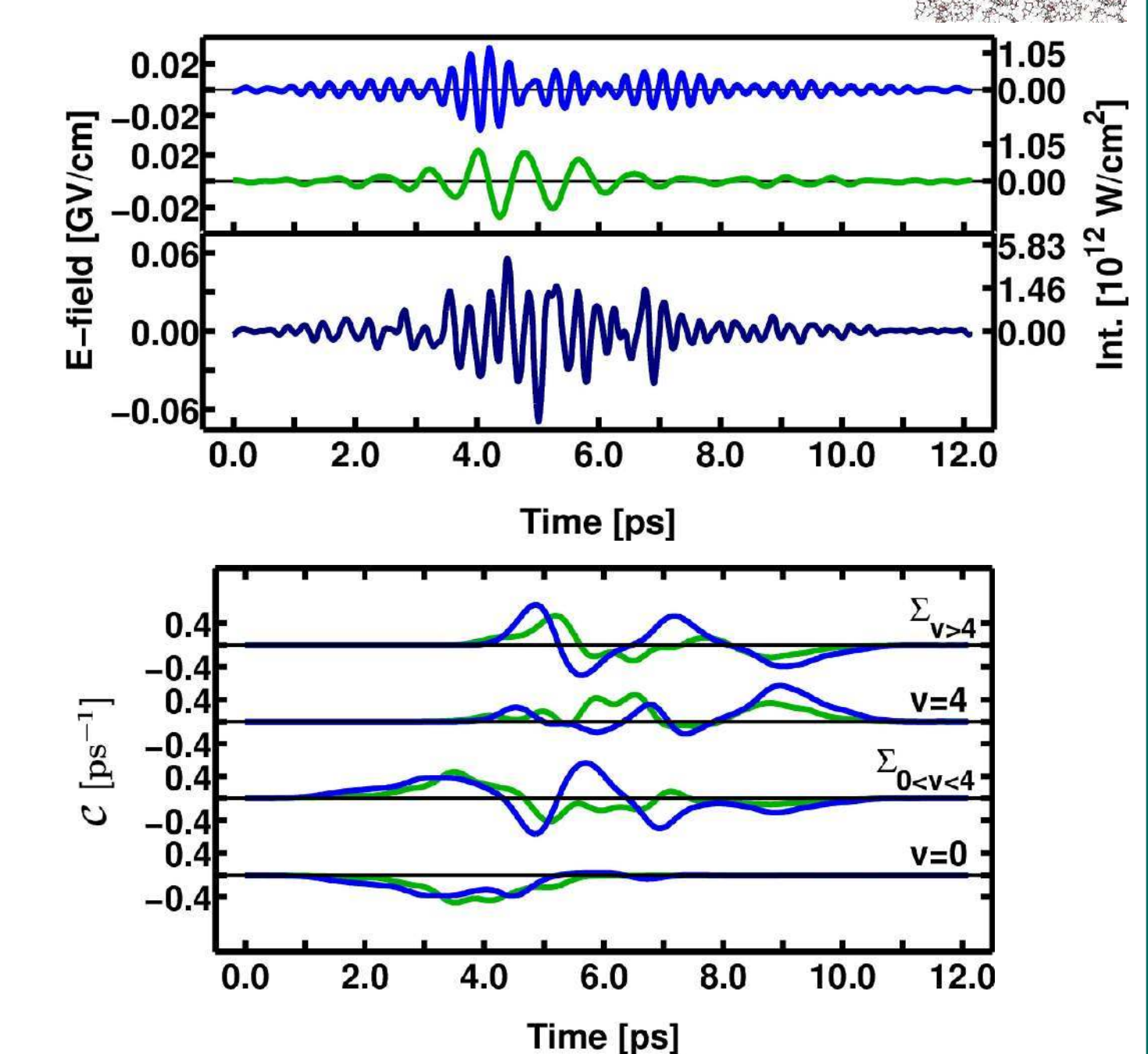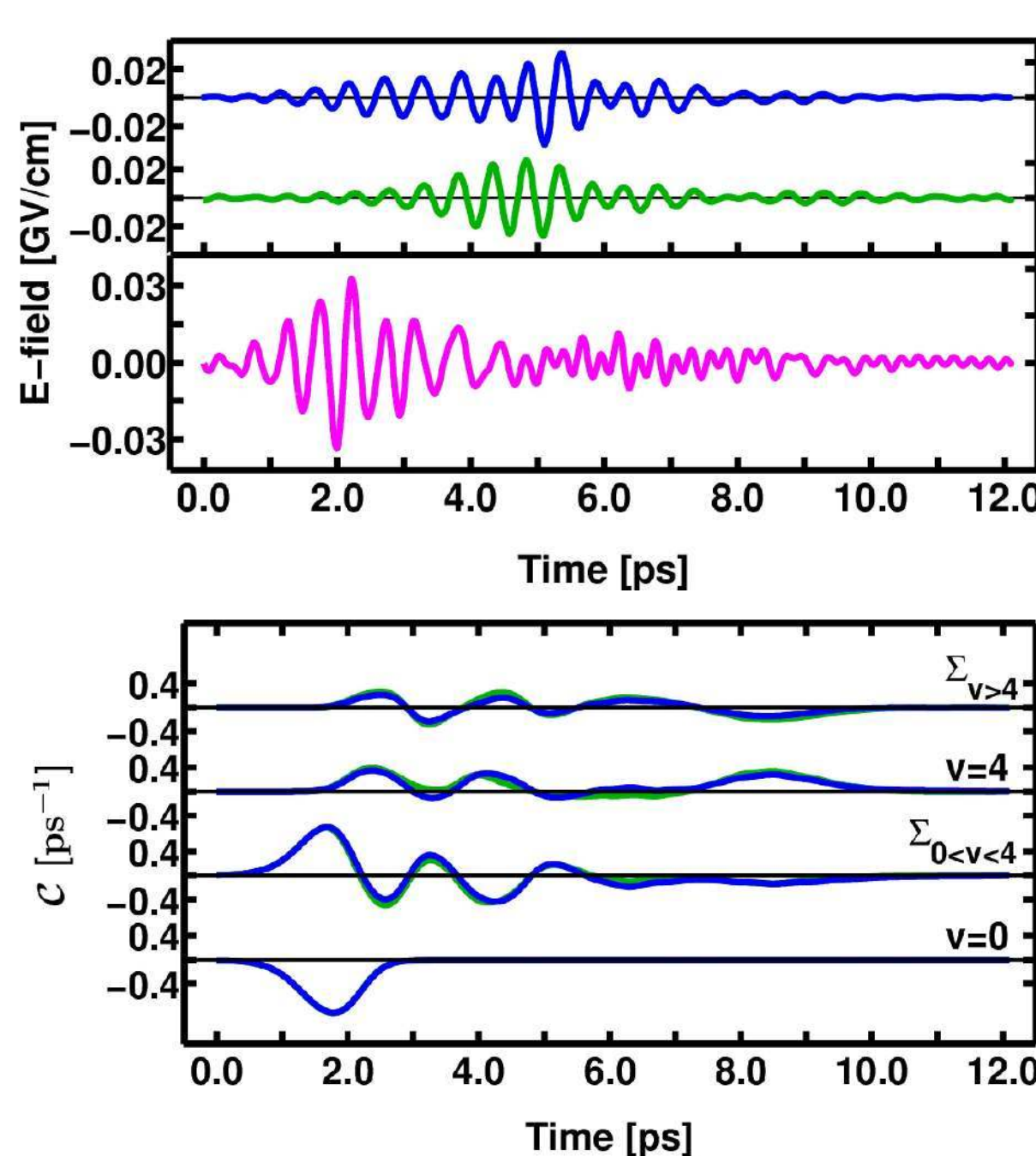
General control mechanism

- Typical ladder climbing
- At the end: discrimination between neighbouring states
- High population yield in the target state
- Smoothened population derivative C indicates times where population is shifted
- Differences in the vibrational level structure in other snapshots lead to significantly different pulse features
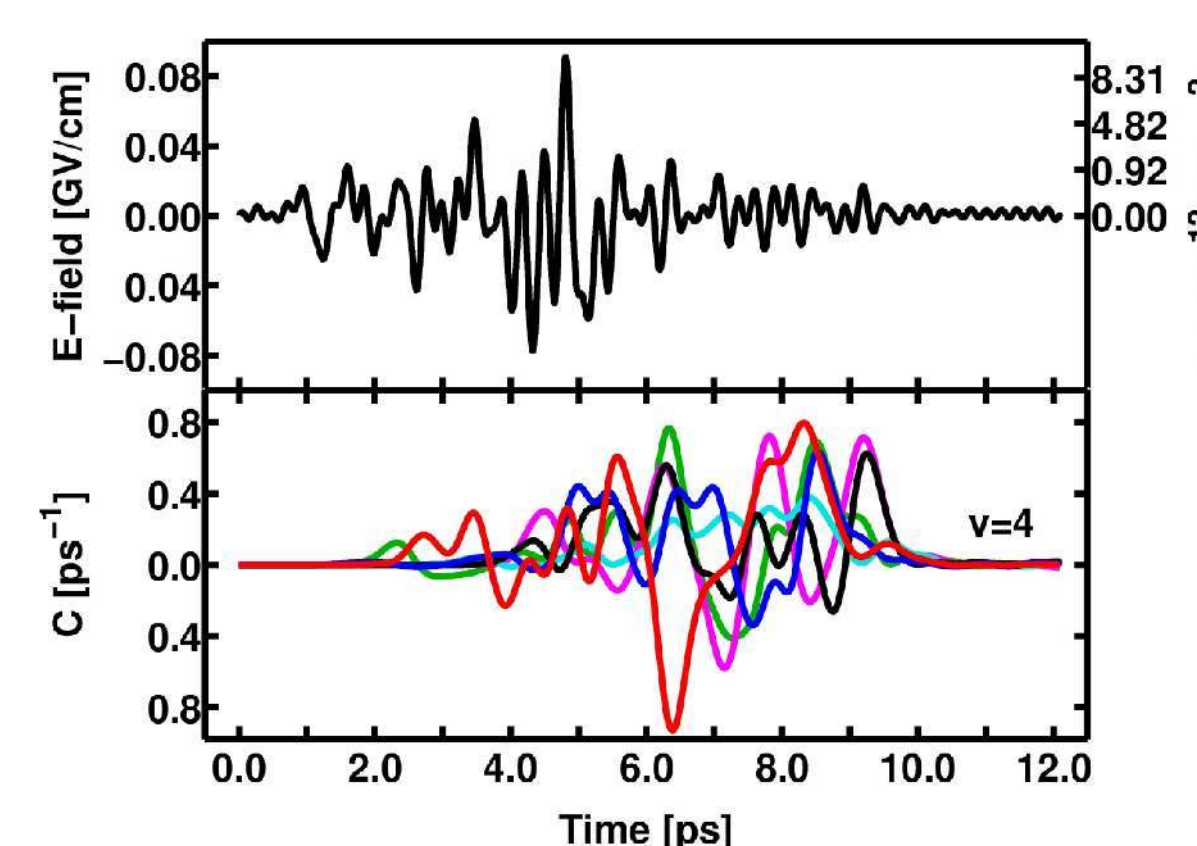
Multi target systems

Two similar snapshots versus two different snapshots

- Pulse complexity and intensity: **lower** vs **higher**
- Population yield in target state: **99.0 %** vs **97.7 %**
- Control mechanism: **homogeneous** vs **heterogeneous**

Increasing the control task complexity: six different snapshots

- Snapshots were chosen to have different vibrational spectra
- The optimal control mechanism consists in a rather individual treatment of the included snapshots
- Population yield still at 94.0 %

Statistical estimate for the thermodynamical ensemble

- **How effective is a pulse which was optimized for a number of L snapshots in the complete thermodynamical ensemble ?**
- Estimate is based on the population yields $Y_{i\rightarrow j}$, which a pulse optimized for snapshot i achieves in j
- Calculate empirical distribution function:

$$F(y) = \frac{1}{N}\sum_{i=1}^{N}\sum_{j>i}^{N}1\{Y_{i\rightarrow j}\leq y\}$$

- The derivative of $F(y)$ is the probability distribution, whose expectation value gives an estimate on the average population yield:

$$\langle y\rangle = \int_0^1 \frac{d}{dy}(F(y))^L\ y\ dy$$

Number of snapshots	Max. pulse intensity [10^{12} W/cm^2]	Y [%]	Y_{eff} [%]
1	1.17	99.4	3.95
2 (sim.)	1.48	99.0	9.4
2 (diff.)	6.33	97.7	9.2
4	12.90	97.1	14.6
6	10.94	94.0	19.2
16	7.86	63.5	23.5

- Multiplying $\langle y\rangle$ with Y gives the **estimated effective yield Y_{eff}** in the complete ensemble

Conclusion

- Explicit solvent environment introduces **inhomogeneity** to the vibrational level structure
  → **MTOCT can handle the challenge**
- Increasing the **control task complexity** by combining different snapshots
  → **System remains controllable**
- **Only six solvent arrangements** have to be considered to have an estimated population yield of almost 20 % in the thermodynamical ensemble
  → **Sufficient for consecutive pulse application**

References

[1] P. von den Hoff, S. Thallmair, M. Kowalewski, R. Siemering, R. de Vivie-Riedle, *Phys. Chem. Chem. Phys.* **14** (2012), 14461-14485.

[2] C. M. Tesch, R. de Vivie-Riedle, *Phys. Rev. Lett.* **89** (2002), 157901

[3] S. Thallmair, J. P. P. Zauleck, R. de Vivie-Riedle, *J. Chem. Theory Comput.* **11** (2015), 1987-1995