



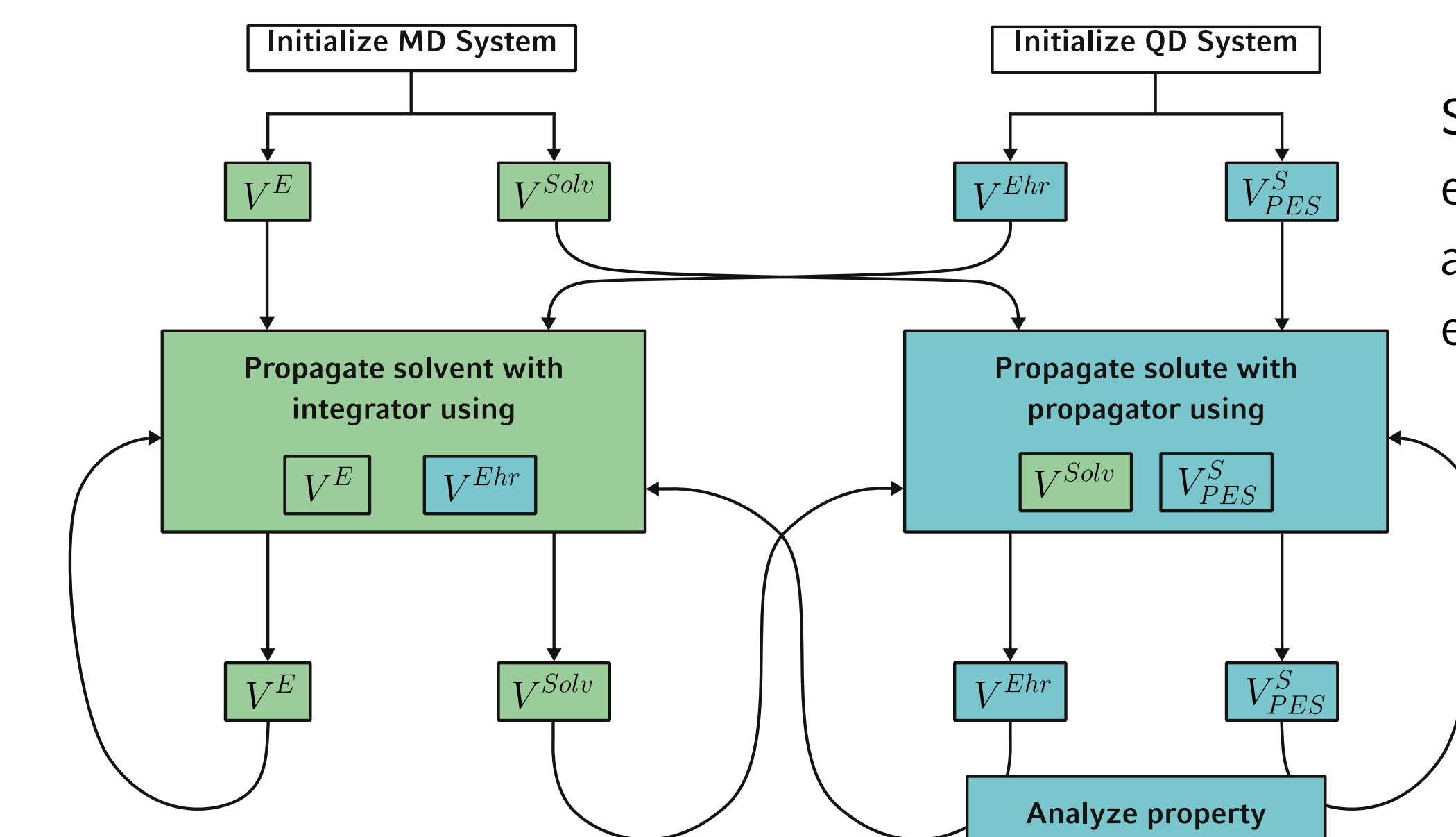
## ABSTRACT

Photochemical reactions often involve highly non-classical phenomena such as tunneling or passing through conical intersections. In these cases a description of motion by a quantum wavepacket is necessary.

Solvents critically influence photochemical reactions [1]. Static solvent effects can for example be treated by QM/MM methods. However, when solvent molecules inhibit or deflect molecular motion, dynamic solvent effects become important. To model these interactions, we present an approach that couples a central quantum wavepacket to a classical molecular dynamics environment (QD/MD).

The coupling uses a quantum classical time-dependent self-consistent field (Ehrenfest dynamics).

## ALGORITHM AND IMPLEMENTATION

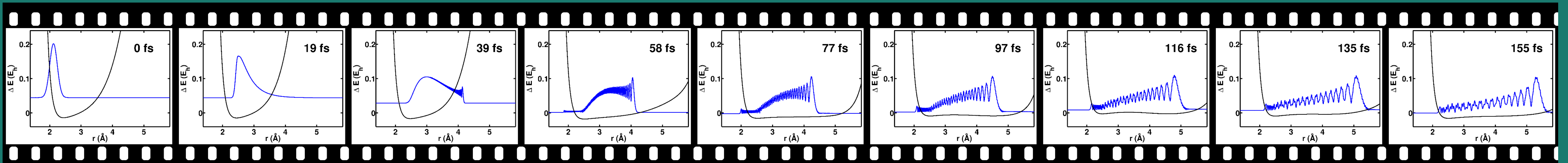


Implementation using a home-built QD program and GROMACS [2]

Simultaneous solution of Newton's equations for the classical **Solvent** and the time-dependent Schrödinger equation for the quantum **Solute**

$$M_I \ddot{R}_I = -\nabla_I \sum_J V_{IJ}^E - \nabla \langle \Psi^S | V_{I,J}^{ES} | \Psi^S \rangle_{V^{Ehr}}$$

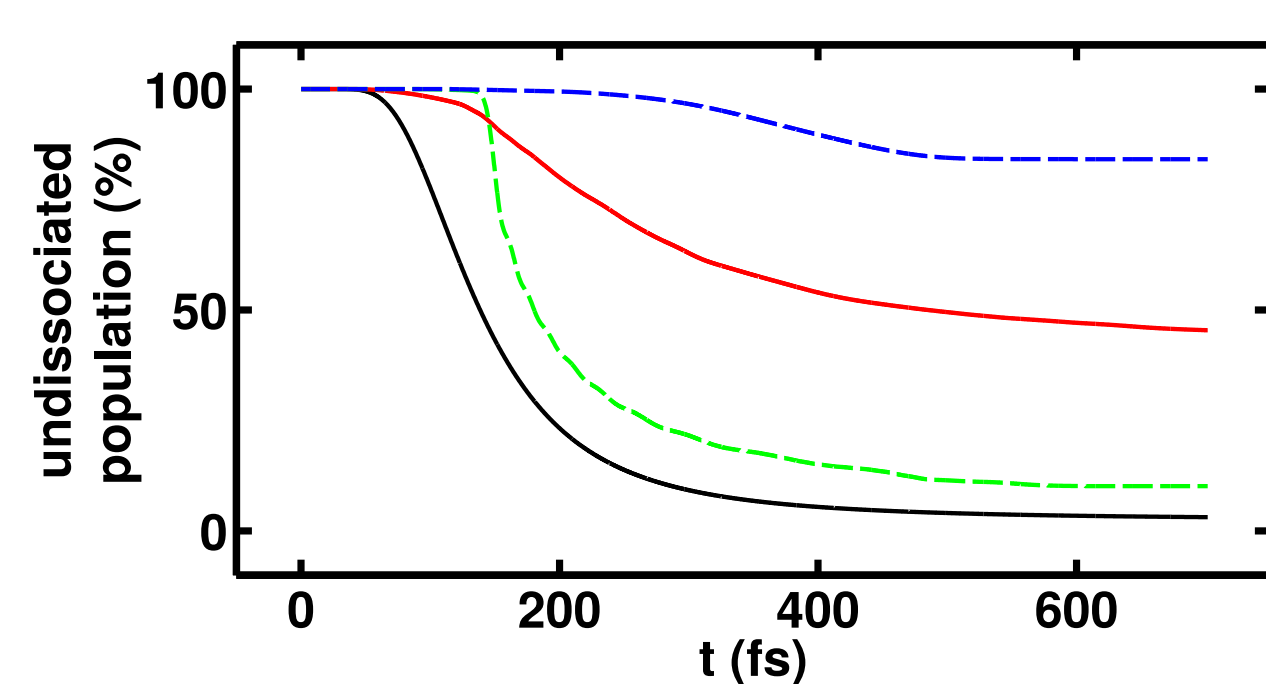
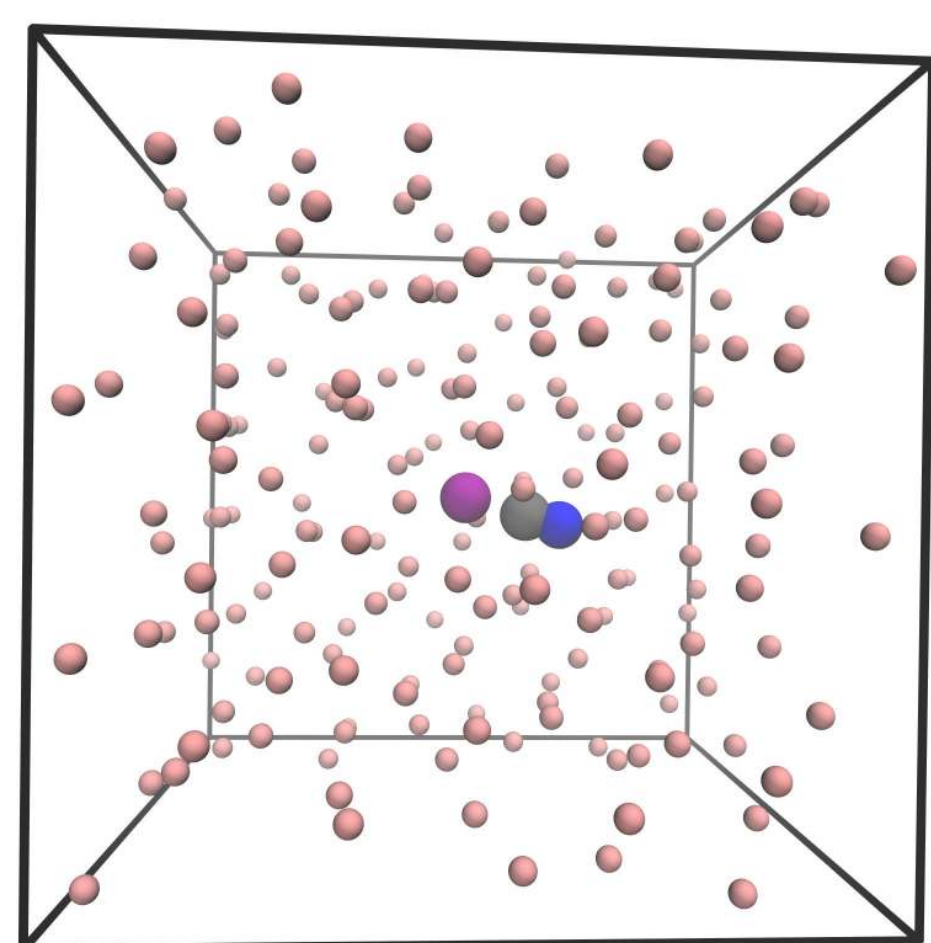
$$i\hbar \frac{\partial \Psi^S}{\partial t} = (T^S + V_{PES}^S + \sum_I V_I^{ES}) \Psi^S$$



## ICN IN LIQUID ARGON

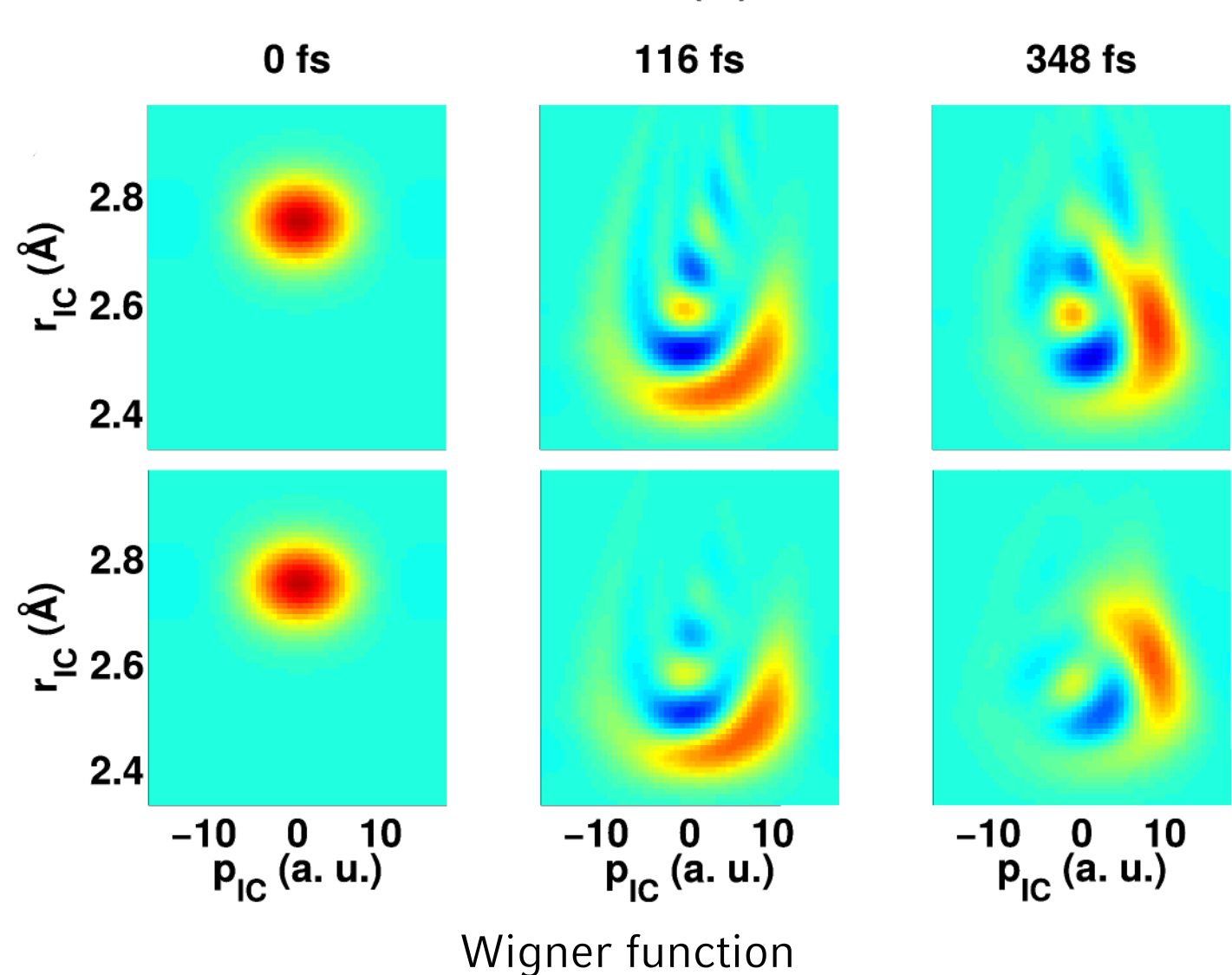
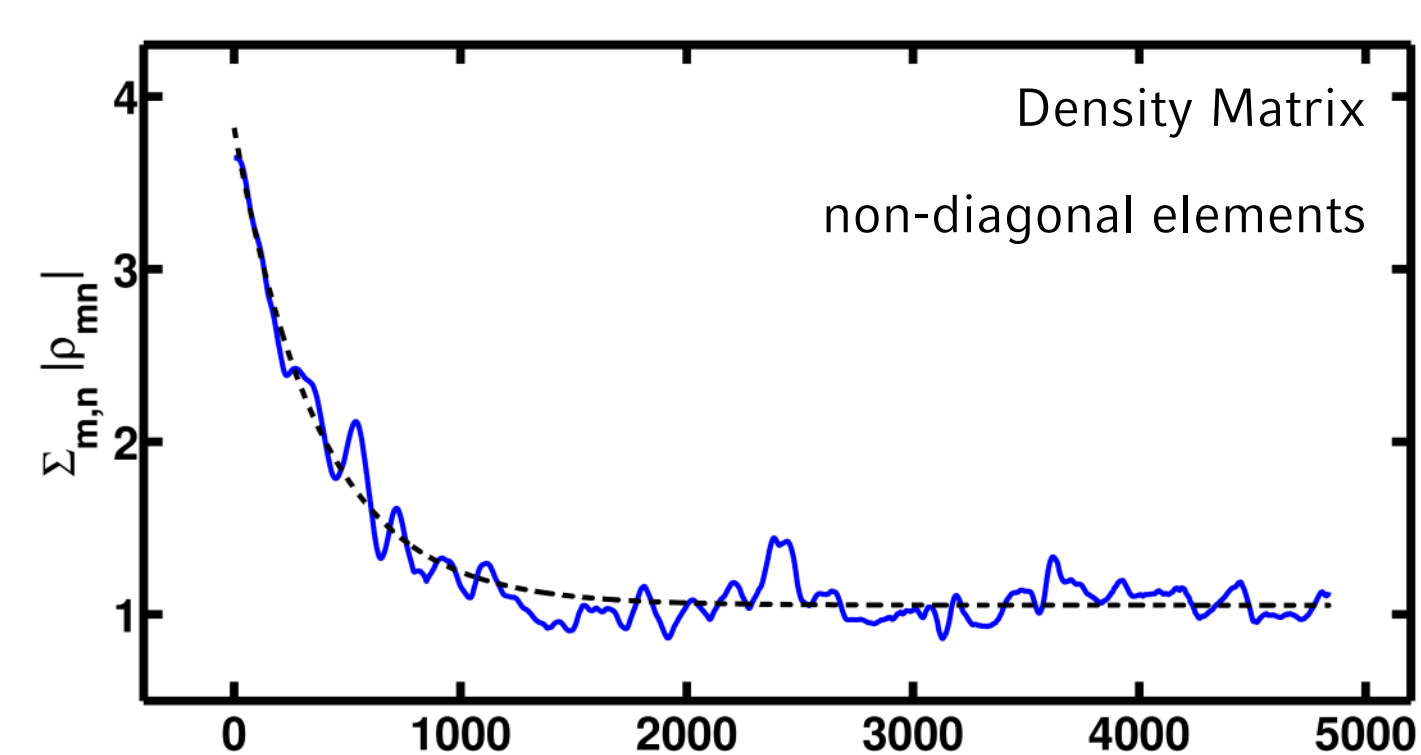
## System:

one ICN molecule, 200 Ar atoms, 84 K, 1 bar, simplified 1D one-state model for dissociation



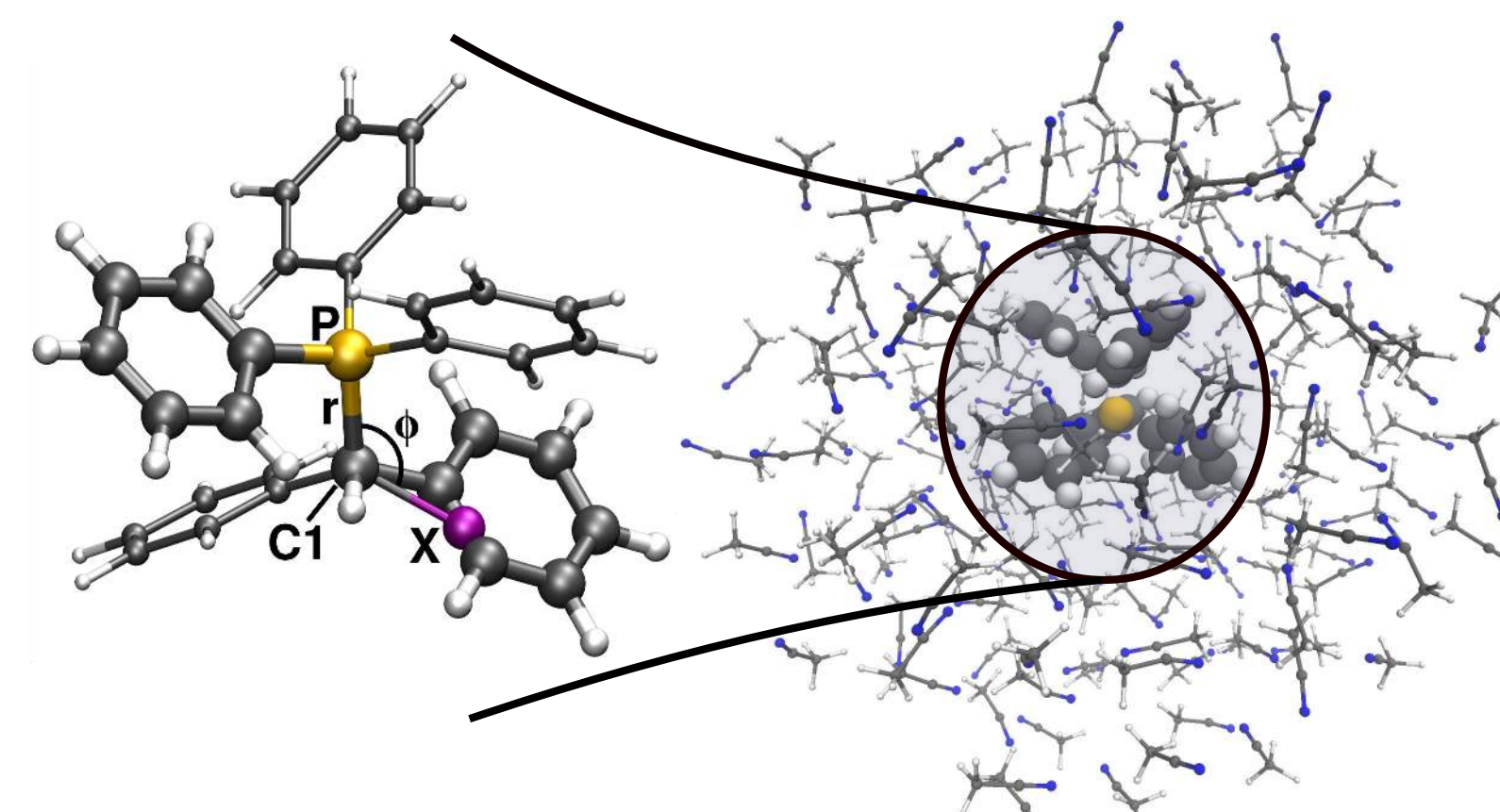
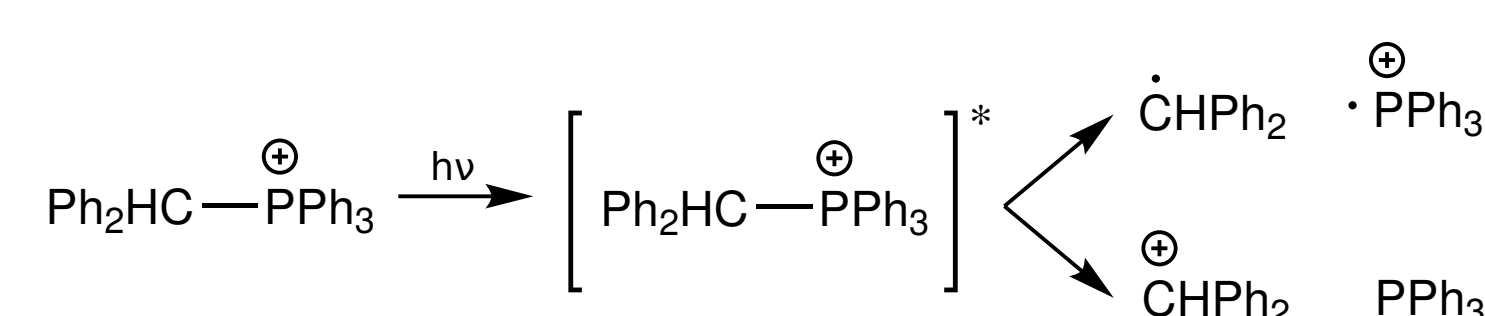
The dissociation outcome strongly depends on the initial solvent configuration.

A sample propagation of the quantum subsystem is shown in the top filmstrip.



When averaging over different solvent configurations, decoherence can be observed in the quantum subsystem.

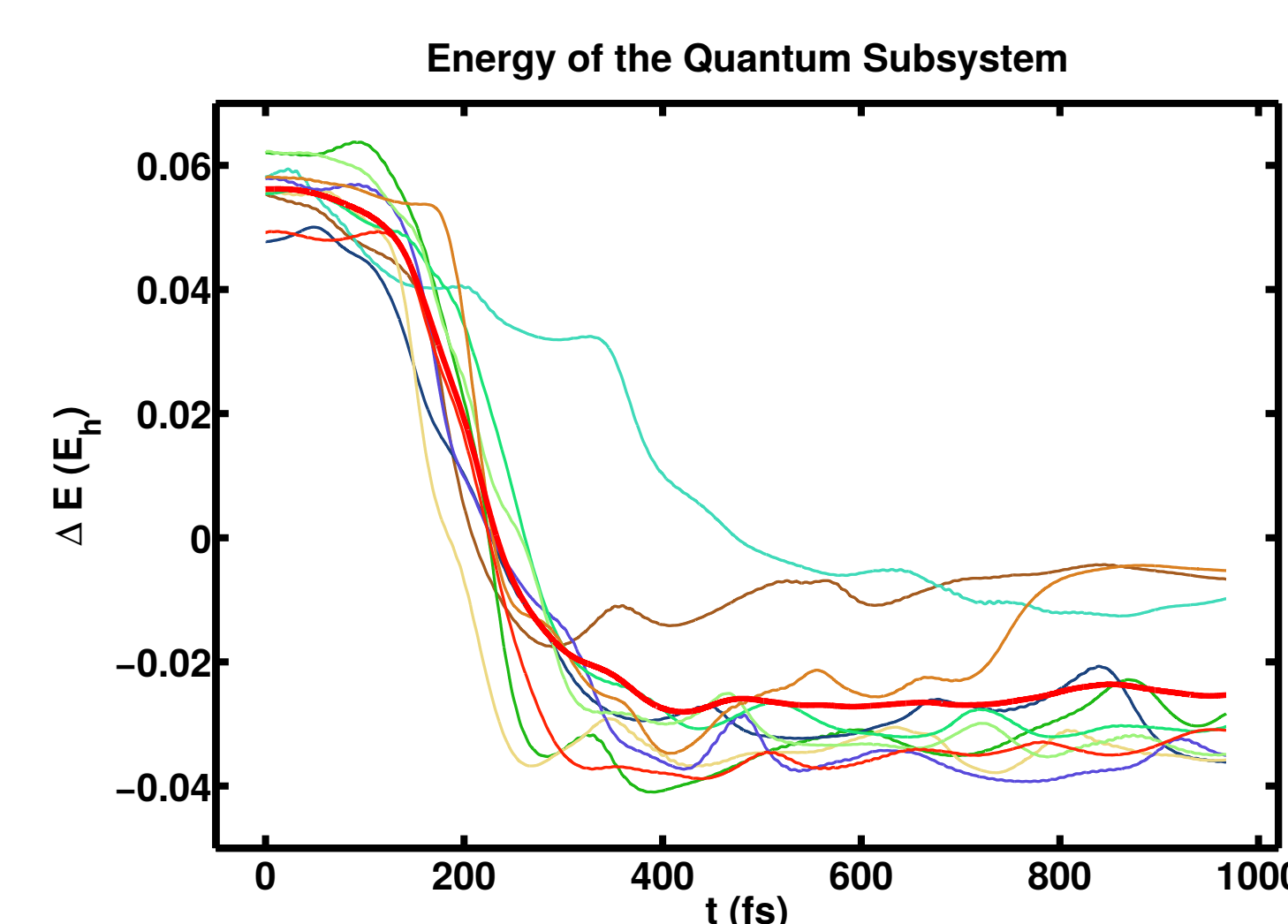
## CARBOCATION PRECURSOR IN ACETONITRILE



The dissociation behavior of diphenylmethyl compounds is strongly influenced by the solvent and can only be explained when considering dynamic solvent effects [3].

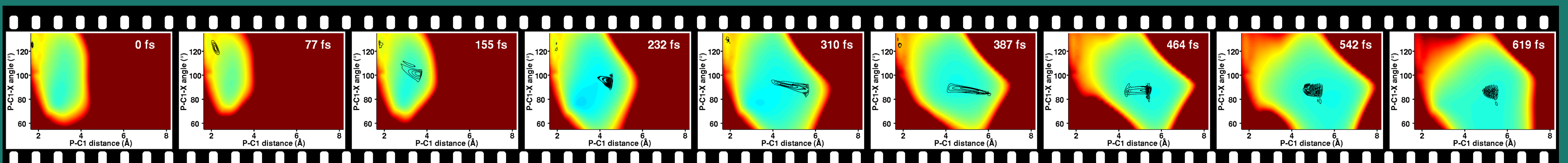
## System:

one diphenylmethyltriphenylphosphonium cation, 484 acetonitrile molecules, 300 K, 1 bar, 2D one or two-state model for dissociation.



During the dissociation, energy transfer in both directions can be observed. In the mean, the energy of the quantum system is dissipated into the classical system after ~400 fs.

A sample propagation of the quantum subsystem is shown in the bottom filmstrip.



## CONCLUSION

The **environment** needs explicit description in some photochemical problems

**Wavepacket Dynamics** accurately describes coherent molecular processes

QD/MD Interaction via Q/C-TDSCF

Simulation of

- deflection/deceleration of molecular motion
  - vibrational decoherence/dephasing
  - solute-solvent energy transfer in a wavepacket picture.

## OUTLOOK

- Multiconfigurational solute-solvent coupling
- high-level System: MCTDH or Gaussian-based methods for higher dimensionality
- Multistate Systems, Laser Interaction (Optimal Control Theory)
- Applications: Photoreactions in complex environments (DNA, proteins), solvent effects on photoswitches

## REFERENCES

- [1] S. Thallmair, J. P. P. Zauleck, R. de Vivie-Riedle *J. Chem. Theory Comput.* **2015**, *11*, 1987-1995.
- [2] M. J. Abraham, T. Murtola, R. Schulz, S. Páll, J. C. Smith, B. Hess, E. Lindahl, *SoftwareX* **2015**, *1-2*, 19-25.
- [3] S. Thallmair, M. K. Roos, R. de Vivie-Riedle *Struct. Dyn.* **2016**, *3*, 043205.