Observing and controlling the coupled nuclear and electron dynamics in the nucleobase uracil

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Abstract

Studying photo-induced processes, like the interaction of a molecule with an ultrashort laser pulse, or the coupling at a conical intersection (CoIn), the interplay between electron dynamics and nuclear motion becomes relevant. The nuclear dynamics usually leads to a fast decoherence of the induced coherent electron dynamics. In some systems also a reappearance of the coherent electron dynamics can be observed [1]. We studied this situation for the nucleobase uracil, which exhibits an ultrafast relaxation mechanism mediated by CoIn's. Applying our ansatz for the coupled description of the nuclear and electron dynamics in molecular systems (NEMol) [2,3] the excitation by a laser pulse and the non-adiabatic relaxation were explicitly simulated and the coherent electron dynamics monitored.

The insights into the electron and nuclear dynamics given by quantum mechanical simulations create the possibility to modify or control the dynamics. Due to their extraordinary properties CoIn's enable optical control possibilities in the few femtosecond regime. We focused on a control scheme relying on the carrier envelope phase (CEP) of a few-cycle IR pulse [4,5,6]. Before the wave packet reaches the CoIn the laser interaction creates an electronic superposition. The imprinted phase information can be modified by the CEP in order to influence the population transfer through the CoIn. This control scheme was applied to the nucleobase uracil, which exhibits multiple crossings of the wave packet over its CoIn seam.

Introduction to the NEMol ansatz

- Ansatz for the total wavefunction:

$$\Phi_{tot}(r,t;\langle R\rangle(t)) = \int \chi^{*}_{tot}(R,t)\Psi_{tot}(r,R,t)dR$$

- determine the coupled one-electron density [1,2,3]:

NEMol

$$\rho(r,t;\langle R\rangle(t)) = \sum_j A_{jj}(t)\,\rho_{jj}(r;\langle R\rangle(t))$$

state specific electronic density

$$+ \sum_{k>j} 2Re\{A_{jk}(t)\,\rho_{jk}(r;\langle R\rangle(t))e^{-i\xi_{jk}(t)}\}$$

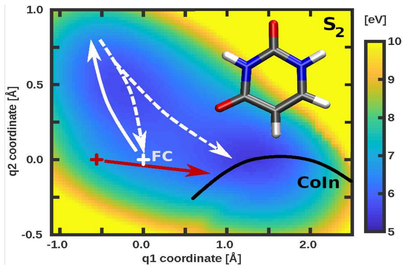
coherent electronic density

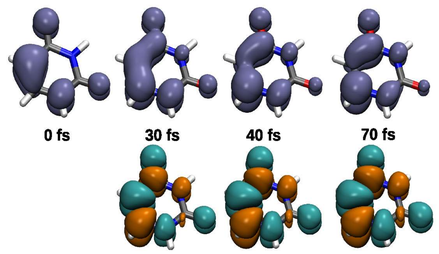
- **NEMol-Grid:**
  - splitting nuclear coordinate space into segments
  - summing up the partial densities of each segment
    - ➔ total electron density coupled to multiple grid points

- **one-electron-two-orbital (1e-2o) approximation [2,3]:**
  - coupled states described by two Slater determinants differing only in occupation of one orbital
  - neglecting the contribution of equally occupied orbitals

Dynamics of uracil

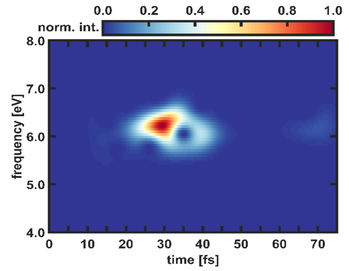
Excitation pulse induced dynamics



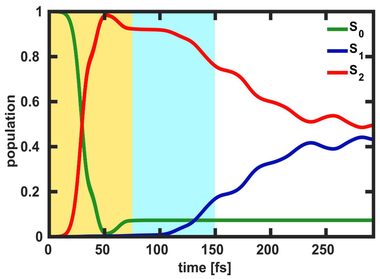


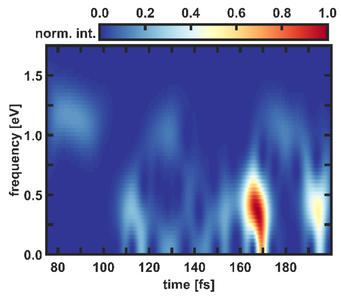
- excitation pulse until 70 fs with a maximum at 40 fs
- fast oscillations of dipole moment (DM) of same frequency as pulse
- reappearance of coherent electron dynamics around 70 fs

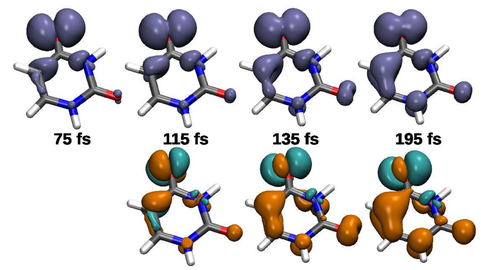
https://vimeo.com/504299040



CoIn induced dynamics







- long lived electronic coherence
- slow oscillations of the DM
- good agreement between results using full electron density and 1e-2o approximation

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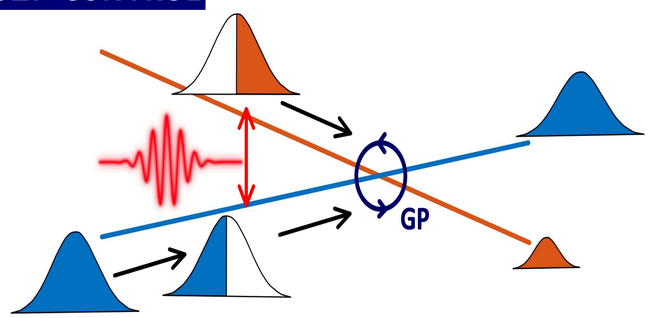
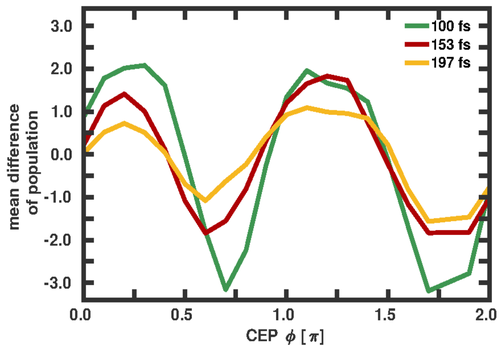
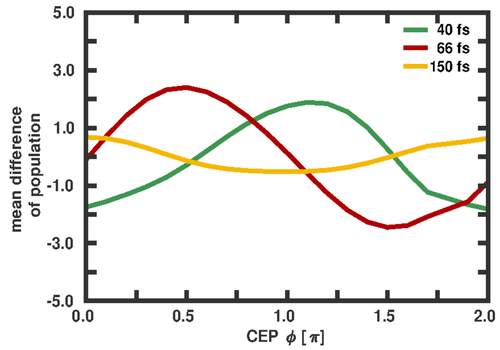
CEP control







- CoIn creates superposition depending on geometric phase (GP)
- steering of population transfer through CoIn by few-cycle IR pulse
- optimizing pulse parameters to achieve maximal population transfer

- starting position at FC

- localized wave packet reaching the CoIn

- two different processes contributing to the CEP control
- distinguishable by their periodicity

References and Funding

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[5] M. Richter, *et al.*, Phys. Chem. Chem. Phys. 2019, 21, 10038.

[6] I. Merritt, *et al.*, J. Phys. Chem. Lett. 2021, 12, 8404.

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