CEP Control of the Coupled Nuclear and Electron Dynamics in the Nucleobase Uracil

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Project Outline

- controlling population transfer through S_2/S_1 conical intersection (CoIn) with the carrier envelop phase (CEP) [1]

- investigating the coupled nuclear and electron dynamics with NEMol [2,3]

- simulating X-ray absorption spectra (XAS) at oxygen K-edge based on a multi-reference protocol [4]

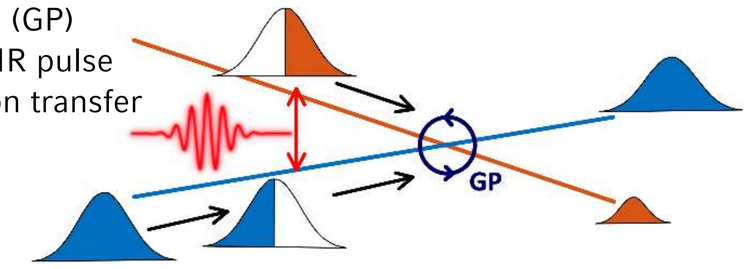
- follow the coupled dynamics and determine the influence of the electronic coherence using time-resolved XAS

References

[1] F. Schüppel, *et al.*, *J. Chem. Phys.* 2020, **153**, 224307.
[2] L. Bäuml, *et al.*, *Front. Phys.* 2021, **9**, 674573.
[3] T. Schnappinger, *et al.*, *J.Chem. Phys.* 2021, **154**, 134306.
[4] F. Rott, *et al.*, *Struct. Dyn.* 2021, **8**, 034104.

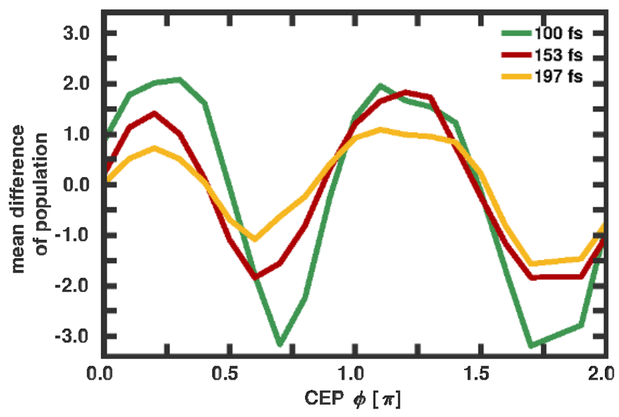
CEP Control

- 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

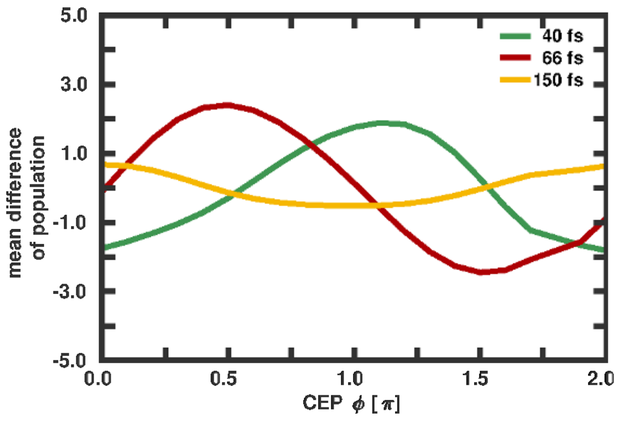


- two different processes contributing to the CEP control
- distinguishable by their periodicity

  - **field-only mechanism:** asymmetry of electric field creates CEP dependence even without NACs
  - **interference mechanism:** CEP pulse creating superposition of electronic states forming the CoIn



- starting position at FC geometry
- periodicity of π ➡ field-only mechanism



- localized wavepacket reaching CoIn
- periodicity of 2π ➡ interference mechanism

Introduction to NEMol

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

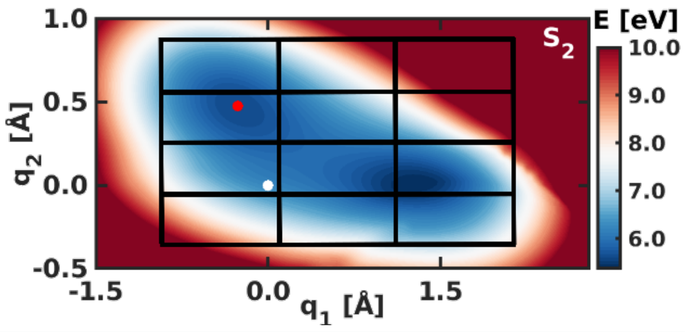
$$\rho(\boldsymbol{r}, t; \langle \boldsymbol{R} \rangle(t)) = \sum_j A_{jj}(t)\, \rho_{jj}(\boldsymbol{r}; \langle \boldsymbol{R} \rangle(t))$$

state specific electronic density

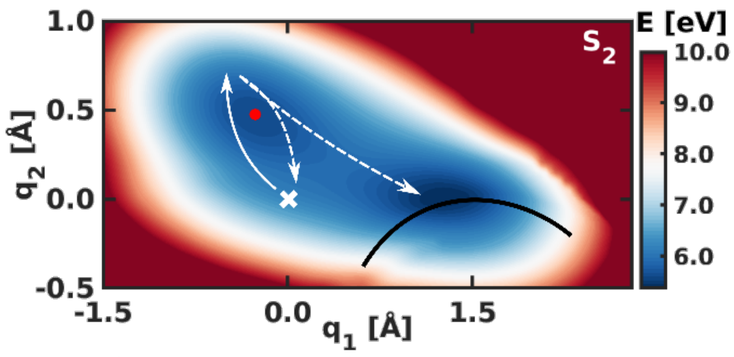
$$+ \sum_{k>j} 2Re\{A_{jk}(t)\, \rho_{jk}(\boldsymbol{r}; \langle \boldsymbol{R} \rangle(t)) e^{-i\xi_{jk}(t)}\}$$

coherent electronic density

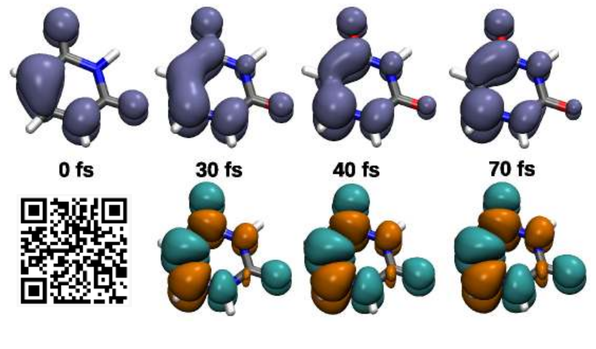
- **NEMol-Grid:**
  - splitting nuclear coordinate space into segments
  - summing up the partial densities of each segment
    ➡ total electron density coupled to multiple grid points



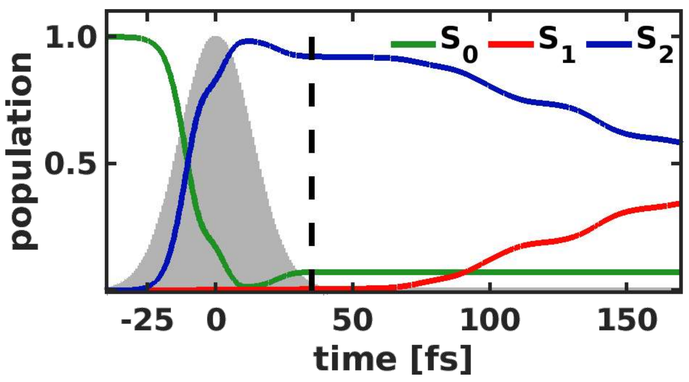
Coupled Dynamics of Uracil



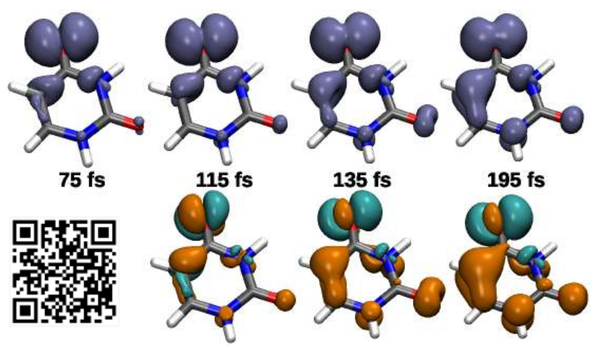
- FC (white cross), S_2 min (red dot), CoIn (black line)



- laser excitation π ➡ π^*
- fast electron dynamics

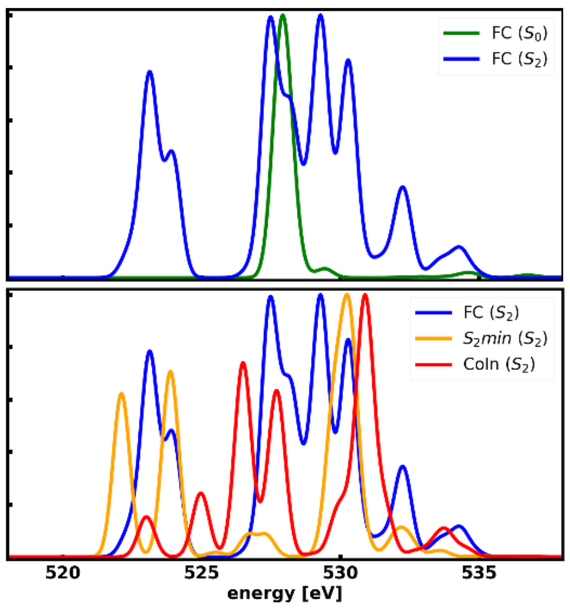


- first parts reaching CoIn around 60 fs



- relaxation through CoIn *lp* ➡ π
- much slower electron dynamics

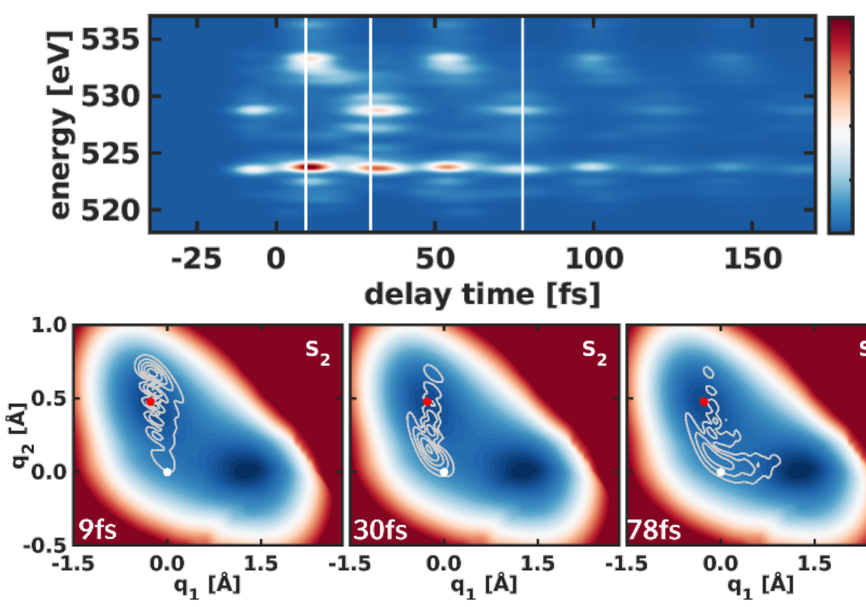
X-Ray Absorption Spectra



- oxygen K-edge XAS

- experimentally distinguishable signals
  excitation: 528 eV (S_0) ➡ 523 eV (S_2)
  S_2 dynamics: 523 eV (FC)
  ➡ 522 eV (S_2 min) ➡ 525, 527 eV (CoIn)

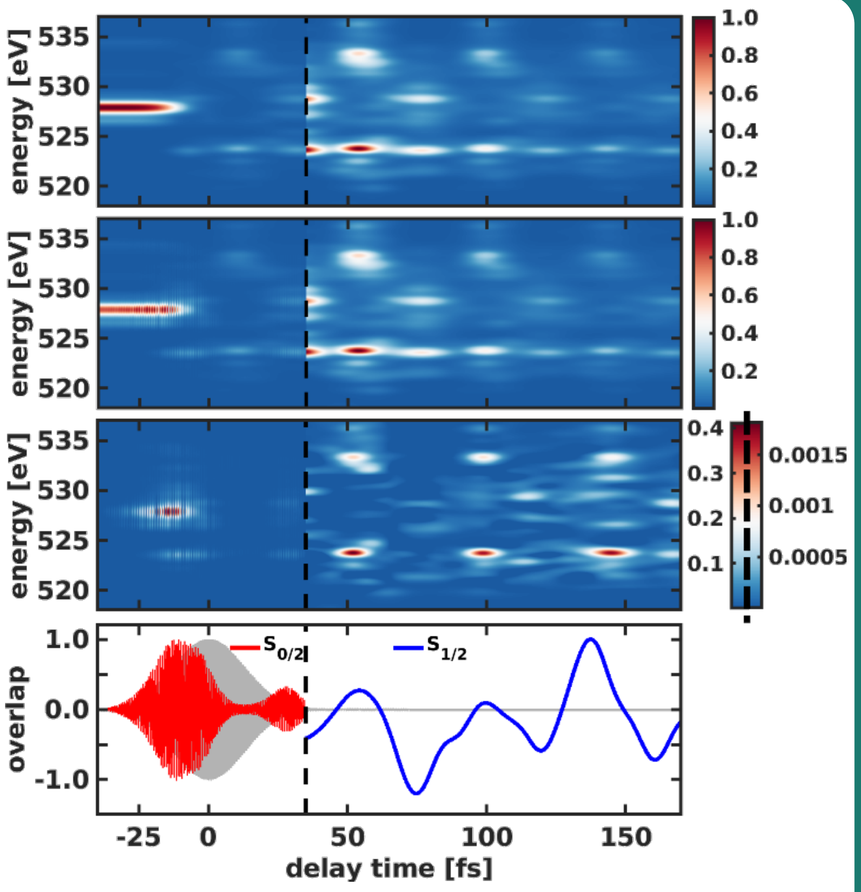
- peaks at higher energies overshadowed by ionization band and Rydberg series



- oscillation of wavepacket between FC and S_2 min seen by shift of signal at 529 eV (FC) and 533 eV (S_2 min)

- passage through CoIn traceable by loss of intensity of signal at 524 eV characteristic for the S_2 state in general and appearance of shallow signals at 525, 527 eV

- very delocalized nuclear WP



- influence of electronic coherence during whole simulation time

- especially strong when WP is very localized