Ultrafast dissociation of vinyl bromide after passage through a conical intersection: an experimental and theoretical study

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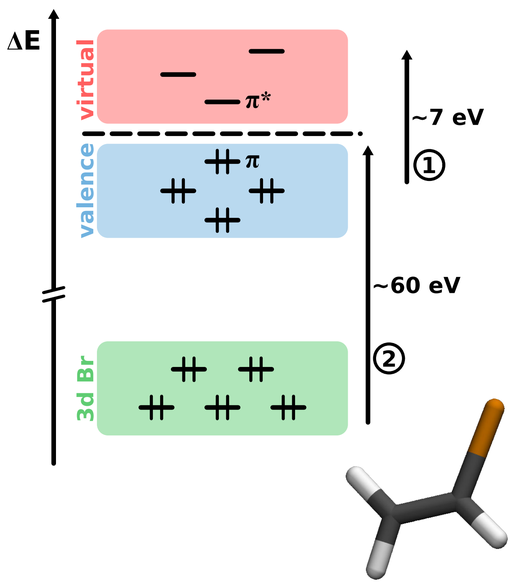
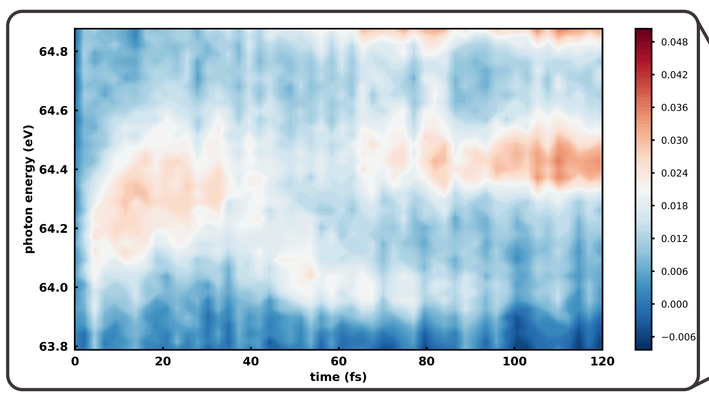
Experiment and Spectrum

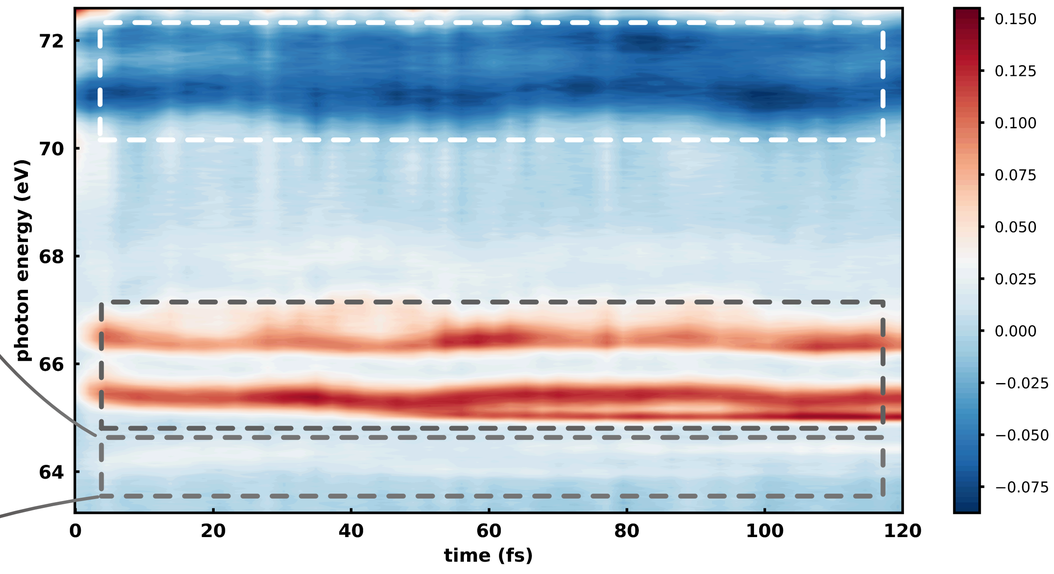
We characterized the ultrafast dissociation of vinyl bromide (C_2H_3Br) after strong-field excitation experimentally and theoretically.
After a multiphoton excitation of the π/π* transition, the relaxation process is illuminated via Attosecond Transient Absorption Spectroscopy (ATAS) using the bromine M-edge.
This method allows to monitor the evolution of the nuclear wave packet during the dissociation of bromine within 100 fs (Experimental setup see [1, 2]).



1. strong-field VIS-NIR pump ▸ initiate dynamics

2. attosecond XUV probe ▸ follow dynamics





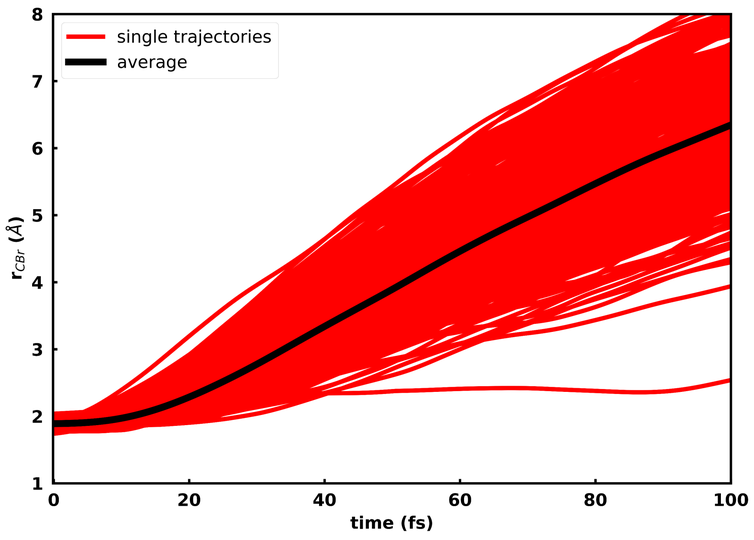
Dynamic Simulations

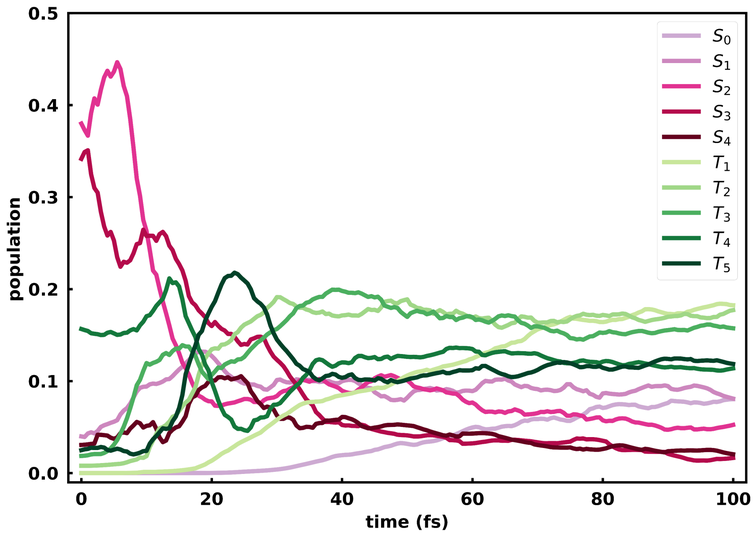
The non-adiabatic molecular dynamics were performt with **SHARC 2.0** [3]

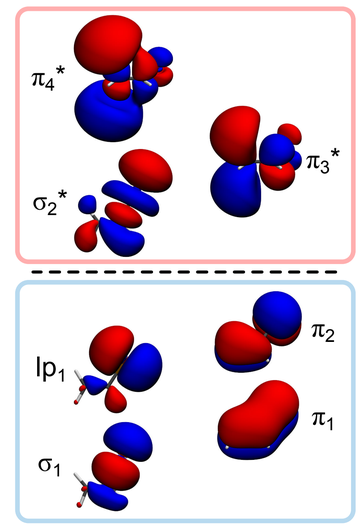
- 400 initial conditions (geometries and velocities) generated based on a Wigner distribution (harmonic vibrational frequencies at CCSD(T)/aug-cc-pVTZ level of theory)
- Energies, gradients and non-adiabatic couplings were calculated at the CASSCF level of theory using **OpenMolcas** [4]
- An (8/7) active space with 5 singulet and 5 triplet states and a modified ATZP basis set was used
- Simulation time: 100 fs (0.5 fs time step)
- Propagator: Velocity-Verlet
- non-adiabatic transitions were treated within the TSH algorithm
- The trajectories started from the bright π/π* state
- 189 trajectories were analyzed

	Character	CAS[1] [eV]	PT2[2] [eV]	CCSD[3] [eV]	Exp. [eV]
S_1	$\pi_2 \rightarrow \sigma_2^*$	6.67 (0.004)	6.12	6.62 (0.001)	5.70
S_2	$\pi_2 \rightarrow \pi_3^*$	7.35 (0.280)	6.99	7.11 (0.257)	6.50
S_3	$lp_1 \rightarrow \sigma_2^*$	7.50 (0.009)	7.03	7.01 (0.003)	-
S_4	$lp_1 \rightarrow \pi_3^*$	7.77 (0.001)	7.20	7.73 (0.002)	-

[1] CASSCF(8,7)/m-ATZP [2] XMS-CASPT2/cc-pVTZ [3] EOM-CCSD/cc-pVTZ



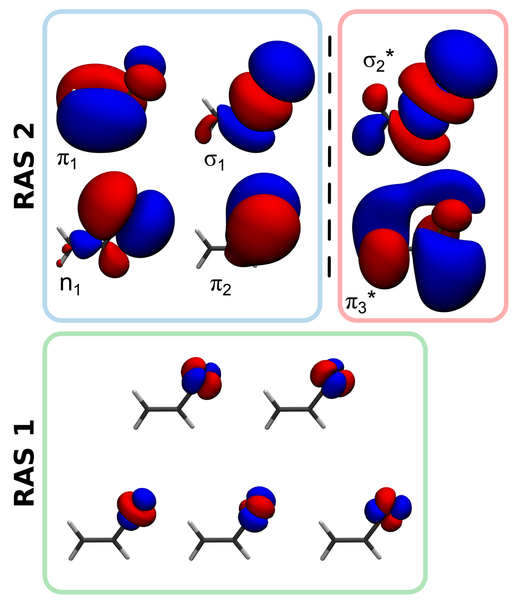


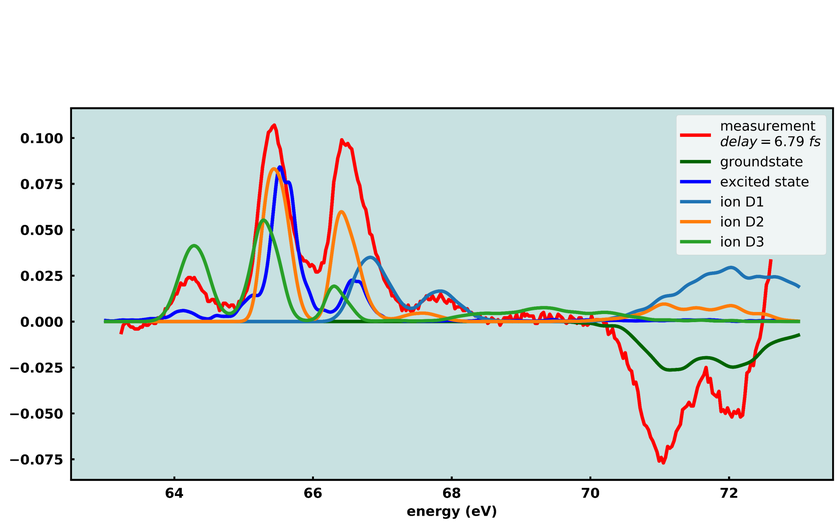


Calculating the spectra

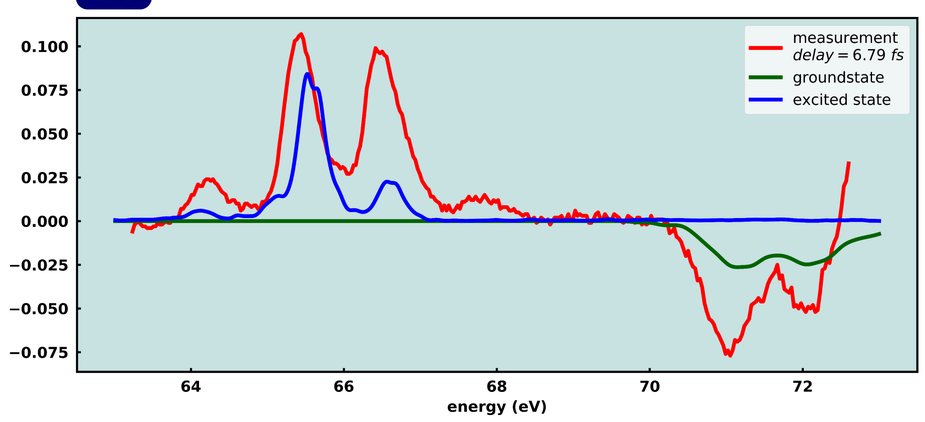
We used the geometries from the dynamics to simulate the XUV absorption spectra:

- We applied the RASSCF method with the ANO-RCC-ATZP basis set as implemented in **OpenMolcas** [4]
- RAS1(10,5), RAS2(8,6) and RAS3(0,0) was used, allowing one hole in RAS1
- Scalar-relativistic effects were treated with the Douglas-Kroll-Hess transformation
- Spin-orbit coupling was included via the RASSI method using AMFI integrals
- 120 singlet states and 230 triplet states were considered
- For both spin wave functions the states were optimized in a SA procedure
- Dynamic correlation was treated via MS-CASPT2

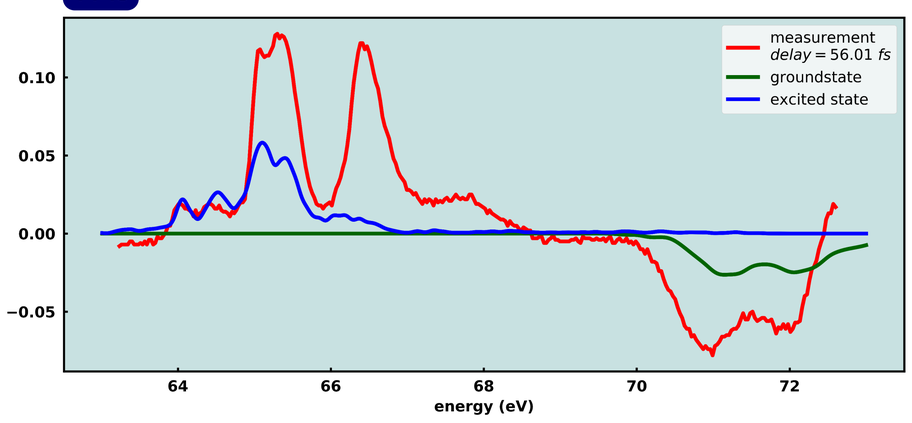




0 fs



11 fs



Summary and Outlook

- Combining non-adiabatic dynamics and the RASSCF/PT2 approach we are able to simulate time-dependent XUV-absorption-spectra
- Completely analyze the dynamic simulation of the ion
- Improve both dynamics using MS-CASPT2 (switch to BAGEL [5])
- Find a second system and do it all over again

References

[1] Lin, M.-F., Pfeiffer, A. N., Neumark, D. M., Leone, S. R. & Gessner, J. Chem. Phys. 137, 244305 (2012).

[2] Lin, M.-F., Neumark, D. M., Gessner, O. & Leone, S. R., J. Chem. Phys. 140, 064311 (2014).

[3] SHARC MD - https://sharc-md.org/

[4] OpenMolcas - https://gitlab.com/Molcas/OpenMolcas

[5] BAGEL - https://nubakery.org/