Simulation of time-dependent ionization processes in acetylene

T. Schnappinger[1], C. Burger[2,3], A. Atia-Tul-Noor[4,5], H. Xu[4,5], P. Rosenberger[2,3], N. Harem[4,5], R.Moshammer[6], R.T. Sang[4,5], B. Bergues[2,3], M.S. Schuurman[7], I.V. Litvinyuk[4,5], M.F. Kling[2,3] and R. de Vivie-Riedle[1]

[1]Department of Chemistry, LMU Munich, [2]Department of Physics, LMU Munich, [3]Max Planck Institute of Quantum Optics, Garching, [4]Centre for Quantum Dynamics, Griffith University, [5]Australian Attosecond Science Facility, Griffith University, [6]Max Planck Institute of Nuclear Physics, Heidelberg, [7]National Research Council of Canada, Ottawa.

Abstract

The ionization of molecules with intense laser pulses typically results in the vibrational and electronic excitation of the molecule. Upon ionization, the molecular structure and the corresponding chemical properties can change drastically, e.g. due to proton migration [1], dissociation [2] or even selective bond-breaking [3]. During bond elongation r-dependent tunnel ionization and enhanced ionization (EI) can occur, if the molecules interact with a second laser pulse [4]. For larger molecular system these process are naturally more complex as multiple degrees of freedom opening various pathways for time-dependent ionization. In this joined experimental and theoretical work we are investigating different ionization processes and the subsequent nuclear dynamics in acetylene ions. Coulomb explosion imaging (CEI) and dynamics simulations are applied to elucidate the underlying ultrafast processes.

Computational Methods

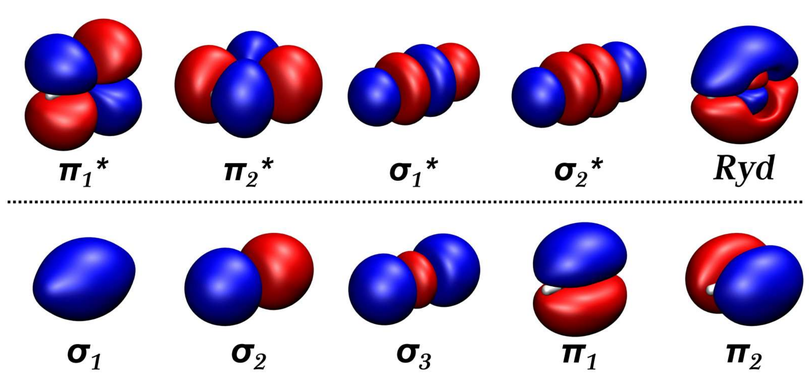
two-step ansatz to simulate time-dependent ionization processes:

1) non-adiabatic on-the fly trajectories simulations
→ nuclear dynamics of relevant states

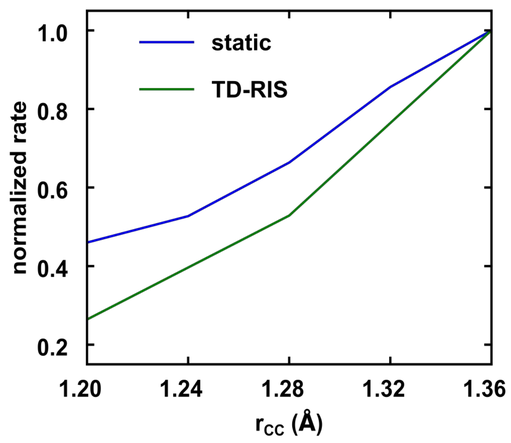
2) static electronic field approach [5,6] to simulate strong field ionization rates along trajectories

$$T(t;\, S) = \int_{V'} \rho(r, t_f) dV' - \int_{V'} \rho(r, t_i) dV'$$

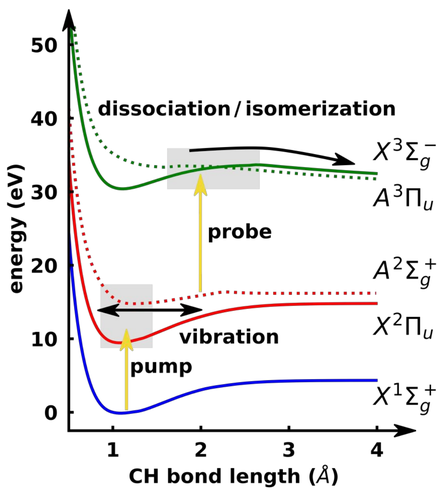
Used Method: SA-CASSCF/6-311++G**



Benchmark against TD-RIS-approach

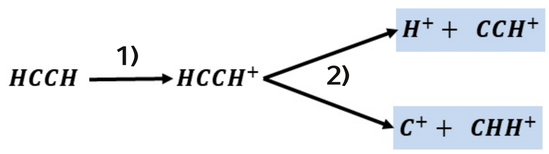


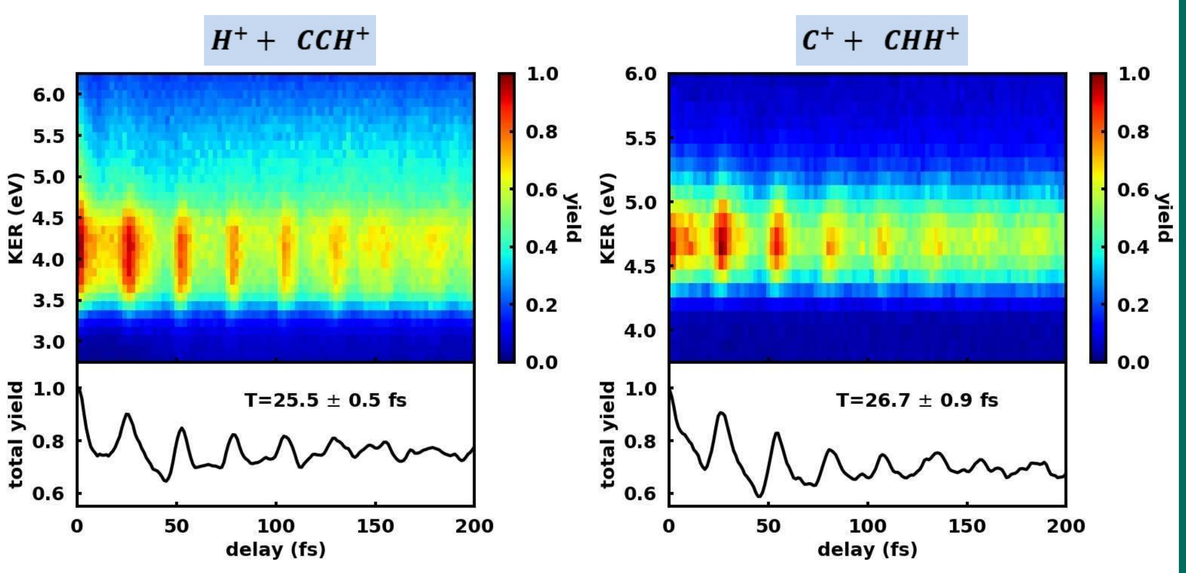
R-dependent ionization in the cation



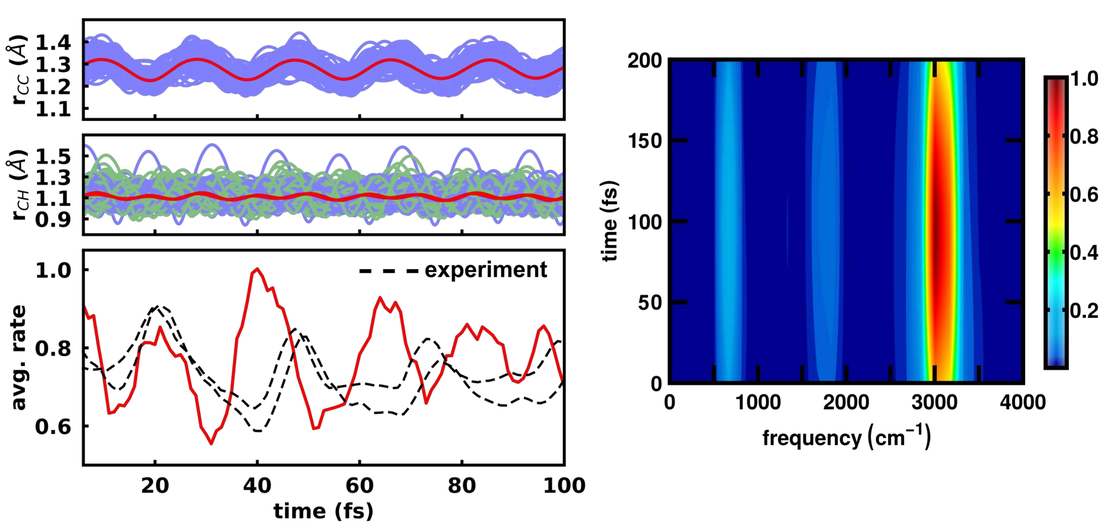
1) pump-pulse:
preparing bounded wave packet in the cation
simulated using full-dimensional trajectories

2) probe-pulse:
populating dissociative states in the dictation
simulated using static field approach



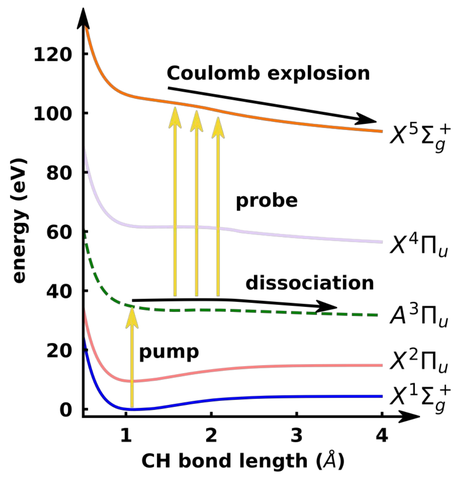


100 trajectories in the $X^2\Pi_u$ state (T = 200 fs, Δt = 0.5 fs) and 3 orbitals included in density



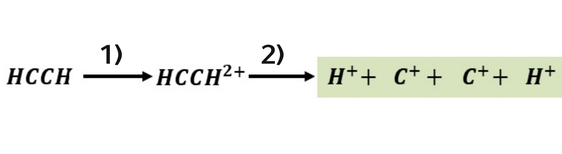
- periodic modulation ionization rate → oszillation periode ~ 20-25 fs
- origin: CC stretching mode in the cation

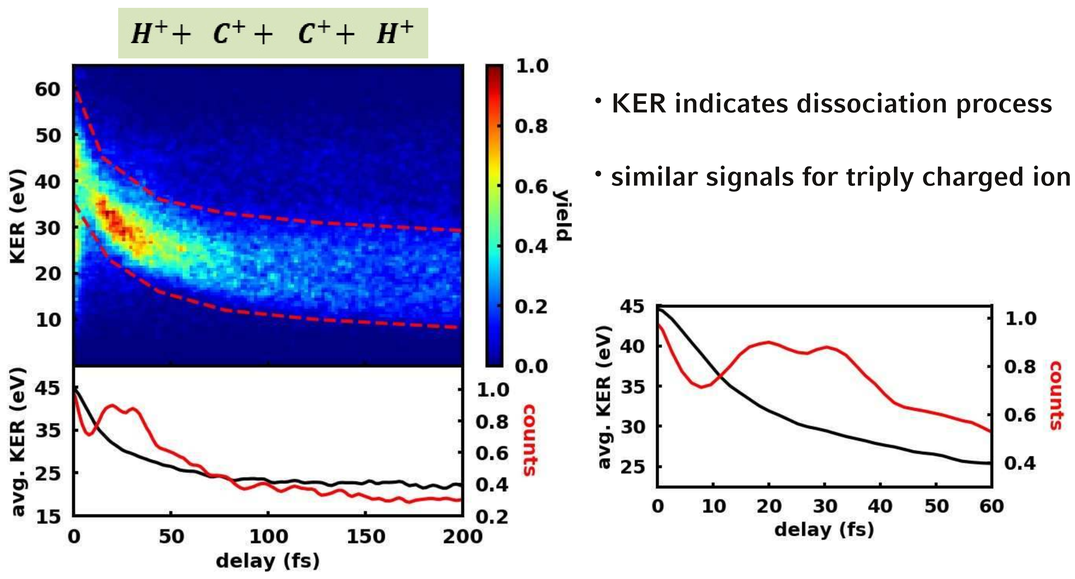
Enhanced ionization in the dication



1) pump-pulse:
preparing dissociative wave packet in the dication
simulated using full-dimensional trajectories

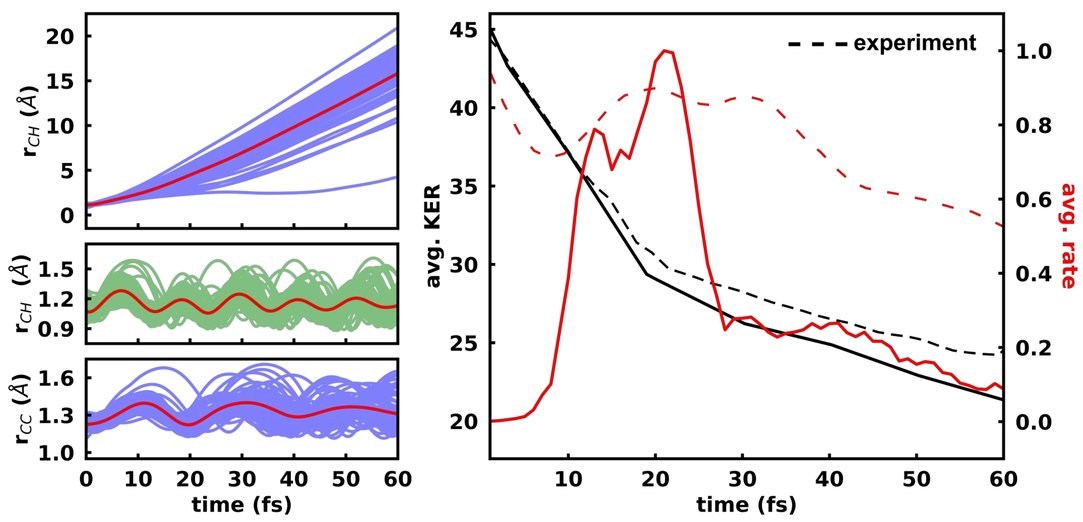
2) probe-pulse:
populating states in the quadruply charged ion
simulated using static field approach





- KER indicates dissociation process
- similar signals for triply charged ion

100 trajectories in the $A^3\Pi_u$ state (T = 100 fs, Δt = 0.5 fs) and 3 orbitals included in density



- clear indication of enhanced ionization from about 10 fs to 40 fs
- origin: deprotonation in the dication

References

[1] Kübel M. *et al.*, Phys. Rev. Lett. **2016**, *116*, 93001.
[2] Wörner H.J. *et al.*, Nature **2010**, *466*, 604.
[3] Assion A. *et al.*, Science **1998**, *282*, 919.
[4] Wu J. *et al.*, Nat. Commun. **2012**, *3*, 1113.
[5] von den Hoff P. *et al.*, Appl. Phys. B **2010**, *98*, 659.
[6] Jochim B. *et al.*, Sci. Rep. **2017**, *7*, 2045.