# Trajectory surface hopping for nonadiabatic dynamics of resonances

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## Hermitian quantum mechanics

- Closed system
- Real Hamiltonian and energies
- Usual quantum chemistry methods


## Non-hermitian quantum mechanics

- Open system: discrete (localized) states of the system are coupled to a continuum (delocalized) of scattering states
- Complex Hamiltonian and energies
- Requires scattering or adapted quantum chemistry methods

# **Metastable electronic states (resonances)**

- Super-excited states
- Core-excited and core-ionized states
- Transient states formed in bimolecular collisions
- Transient anions

These resonances may decay by electron autodetachment, and thus have a complex-valued energy

$\varepsilon = E - i\ \Gamma/2$

E is the resonance energy

$\Gamma$ is the resonance width (detachment rate)

# Methods for dynamics of resonances

**Current approaches**

- Quantum propagation of nuclear wavepacket
- PES: precomputed with (expensive) scattering methods
- Accurate, costly, few degrees of freedom

Check for updates

# Nonadiabatic dynamics in multidimensional complex potential energy surfaces†

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Despite the continuous development of theoretical methodologies for describing nonadiabatic dynamics of molecular systems, there is a lack of approaches for processes where the norm of the wave function is not conserved, *i.e.*, when an imaginary potential accounts for some irreversible decaying mechanism. Current approaches rely on building potential energy surfaces of reduced dimensionality, which is not optimal for more involving and realistic multidimensional problems. Here, we present a novel methodology for describing the dynamics of complex-valued molecular Hamiltonians, which is a generalisation of the trajectory surface hopping method. As a first application, the complex surface fewest switches surface hopping (CS-FSSH) method was employed to survey the relaxation mechanisms of the shape resonant anions of iodoethene. We have provided the first detailed and dynamical picture of the $\pi^*/\sigma^*$ mechanism of dissociative electron attachment in halogenated unsaturated compounds, which is believed to underlie electron-induced reactions of several molecules of interest. Electron capture into the $\pi^*$ orbital promotes C≡C stretching and out-of-plane vibrations, followed by charge transfer from the double bond into the $\sigma^*$ orbital at the C−I bond, and, finally, release of the iodine ion, all within only 15 fs. On-the-fly dynamics simulations of a vast class of processes can be envisioned with the CS-FSSH methodology, including autoionisation from transient anions, core-ionised and superexcited states, Auger and interatomic coulombic decay, and time-dependent luminescence.

# Methods for dynamics of resonanes

**<u>Current approaches</u>**

- Quantum propagation of nuclear wavepacket
- PES: precomputed with expensive scattering methods
- Accurate, costly, few degrees of freedom

**<u>Our novel approach</u>**

- Classical propagation of nuclei
- PES: obtained on-the-fly, with hopefully cheap bound state and/or scattering methods
- More approximate, affordable, all degrees of freedom

# Complex surface fewest switches surface hopping (CS-FSSH)

Time dependent Schrödinger equation:

$$i\hbar \frac{\partial}{\partial t} \Phi(\boldsymbol{r}, \boldsymbol{R}, t) = H(\boldsymbol{r}, \boldsymbol{R}, t) \Phi(\boldsymbol{r}, \boldsymbol{R}, t)$$

Expanding in a set of orthornormal basis functions {$\psi_j$}:

$$\Phi(\boldsymbol{r}, \boldsymbol{R}, t) = \sum_j c_j(t)\, \psi_j(\boldsymbol{r}; \boldsymbol{R}(t))$$

EOM for the expansion coefficients:

$$\frac{dc_j}{dt} = -\frac{i}{\hbar} E_j c_j - \frac{1}{\hbar}\frac{\Gamma_j}{2} c_j - \sum_{k \neq j} \left( \frac{i}{\hbar} H_{jk}^R + \frac{1}{\hbar}\frac{\Gamma_{jk}}{2} + \boldsymbol{F}_{\boldsymbol{jk}} \cdot \boldsymbol{v} \right) c_k$$

The propagation of each state j involves 3 terms:
- Phase term: real energy $E_j$
- Decay term: width $\Gamma_j$
- Coupling term: involving diabatic couplings $H^R_{jk}$, continuum-mediated couplings $\Gamma_{jk}$, and non-adiabatic couplings $\boldsymbol{F}_{jk}$

For the nuclei:

$$\frac{d^2 \boldsymbol{R}_\alpha}{dt^2} = -\frac{\nabla_{\boldsymbol{R}} E_j}{M_\alpha}$$

Coupling between electrons and nuclei with the FSSH formula:

$$P_{j \to k} = max\left[-\frac{2\Delta t}{\rho_{jj}} \Re(\rho_{jk})(\boldsymbol{F}_{\boldsymbol{kj}} \cdot \boldsymbol{v} - \frac{\Gamma_{jk}}{2\hbar}), 0\right]$$

# Benchmark CS-FSSH against quantum dynamics (QD)
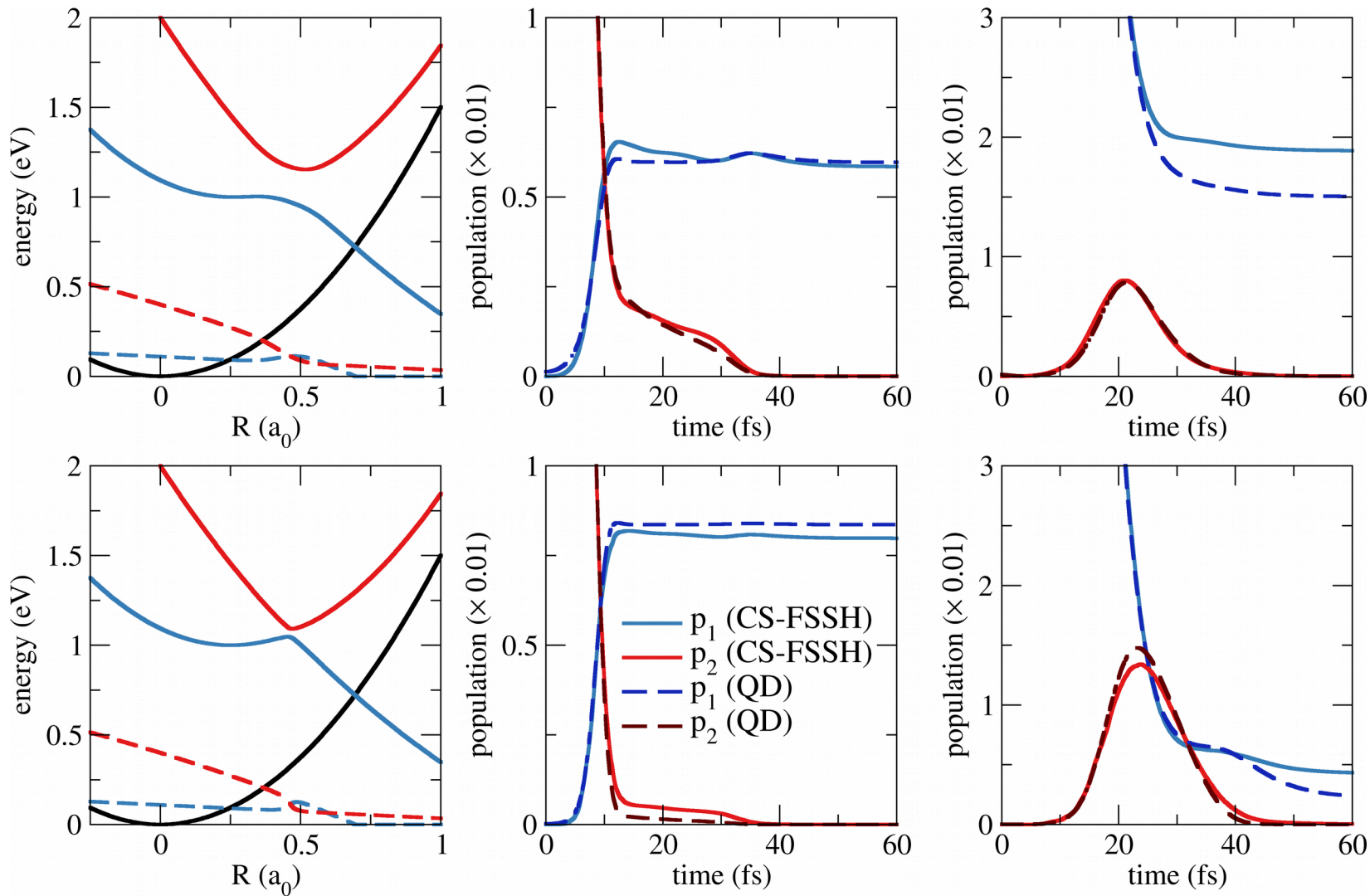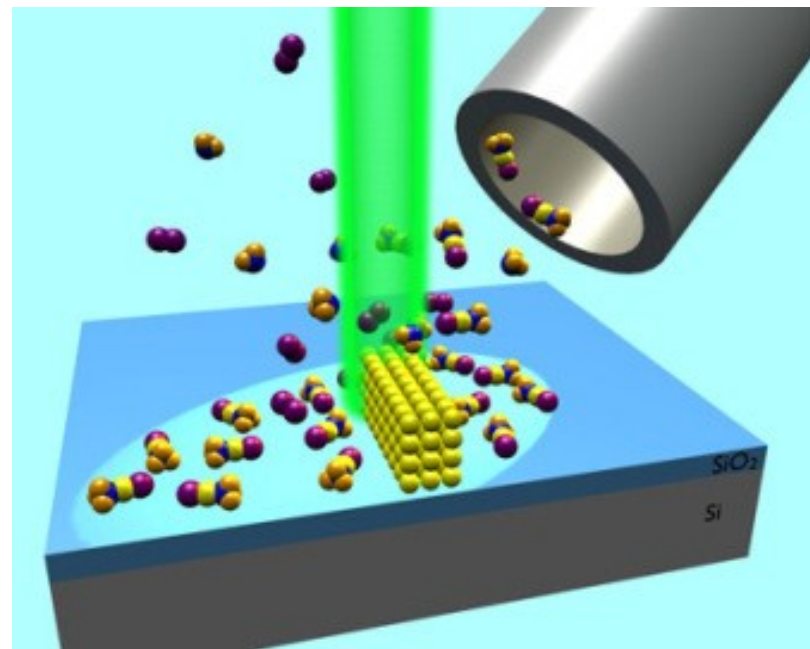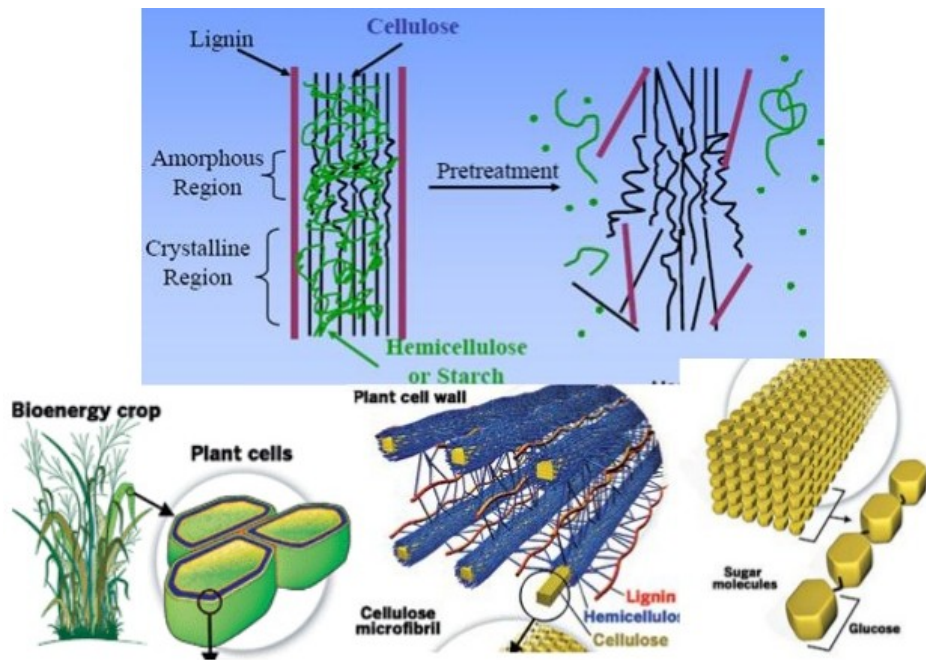
Low energy electron (<10 eV) encounters a molecule

At particular electron impact energies, a **transient anion** state $AB^-$ is formed, which decay by one of the following:

$e^- + AB \rightarrow AB^- \rightarrow e^- + AB$ **autodetachment**

$e^- + AB \rightarrow AB^- \rightarrow A + B^-$ **dissociative electron attachment (DEA)**

# Low-energy electron induced chemistry
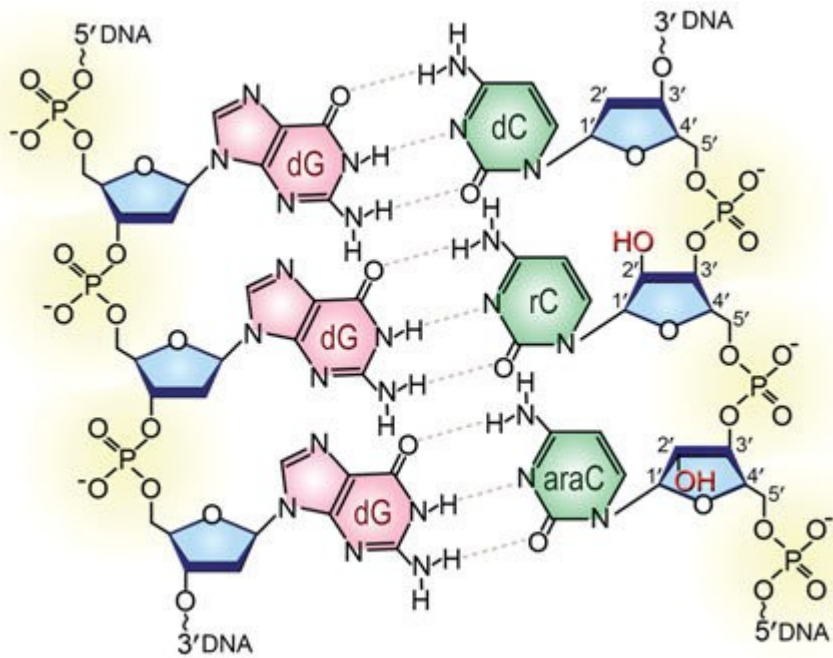
# Low-energy electron induced chemistry

# Iodoethene
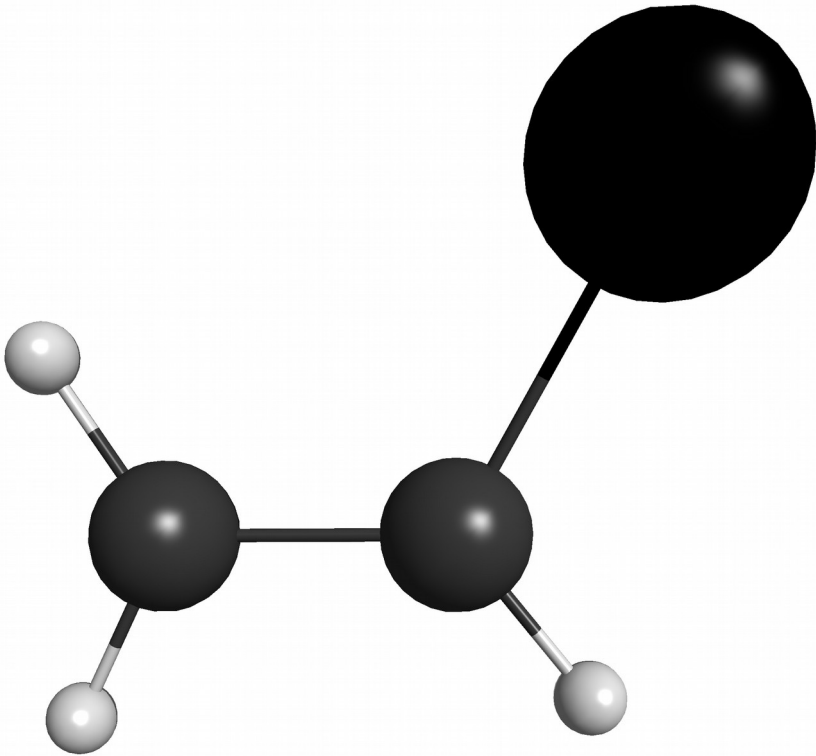


- Rather small, fast calculations

- Prototypical DEA mechanisms, model for larger halogenated molecules

# Iodoethene
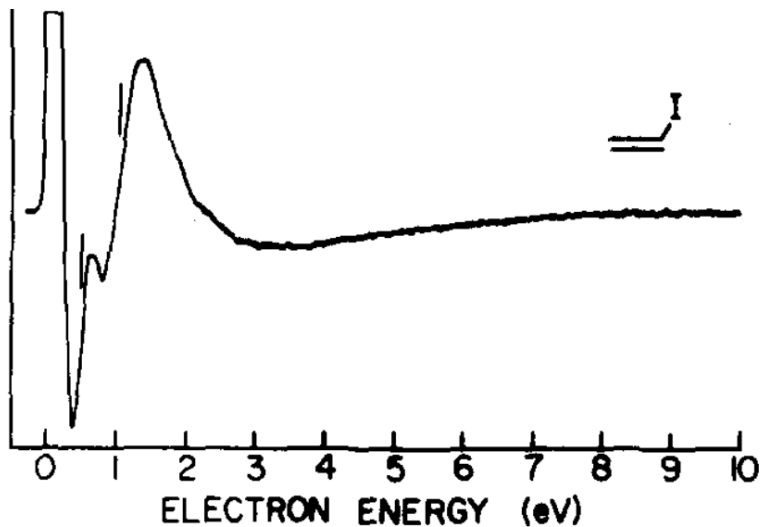


σ* resonance at 0.5 eV
π* resonance at 1.05 eV
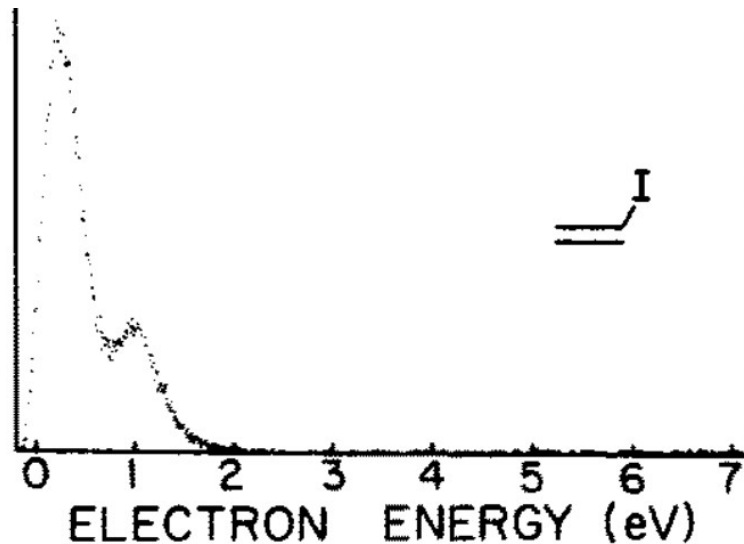
Both resonances promote
dissociation of the I⁻ ion

Olthoff et al. J. Chem. Phys. 83, 5627 (1985)

# Computational details

- Dynamics with MRCIS (800 trajectories for each precursor anion)
- Orbitals from a SA(3)-CASSCF(8,6) calculation for the neutral
- cc-pVDZ basis set for C and H, ADZP basis set for I
- Systematic shift to match the equilibrium geometry scattering results
- Initial conditions sampled from the Wigner distribution for 333 K
- 0.25 fs time step for the classical integration, until ~25 fs
- At each time step, one extra energy calculation for the neutral
- 0.002 fs time step for the quantum propagation
- Decoherence correction for the standard $\alpha = 0.1$ Hartree
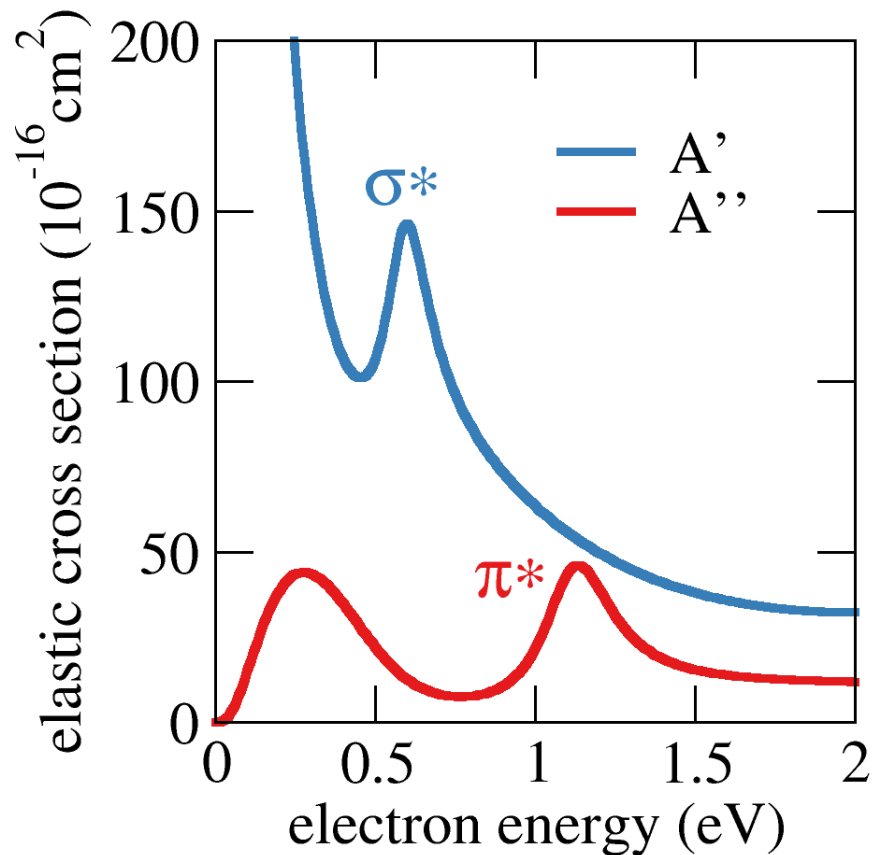
- Elastic scattering calculations

- σ* at 0.58 eV (exp. 0.5 eV)
  π* at 1.11 eV (exp. 1.05 eV)
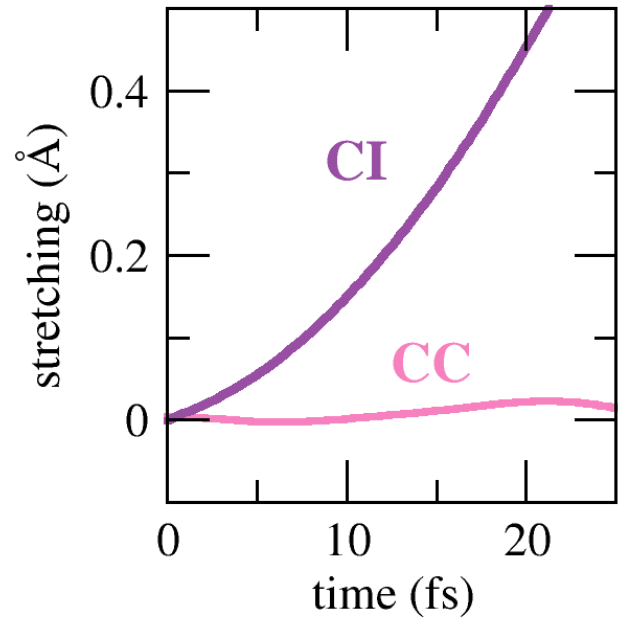
- Vertical detachment lifetimes:
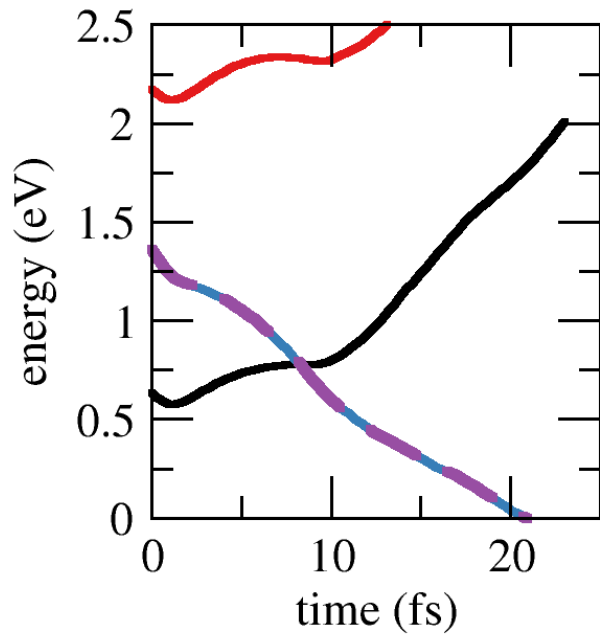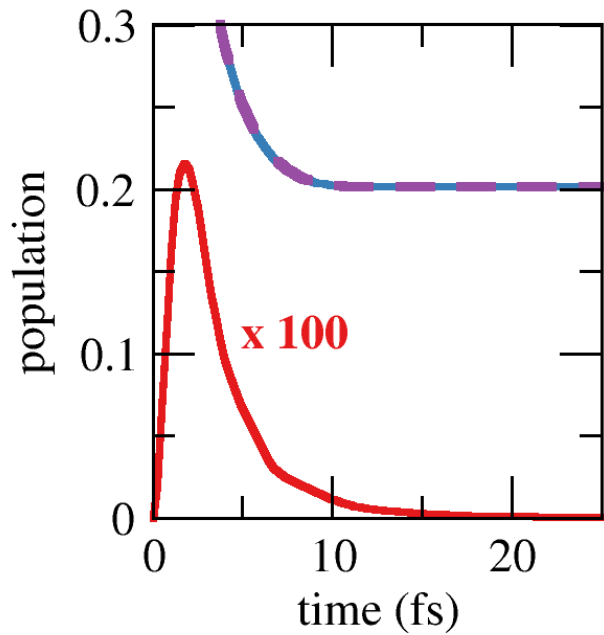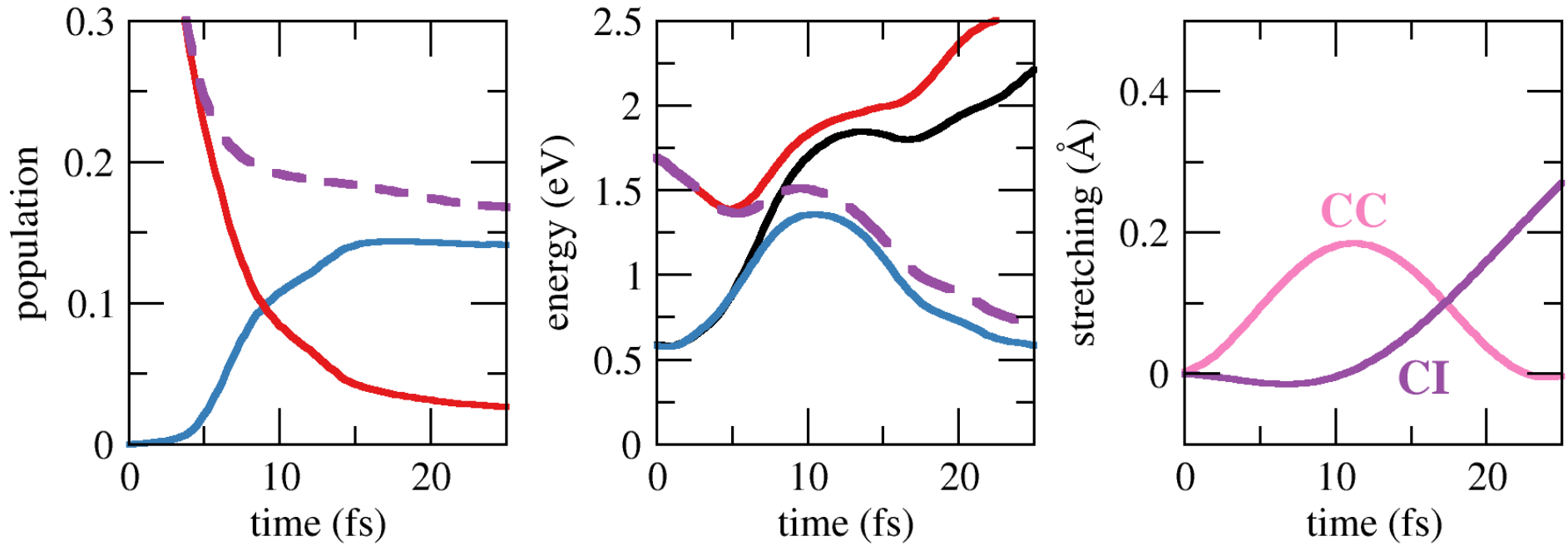  4.2 fs σ*, 2.5 fs π*
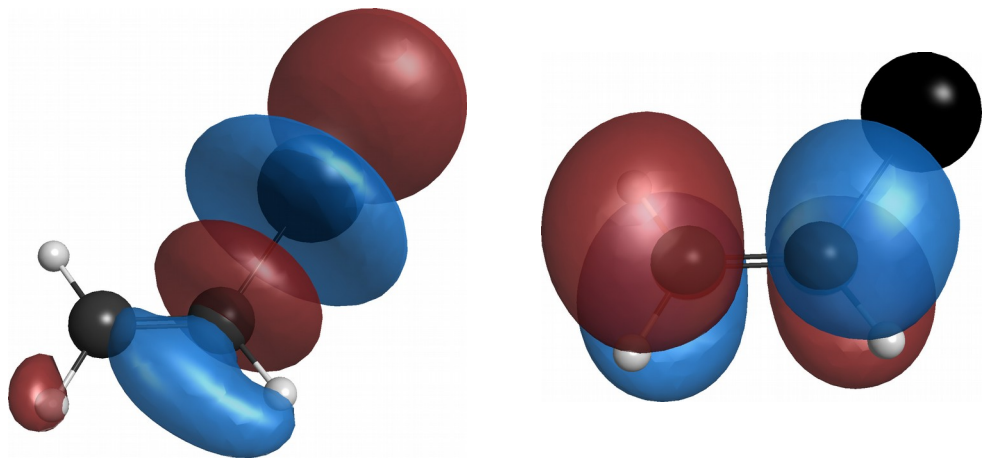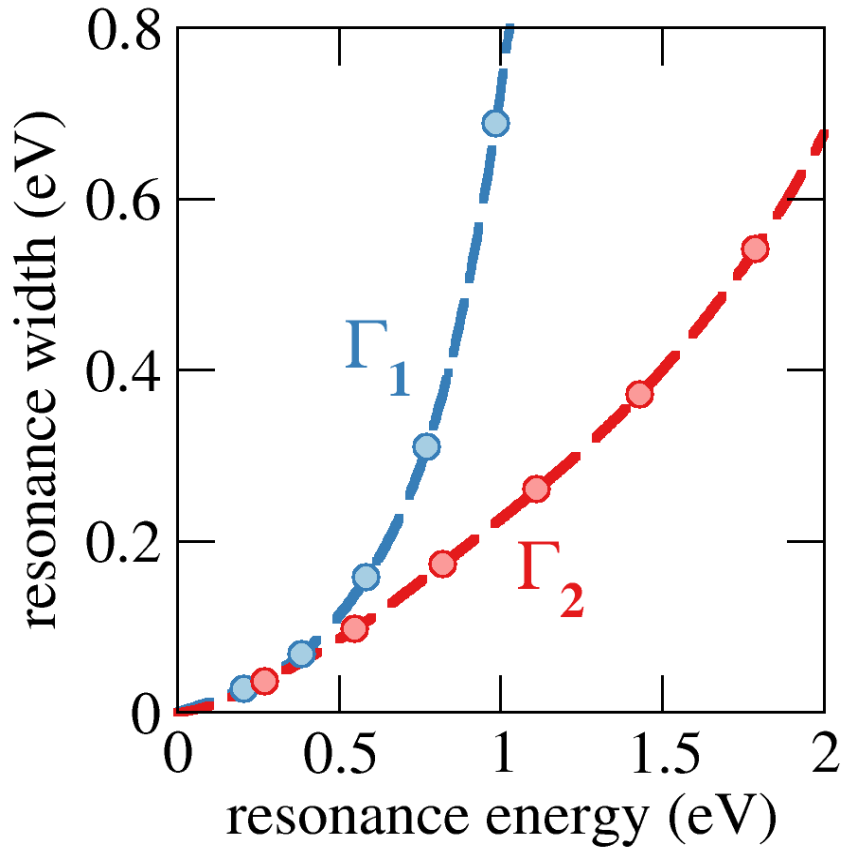
Autodetachment model employed in the dynamics: combination of quantum chemistry and few scattering calculations

$\Gamma_1$ : width of the lower state

$\Gamma_2$ : width of the upper state

- Population decay is extremely fast, and converges to 0.2

- Anion remains in the lower PES

- C-I cleavage and elimination of the I⁻ ion

- Fast decay before 5 fs, slower decay later, converging to 0.17

- Between 5 and 15 fs, π* couples to σ* by C=C stretching and out-of-plane vibrations, followed by C-I bond breaking

- Potential barrier could hinder the DEA reaction, but not in the present case
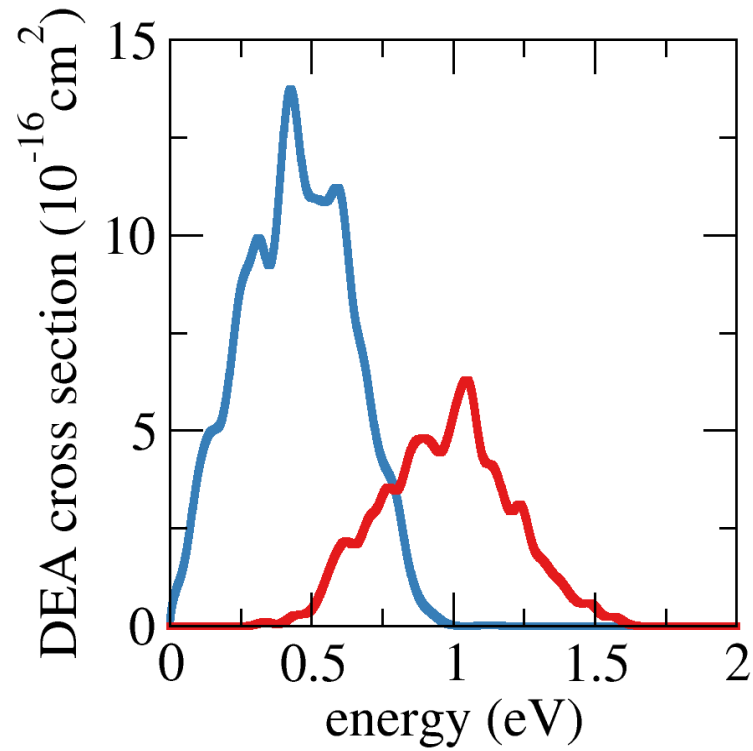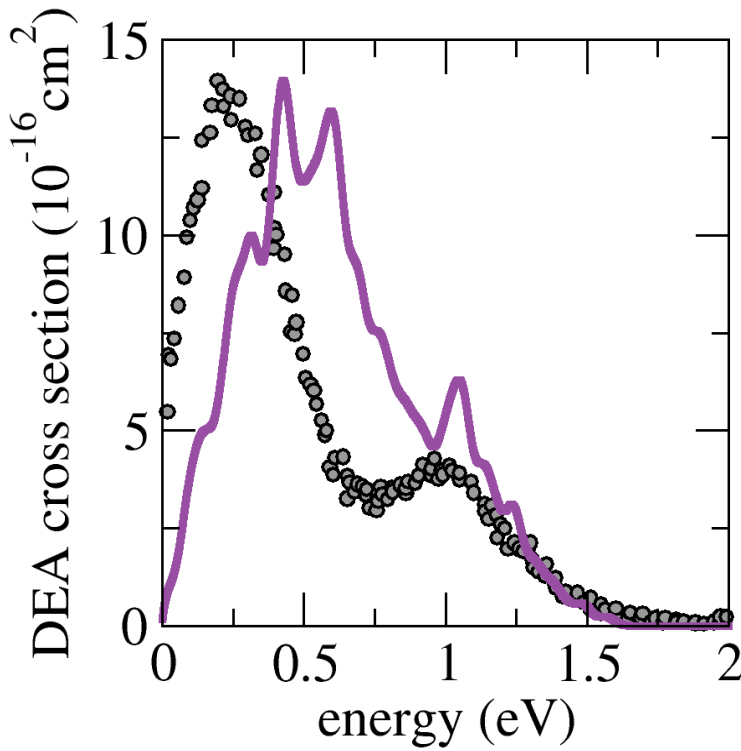
$$\sigma_k(E) = \frac{\pi}{E} \frac{1}{N_t} \sum_{i=1}^{N_t} \frac{\gamma(E)\Gamma_i^0(E)}{\gamma(E_i^0)} g_i(E) p_i(t \to \infty)$$

- Experimental data (dots) is normalized to the first peak

- Profile of the DEA cross section is quite similar
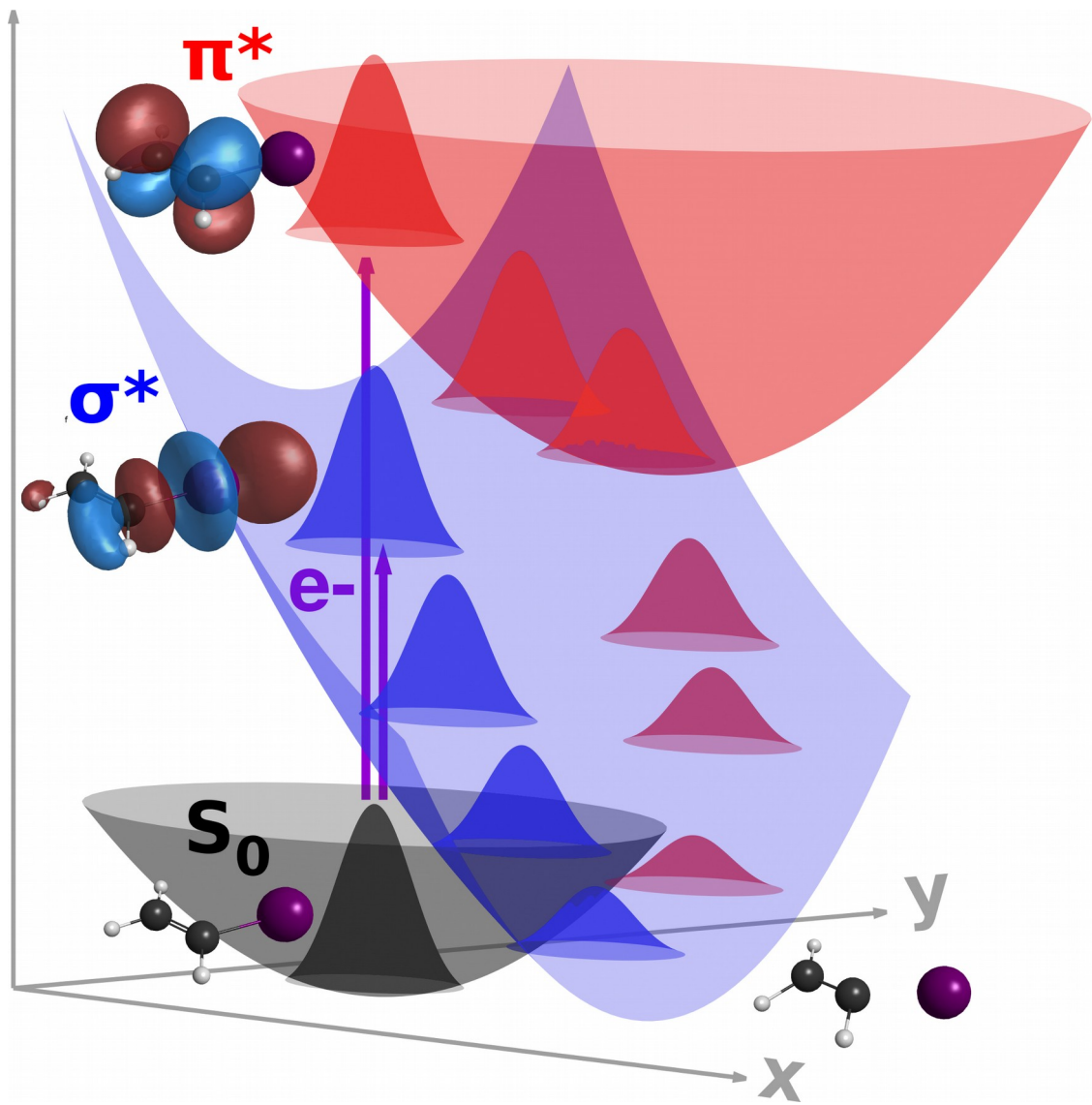
# Other potential applications

- **<u>Autoionizing states</u>**: transient anions, superexcited, core-excited and core-ionized states, transient complexes in bimolecular collisions

- **<u>Radiative decay</u>**: fluorescence and phosphorescence decay described with an imaginary potential

- **<u>Molecules on surfaces</u>**: discrete states of adsorbed molecule coupled to the continuum of bulk states

# Conclusions

- **CS-FSSH**, a novel methodology for nonadiabatic dynamics of resonances, implemented into Newton-X

- **Any type of continuum**, autoionizing states, radiative decay, surfaces, cavities

- **DEA to iodoethene**, detailed picture of the underlying dynamics

# Acknowledgements