Trajectory Ensemble Analysis with SHARC

Sebastian Mai

Institute of Theoretical Chemistry, Faculty of Chemistry, University of Vienna, Austria

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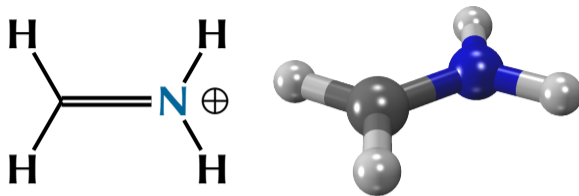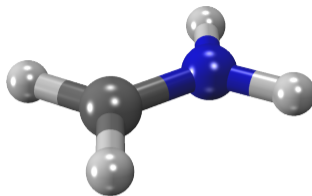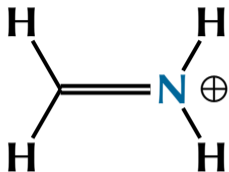"Excited States and Nonadiabatic Dynamics CyberTraining Workshop 2022" in Buffalo, NY

Outline

What was it again that we were interested in about this molecule?

- Ultrafast dynamics after photo-excitation of **methylene immonium cation** $CH_2NH_2^+$
- Dynamics similar to ethylene? ($\pi\pi^*$ state, torsion around double bond)

The chemical problem

- Ultrafast dynamics after photo-excitation of **methylene immonium cation** $CH_2NH_2^+$
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Questions:

- Involved electronic states?
- Deactivation processes?
- Time scales?
- Photochemical products and yields?

After taking days or weeks to ...

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your simulations are finished and the fun of analyzing them starts!

Did anything go wrong?

Possible error sources

Computational errors:

- ▶ Network problems
- ▶ I/O errors
- ▶ Job was killed
- ▶ **Recoverable**

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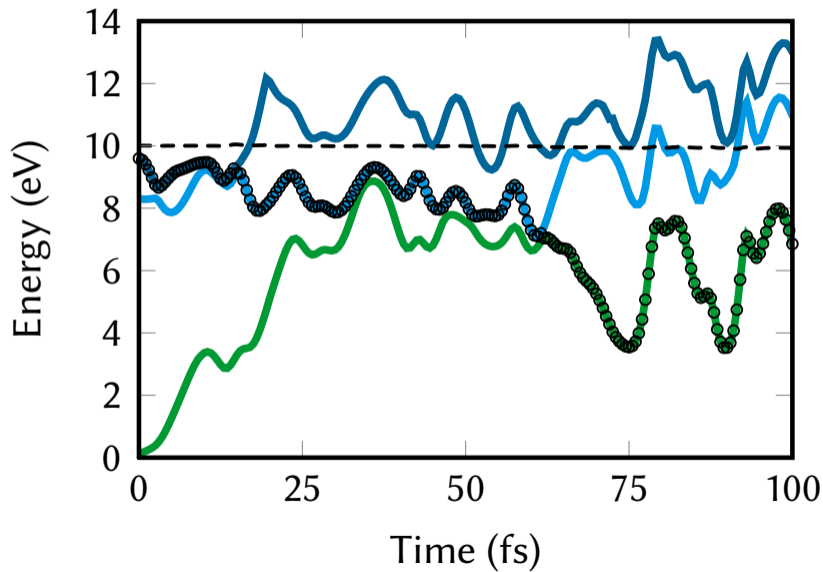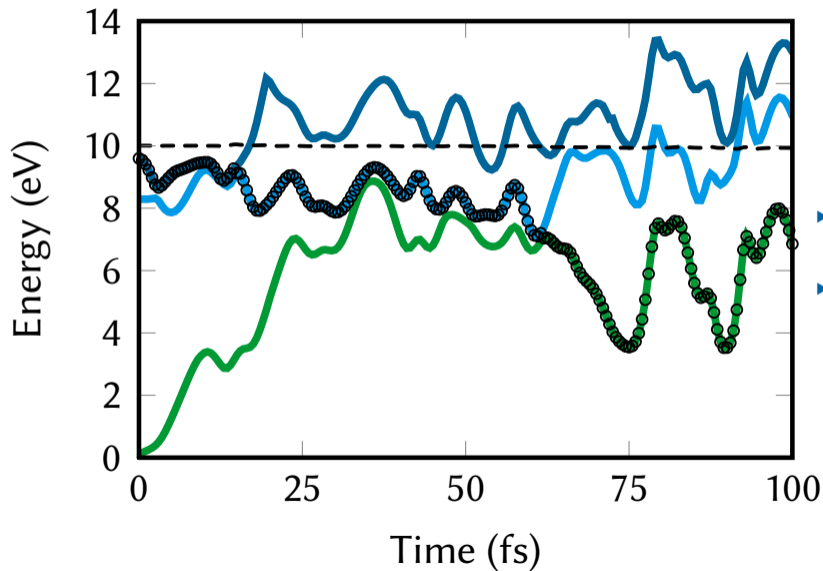
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Numerical artifacts:

- Total population not conserved
- Total energy not conserved
- Non-continuous potential energy surfaces
- Non-continuous kinetic energy
- Intruder states
- Surface hops over large energy gaps
- …
- **Might go unnoticed!**
- **Checks required**

- Trajectory does not show numerical artifacts.
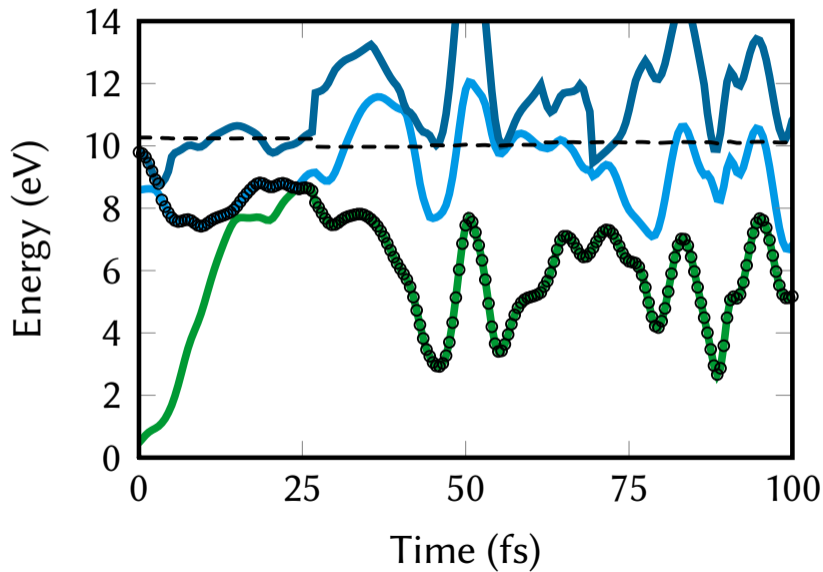- Intruder state at 21 fs (but no problem).
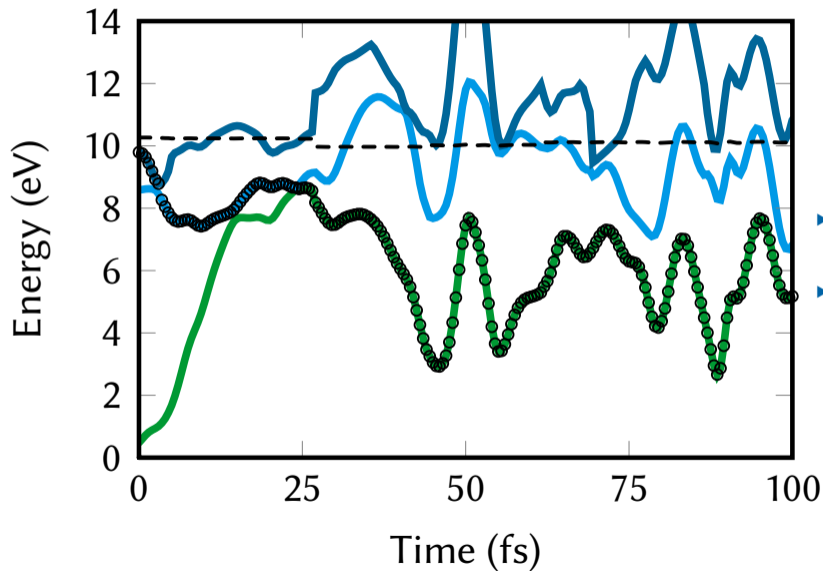
- Total energy and potential energies jump at 26 fs.
- Sudden exchange of active orbitals.
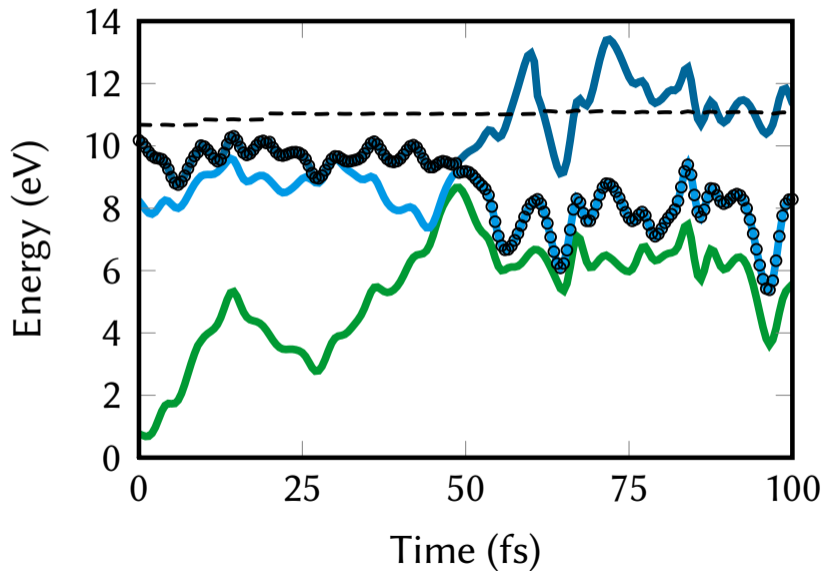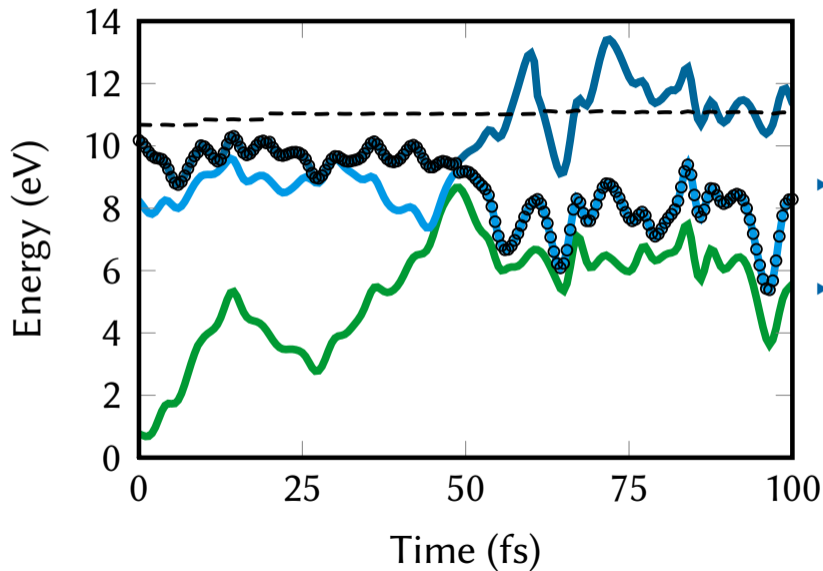
- Jumps in the total energy while potential energies are smooth.
- Badly converged gradient computation or too long time steps.
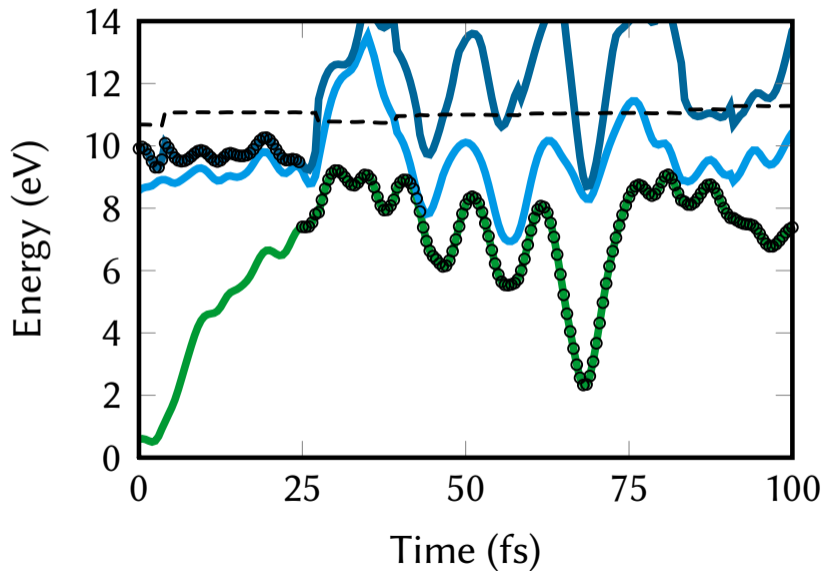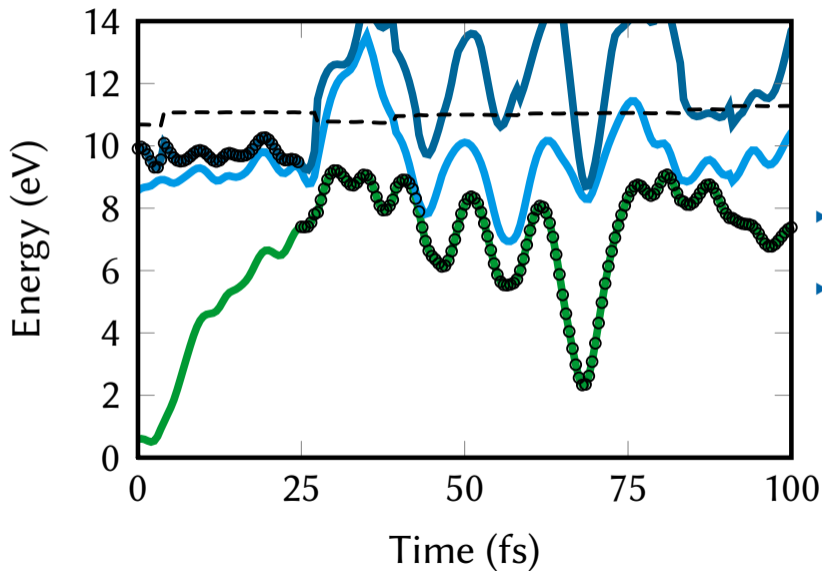
- Surface hop over large energy difference.
- Different possible reasons, needs closer analysis.

Checking all 210 trajectories shows many problems.

- ▶ Simulations should possibly be repeated with larger active space, like CAS(12,7).
- ▶ Might need different electronic structure settings
- ▶ For larger projects, this is usually not feasible.

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Result: **We keep 90 out of 210 trajectories for analysis**.

Isn't this a surprising behaviour?

Goals of the individual analysis

Important:
Analyzing the trajectories individually is **not the main way to analyze the results**:

- ▶ It is tedious.
- ▶ It is subjective.
- ▶ It is non-reproducible.
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It can still be useful:

- Use pattern recognition of human brain to find interesting trends/behaviors/aspects.
- Formulate hypotheses that can then be tested.
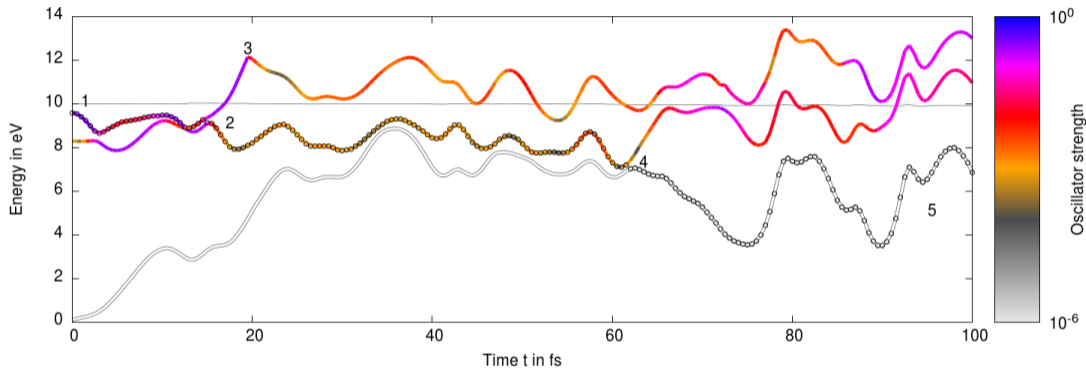
- Oscillator strength indicates state ($\pi\pi^*$, $\sigma\pi^*$, closed shell), see coloring.
- Two surface hops bring trajectory to ground state, where strong vibrations appear.
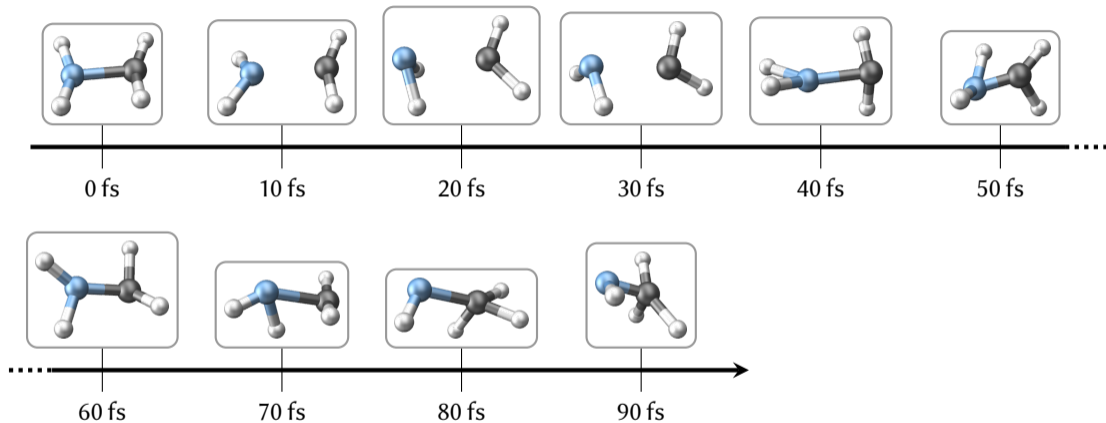
▶ Strong C=N stretch, pyramidalization, torsion, hydrogen migration

... after inspecting all trajectories:

Hypotheses

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1. **Relaxation time scale**: Sequential decay from S_2 ($\pi\pi^*$) to S_1 ($\sigma\pi^*$) and then to S_0 (closed shell) in less than $100\,\text{fs}$.

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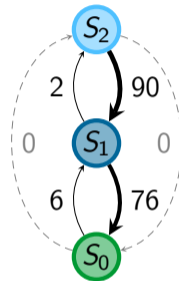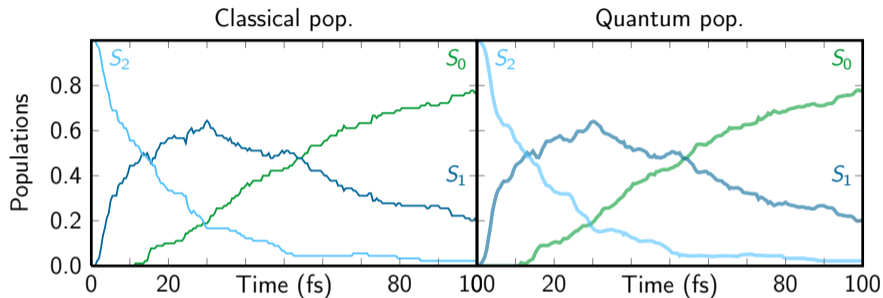
Outline

How can we make sense of all this data?
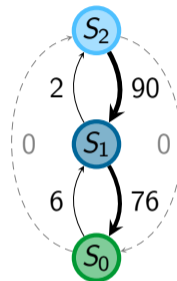
Electronic evolution
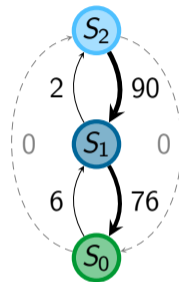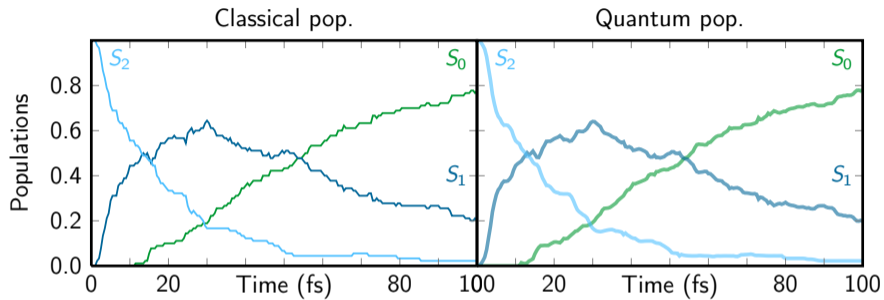
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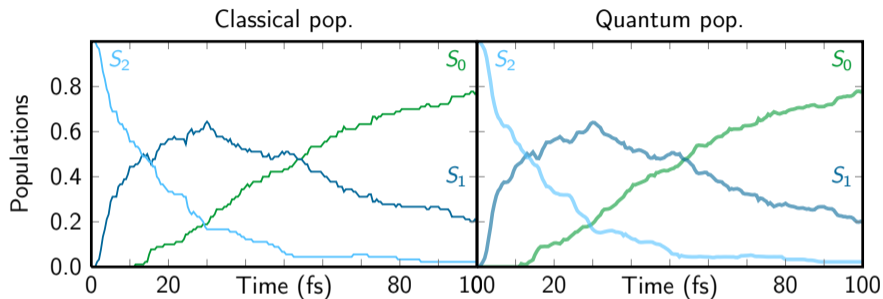
- ▶ Initially in S_2
- ▶ S_1 is intermediate state
- ▶ Quick return to S_0
- ▶ Sequential transfer (verified with hopping analysis)

Electronic evolution: Kinetic modeling

Sequential, uni-molecular, first-order kinetic model:

$$S_2 \xrightarrow{k_{21}} S_1 \xrightarrow{k_{10}} S_0, \tag{1}$$

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Corresponding differential equation system:

$$\frac{\mathrm{d}}{\mathrm{d}t} S_2(t) = - k_{21} S_2(t),$$

$$\frac{\mathrm{d}}{\mathrm{d}t} S_1(t) = + k_{21} S_2(t) - k_{10} S_1(t),$$

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Solutions:

$$S_2(t) = \mathrm{e}^{-k_{21}t},$$

$$S_1(t) = - \frac{k_{21}}{k_{21} - k_{10}} \mathrm{e}^{-k_{21}t} + \frac{k_{21}}{k_{21} - k_{10}} \mathrm{e}^{-k_{10}t},$$

$$S_0(t) = + \frac{k_{10}}{k_{21} - k_{10}} \mathrm{e}^{-k_{21}t} - \frac{k_{21}}{k_{21} - k_{10}} \mathrm{e}^{-k_{10}t} + 1.$$

- ▶ Fitting functions
- ▶ Fitting parameters:
  $\tau_{S_2 \to S_1} = \frac{1}{k_{21}}$ and $\tau_{S_1 \to S_0} = \frac{1}{k_{10}}$
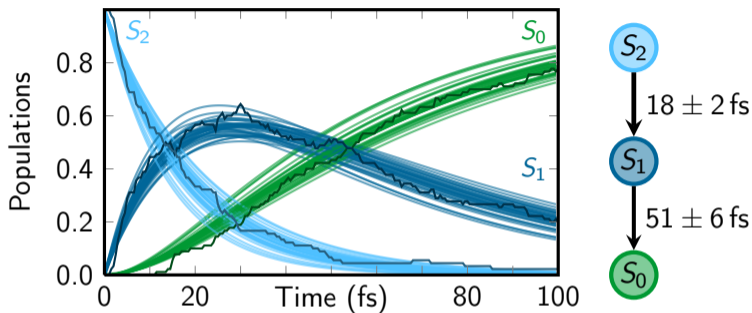
Electronic evolution: Time constants
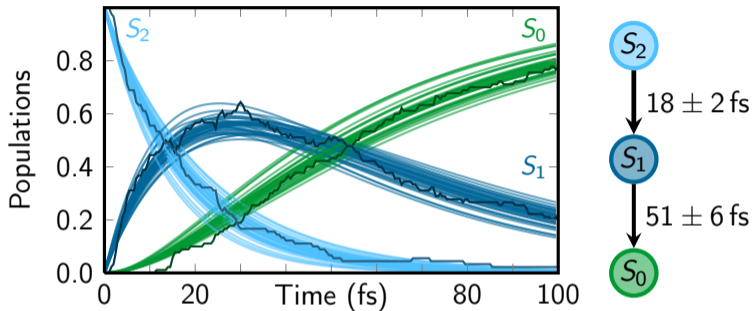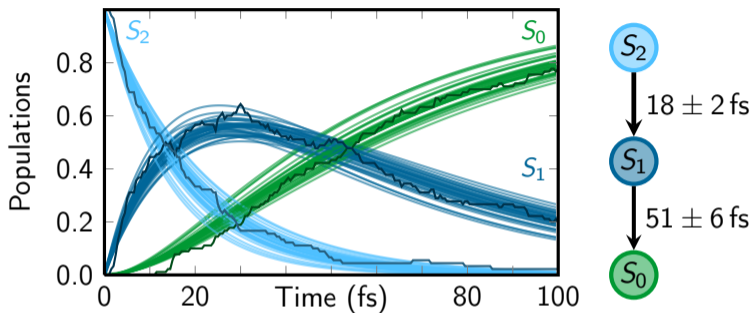
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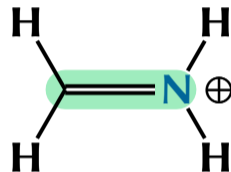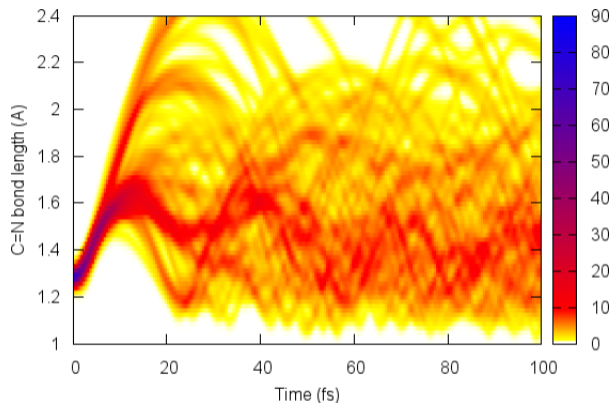
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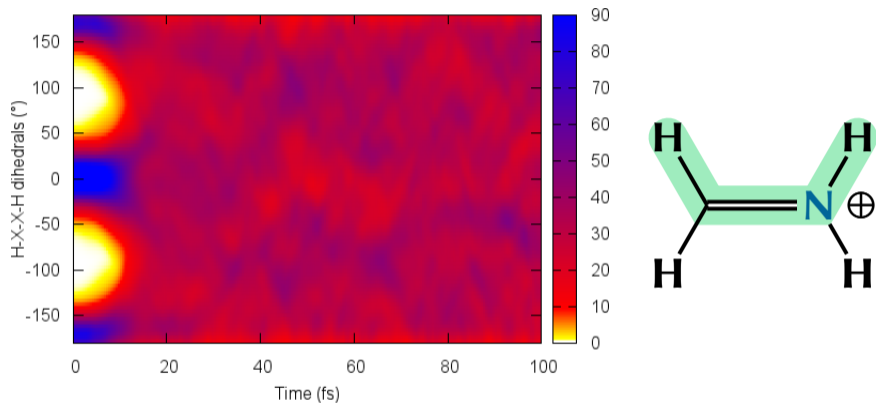
- ▶ Strong increase in bond length
- ▶ Some coherent motion
- ▶ Splitting of trajectory swarm

Nuclear evolution: C–H and N–H bonds
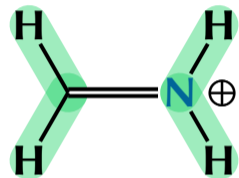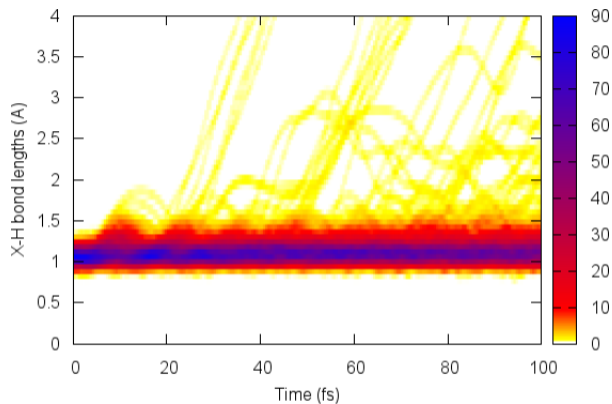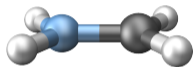

- ▸ Most bonds are stable
- ▸ Some dissociation
- ▸ Some migration

Nuclear evolution: Dihedral angles

- Initially planar
- Double bond is broken in excited state, free rotation around bond
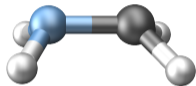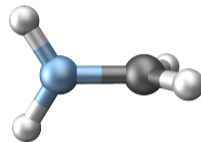
S_0 minimum S_2/S_1 minimum-energy CoIn S_1/S_0 minimum-energy CoIn

- Extract hopping geometries: find what motion leads to S_2/S_1 and S_1/S_0 crossing points.
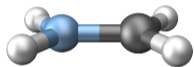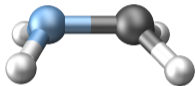
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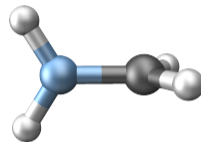
- Extract hopping geometries: find what motion leads to S_2/S_1 and S_1/S_0 crossing points.
- S_2/S_1 transfer is mediated by pyramidalization and C=N stretch
- S_1/S_0 transfer is mediated by torsion

Nuclear evolution: Importance of minimum crossing points
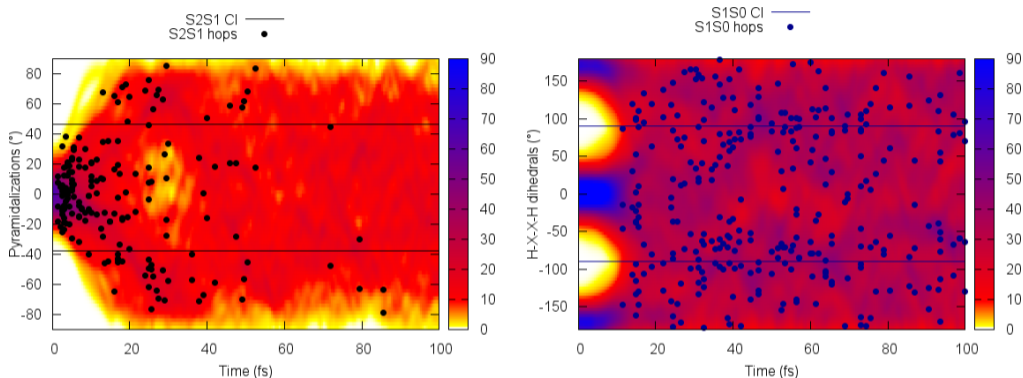
- In this molecule, there is a 10-dimensional intersection space.
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- Optimized conical intersections are only one point in this space.
- Trajectories hop at many different geometries distributed around the conical intersection.

- ▶ Path from starting point to conical intersections to end point.
- ▶ Path is barrierless.

Nuclear evolution: Potential energy surfaces
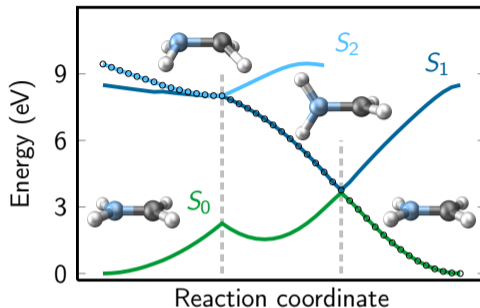
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❷ **Relaxation mechanism**: Important motion is a combination of C=N stretch, pyramidalization, and torsional motion. The conical intersections are easy to reach (no barriers). **CONFIRMED**

Some trajectories did not return to initial S_0 minimum.

Photochemistry products

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Different products:

- H migration to $CH_3\text{-}NH^+$
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- Dissociation to CH_2 and NH_2 fragments
- Any others?

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Automatically identify products: through geometry parameters.

Photochemistry products: Branching ratios
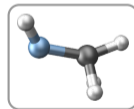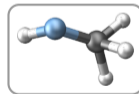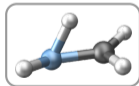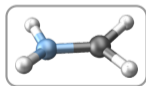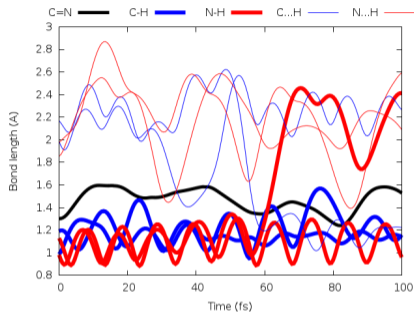
Reaction pathway	Trajectories	Percentage
Unreactive	65	72%
H_2 elimination to $C=N_2^+$	10	11%
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Simulating time-dependent spectra

Most nonadiabatic dynamics is experimentally measured with time-dependent spectroscopy. Examples:

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- Transient absorption
- Photoionization
- X-ray scattering
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How to compute time-dependent photoluminescence spectrum:

$$S(E, t) = \frac{1}{N_{\text{traj}}} \sum_{j}^{\text{traj}} \sum_{\beta}^{\text{states}} (f_{\text{osc}})^{j}_{\alpha \to \beta}(t) \cdot e^{-\frac{4 \ln 2}{\text{FWHM}_E^2} \left(E - \Delta E^{j}_{\alpha \to \beta}(t) \right)^2}. \tag{2}$$

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With broadening through an instrument response function:

$$S^{\text{conv}}(E, t) = \sum_{i}^{\text{time steps}} S(E, \Delta t_i) \; \cdot \; e^{-\frac{4 \ln 2}{\text{FWHM}_t^2}(t - \Delta t_i)^2}. \tag{3}$$

▶ Computed fs luminescence spectrum with broadening of 2.0 eV and 10 fs

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- Quick decrease in luminescence energy: decay to ground state
- Splitting of swarm can be discerned

Simulating time-dependent spectra: Results
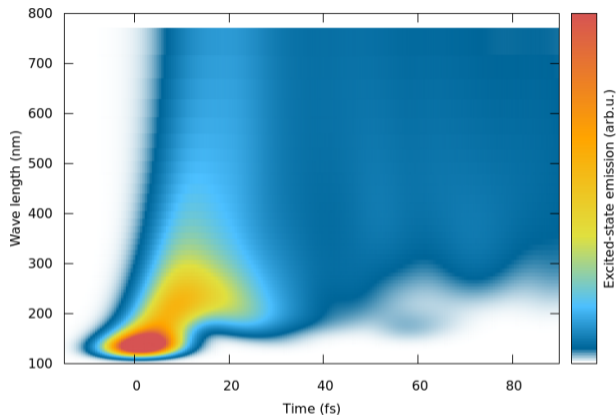
- ▶ Computed fs luminescence spectrum with broadening of 2.0 eV and 10 fs
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- ▶ Splitting of swarm can be discerned
- ▶ Can be compared to suitable experiment

Chemical problem

Simulate the photo-induced nonadiabatic dynamics of the methylene immonium cation $CH_2NH_2^+$.

Summary I

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Surface hopping coupled to multi-reference configuration interaction (MRCI) with a CAS(6,4) active space.

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Methods

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Initial conditions

Wigner distribution around S_0 minimum, excited vertically at 9.29–9.59 eV to the S_2 $(\pi\pi^*)$ state.

Summary II

Settings

210 trajectories were propagated for 100 fs with a 0.5 fs time step. Typical settings for surface hopping were used (decoherence, kinetic energy rescaling, …).

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Execution

A single time step took about 5 min. Therefore, 200 steps took 19 hours and 210 trajectories then cost 4000 CPU hours.

Summary II

Settings

210 trajectories were propagated for 100 fs with a 0.5 fs time step. Typical settings for surface hopping were used (decoherence, kinetic energy rescaling, …).

Execution

A single time step took about 5 min. Therefore, 200 steps took 19 hours and 210 trajectories then cost 4000 CPU hours.

Validation

Many trajectories had numerical artifacts so that the swarm was reduced to 90 suitable trajectories.

Summary III

Individual analysis

Four hypotheses:

1. Fast, sequential $S_2 \rightarrow S_1 \rightarrow S_0$ decay.
2. Important motion C=N stretch, pyramidalization, and torsion.
3. We can have H migration, H_2 elimination, or other processes.
4. Most trajectories do nothing.

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4. Most trajectories do nothing.

Statistical analysis

1. $S_2 \rightarrow S_1$ decays with 18±2 fs and $S_1 \rightarrow S_0$ with 51±6 fs without barriers.
2. Conical intersections involve C=N stretch, pyramidalization, and torsion.
3. We find H_2 elimination (11%), H migration (8%+6%), and C=N dissociation (3%).
4. Most trajectories do nothing (72%).

Thank you for your attention!

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My further thanks goes to: