A 3D visualization of molecular dynamics on a complex grid landscape. In the center, a large orange sphere contains a red wireframe molecular model. Surrounding it are several translucent pink molecular models. The background consists of a dark blue space with a white grid, and the foreground features a green wireframe mountain range.

Can we describe
photochemistry
without
nonadiabatic
dynamics?

Elisa Pieri

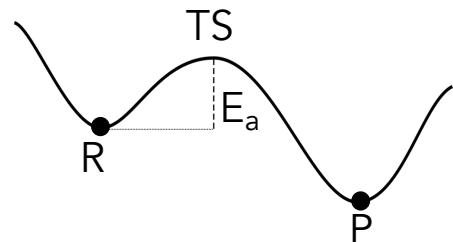
VISTA

February 14, 2023

Stanford University

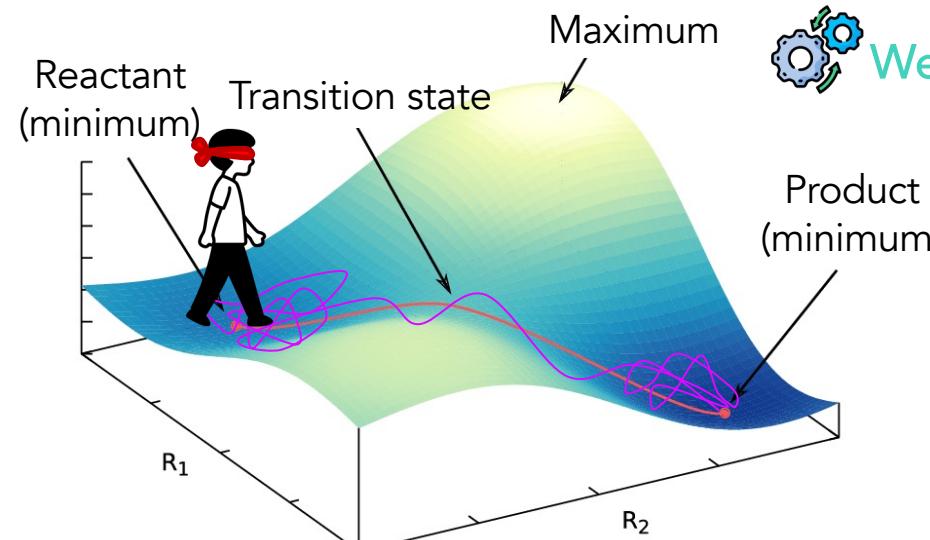
Paradigms in chemical simulations

Static approach



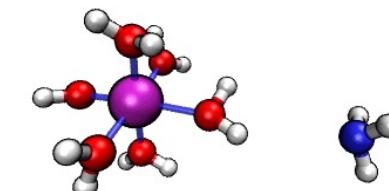
Good for:

- ✓ Isolate reactions coordinates
- ✓ Compare potential energies
- ✓ Build reaction networks



We need walking algorithms!

Dynamic approach



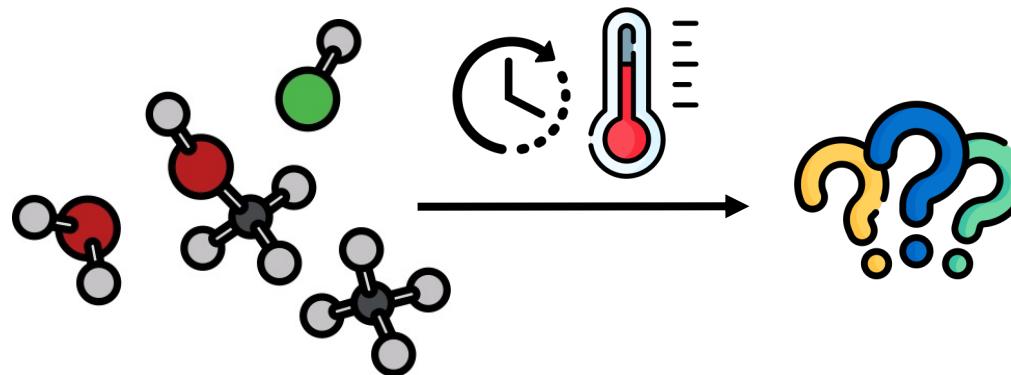
Good for:

- ✓ Sampling conformations
- ✓ Get statistics
- ✓ Get time information

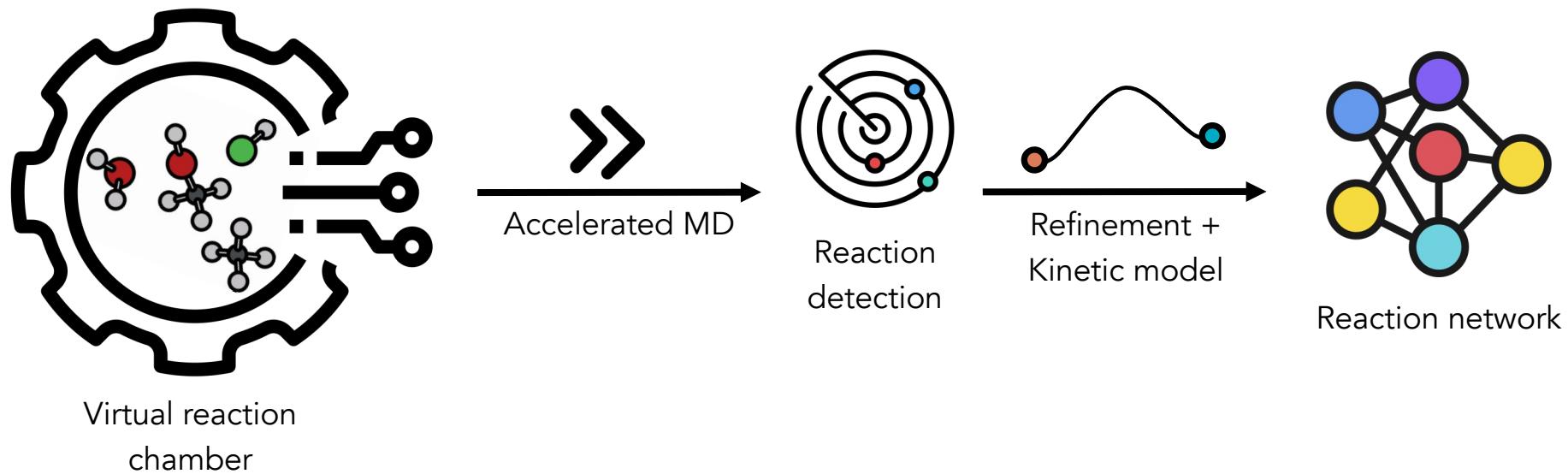
How can we get the best of both worlds?



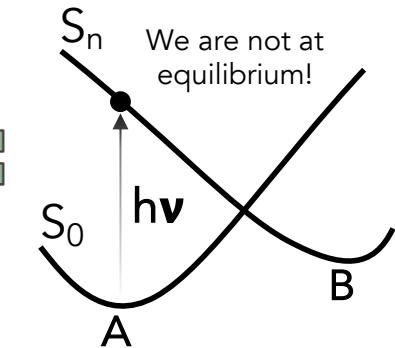
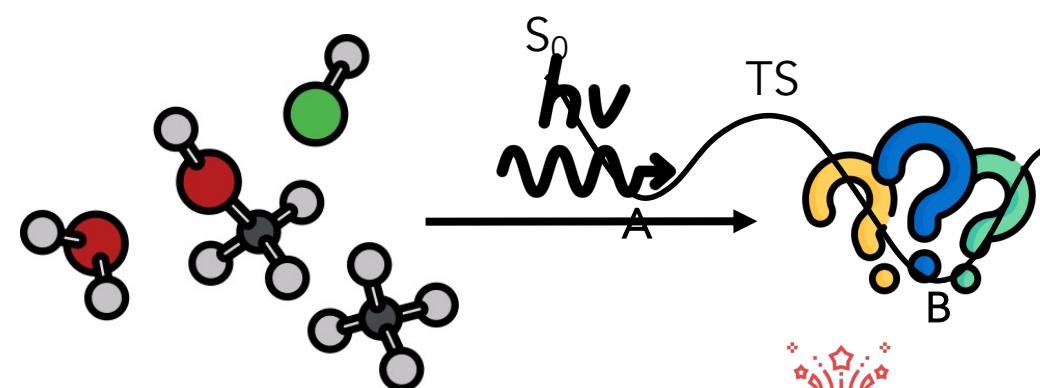
Reactivity prediction



The *ab initio* NanoReactor

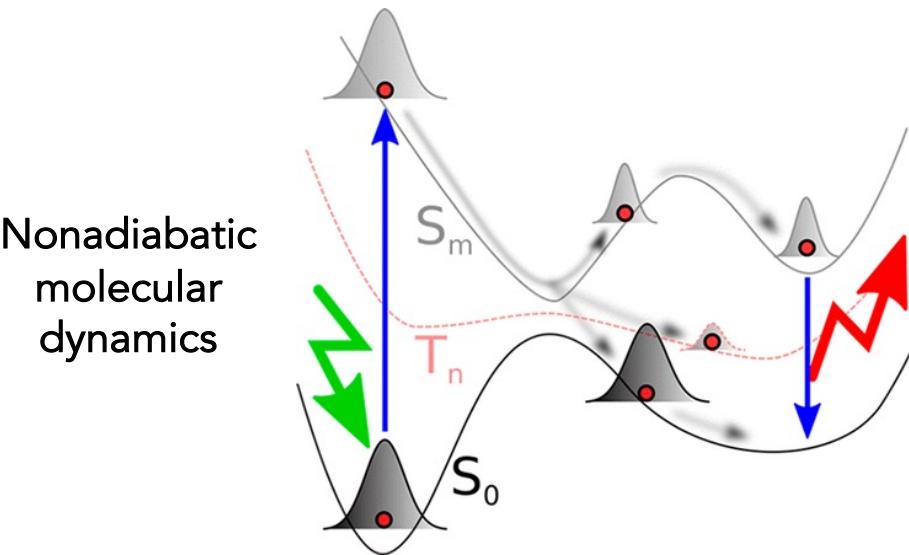


What about photochemistry?



 **The Nonadiabatic NanoReactor**

A “black-box” tool to discover all photoproducts.



- Requires accurate description of multiple electronic states, coupling and population transfers
- Difficult to catch rare events

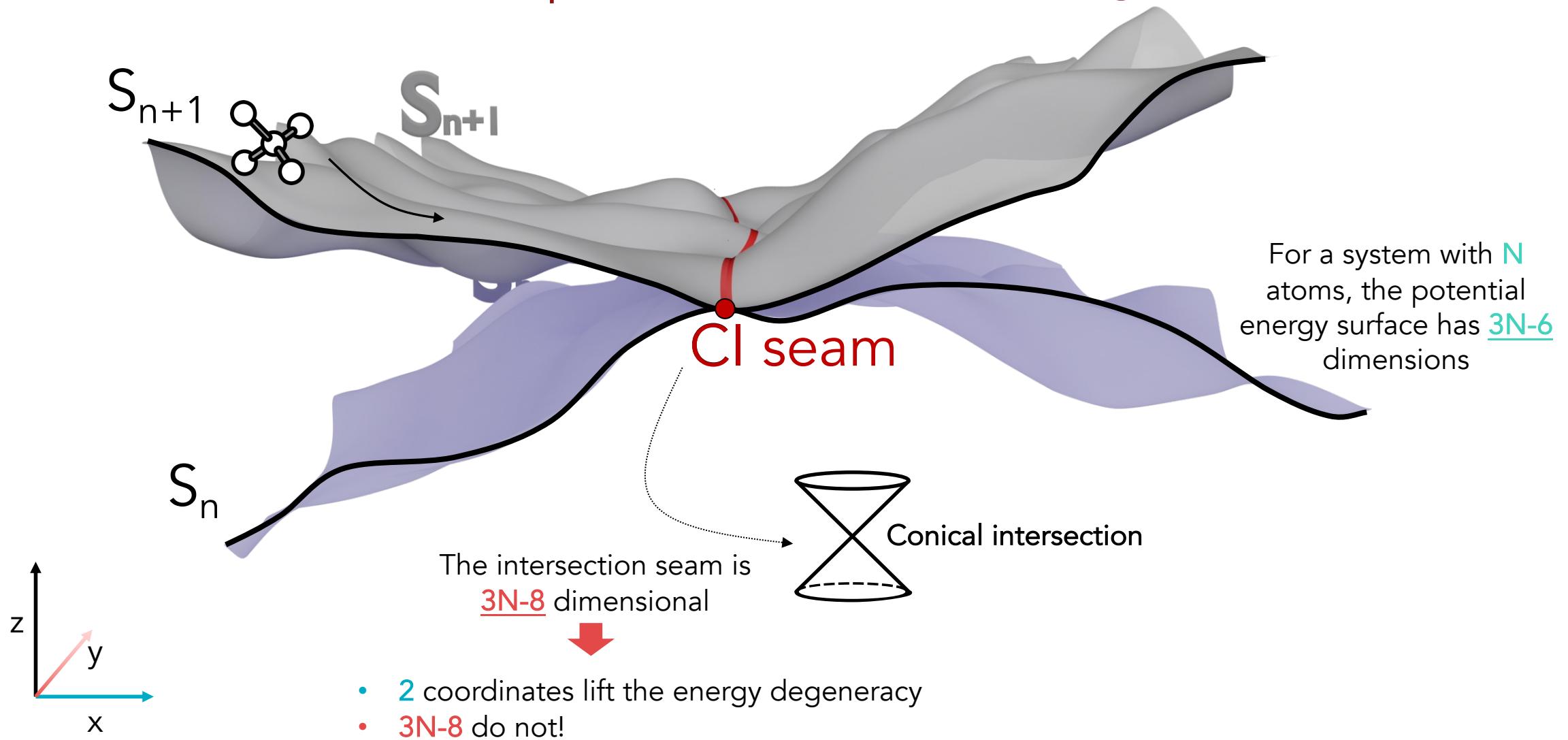


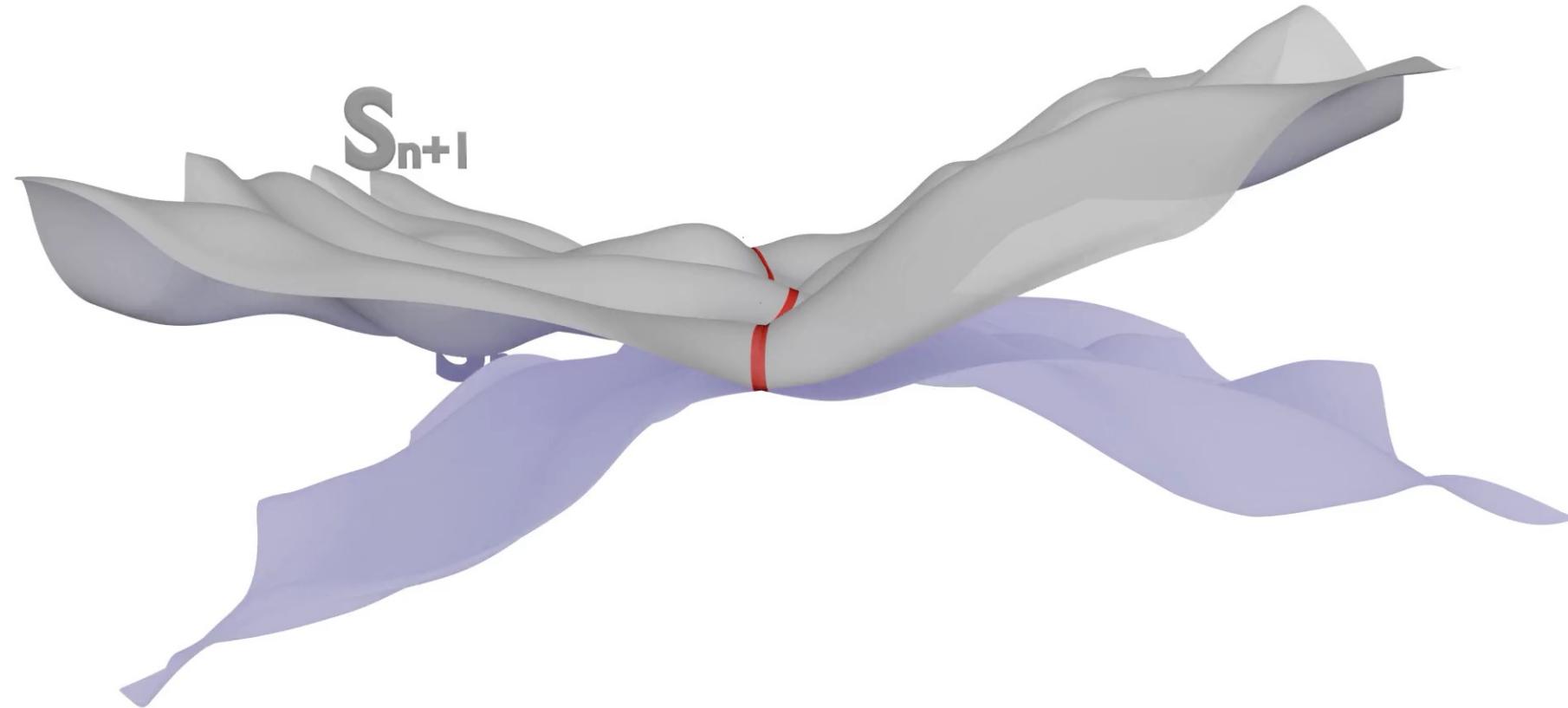
Find all accessible conical intersections



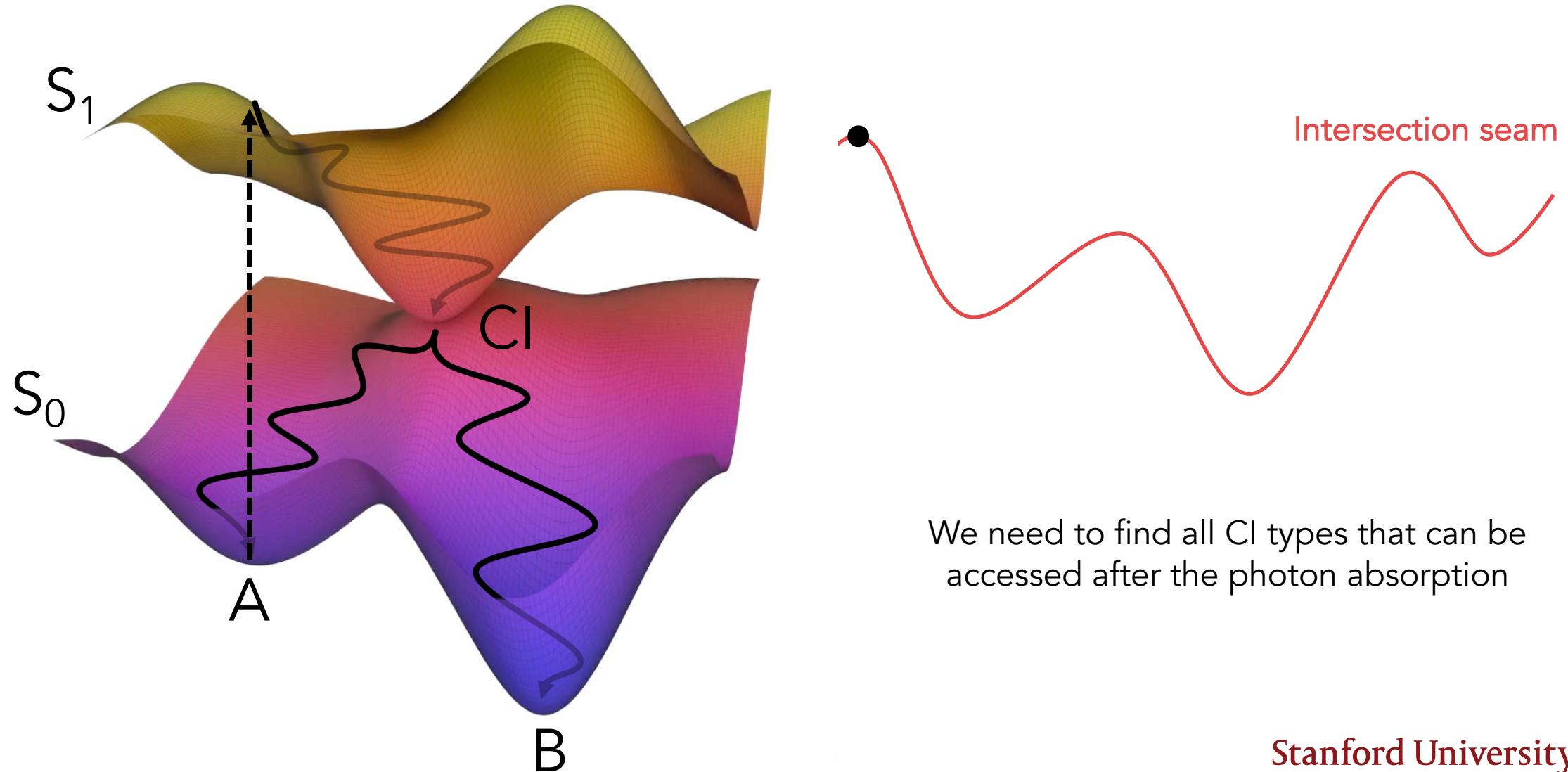
From them, find all possible photoproducts

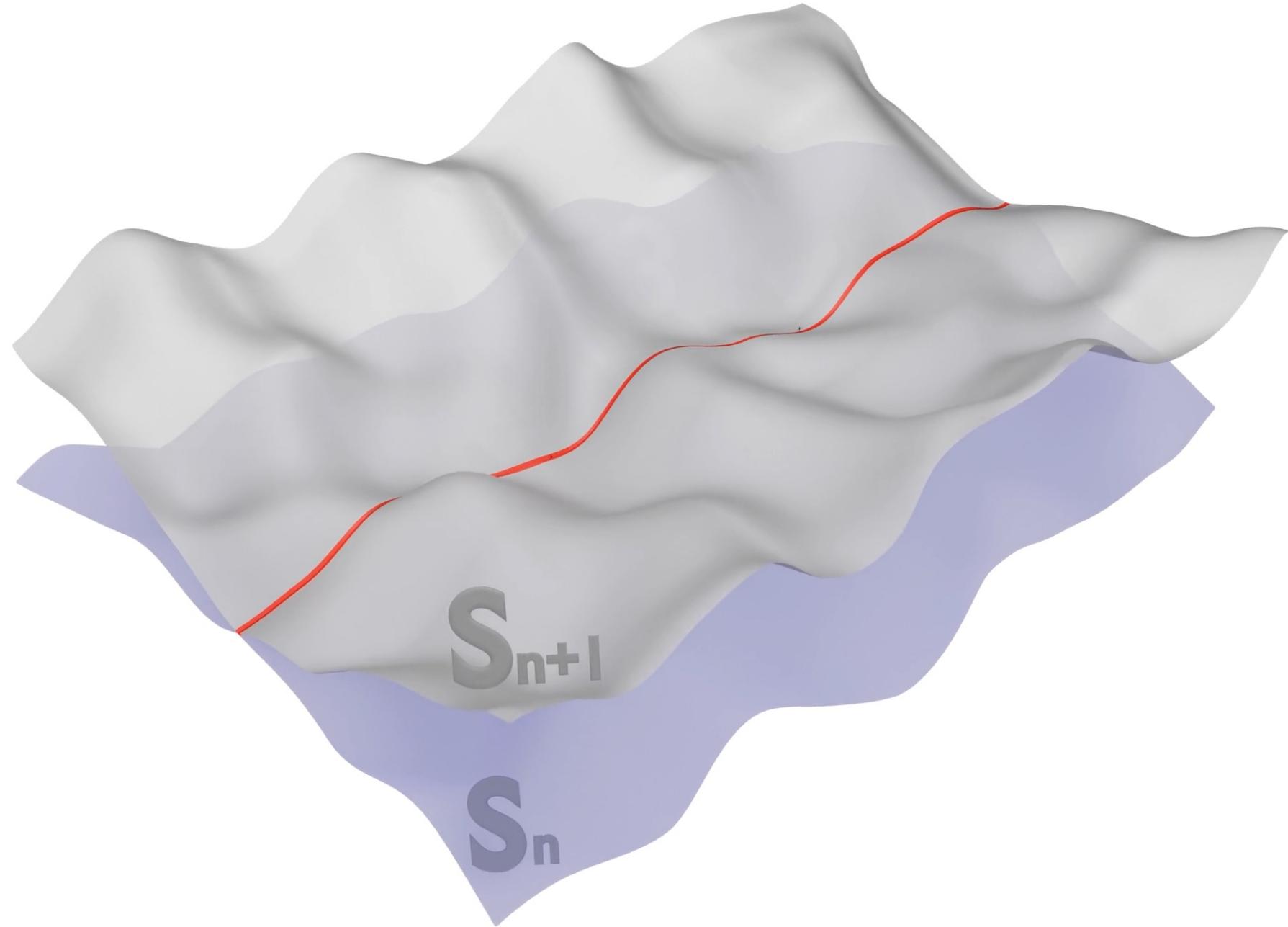
Multidimensional spaces are hard to imagine





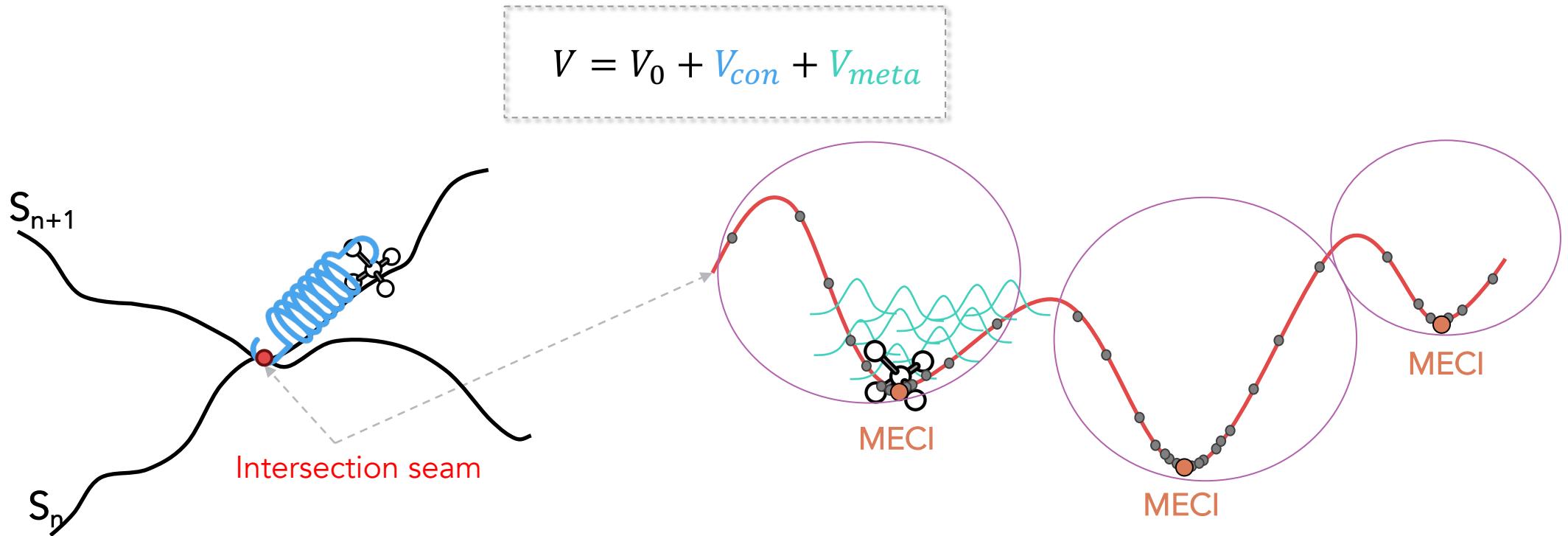
There are infinite conical intersections







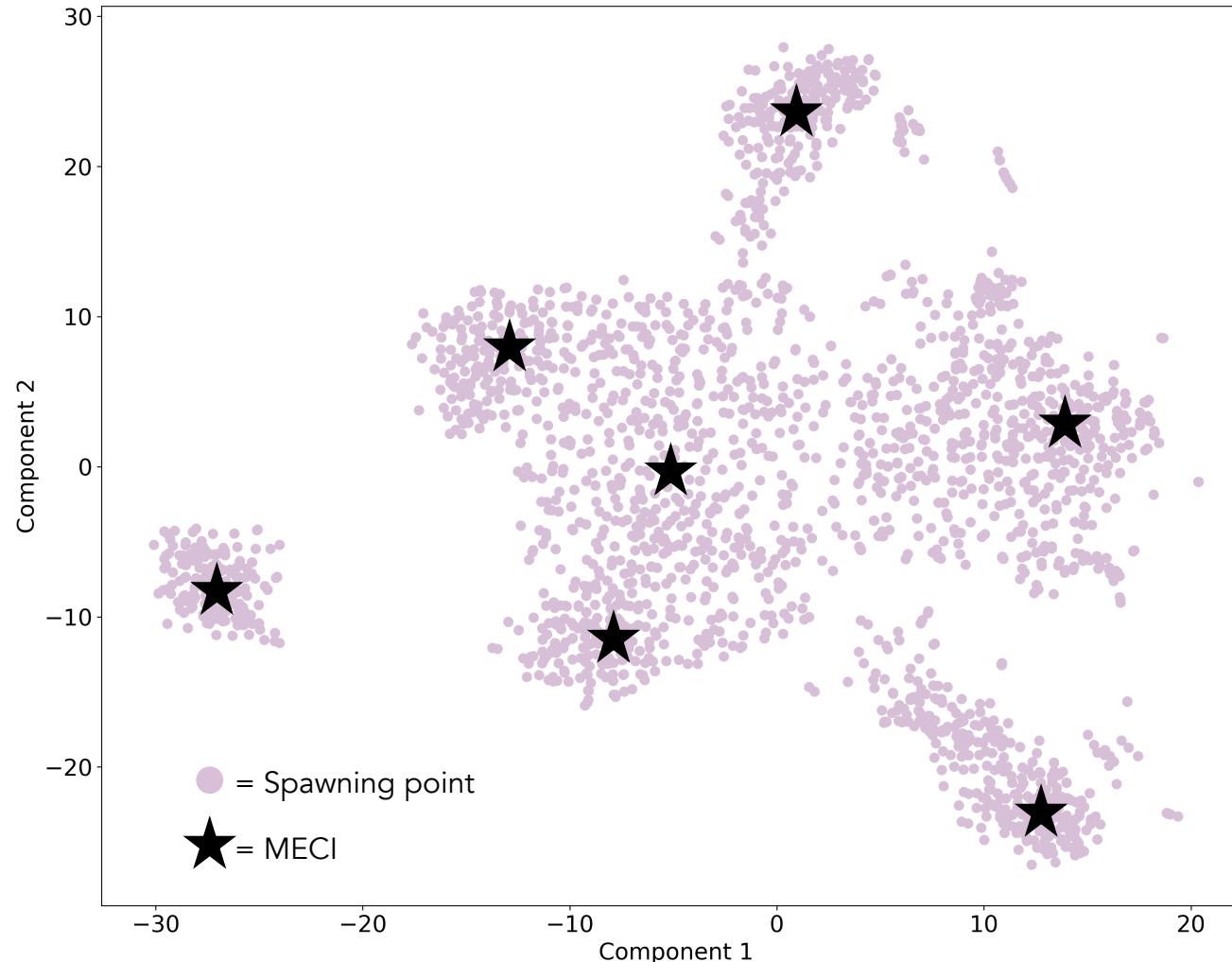
Seam-constrained meta-dynamics



WHY MECIs?

- Collect thousands of **conical intersections**
- **Cluster** them
- Search **minimum energy conical intersections** (MECI) from centroids

MECIs represent conformational wells on the seam space



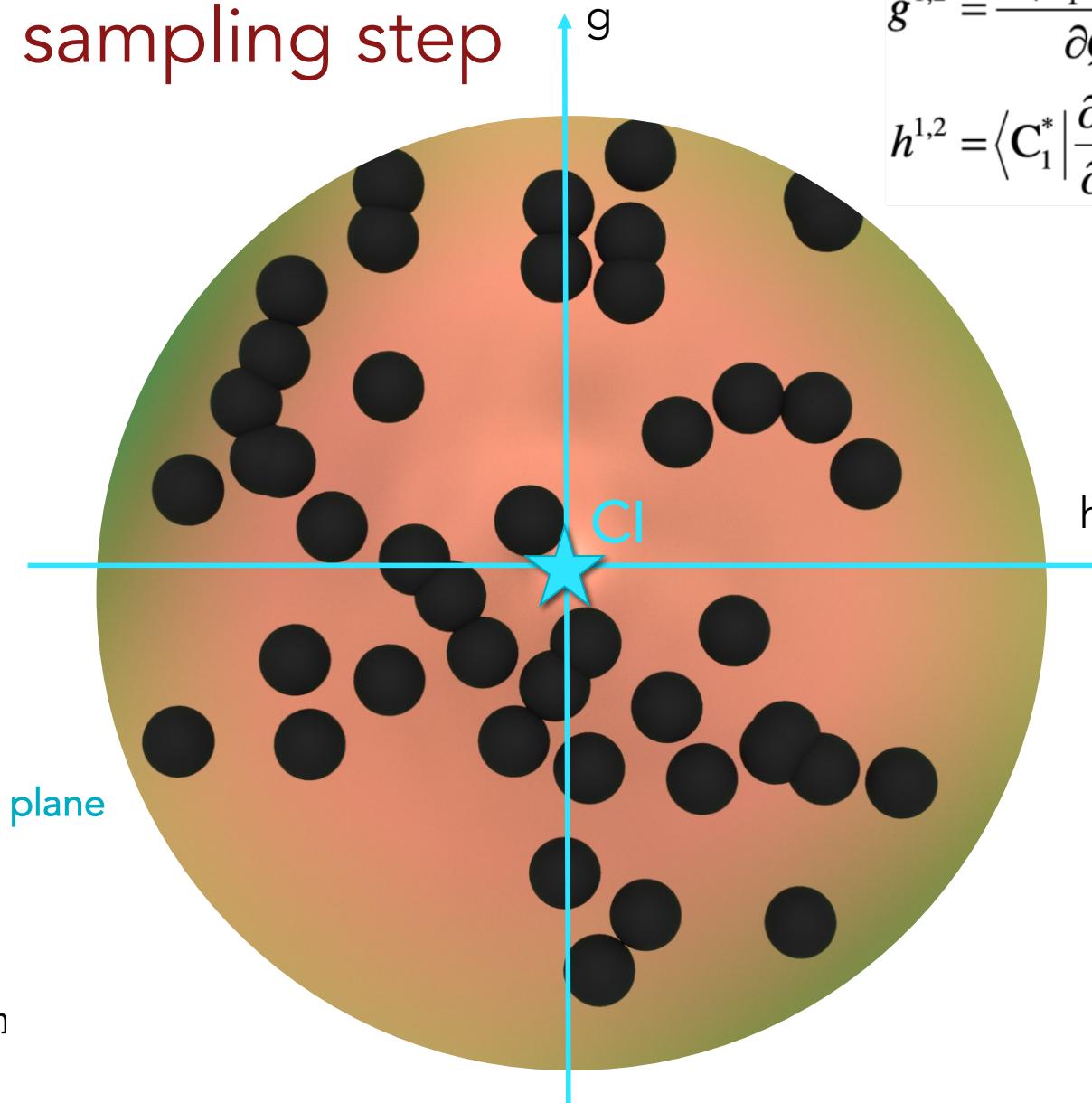
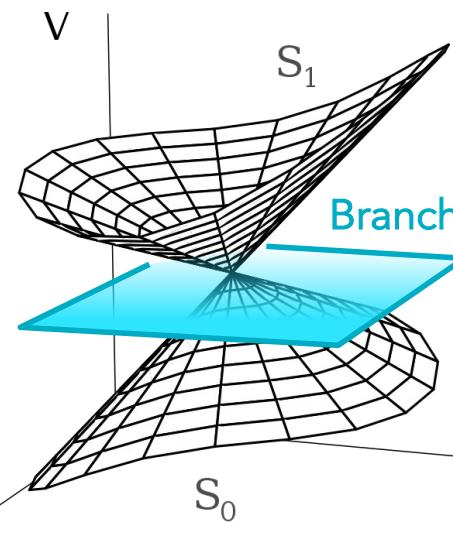
t-SNE analysis on the coordinates of the S_1/S_0
AIMS spawning geometries for benzene

FOMO-CASCI(6,5)/6-31G

MECIs seem to be suitable to represent
a basin of CIs on the intersection space



The cone sampling step



$$g^{1,2} = \frac{\partial(E_1 - E_2)}{\partial Q}$$

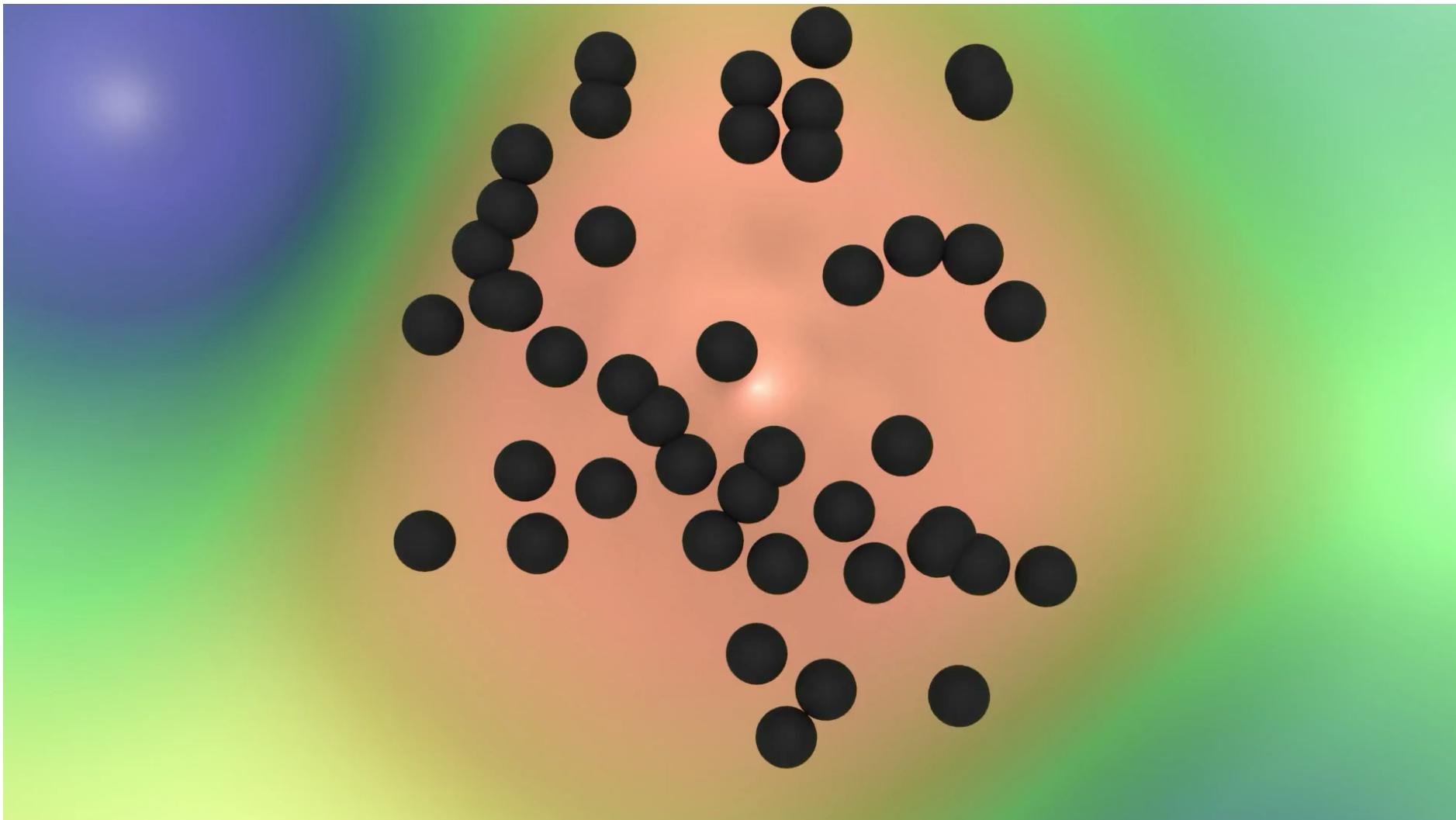
$$h^{1,2} = \left\langle C_1^* \right| \frac{\partial H}{\partial Q} \left| C_2^* \right\rangle$$

gradient difference
vector

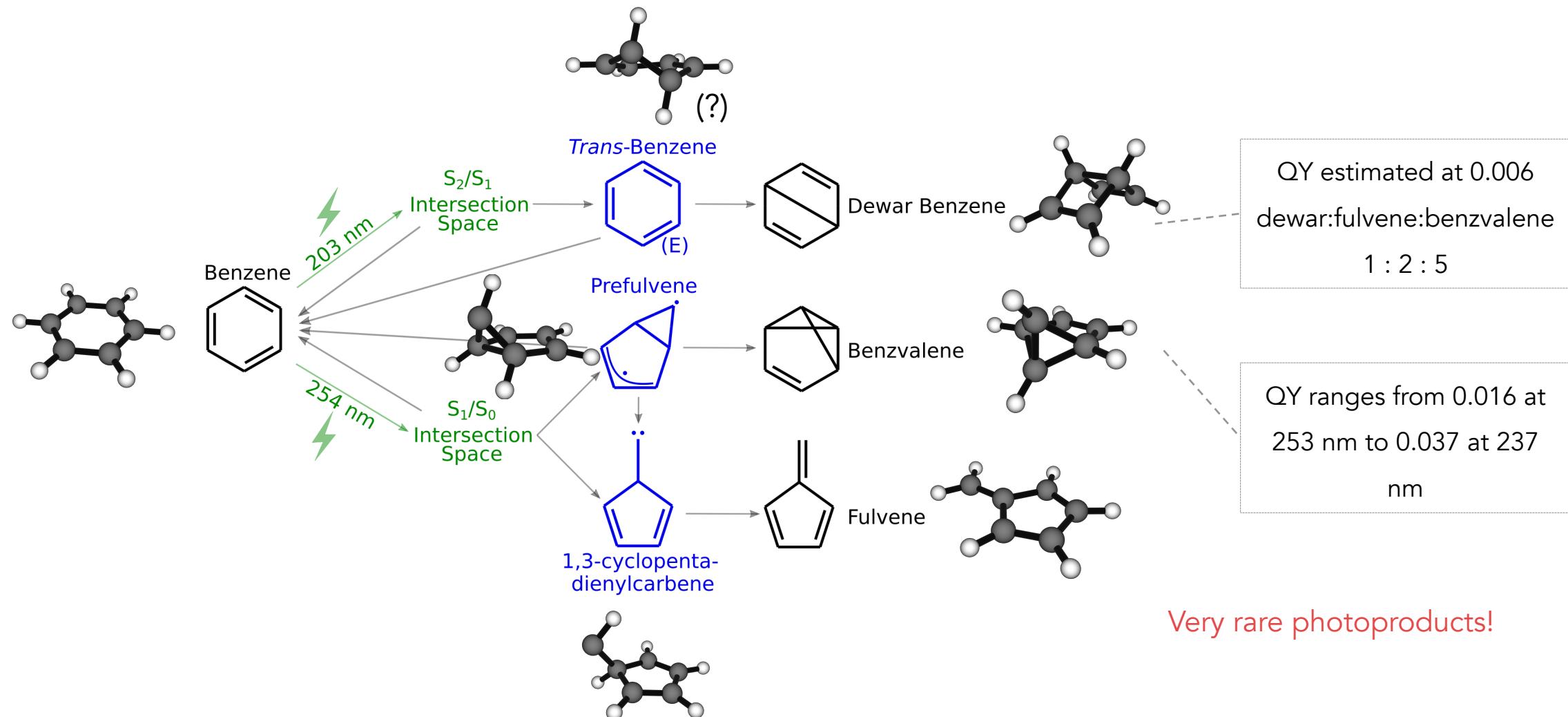
interstate coupling
vector



The photoproduct search



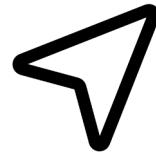
Benzene as a case study



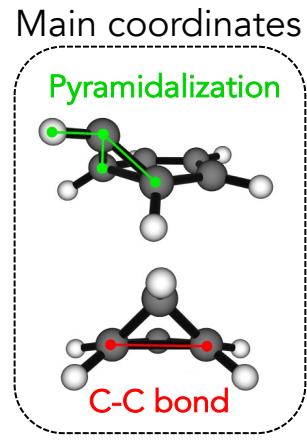
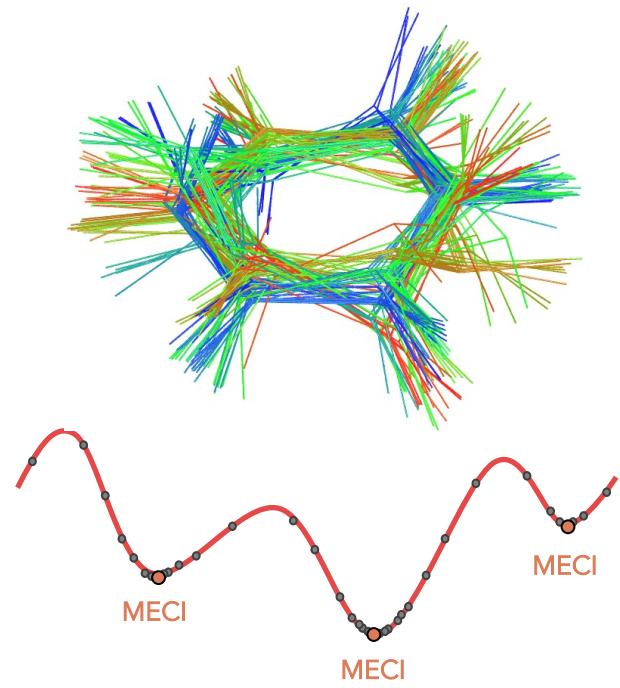
Kaplan et al., 1968, J. Am. Chem. Soc.

Dreyer et al., 1996, Chemistry A European Journal

Domcke et al., 2004, Conical Intersections: Electronic Structure, Dynamics & Spectroscopy

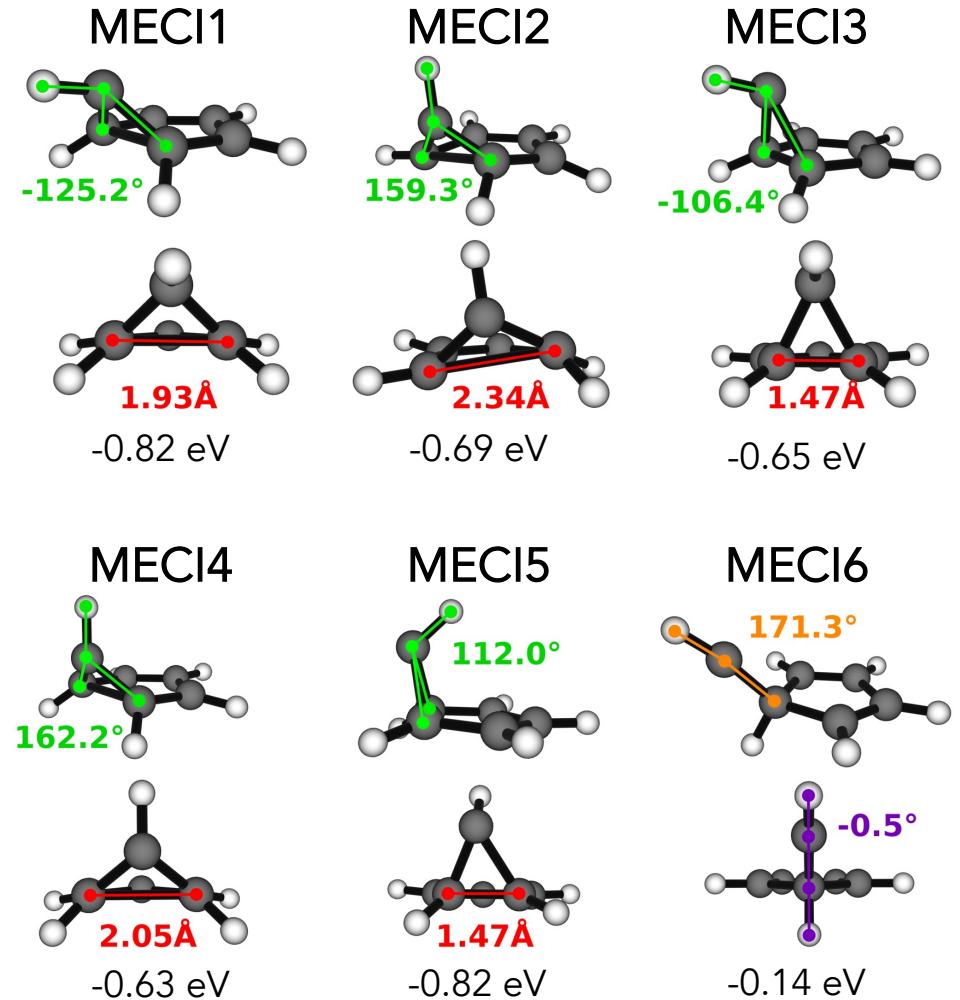


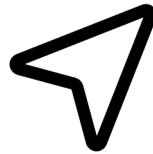
We found many accessible S_0/S_1 MECIs



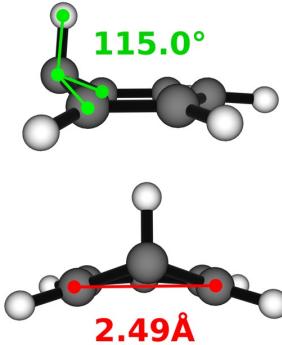
S_1/S_0 seam exploration:

from ~2000 Cls
to 6 MECIs

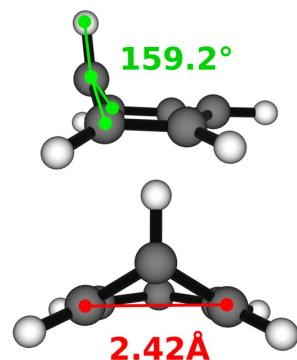
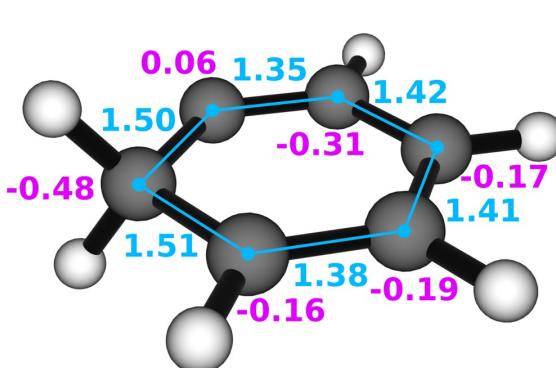




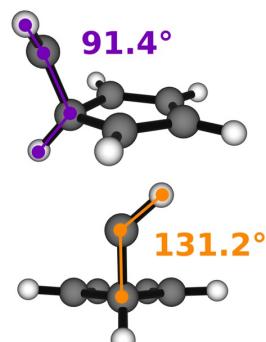
Exploration of the S_1/S_2 seam



S_2/S_1 MECI1
 $\Delta E = -0.80$ eV



S_2/S_1 MECI2
 $\Delta E = -0.61$ eV



S_2/S_1 MECI3
 $\Delta E = -0.10$ eV

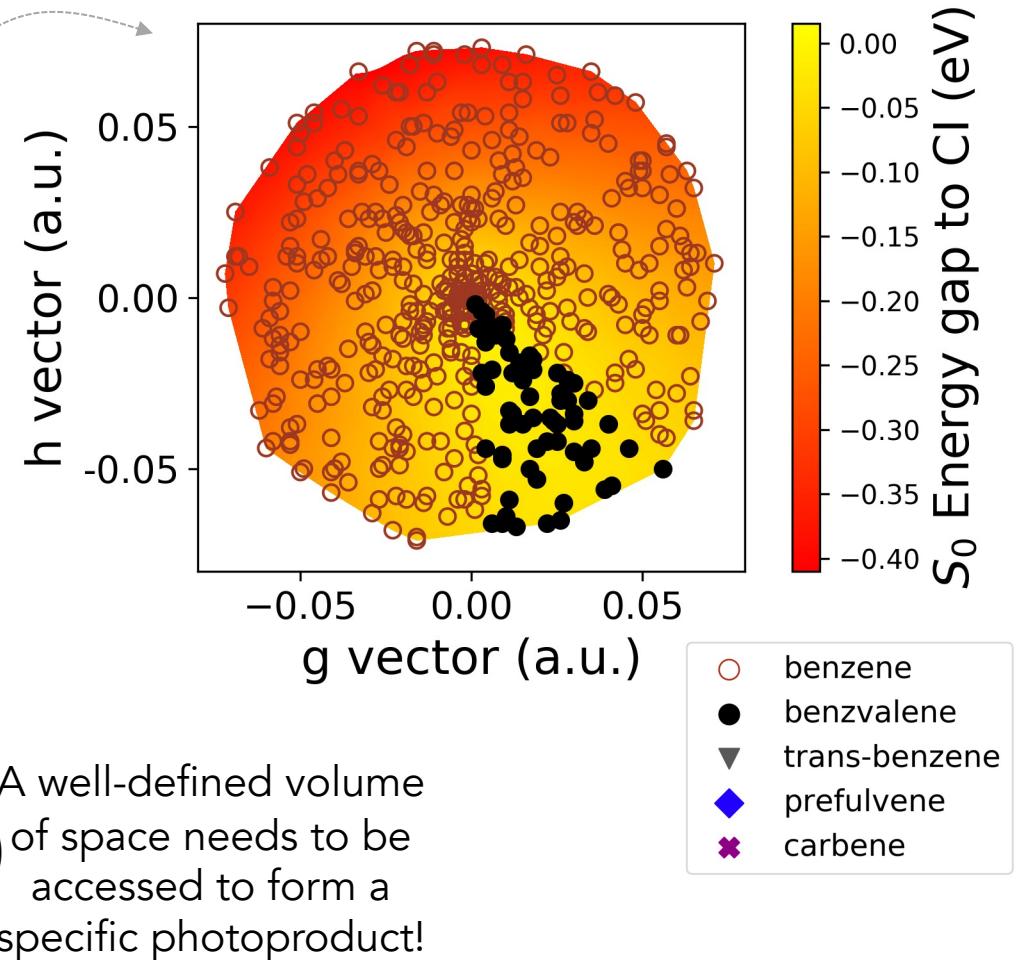
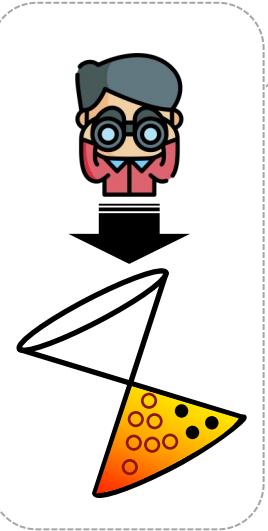
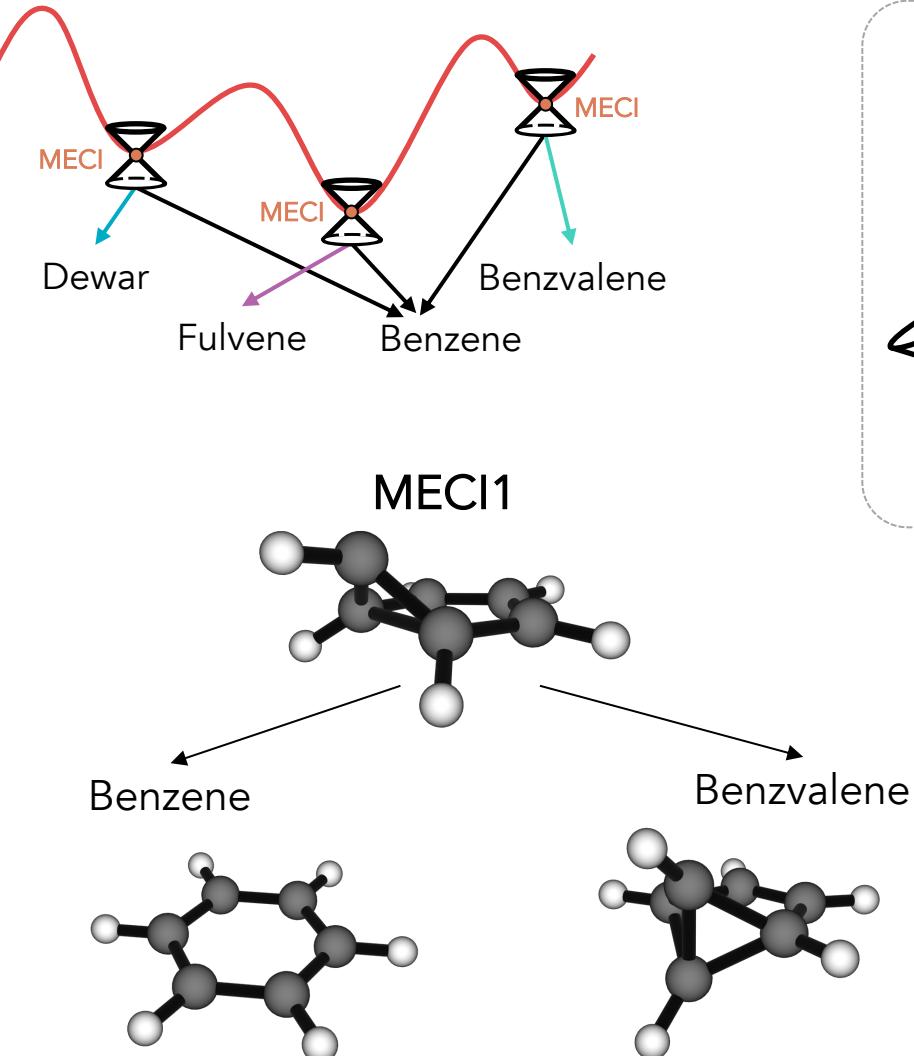
Exploration of the S_1/S_0 starting from the S_2/S_1 MECIs reaches many of the S_1/S_0 already characterized

S_1/S_0 MECI7 can only be reached when benzene is excited to S_2

- 1.5 eV lower in energy than MECI1



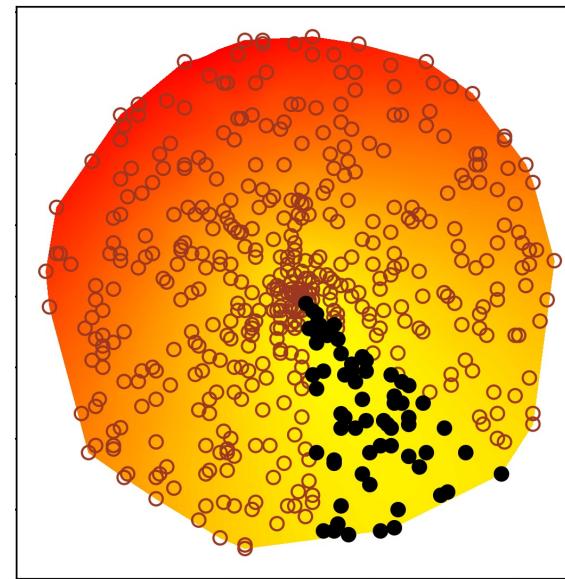
The photoproduct search



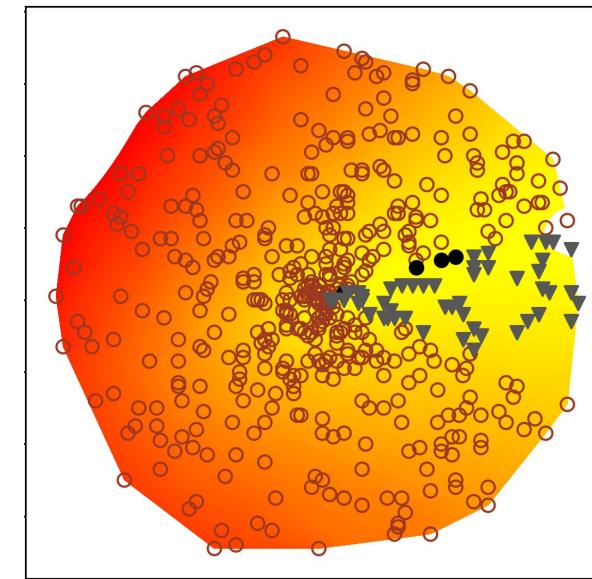
Each MECI leads to different photoproducts

- benzene
- benzvalene
- ▼ trans-benzene
- ◆ prefulvene
- ✗ carbene

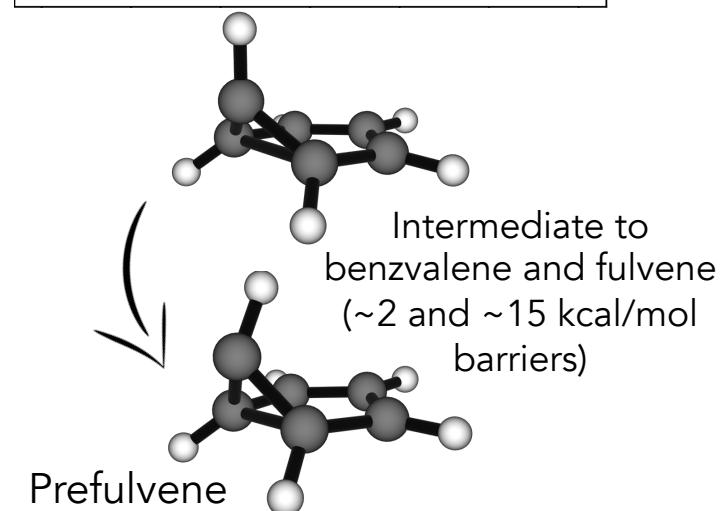
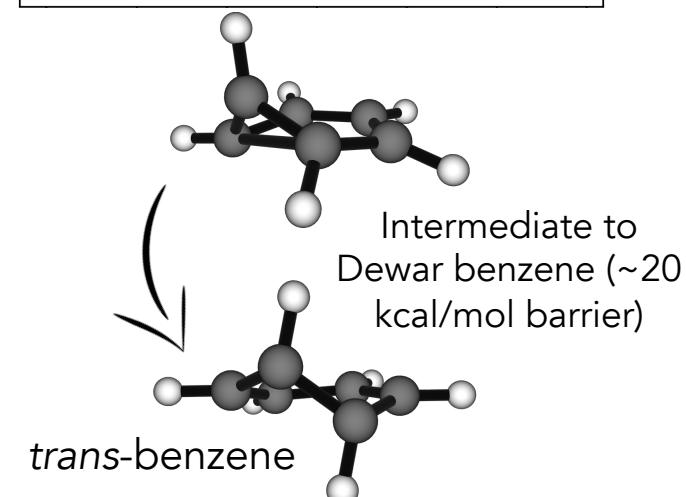
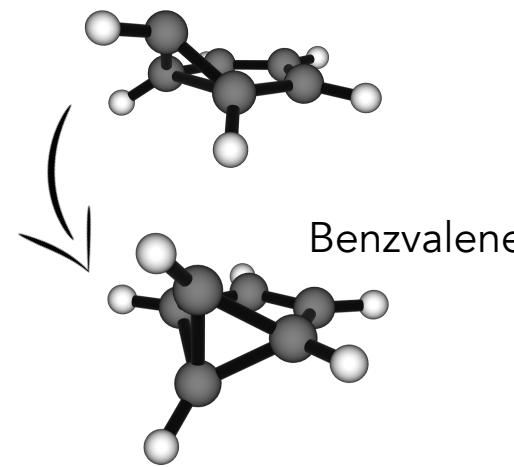
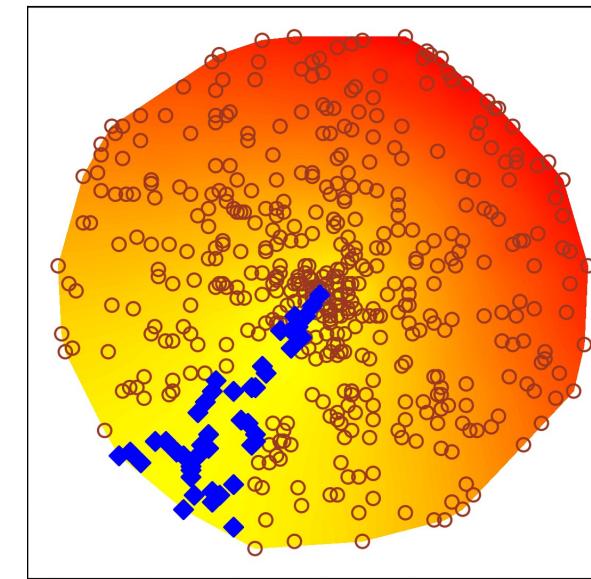
MECI1



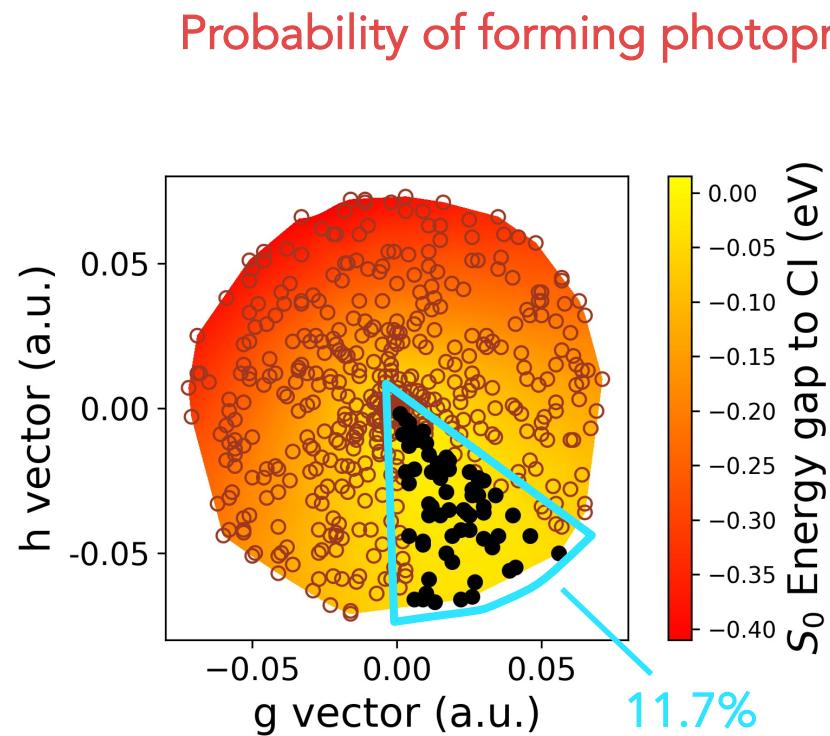
MECI2



MECI3



A crude model to estimate quantum yields



$$p(P_j) = \sum_i p(I_i) p(P_j | I_i)$$

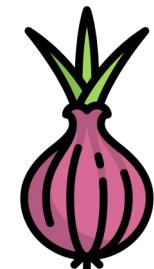
Probability of reaching the i -th CI

Probability of forming j from i

$$p(I_i) = \frac{1}{Q} e^{-\frac{\Delta E}{K_B T}}$$

QY(benzvalene)
Theo.=0.10
Exp. = 0.04

QY(Dewar benzene)
Theo.=0.005
Exp. = 0.006

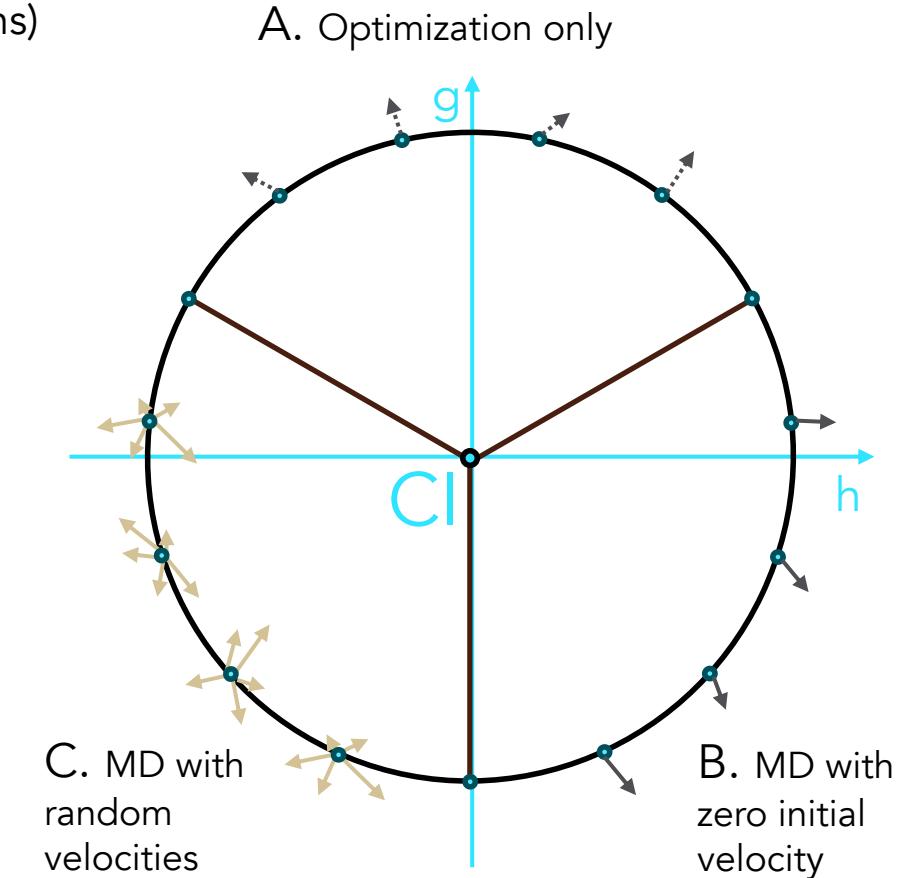
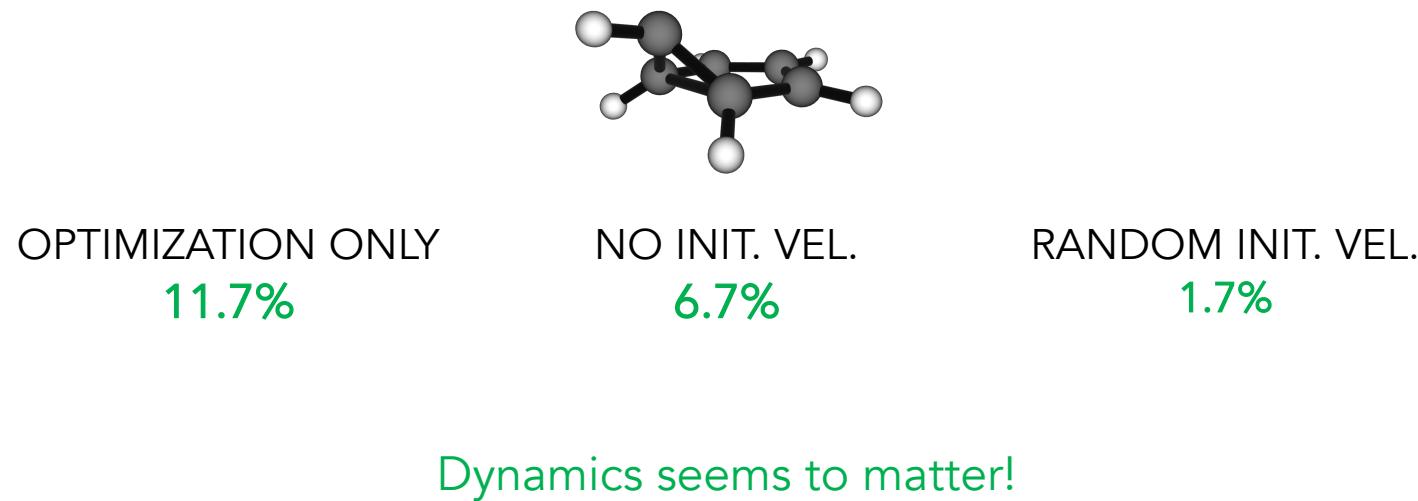


Approximations:

- Equilibrium between the MECIs
- Each part of the cone is equally accessible
- Temperature estimated from the kinetic energy as $K = E_{FC} - E_{S_1 MIN}$

Directions to improve the model

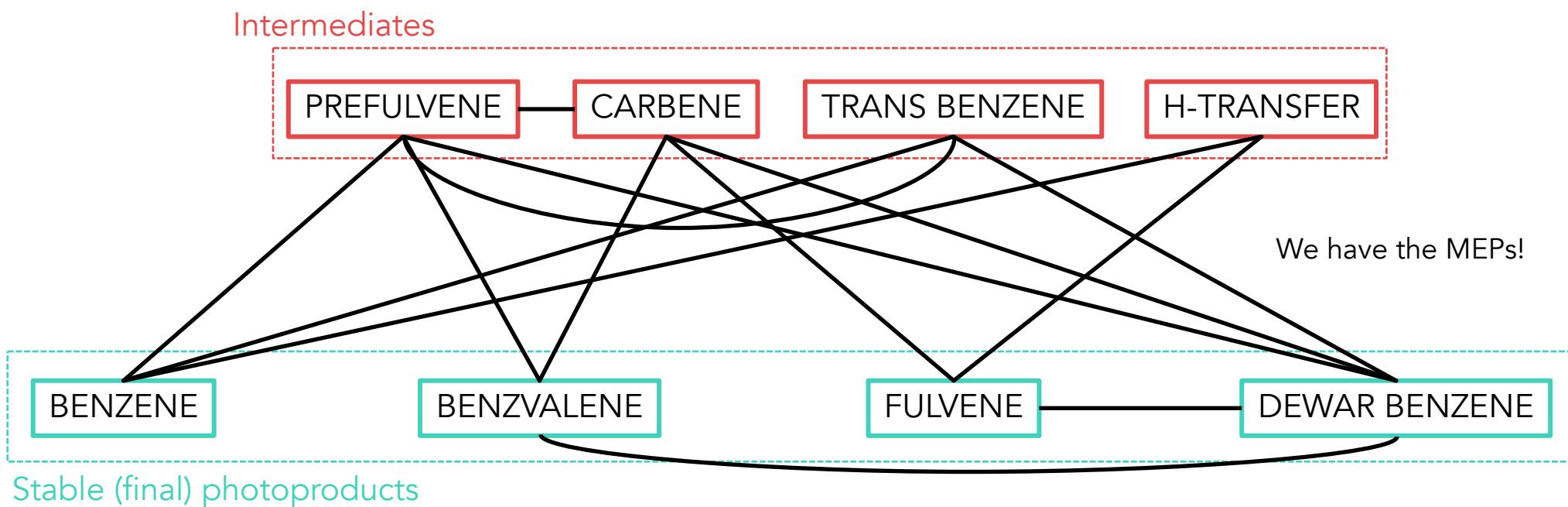
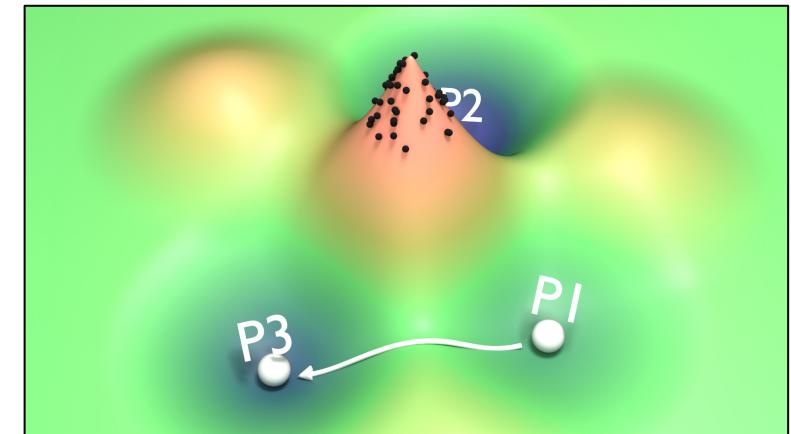
- Dynamics in the photoproduct search phase (instead of optimizations)



Directions to improve the model

- Dynamics in the photoproduct search phase (instead of optimizations)

Include the transformation of intermediates into final products → branching ratios



Directions to improve the model

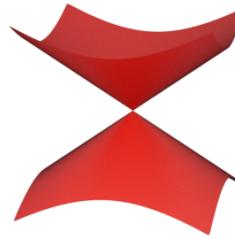
- Dynamics in the photoproduct search phase (instead of optimizations)
- Impact of conical intersection topography

$$\vec{S} = \lim_{R_0 \rightarrow R_{\text{CI}}} \nabla \left(\frac{E_1(R) + E_2(R)}{2} \right) \Big|_{R=R_0}$$

σ = length of the projection of \vec{S}

{ $\sigma = 0 \rightarrow$ ideally peaked CI
 $\sigma > 0 \rightarrow$ more and more sloped CI

Benzene S_0/S_1 MECIs \rightarrow 3 sloped, 3 peaked



Peaked



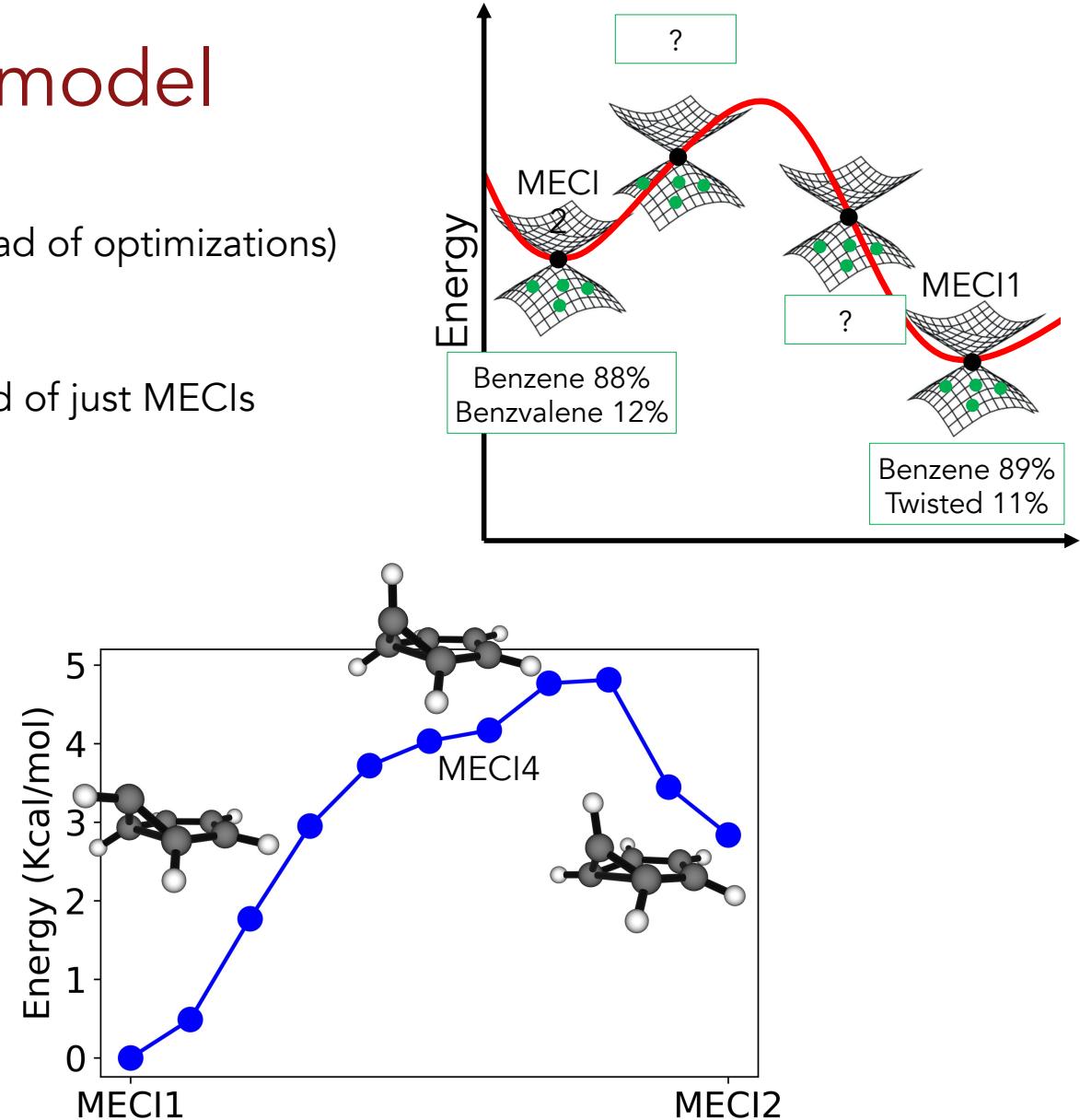
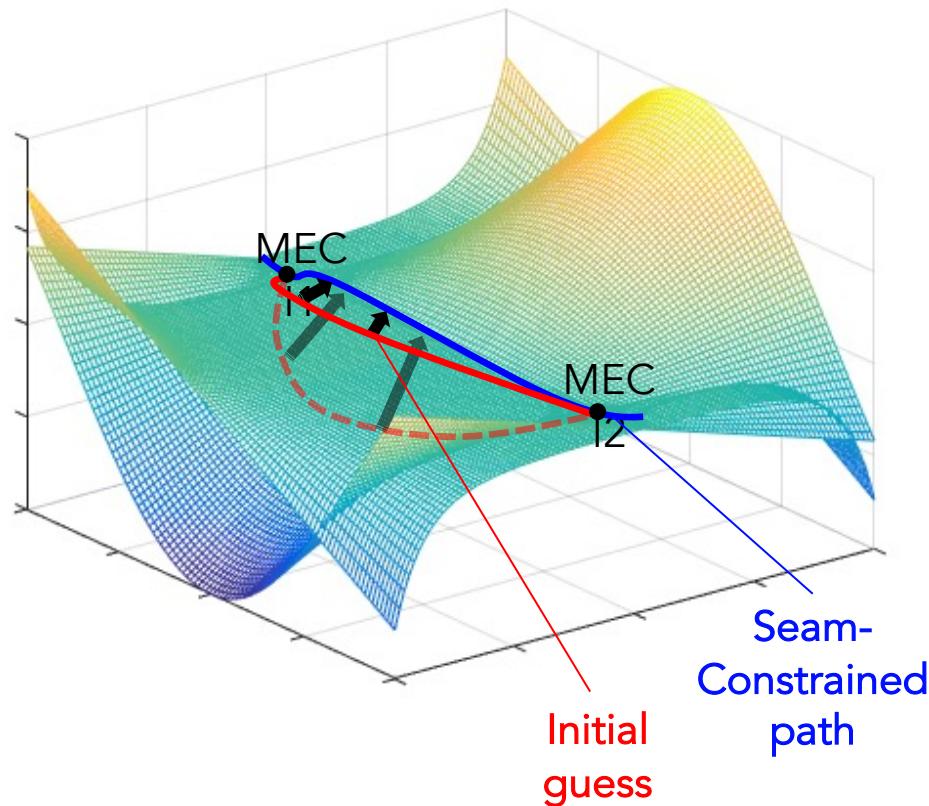
Sloped

VS.

Does the topography impact
the accessibility of cone?

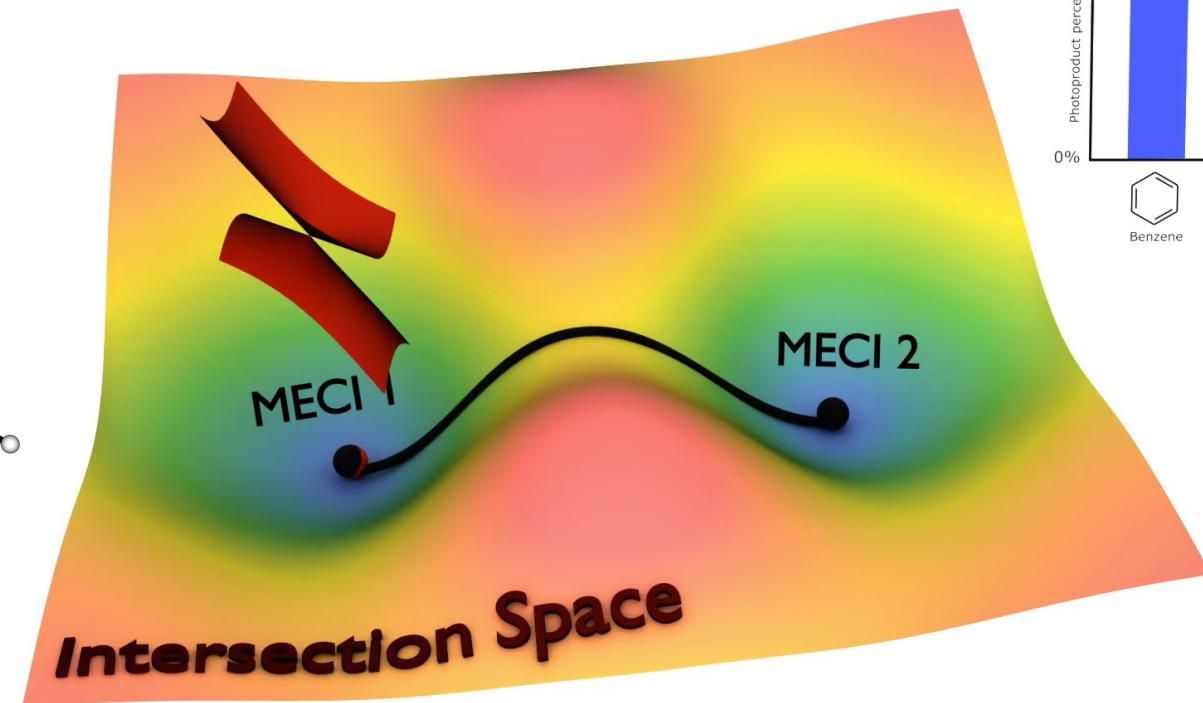
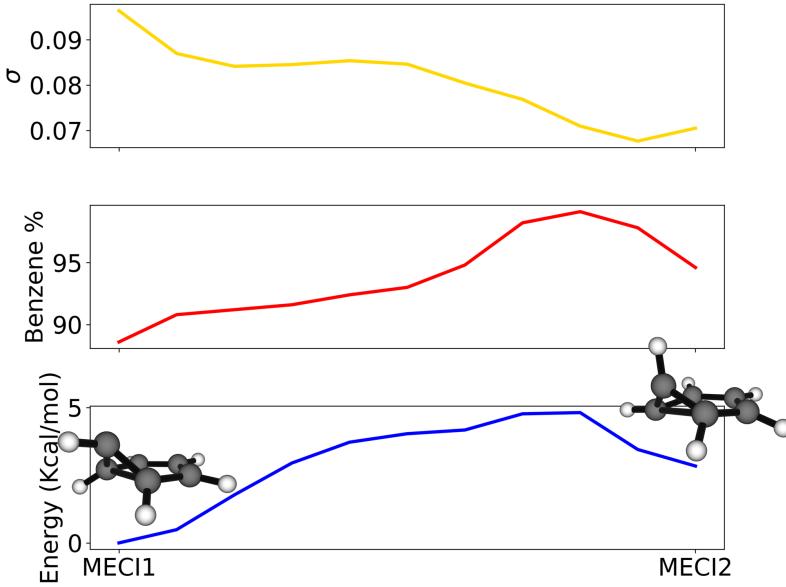
Directions to improve the model

- Dynamics in the photoproduct search phase (instead of optimizations)
- Impact of conical intersection topography
- Sampling from the whole intersection seam instead of just MECl

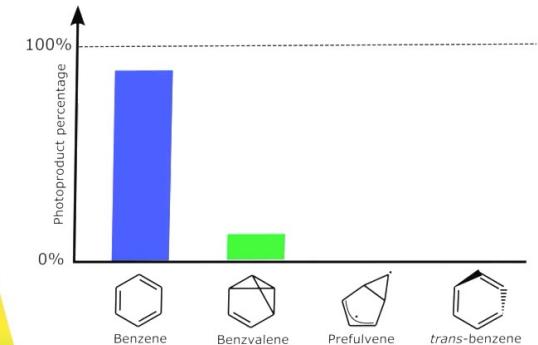


Directions to improve the model

- Dynamics in the photoproduct search phase (instead of optimizations)
- Impact of conical intersection topography
- Sampling from the whole intersection seam instead of just MECIs



Is there a relationship between the selectivity of a CI and its topography?



Conclusions



The Nonadiabatic NanoReactor

A hypothesis-free tool to systematically explore photochemistry.

Step 1



Find all accessible conical intersections

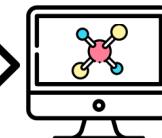
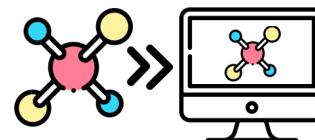


From them, find all possible photoproducts

So many remaining questions on the foundations of photochemistry!

FINDINGS:

- Qualitatively accurate, even for rare photoproducts, through systematic sampling.
- Quantitative description → work in progress!
- Great exploration tool



Experimental results reproduced.



Trans-benzene is a possible intermediate to Dewar benzene; new path to fulvene found



New predictive tool!

Acknowledgements

- ✓ Todd Martinez
- ✓ Keiran Thompson
- ✓ Dean Lahana
- ✓ Alex Chang
- ✓ Cody Aldaz
- ✓ Alessio Valentini
- ✓ Ethan Curtis

Thank you for
listening!

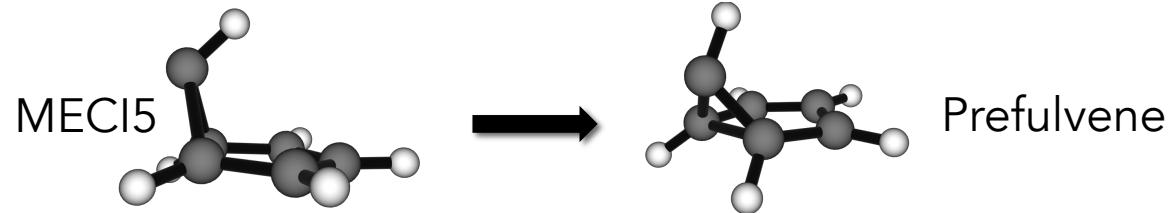
Questions??

Lake Shasta 2022

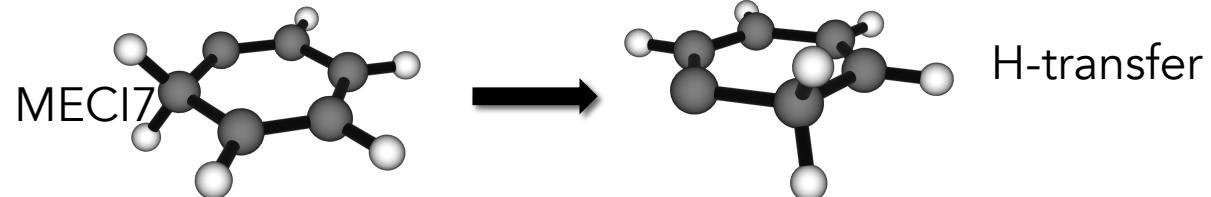
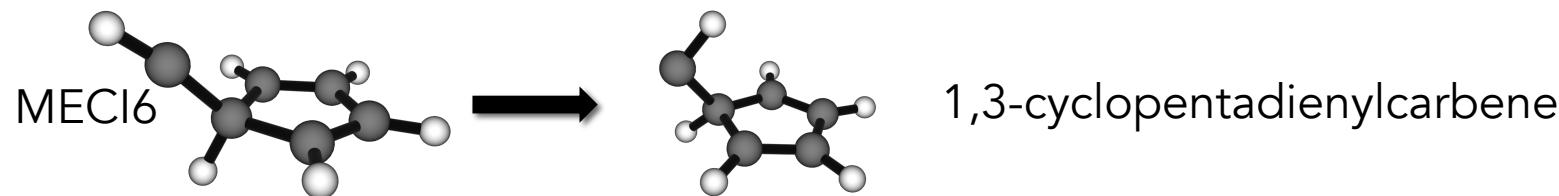


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The other MECIs



Open question: how “rare”
each MECI type is?



Info on crude model

$$Q = \sum_i e^{-\frac{\Delta E_i}{k_B T}}$$

$$K = \Delta E = E_{FC} - E_{S_1 MIN}$$

$$T = \frac{K}{\frac{1}{2}(3N - 6)k_B T}$$

Initial velocity sampling

$$\mathbf{v}_k = \frac{1}{\sqrt{M_k}} \gamma_g$$

Vector of gaussian distributed random numbers

$$\mathbf{v}_{\text{rot},k} = (\mathbf{T}_I^{-1} \mathbf{L}) \times \mathbf{v}_k$$

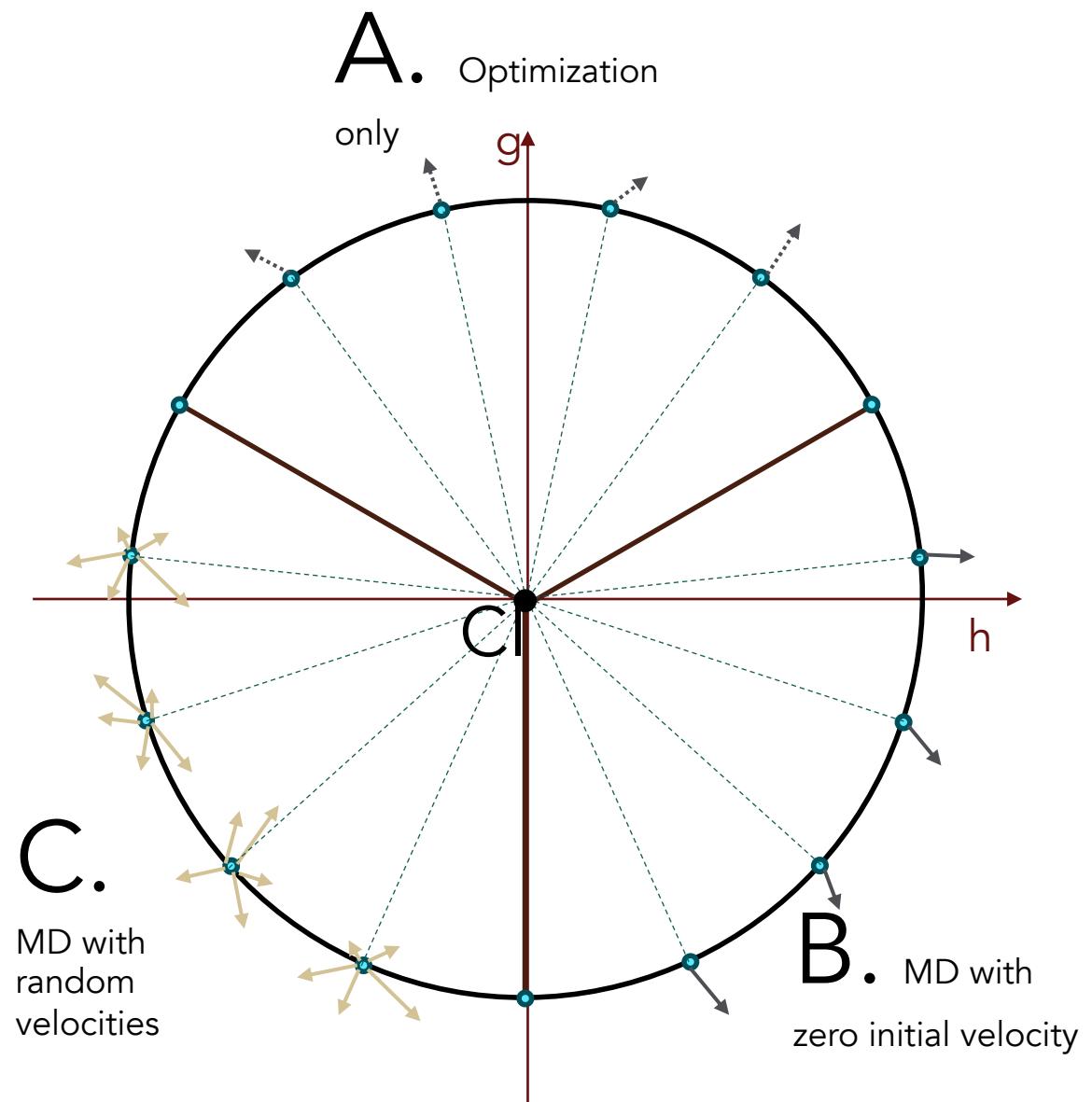
Tensor of inertia

Total classical angular momentum

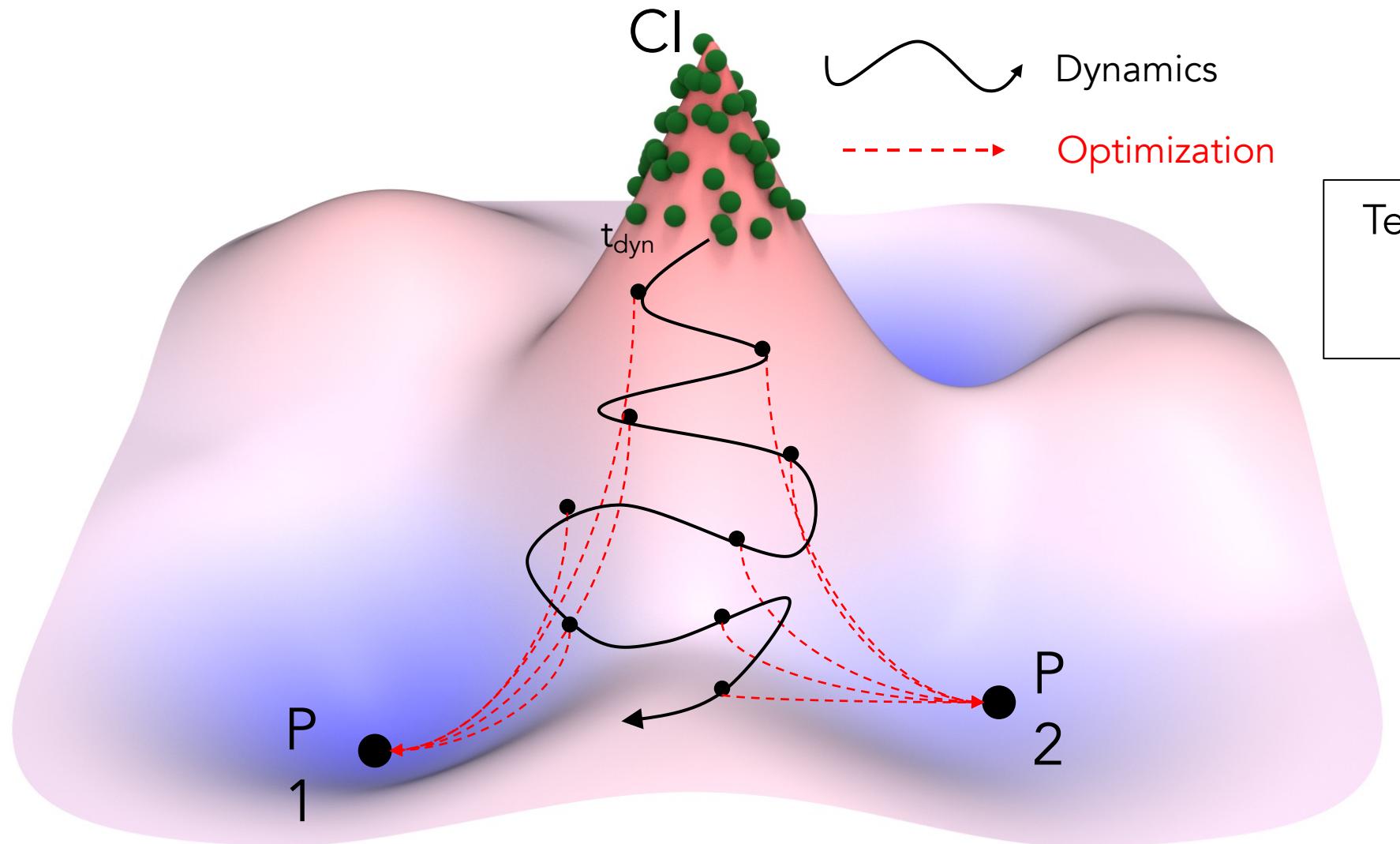
$$\mathbf{v}_k = \mathbf{v}_k - \mathbf{v}_{\text{rot},k}$$

$$\mathbf{v}^{\text{ini}} = \sqrt{\frac{2E_{\text{ini}}}{\sum_k M_k v_k^2}} \mathbf{v}$$

Desired initial kinetic energy

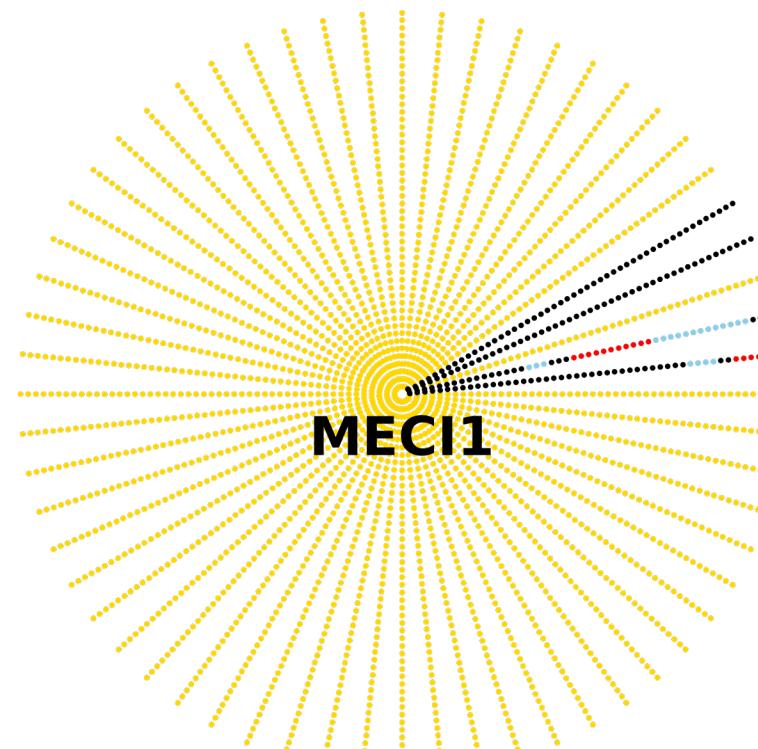
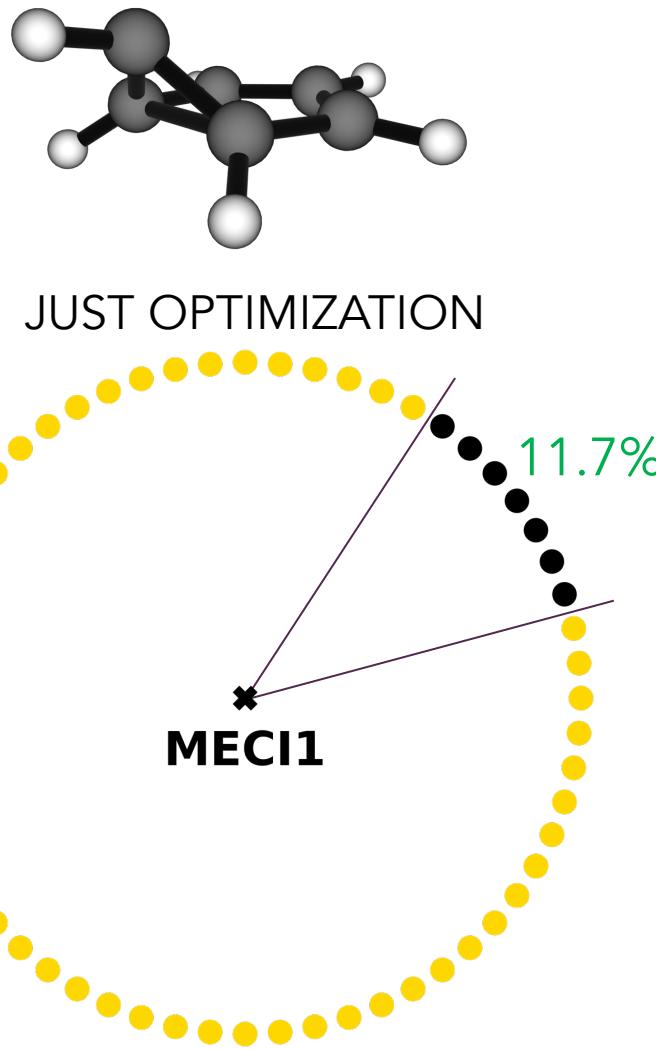


Length of MD before quenching



Test different t_{dyn}
and monitor
convergence

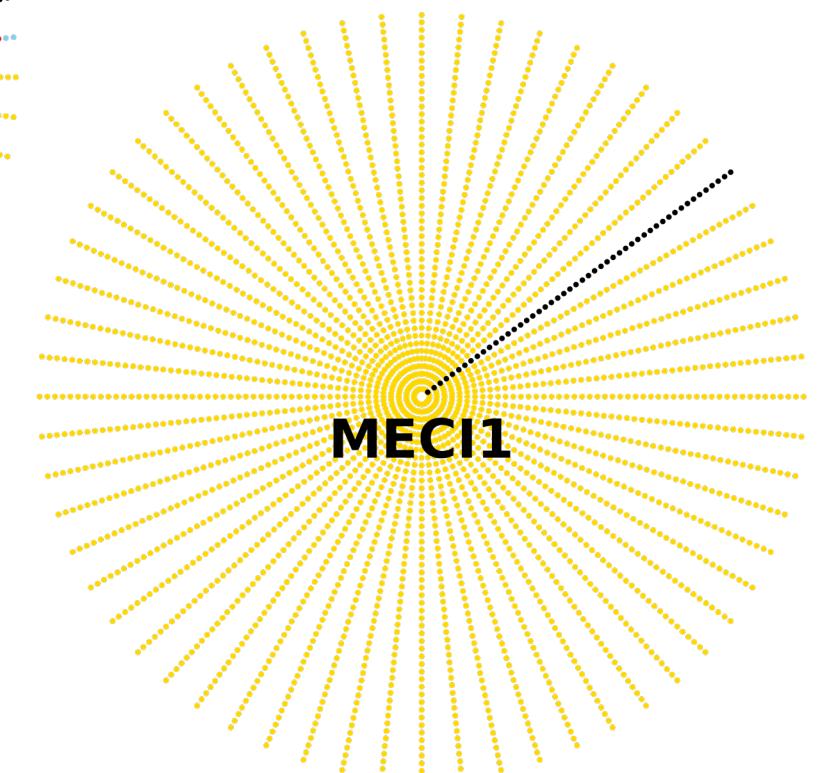
Inclusion of dynamics in the photoproduct search



DYNAMICS WITH ZERO
INITIAL VELOCITY

$t_{dyn}=10$ fs : 8.3%
 $10 \text{ fs} < t_{dyn} < 180$ fs : 6.7%
 $t_{dyn} \geq 180$ fs : <6.7%

DYNAMICS WITH RANDOM
INITIAL VELOCITY
Always 1.7%



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