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Strain-driven photochemical reactivity of a small molecule

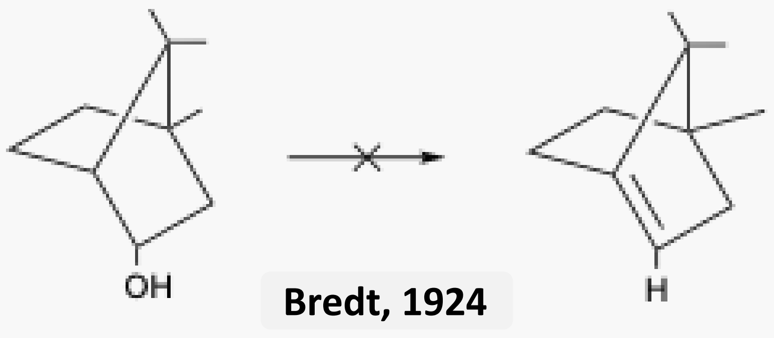
Laboratory of computational photochemistry and photobiology

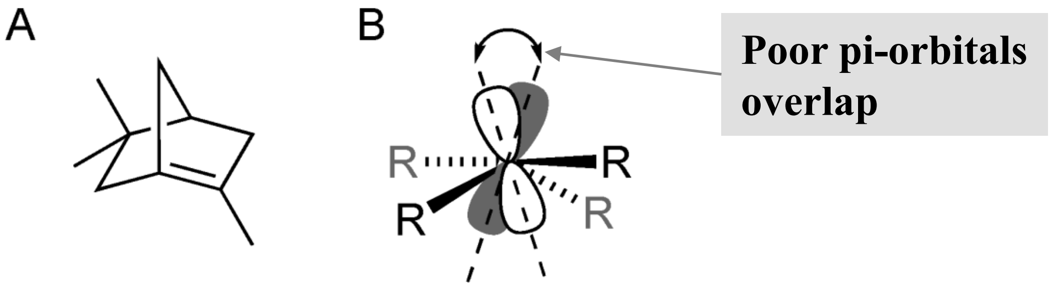
Center for Photochemical Sciences

Introduction

- Bridgehead olefins are a sub-class of polycyclic compounds containing a C=C double bond at the bridgehead position of a bicyclic system.

Julius Bredt
[1855 - 1937]





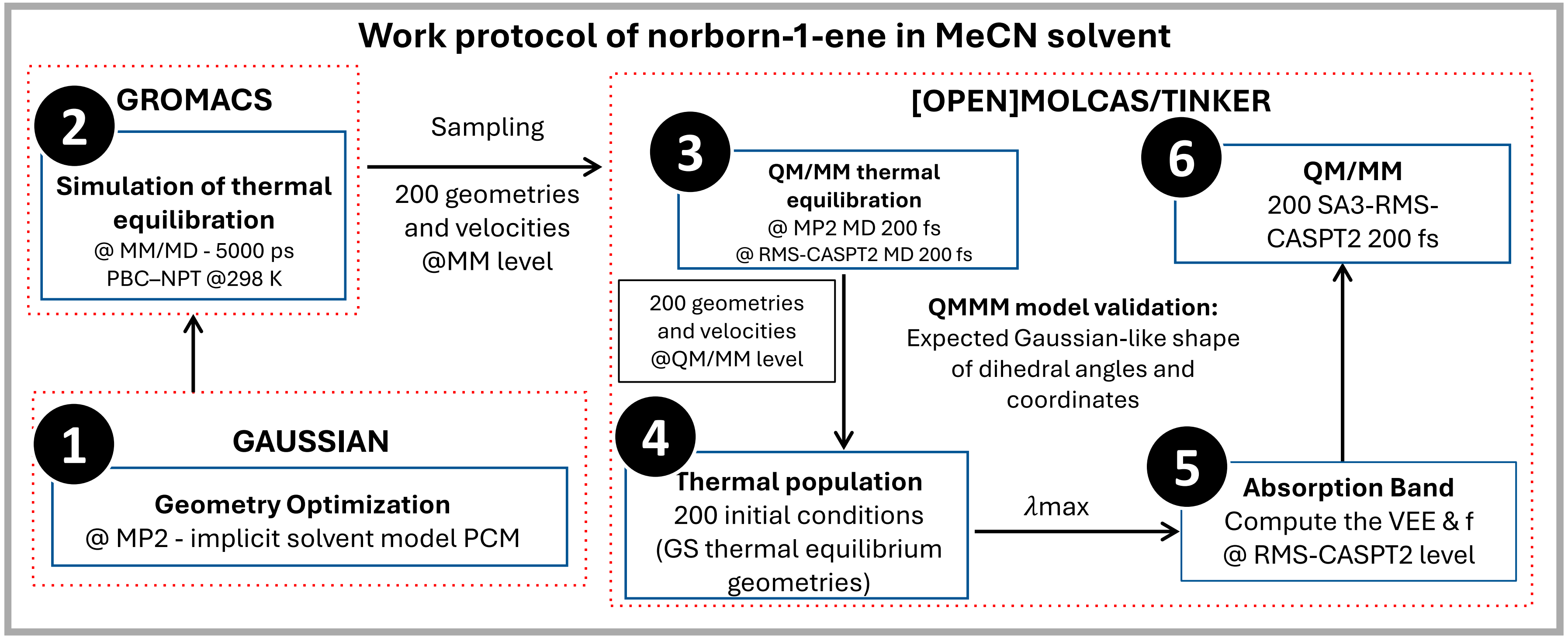
(A) A typical bridgehead olefins considered as too strained to exist. (B) The twisting of one p-orbital relative to the other as required to form a C=C bond in a strained bridgehead alkene.

- **Bredt's rule:** Double bonds at the bridgehead position in a bicyclic molecules of ring size <8 cannot synthesize.

Why a computational study on norborn-1-ene?

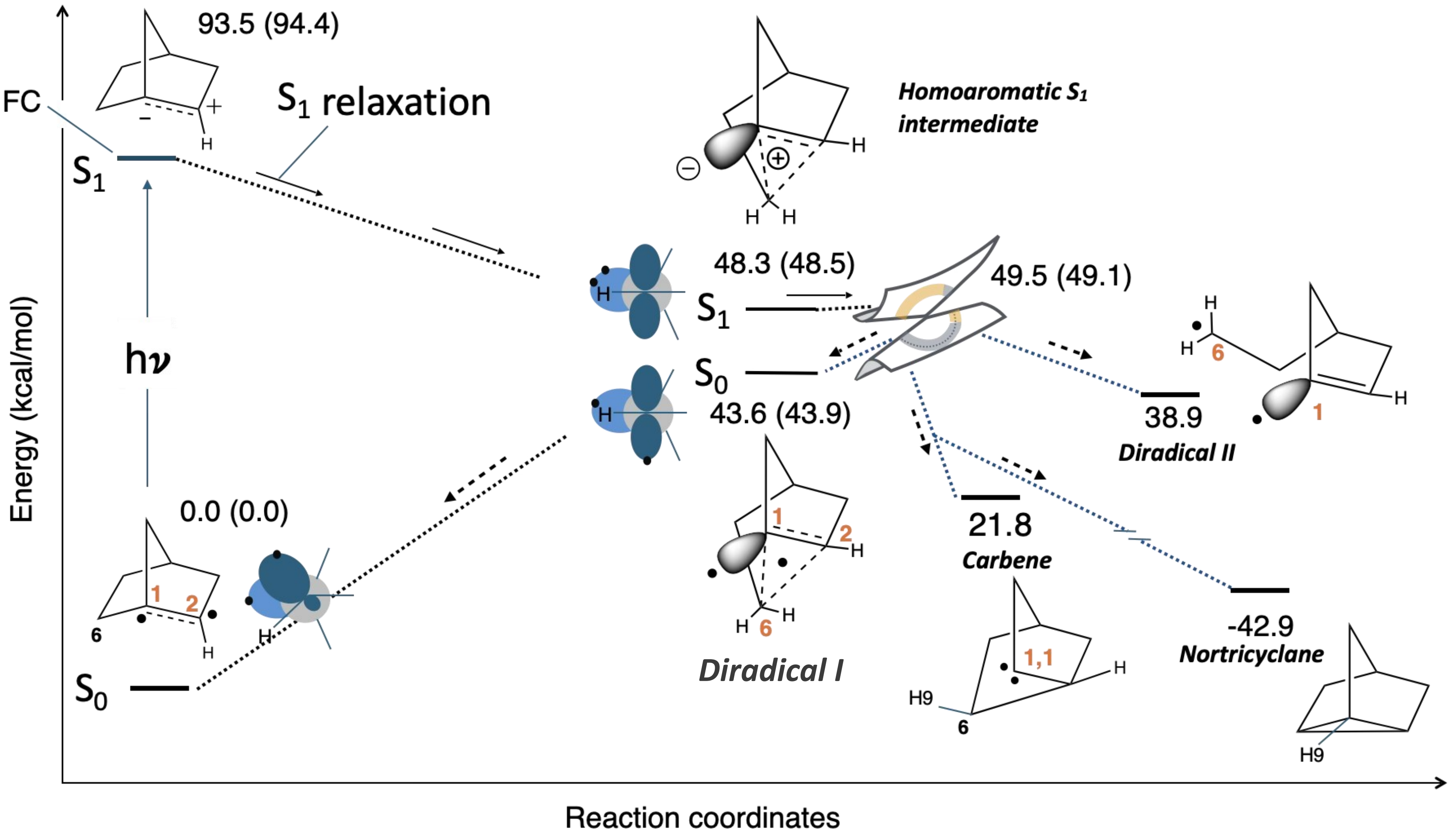
- No photochemistry studied before
- The distorted C=C bond makes it to absorb photon at the longer wavelength
- Size of the molecule allow us to use an accurate quantum chemical gradients available

Details of computational methods



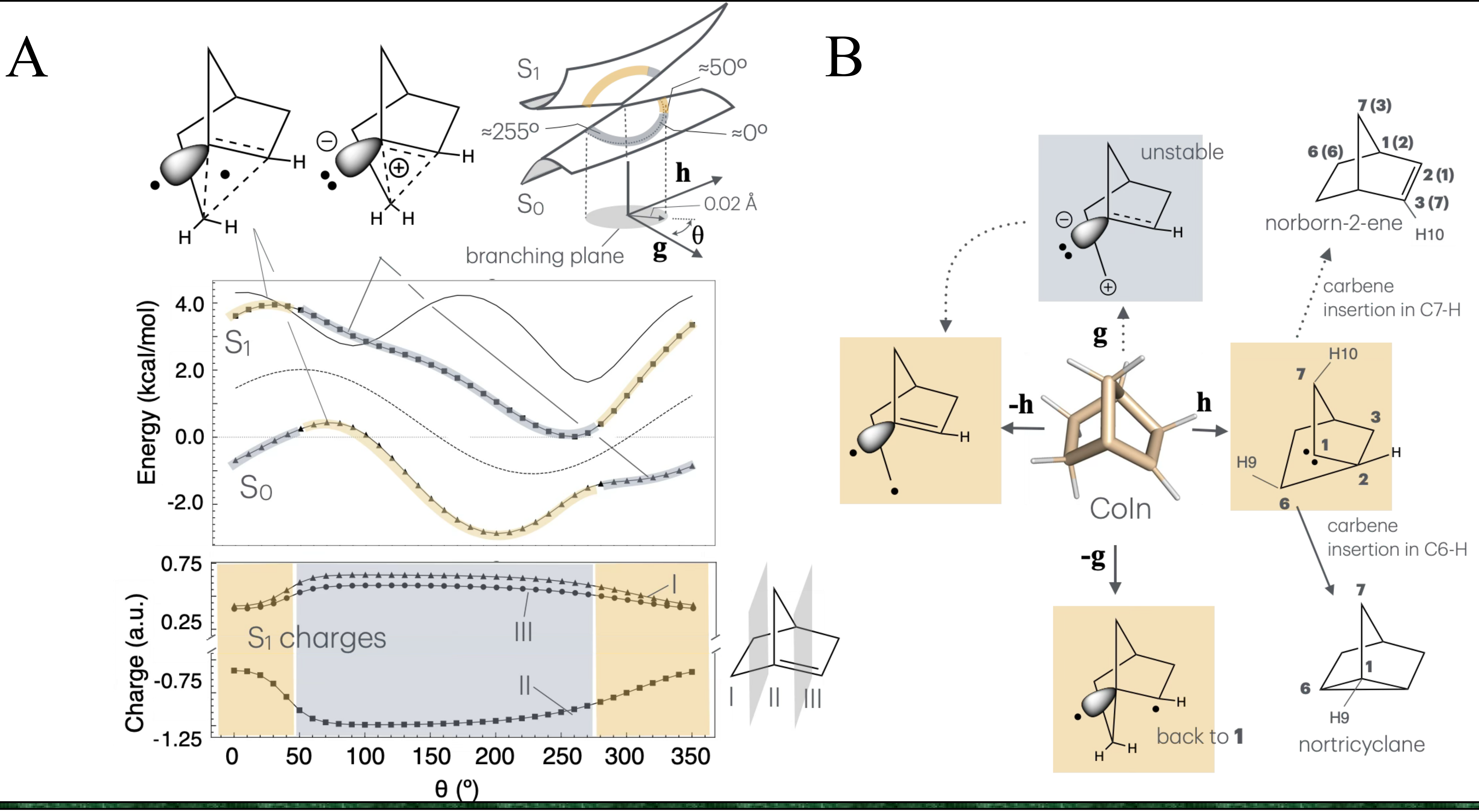
- Olivucci M., *et al*. J. Phys. Chem. B **2023**, 127, 10871–10879.
- Blanco A. (2023), Impact of vibrational mode coupling on the isomerization of natural and synthetic molecular switches, Ph.D. dissertation, Pp. 48.

Potential energy surface



J. Am. Chem. Soc. **2026**, *148*, 17736–17744

Analyzing conical intersection



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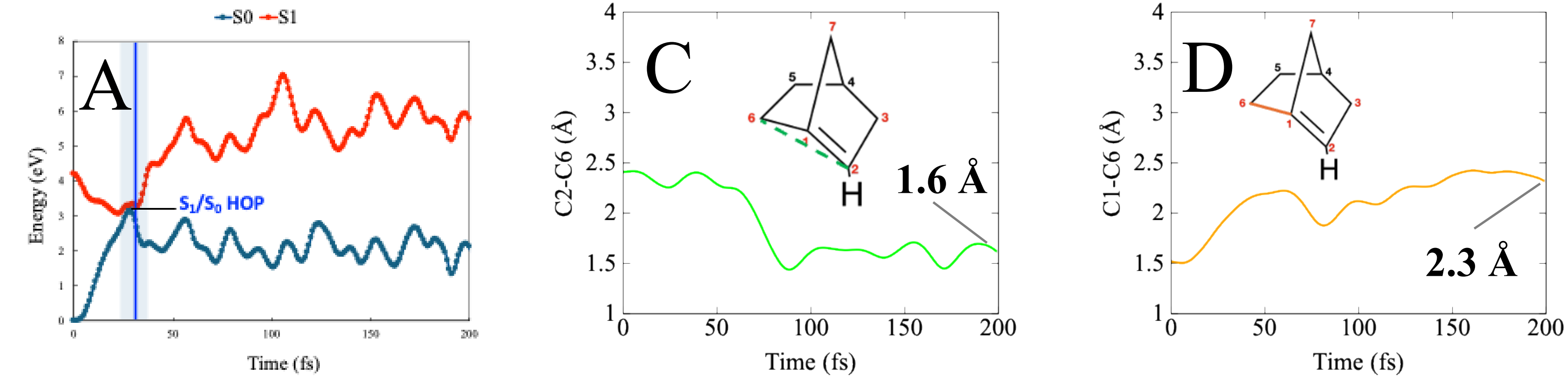
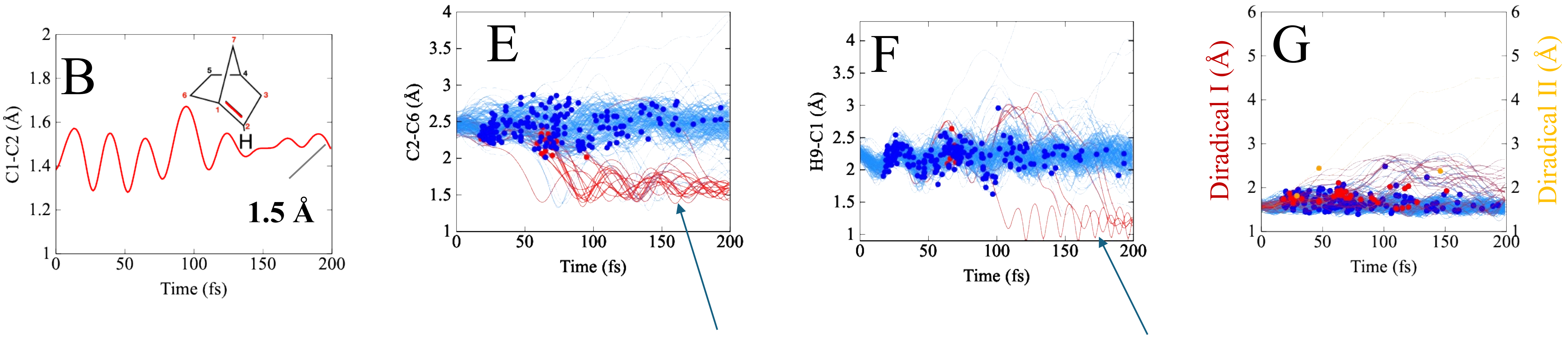
Quantum-classical dynamics



Key:

- ***S_2/S_1 CI – Unreactive***
- ***S_1/S_0 CI – Productive***

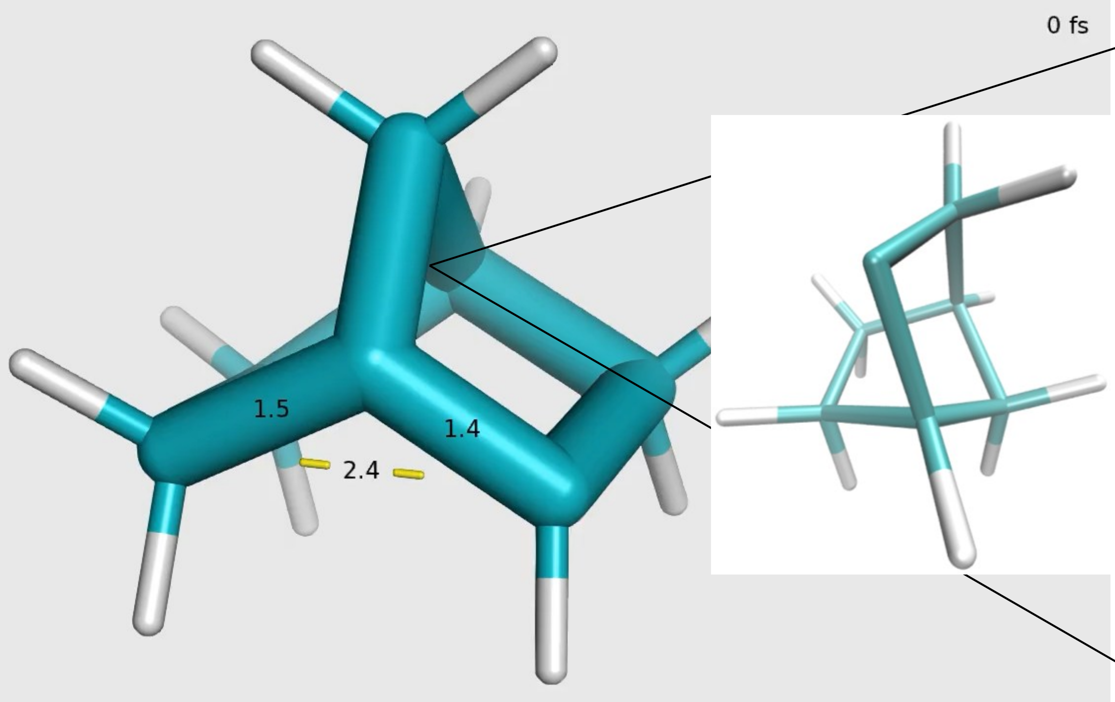


C1=C2 bond length

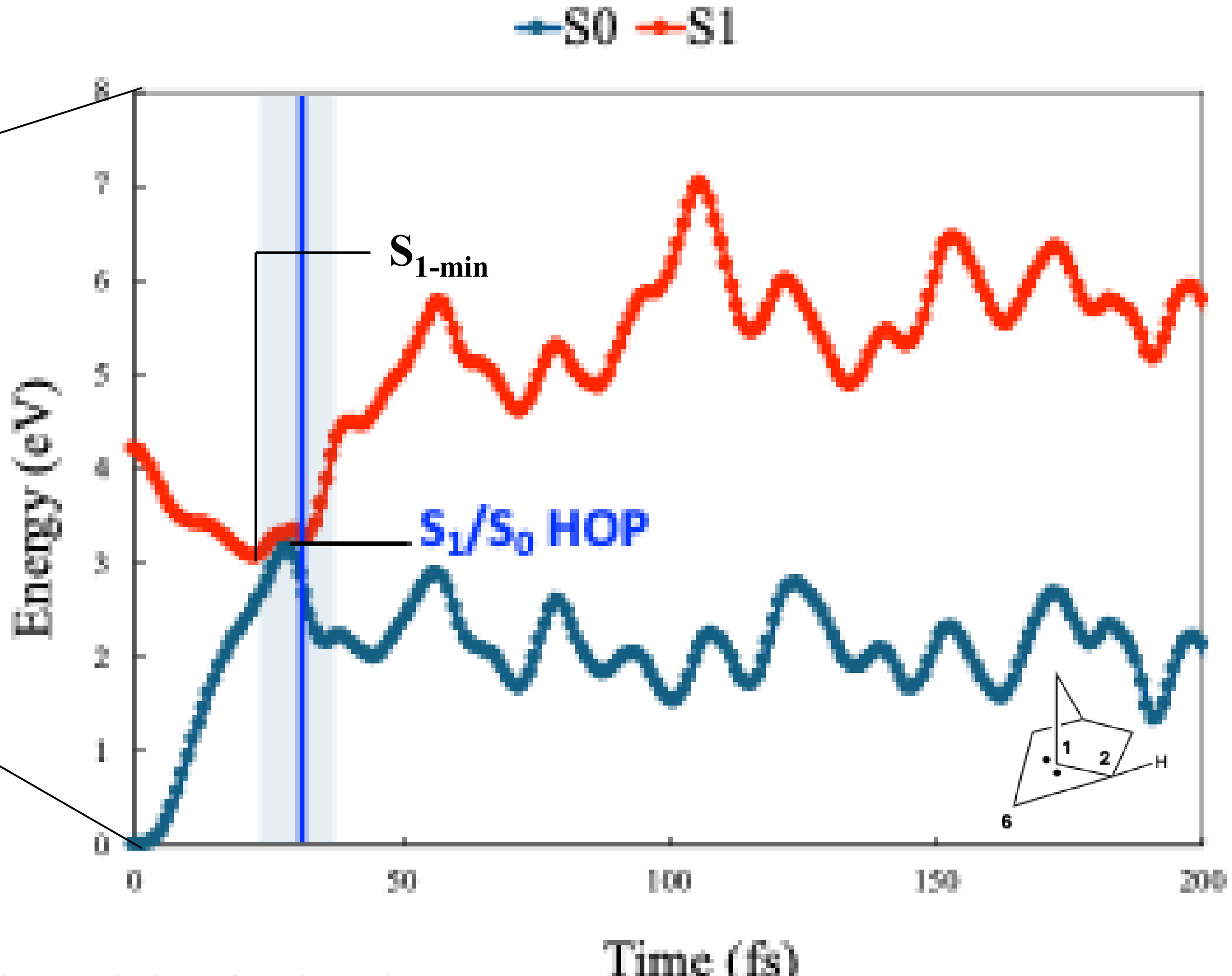
Carbene

Nortricyclane

Representative photoproduct from trajectory

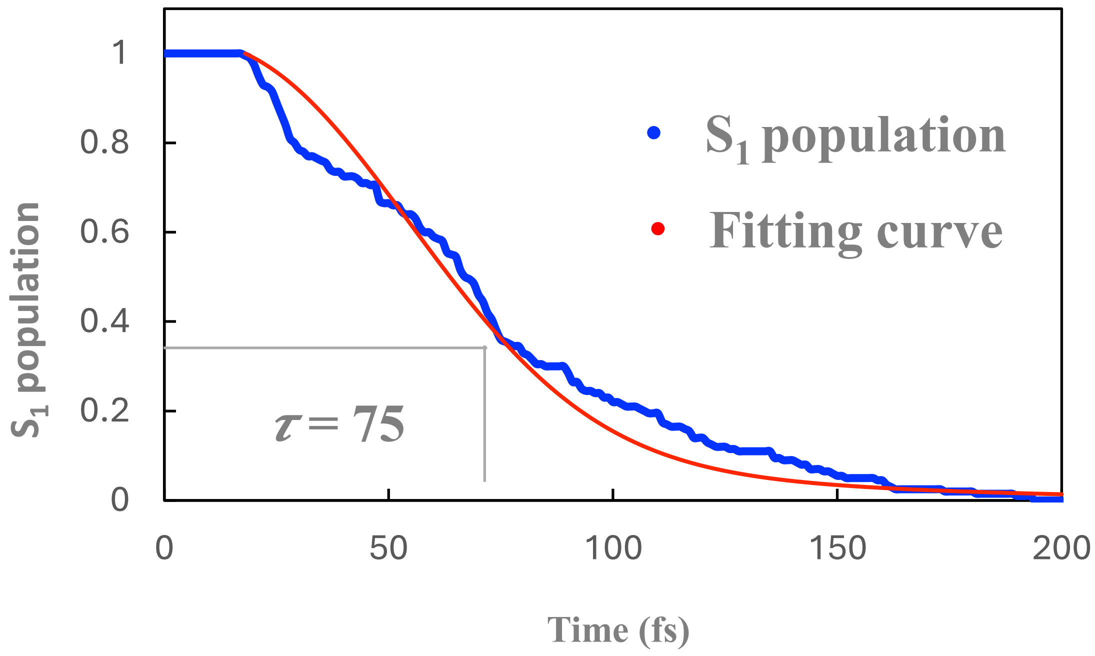


The movie shows the carbene product followed by the CoIn structure



Time evolution of norborn-1-ene

Excited state lifetime and QE



$$f(x) = a_1 e^{\left(-\left(\frac{t-t_1}{t_2}\right)^2\right)} + y_0 + ((1 - a_1) - y_0) e^{\left(-\left(\frac{t-t_1}{t_3}\right)\right)}$$

$$\tau = t_1 + a_1 + t_2 + (1 - a_1 - y_0) t_3$$

Quantum Efficiency

$$\Phi_{\text{photochem}} = \frac{\text{Number of photoproduct}}{\text{Number of } \textbf{total trajectories}}$$

a_1 = weight of gaussian decay component
y_0 = fitting parameter
t_1 = latency time
t_2 = decay time of gaussian component
t_3 = decay time of exponential component

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