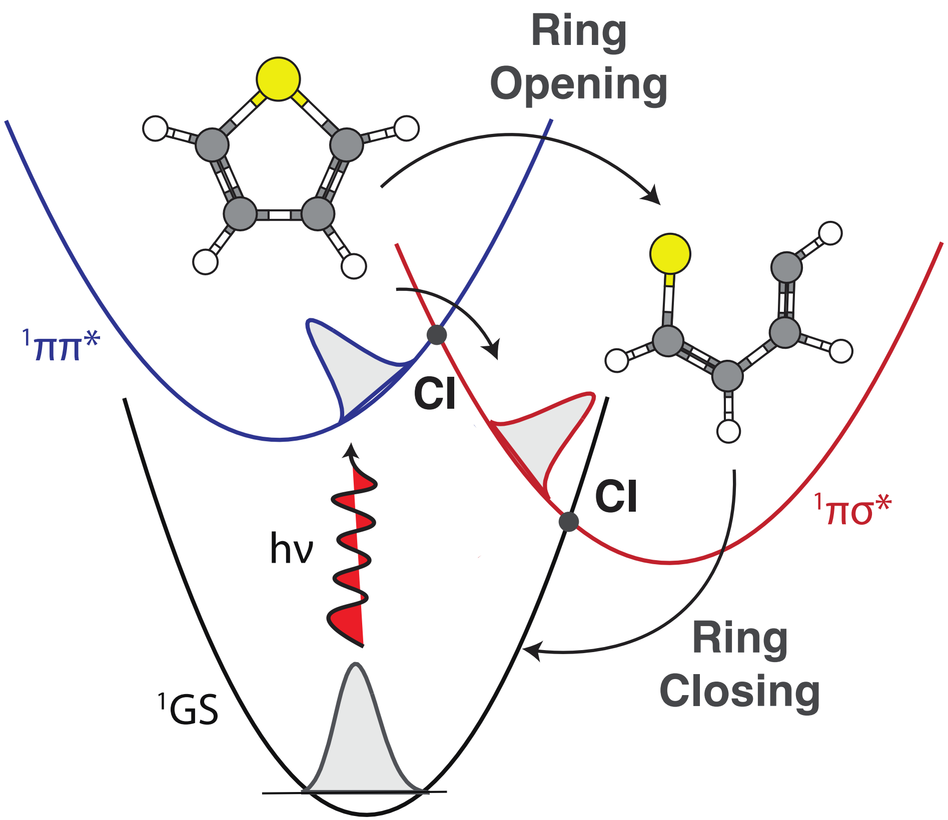
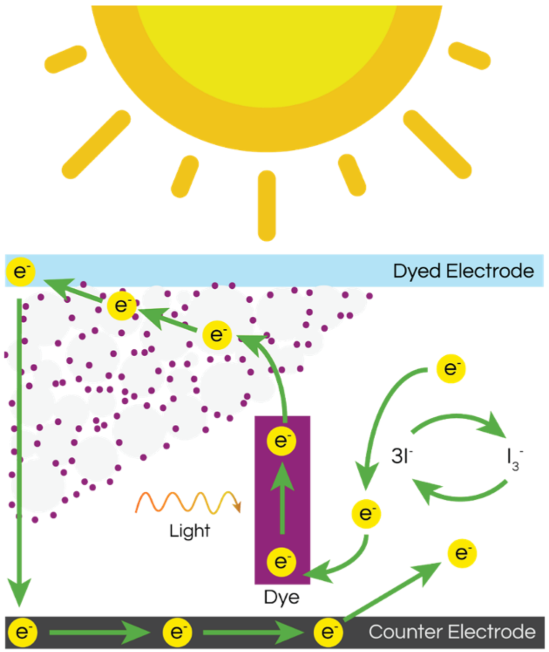
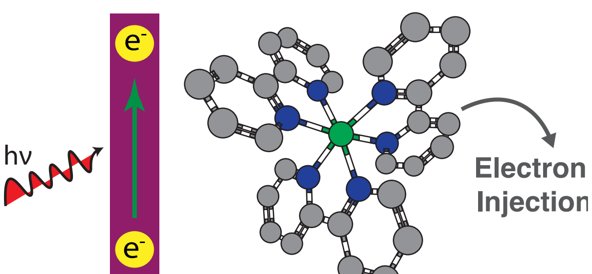
Addressing Challenges and Artifacts on Excited State Potential Energy Surfaces: Insights from Quantum Chemistry and Quasi-Classical Dynamics



Justin J. Talbot
VISTA Seminar
Clemson University
February 26, 2025

Solar Energy Catalysis





tris(2,2'-bipyridine)ruthenium(2+)

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Castro, P. J.; Maeda, S.; Morokuma, K., *Int. J. Quantum. Chem.*, **2021**, 121(14), e26663
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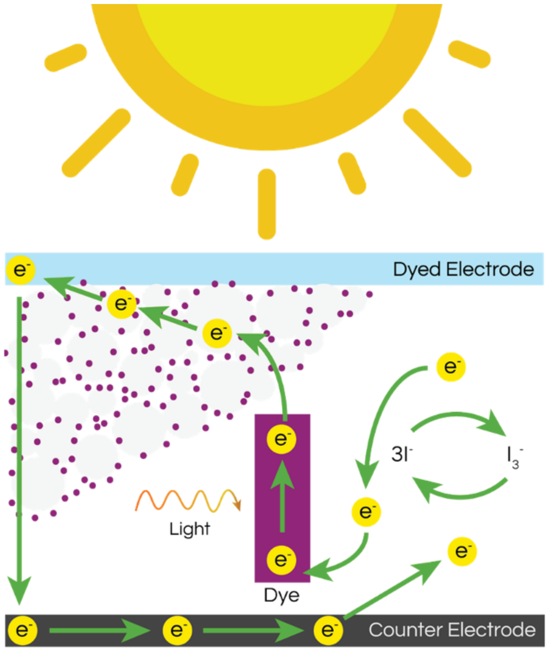

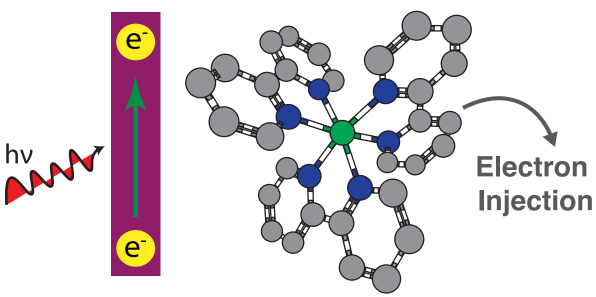

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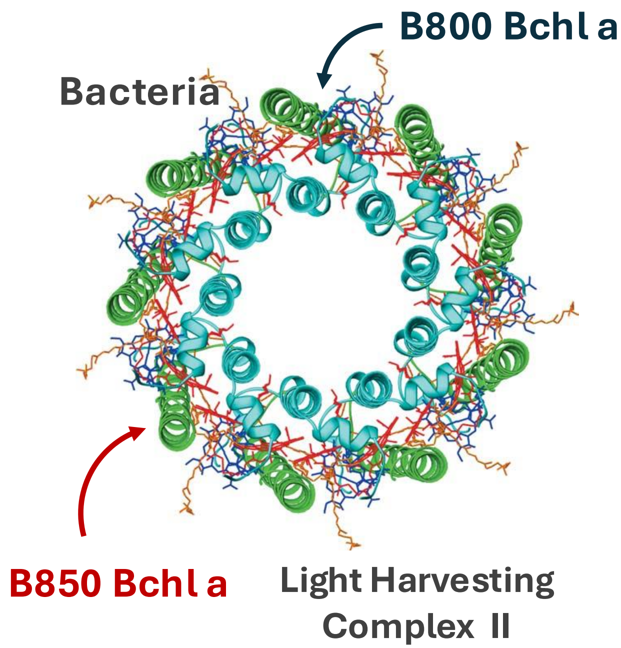
Biological Systems



Energy Transfer Time:

B800 → B800	~0.5ps
B800 → B850	~0.9ps
B850 → B850	~50 – 150fs

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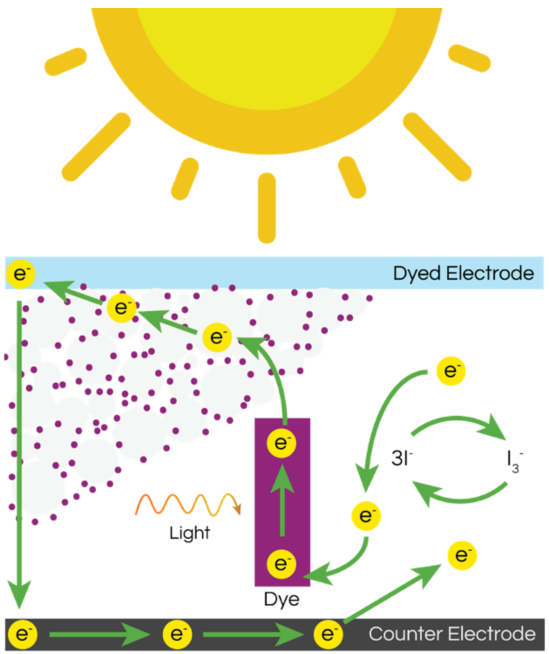

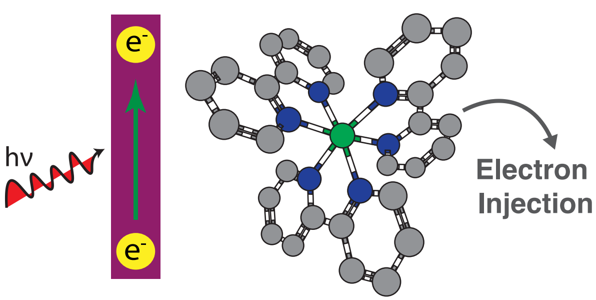

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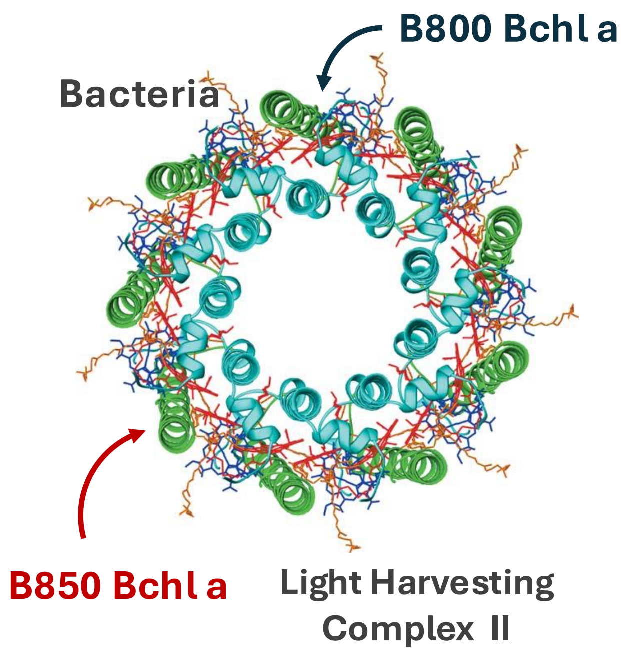

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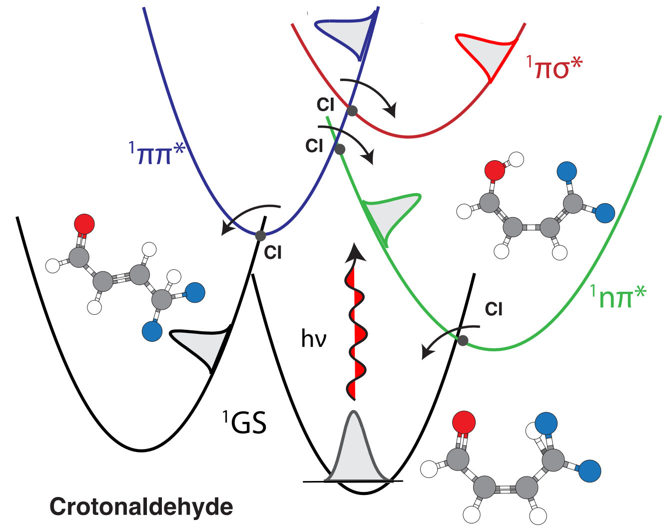
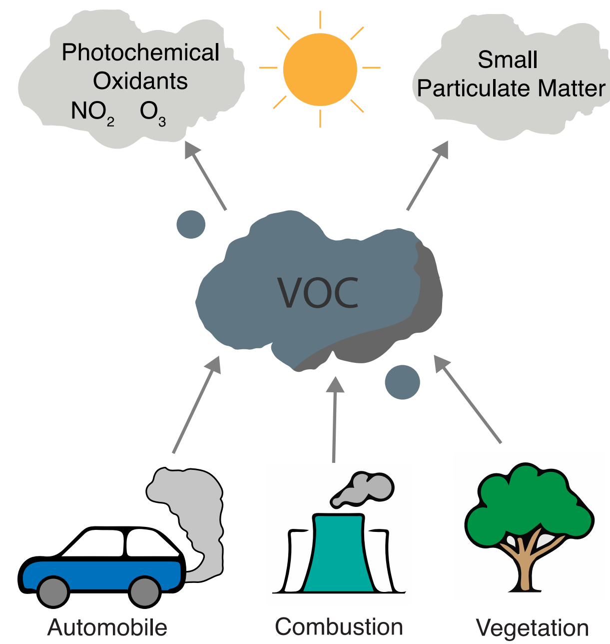
Atmospheric Chemistry





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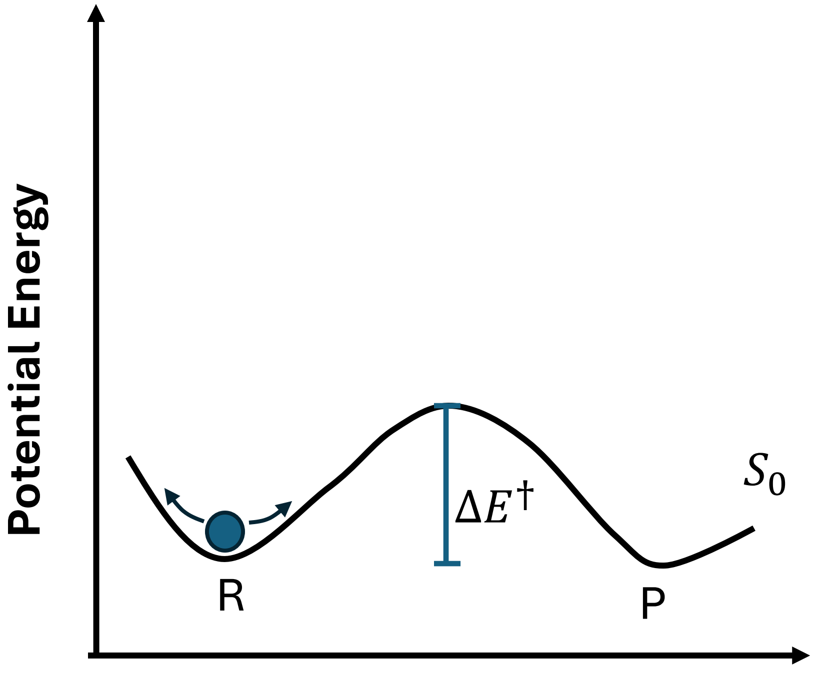

$$E_{particle} < \Delta E^\dagger$$

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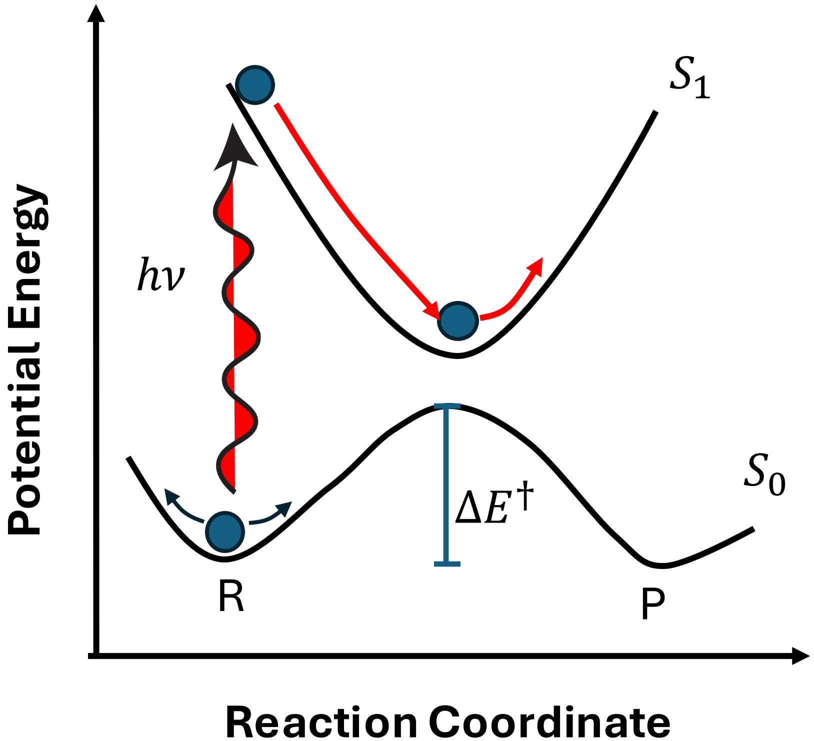

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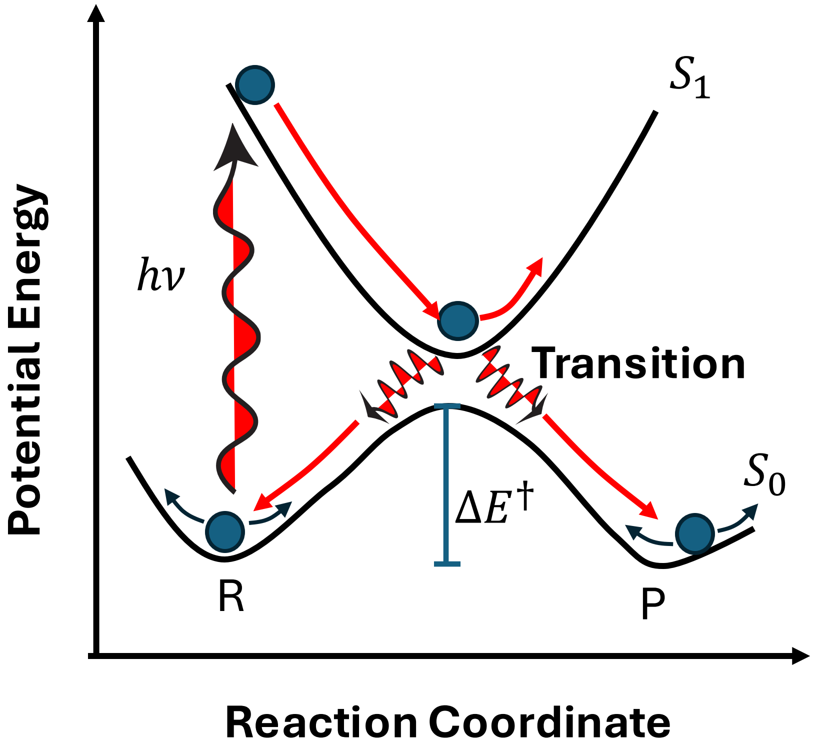

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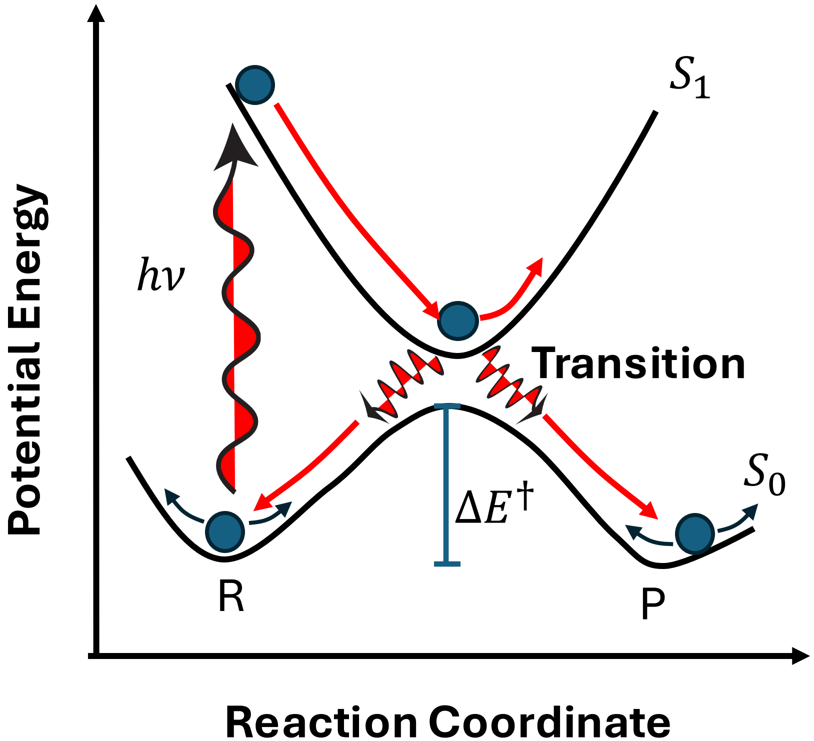
What are the electronic and nuclear rearrangements that drive electron-nuclear coupling?



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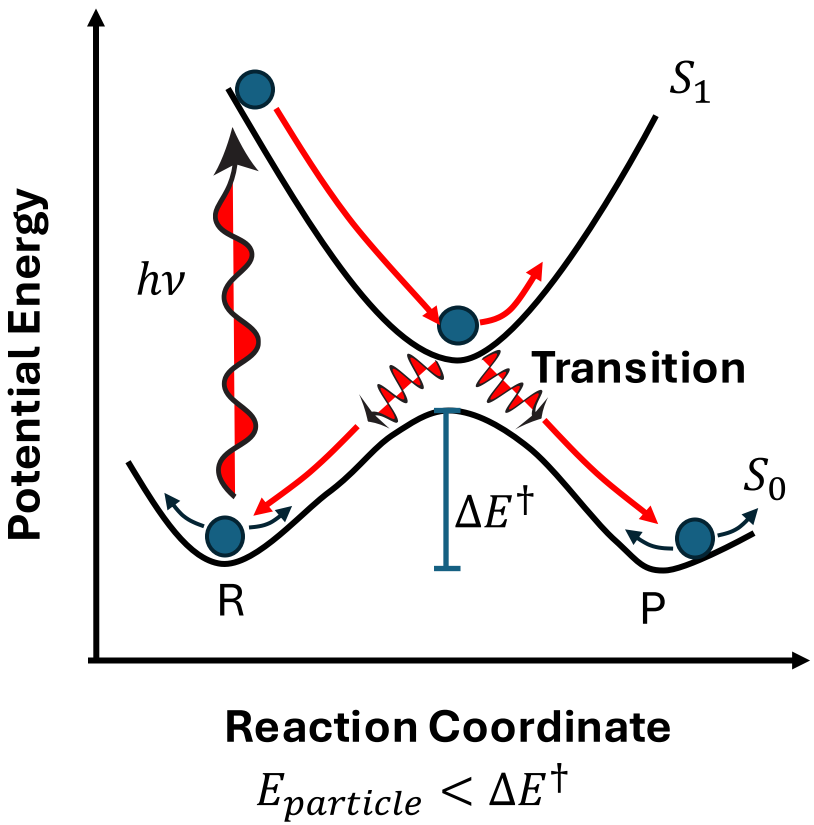

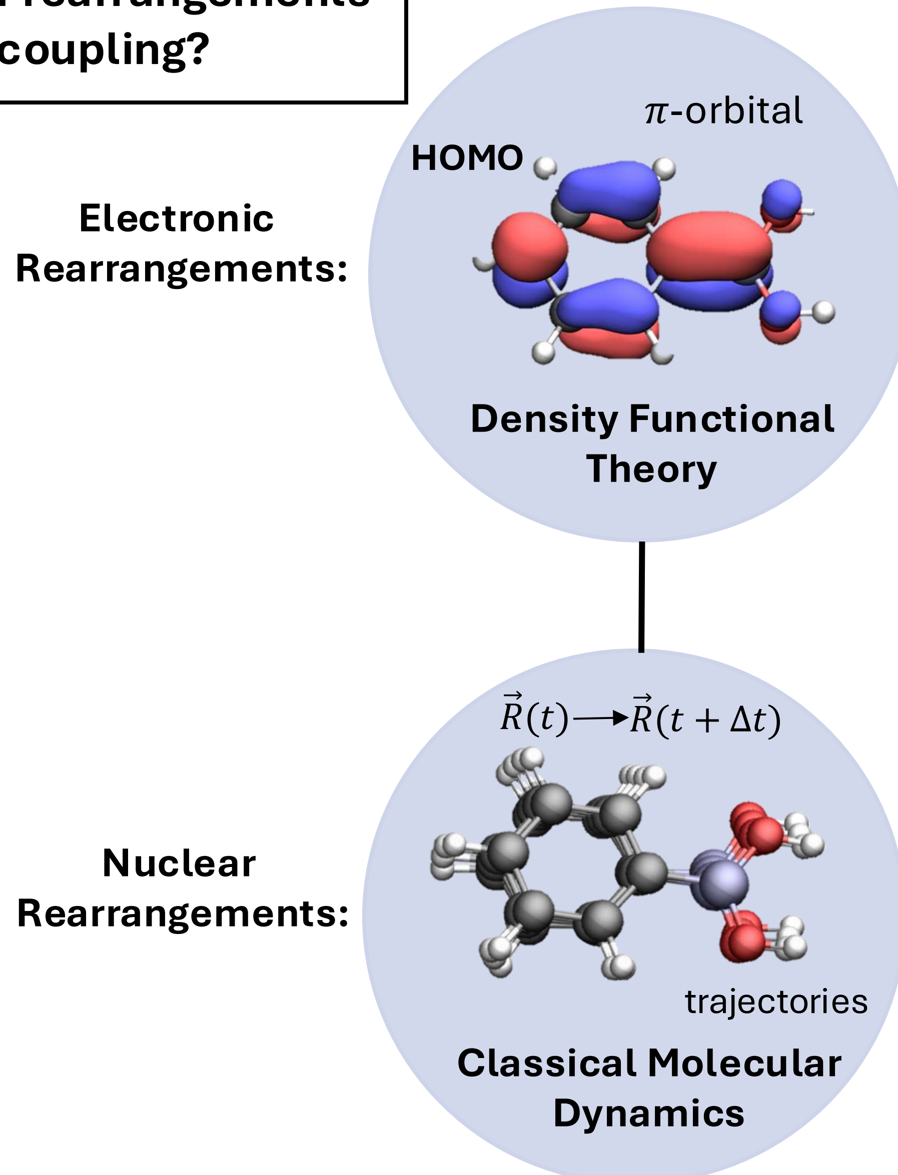

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Domcke, W., Yarkony, D., Koppel, H., Conical Intersections., (**2004**), 15th edition.

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Molecular Hamiltonian

$$\hat{H}_{mol} = \frac{\hat{\boldsymbol{P}}^2}{2\boldsymbol{M}} + \hat{T}_e(\vec{\mathbf{r}}) + \hat{V}_{NN}(\vec{\mathbf{R}}) + \hat{V}_{eN}(\vec{\mathbf{r}}, \vec{\mathbf{R}}) + \hat{V}_{ee}(\vec{\mathbf{r}})$$

$$= \frac{\hat{\boldsymbol{P}}^2}{2\boldsymbol{M}} + \hat{T}_e(\vec{\mathbf{r}}) + \hat{U}(\vec{\mathbf{r}}, \vec{\mathbf{R}})$$

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$$= \frac{\hat{\boldsymbol{P}}^2}{2\boldsymbol{M}} + \hat{T}_e(\vec{\mathbf{r}}) + \hat{U}(\vec{\mathbf{r}}, \vec{\mathbf{R}})$$

Assume time-scale separability between the nuclear degrees of freedom $(\vec{\mathbf{R}})$ and the electronic degrees of freedom $(\vec{\mathbf{r}})$ which allows $\hat{H}_{mol}$ to be separated into two parts.

$$\hat{H}_{elec} = \hat{T}_e(\vec{\mathbf{r}}) + \hat{U}\,(\vec{\mathbf{r}}, \vec{\mathbf{R}})$$

$$\hat{H}_{elec}\phi_I(\vec{\boldsymbol{r}}; \vec{\mathbf{R}}\,) = V_I(\vec{\mathbf{R}})\phi_I(\vec{\mathbf{r}}; \vec{\mathbf{R}}\,)$$

$$\hat{H}_{Nuc} = \frac{\hat{\boldsymbol{P}}^2}{2\boldsymbol{M}} + \hat{V}_I(\vec{\mathbf{R}})$$

$$\hat{H}_{Nuc}\chi_I(\vec{\mathbf{R}}) = E_I\chi_I(\vec{\mathbf{R}})$$

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Propagate the electronic degrees of freedom (TDSE)

$$i\hbar\dot{C}_K + i\hbar\sum_J C_J\langle\phi_K|\dot{\phi}_J\rangle = C_K V_K(\vec{\mathbf{R}})$$

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Assume that the nuclear motion can be described a trajectory $\vec{\boldsymbol{R}}(t)$

$$i\hbar\dot{C}_K = C_K V_K(\vec{\mathbf{R}}) - i\hbar\sum_J C_J\dot{\vec{\boldsymbol{R}}}d_{kJ}(\vec{\boldsymbol{R}})$$

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Meyer-Miller dynamics require that the electronic coefficients evolve according to Hamilton's equations

$$C_K = \frac{1}{\sqrt{2}}[x_K + ip_K]$$ ← canonically-conjugate electronic positions & momenta

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Putting this together the Meyer-Miller Hamiltonian is

$$H\,(\mathrm{x},\mathrm{p},\mathbf{R},\mathbf{P}) = \frac{\mathbf{1}}{2\boldsymbol{M}}\left(\vec{\mathbf{P}} + \sum_{JK}^{F} x_J p_K \boldsymbol{d}_{JK}(\vec{\mathbf{R}})\right)^{\mathbf{2}} + \sum_{K}^{F}\left(\frac{1}{2}p_K^2 + \frac{1}{2}x_K^2 - \gamma_K\right)V_K(\boldsymbol{R})$$

n_K Ehrenfest $\gamma_K = 0$

Notes provided to me by Bill Miller.

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Propagate the dynamics classically by applying Hamilton's equations to the Hamiltonian

$$\dot{x}_I = \frac{\partial H}{\partial p_I} \qquad \dot{p}_I = -\frac{\partial H}{\partial x_I} \qquad \dot{\vec{\mathbf{R}}} = \frac{\partial H}{\partial \vec{\mathbf{P}}} \qquad \dot{\vec{\mathbf{P}}} = -\frac{\partial H}{\partial \vec{\mathbf{R}}}$$

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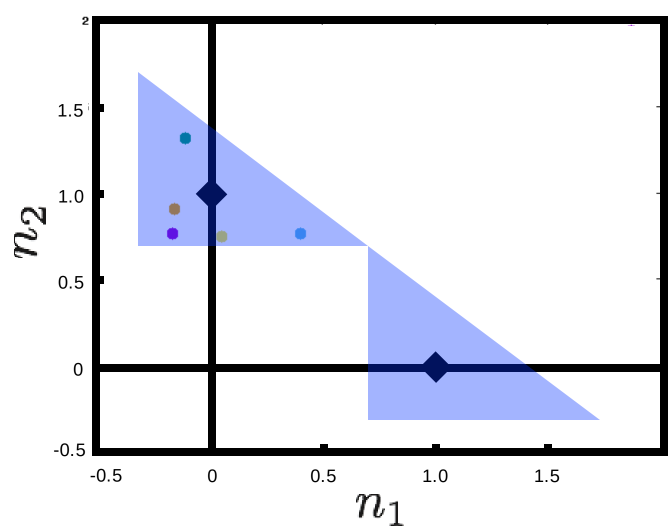
Symmetric Quasi-classical Approach (SQC)

Quantize the action variables by binning according to windowing functions



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The Tamm-Dancoff Approximation (TDDFT)

$$\boldsymbol{A}\boldsymbol{X}^{\boldsymbol{I}} = \omega_I \boldsymbol{X}^{\boldsymbol{I}}$$

$$|\phi_I\rangle = \sum_{ia} X_{ai}^I |\Phi_i^a\rangle$$

Zhang, X., Herbert, J.M. *J. Chem. Phys.*, **2014**, 141, 064104
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Hellmann-Feynman Derivative Coupling

$$\widehat{\boldsymbol{d}}_{IJ}(\vec{\mathbf{R}}) = \left\langle \phi_I \middle| \phi_J^{[\mathbf{R}]} \right\rangle = \frac{\left\langle \phi_I \middle| \widehat{H}_{elec}^{[\mathbf{R}]} \middle| \phi_J \right\rangle}{\omega_J - \omega_I} = \frac{1}{\omega_J - \omega_I} \sum_{ijab} X_{ai}^{I} A_{ai,bj}^{[\mathbf{R}]} X_{bj}^{J}$$

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$$\sum_{ijab} X_{ai}^{I} A_{ai,bj}^{[\mathbf{R}]} X_{bj}^{J} = \mathbf{P}_{\boldsymbol{\Delta}}^{\mathbf{IJ}'} \cdot \mathbf{H}^{[\mathbf{R}]} + \boldsymbol{\Gamma}^{\mathbf{IJ}'} \cdot \boldsymbol{\Pi}^{[\mathbf{R}]} + \mathbf{W}^{\mathbf{IJ}'} \cdot \mathbf{S}^{[\mathbf{R}]} + \mathbf{P}_{\boldsymbol{\Delta}}^{\mathbf{IJ}'} \cdot \mathbf{F}_{\mathbf{xc}}^{[\mathbf{R}]} + \mathbf{T}^{\mathbf{I}\dagger} \cdot \boldsymbol{\Omega}^{[\mathbf{R}]} \cdot \mathbf{T}^{\mathbf{J}}$$

Relaxed 1PDM	Relaxed 2PDM	Relaxed EWDM	Transition DM
$\mathbf{P}_{\boldsymbol{\Delta}}^{\mathbf{IJ}'}$	$\boldsymbol{\Gamma}^{\mathbf{IJ}'}$	$\mathbf{W}'$	$\mathbf{T}^{\mathbf{I}}$
$\mathrm{F}(\mathrm{F}+1)/2$	$\mathrm{F}(\mathrm{F}+1)/2$	$\mathrm{F}(\mathrm{F}+1)/2$	F

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<u>Relaxed 1PDM</u>	<u>Relaxed 2PDM</u>	<u>Relaxed EWDM</u>	<u>Transition DM</u>
$\mathbf{P}_{\boldsymbol{\Delta}}^{\mathbf{IJ}'}$	$\boldsymbol{\Gamma}^{\mathbf{IJ}'}$	$\mathbf{W}'$	$\mathbf{T}^{\mathbf{I}}$
$\mathrm{F}(\mathrm{F}+1)/2$	$\mathrm{F}(\mathrm{F}+1)/2$	$\mathrm{F}(\mathrm{F}+1)/2$	F

Parallelize contractions!

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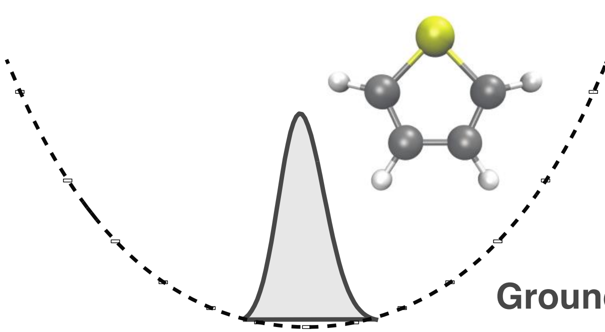
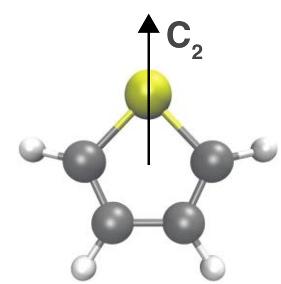
Selenophene (SeC_4H_4)





SeC_4H_4
Selenophene (C_{2V})

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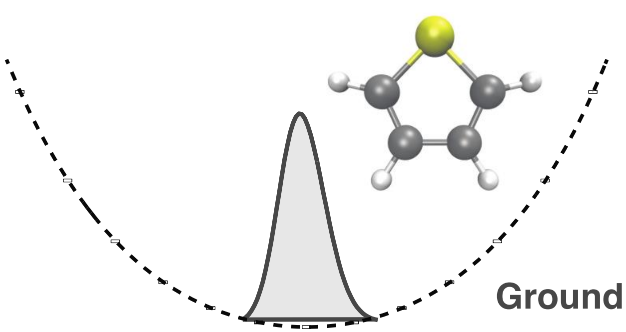
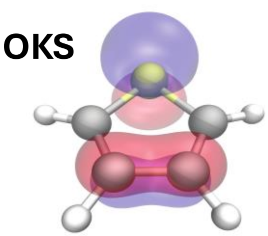
LRC-ωPBE/6-311G**

Selenophene (SeC_4H_4)



Ground State S_0

HOKS



π-orbital

SeC_4H_4

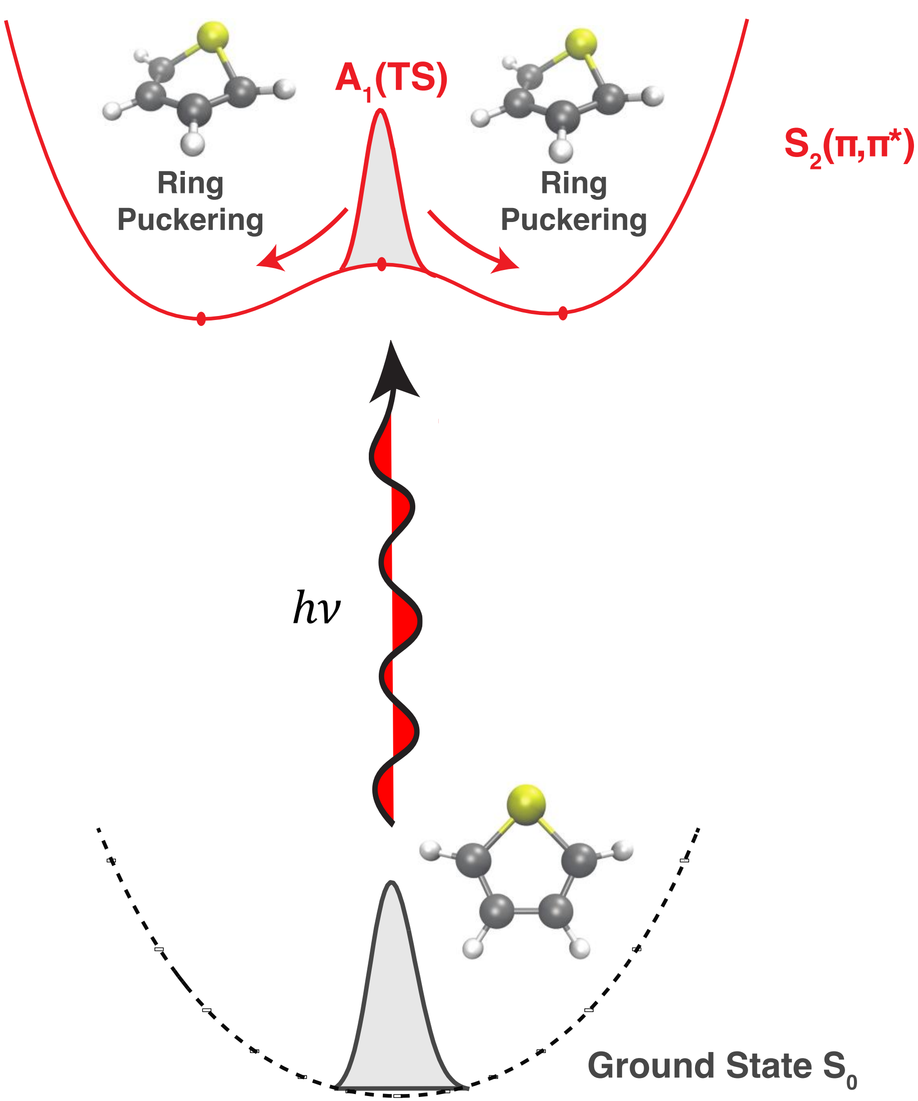
Selenophene (C_{2V})

Talbot, J.J.*, Head-Gordon, M., Cotton, S. J., *Mol. Phys.*, **2022**, 121, 7-8

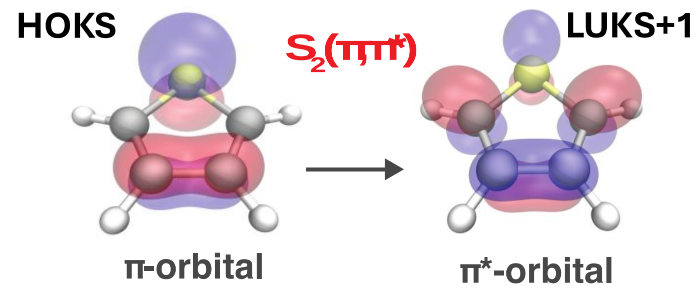
LRC-ωPBE/6-311G**

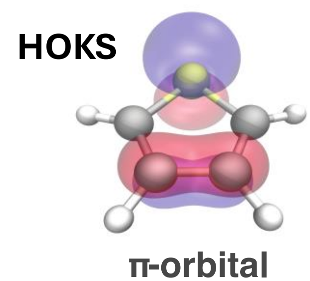
Selenophene (SeC_4H_4)

Nuclear Rearrangement



Electronic Rearrangement





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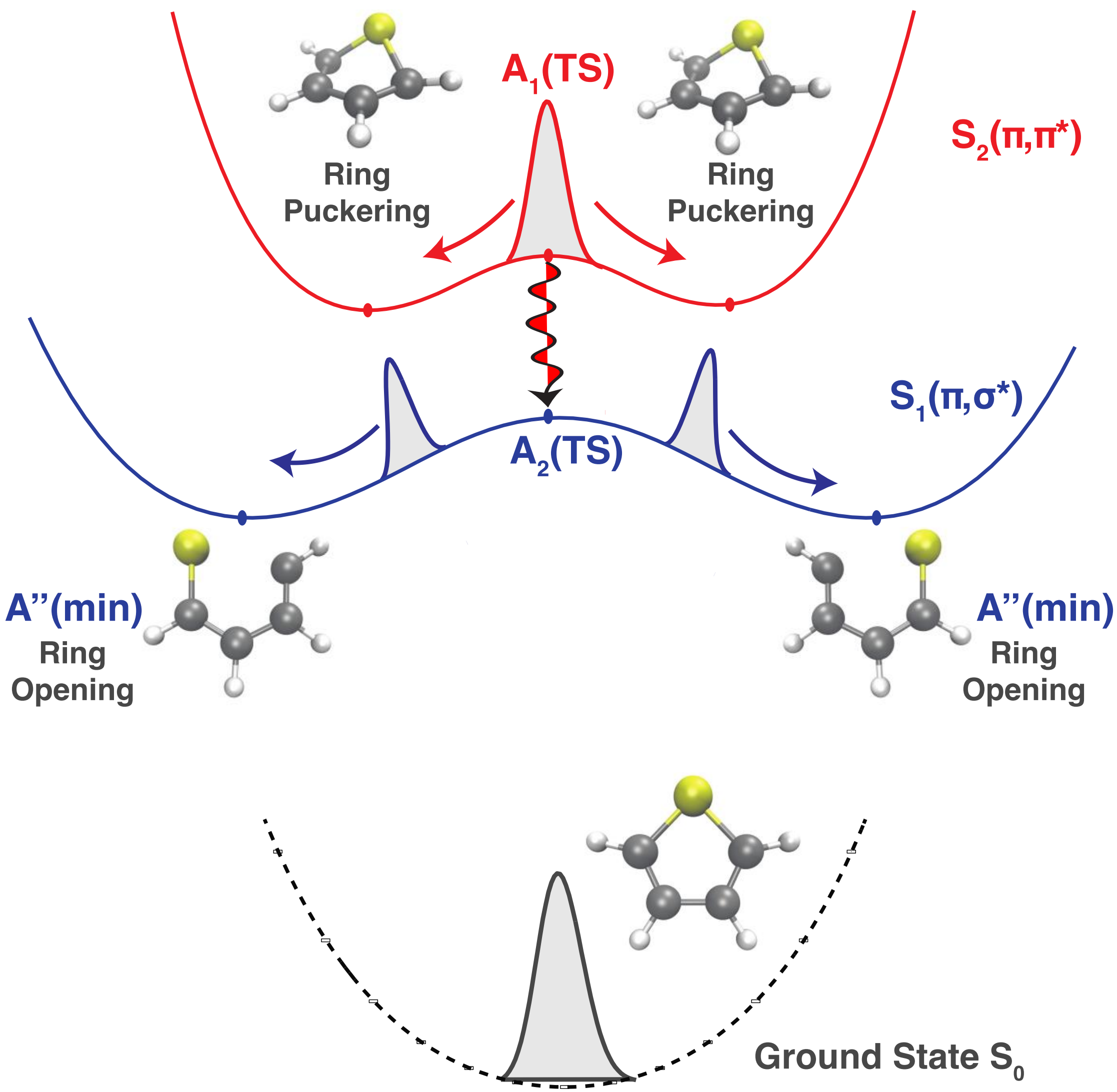

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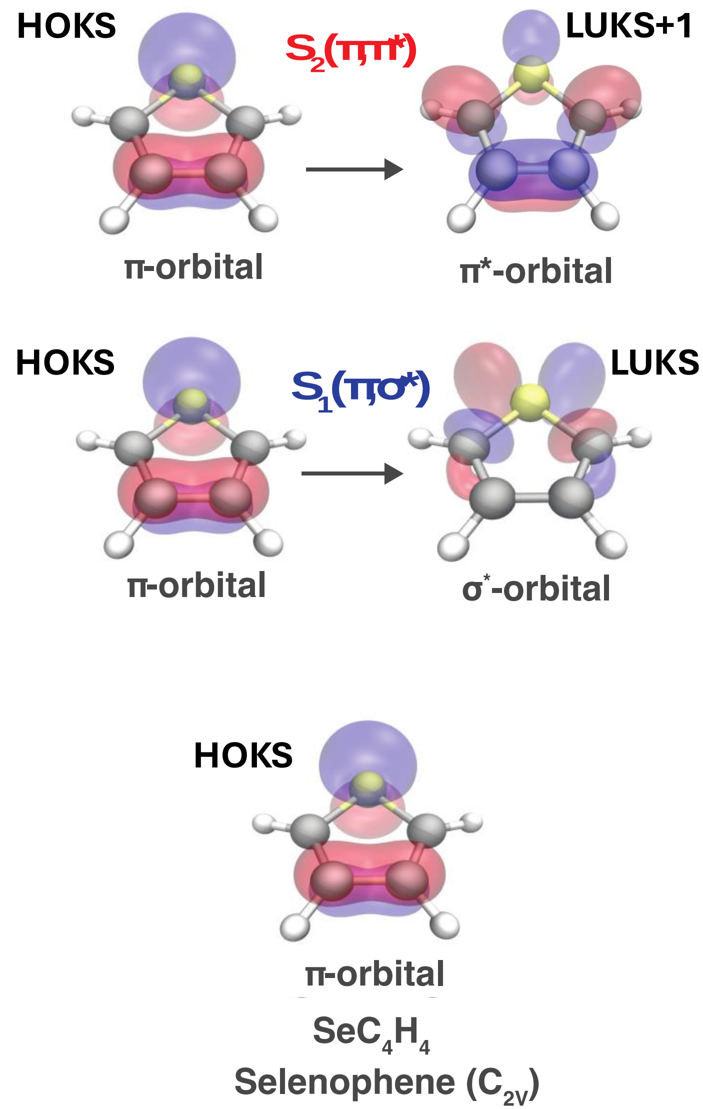

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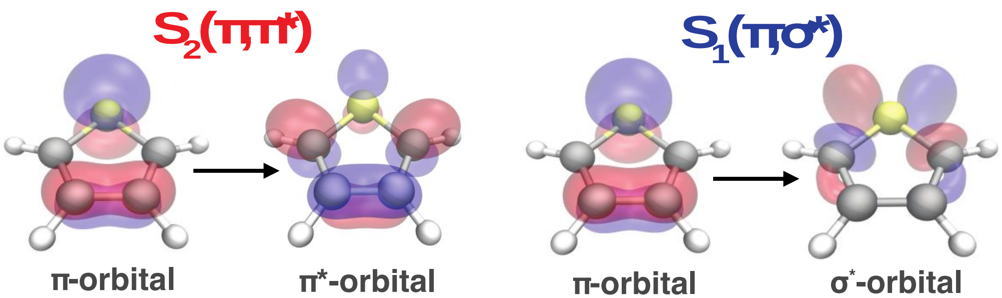

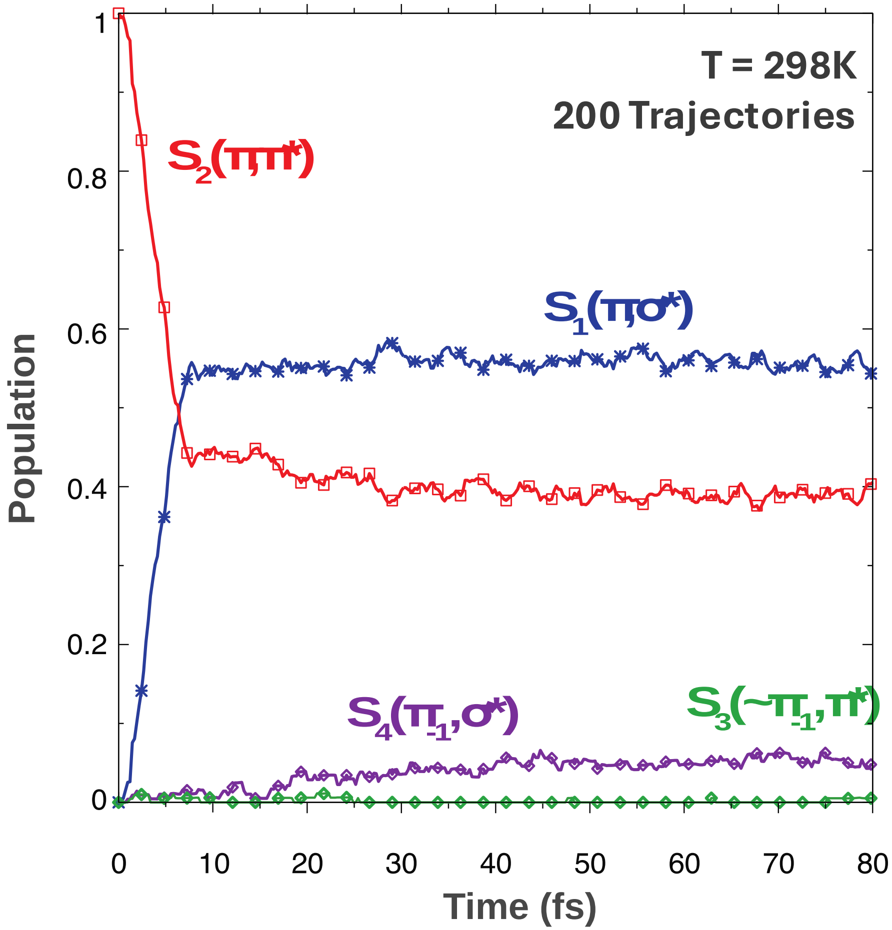

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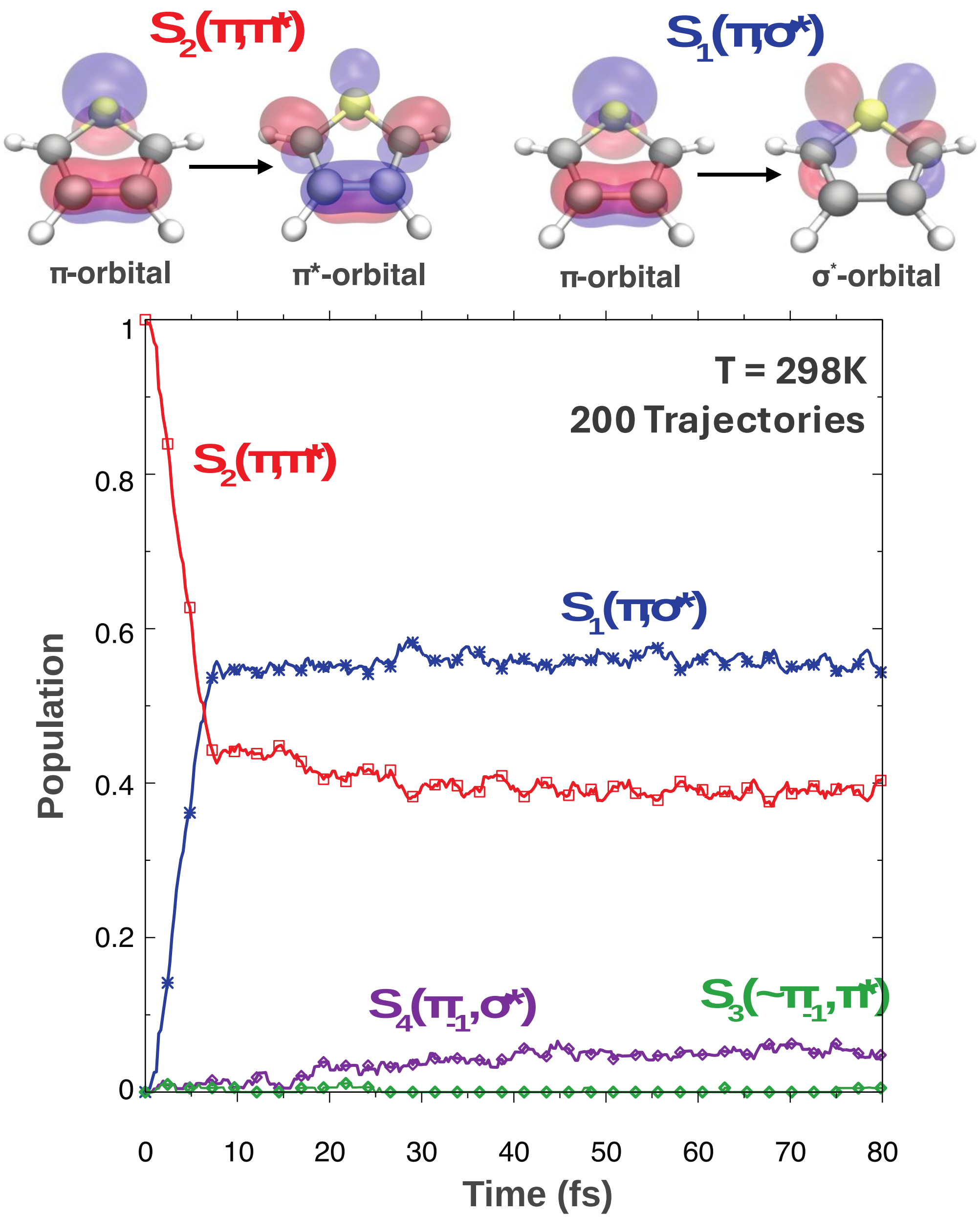

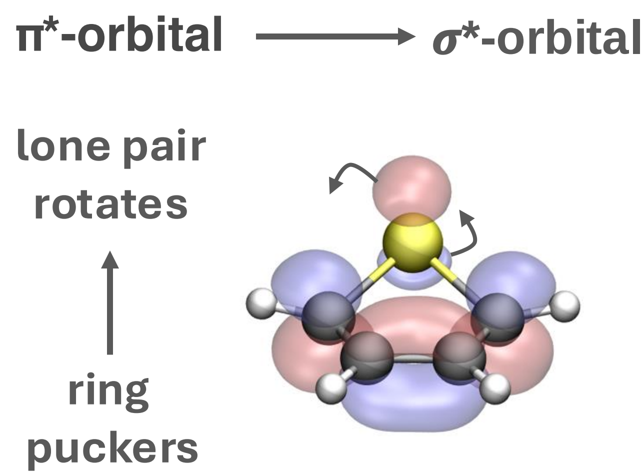

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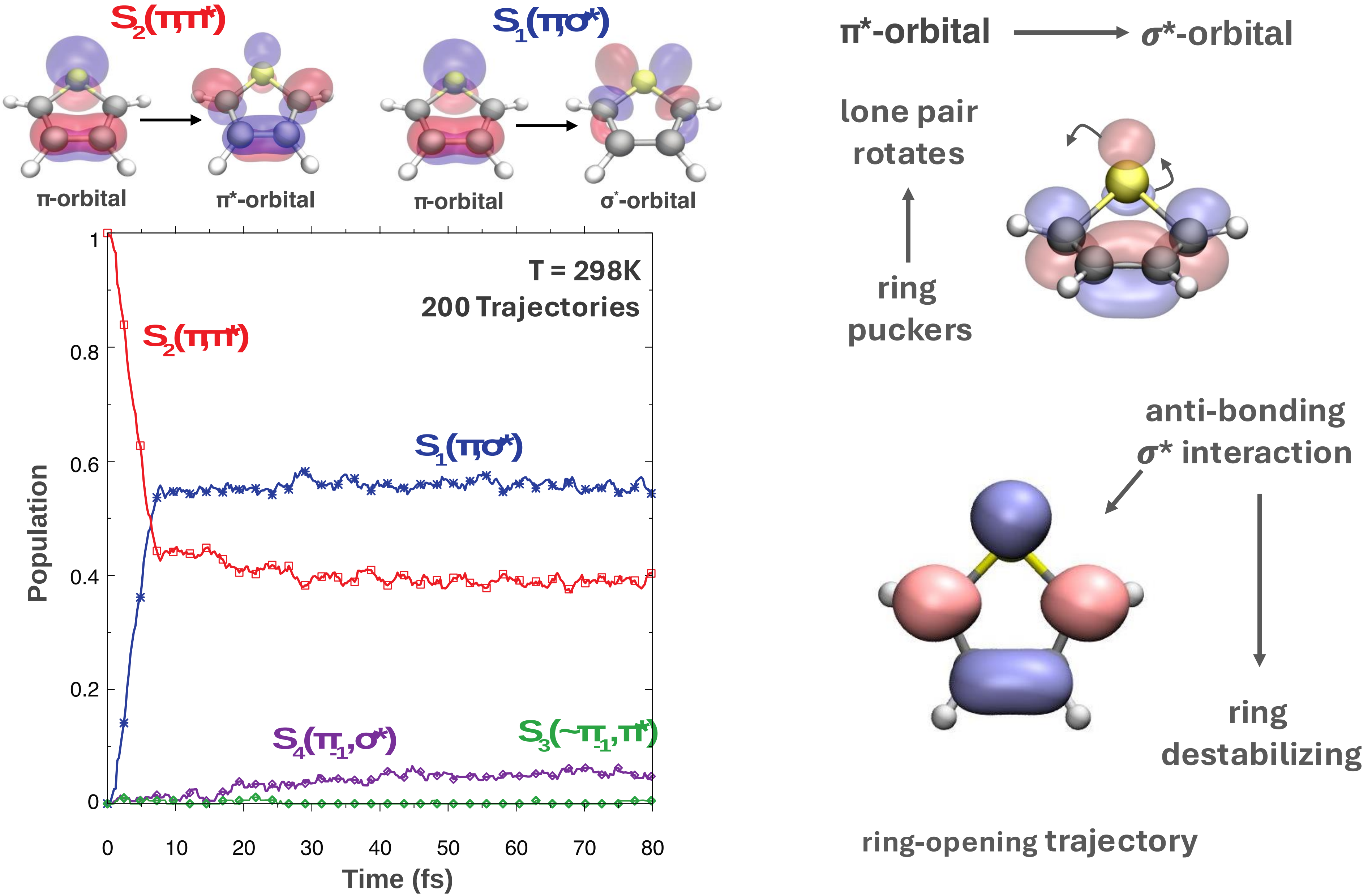

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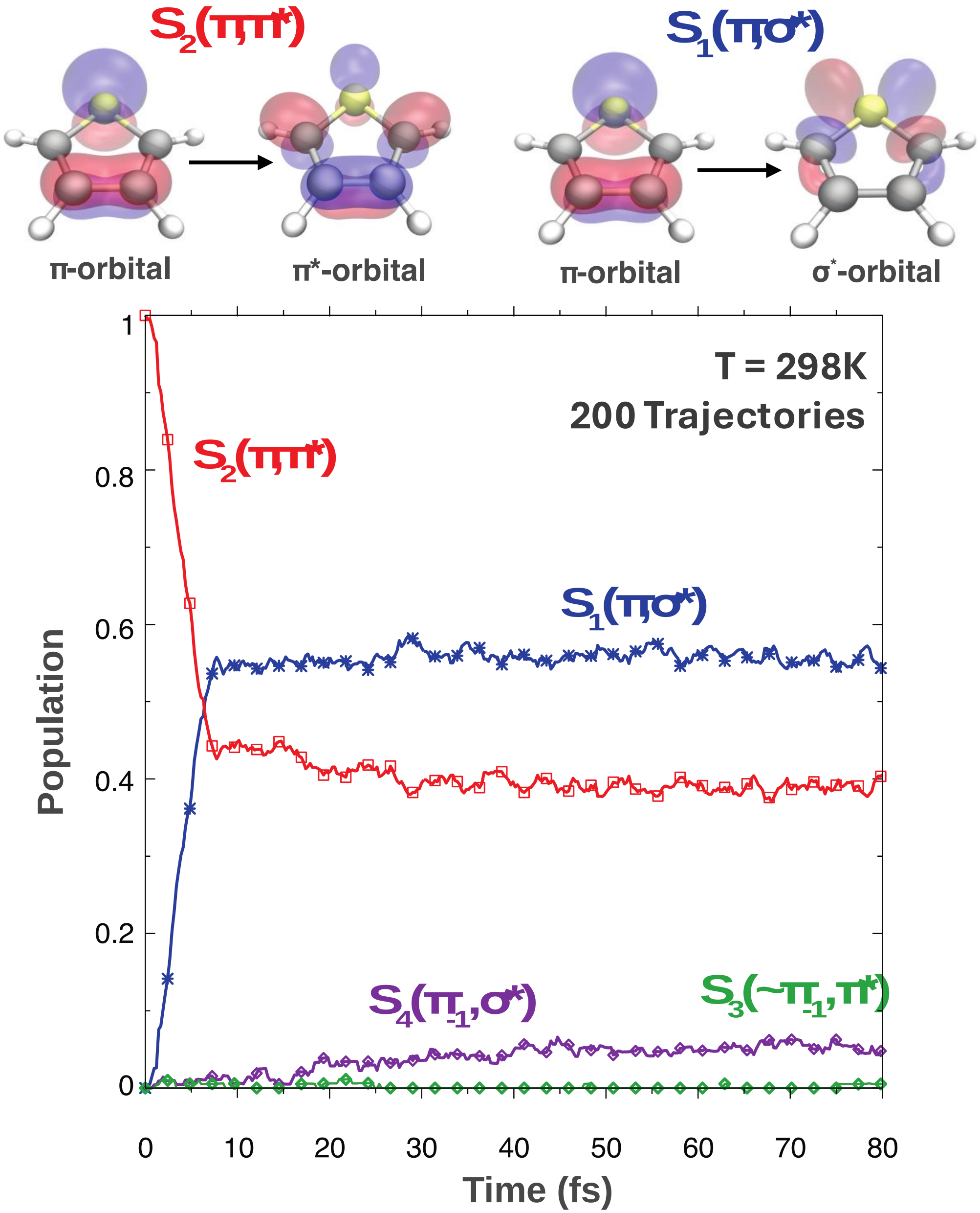

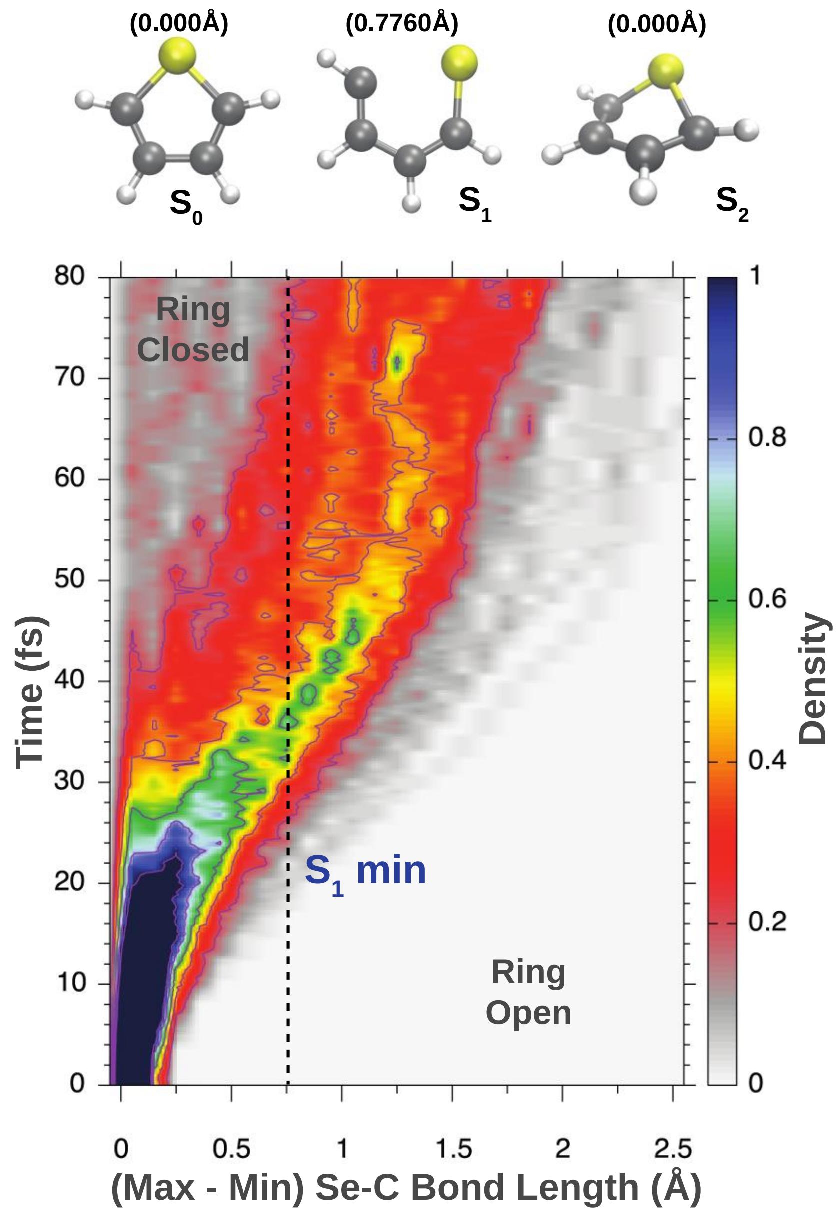

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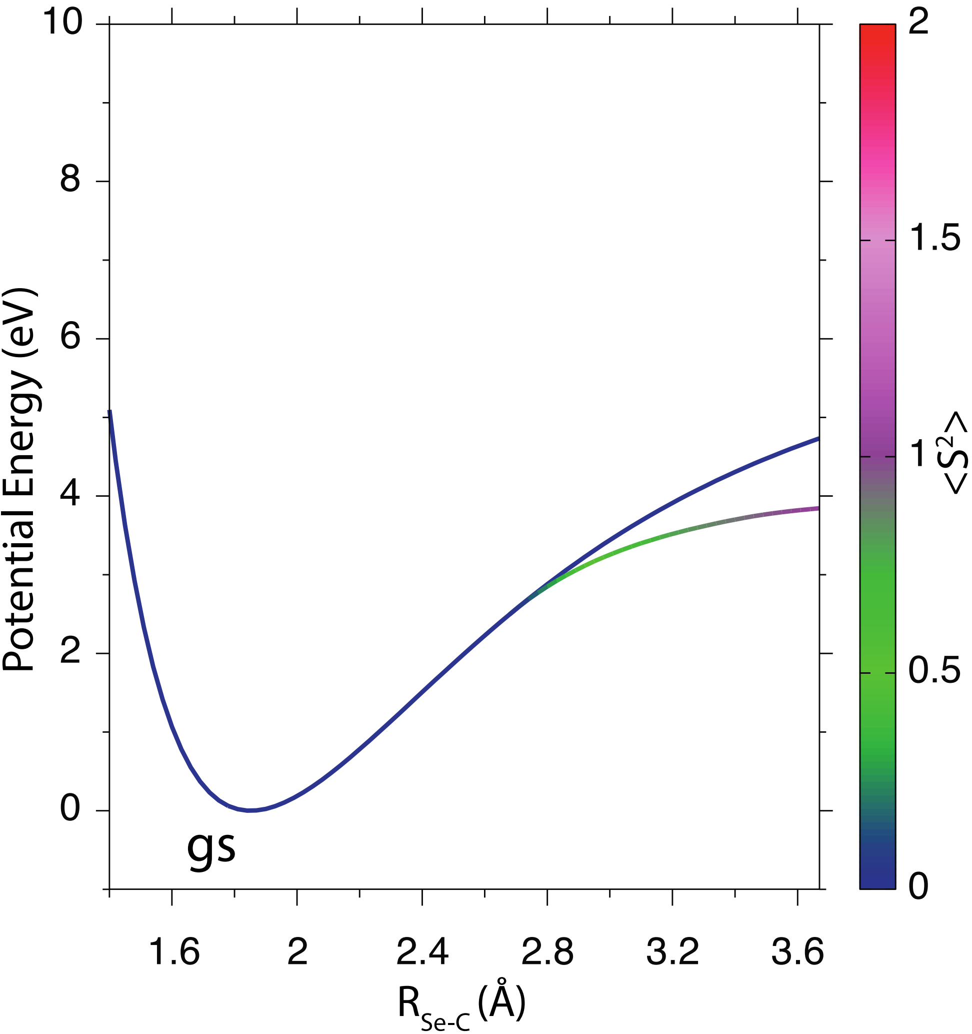
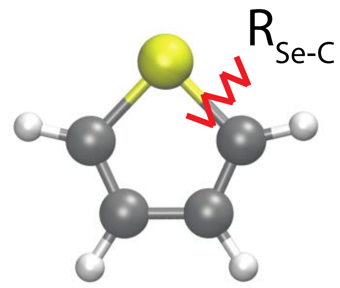
LRC-ωPBE/6-311G**

Realistic predictions of bond-breaking requires electronic structure theories that include static correlation.





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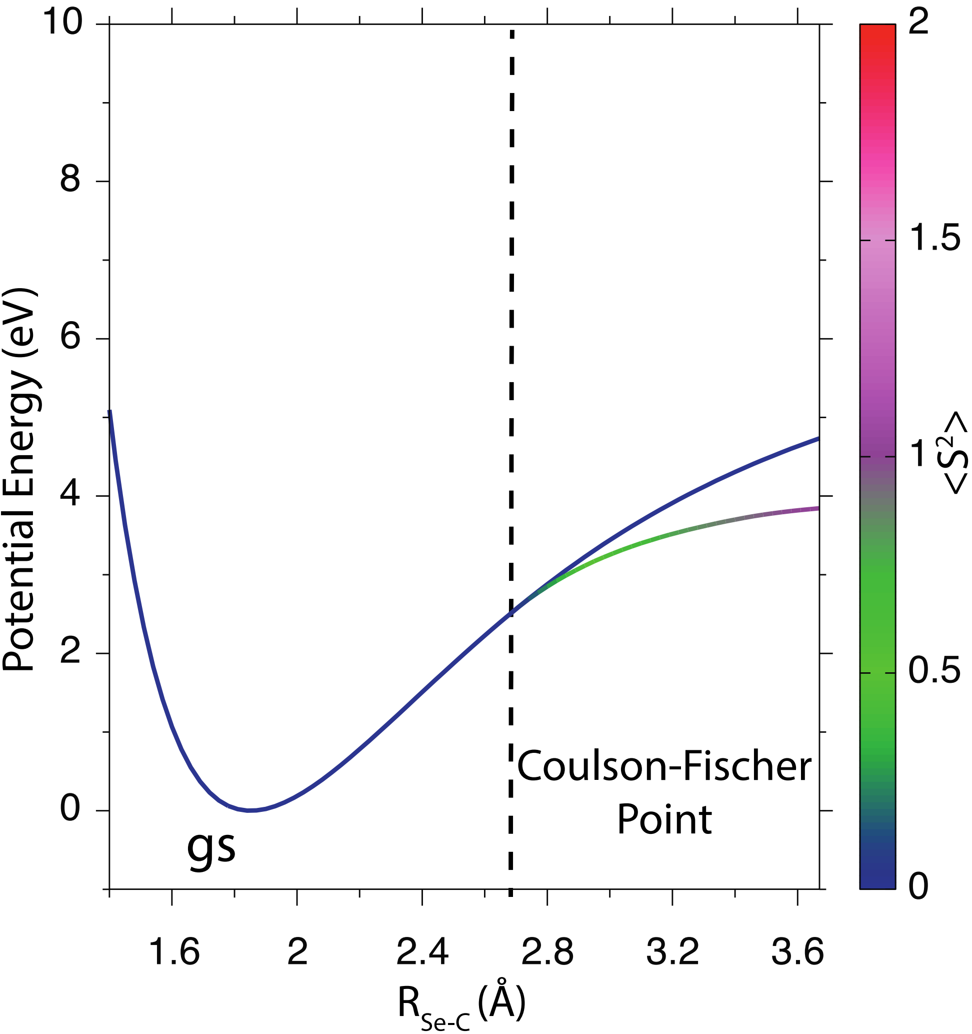

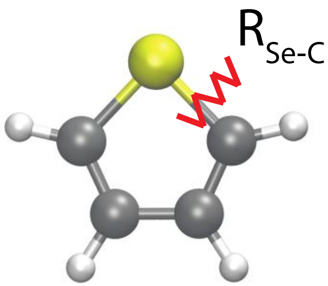

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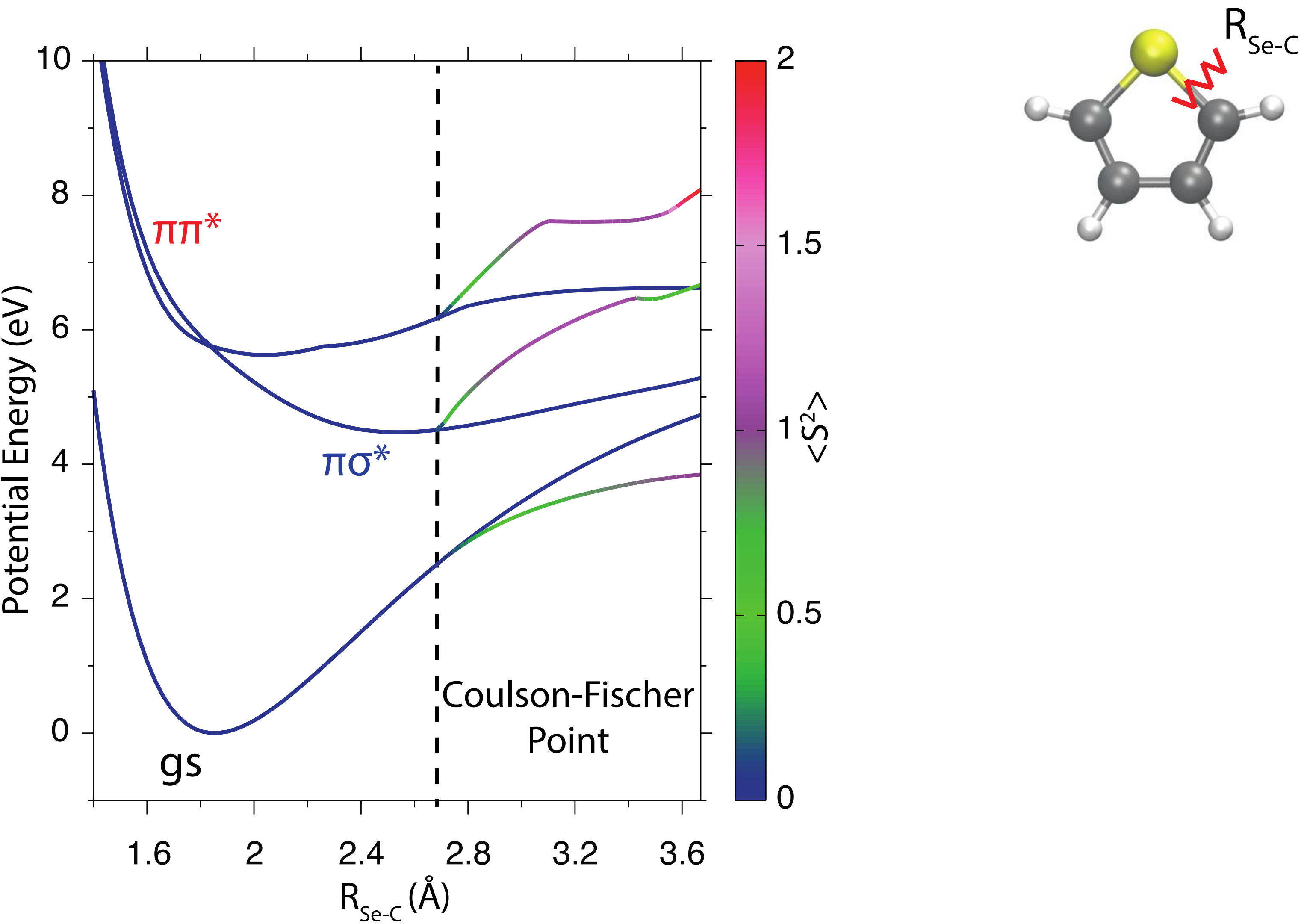

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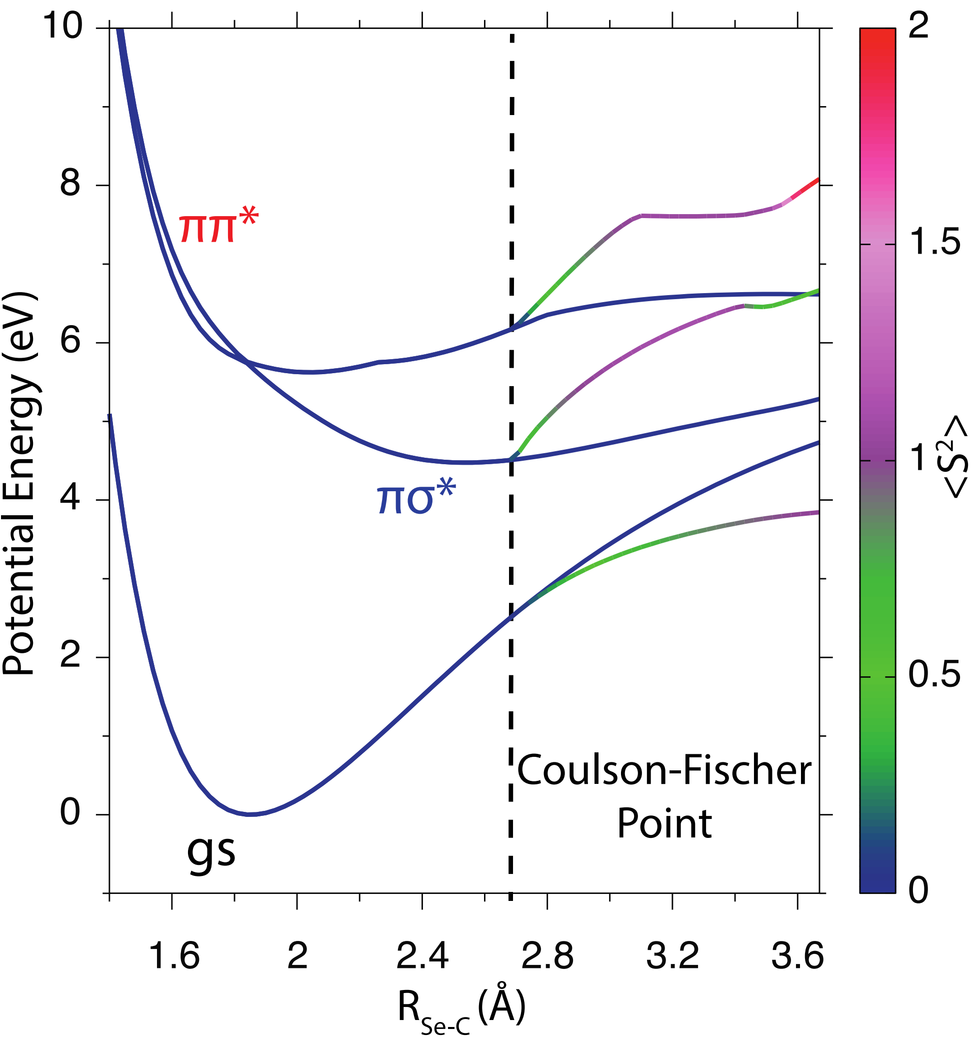

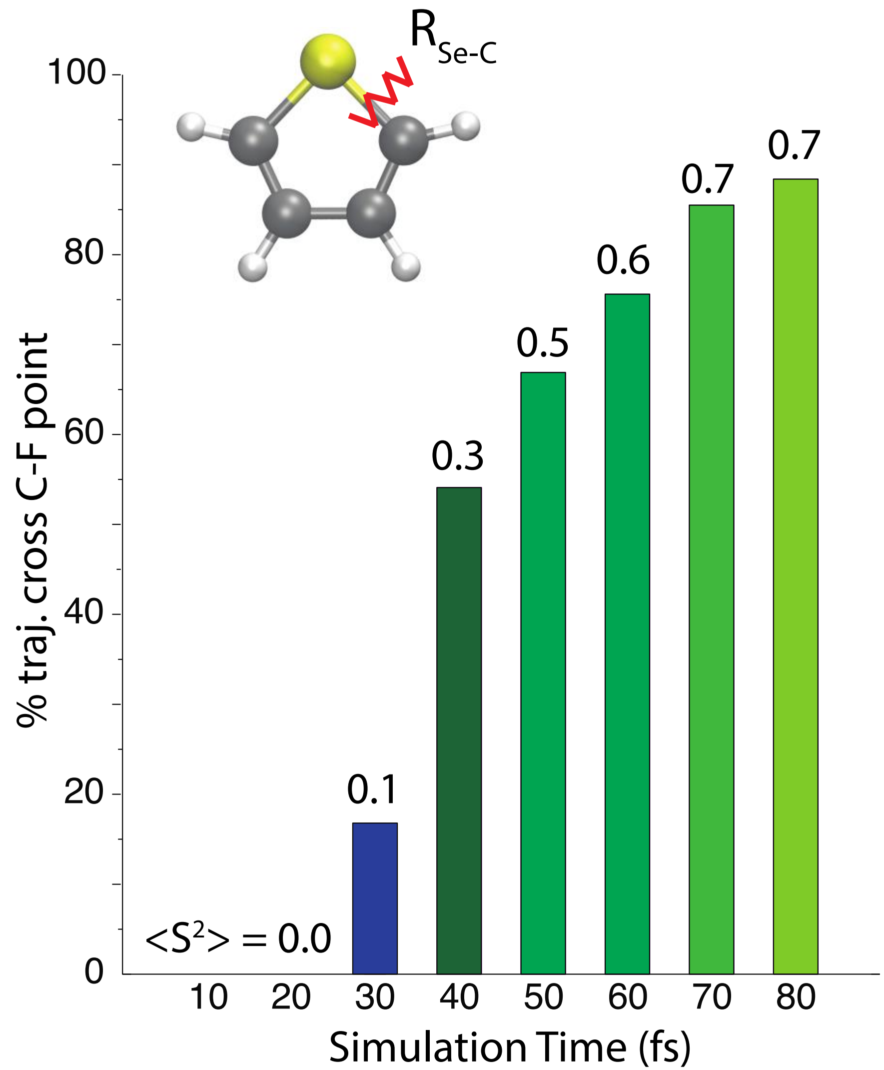

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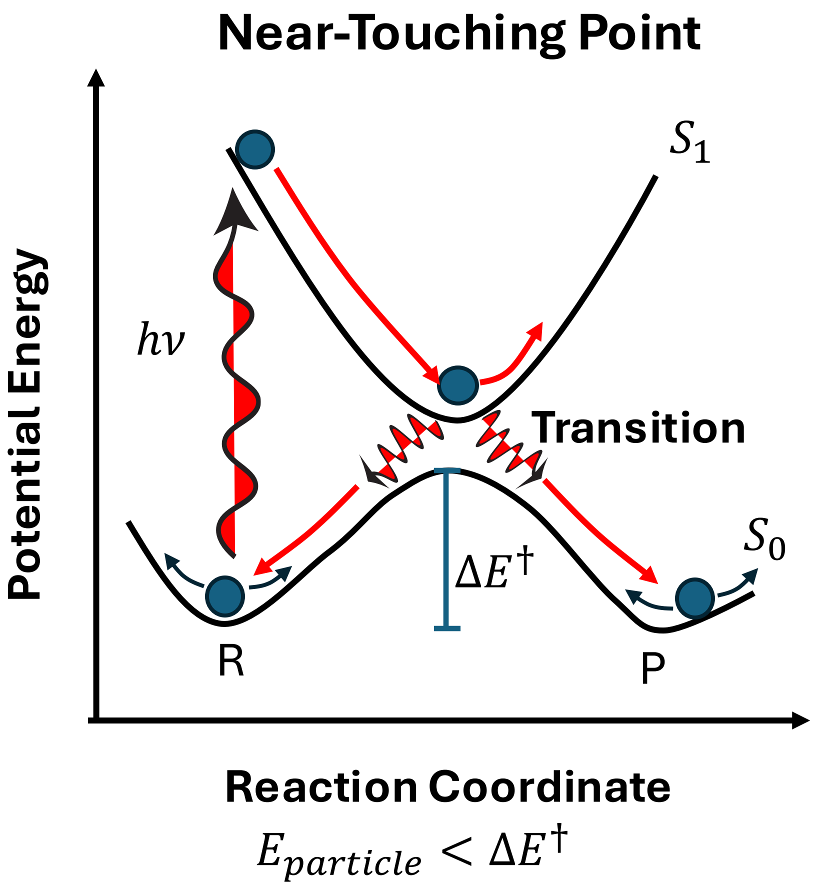
LRC-ωPBE/6-311G**

Fantastical excited state minimum energy configurations can appear stable near conical intersections.



Yarkony, D.R., *J. Chem. Phys.*, **1990**, 92, 2457
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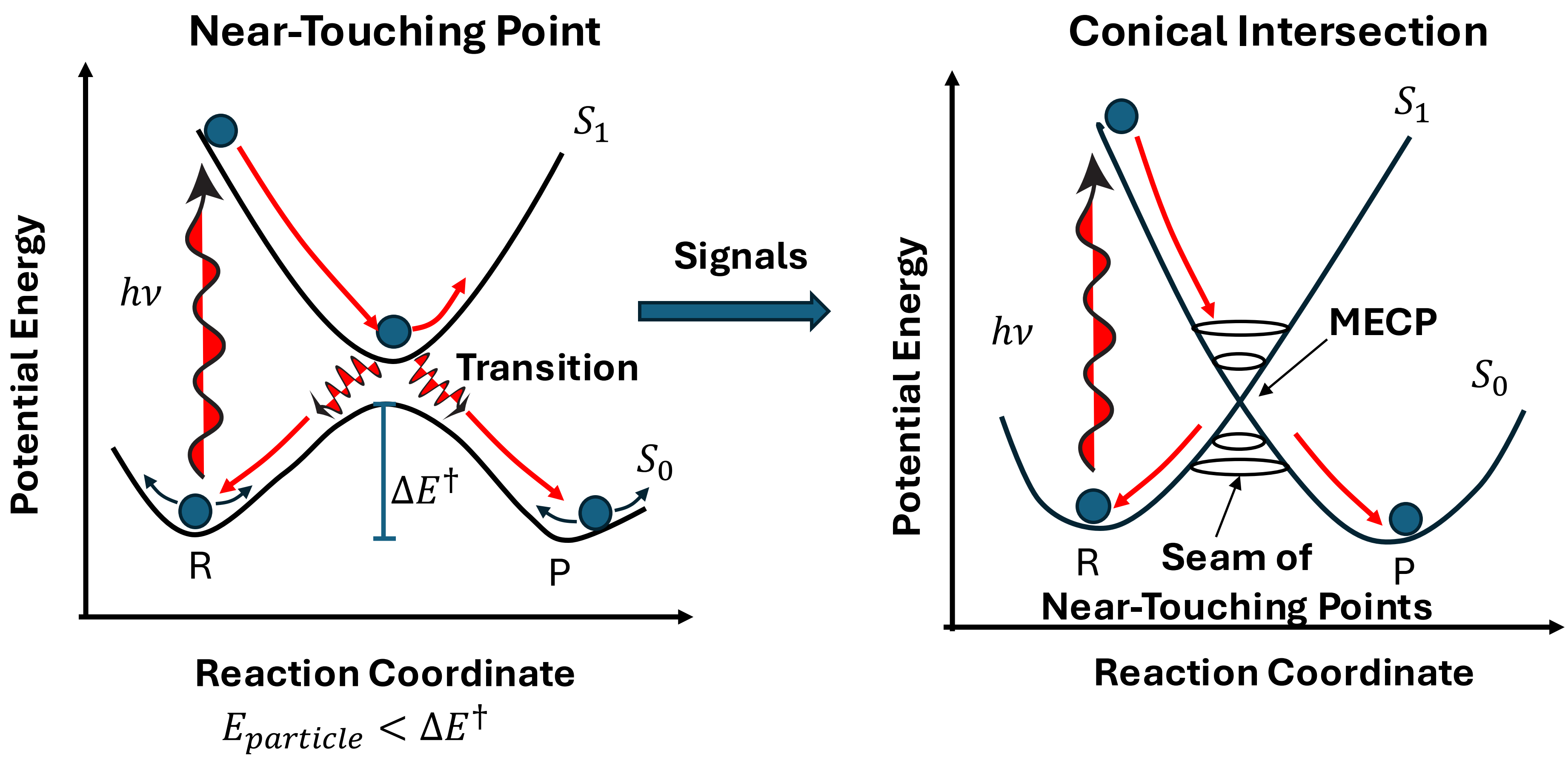

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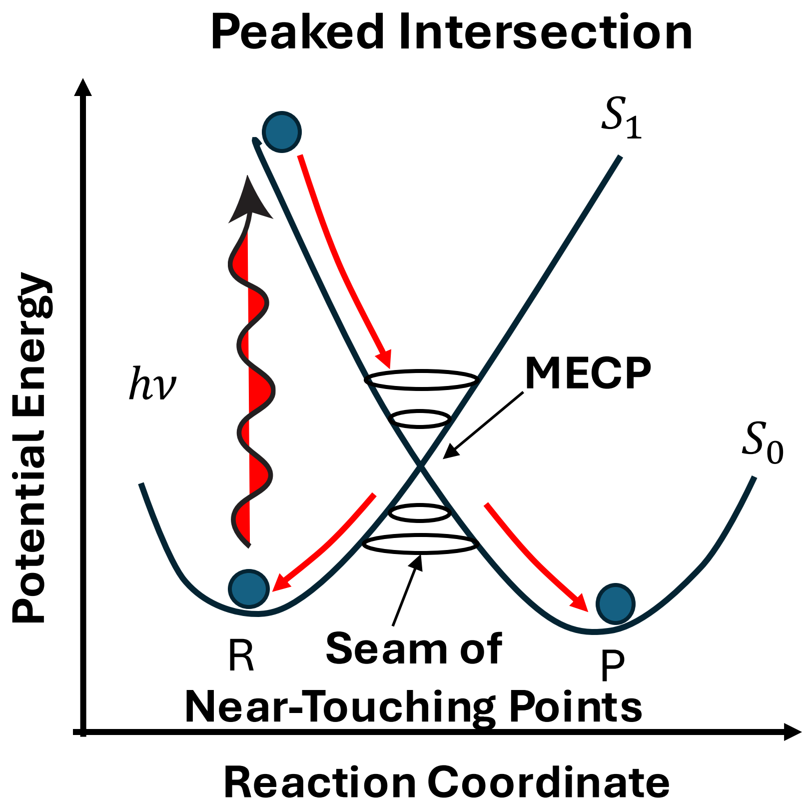

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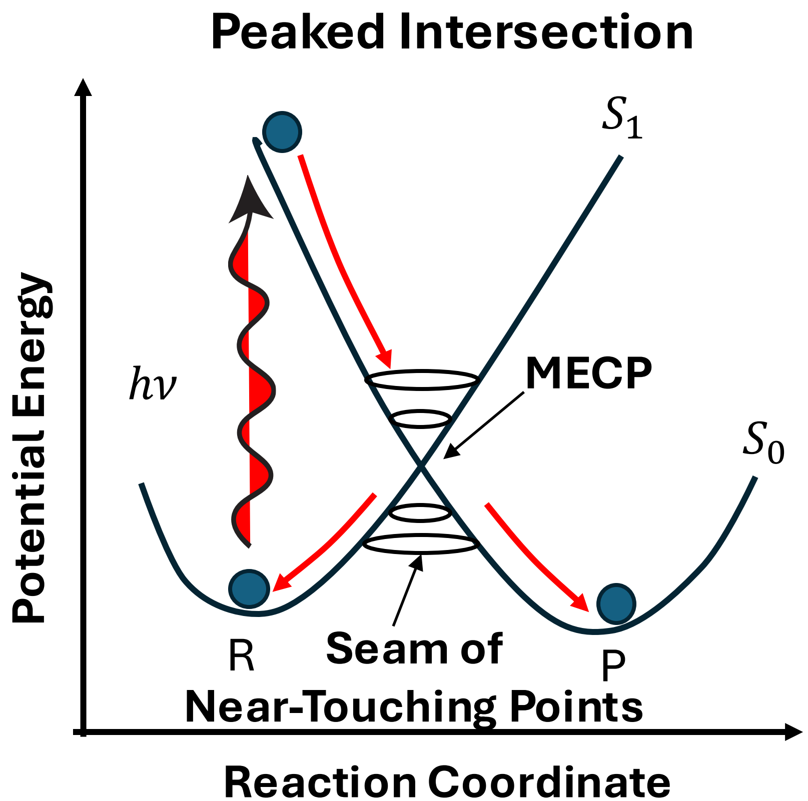

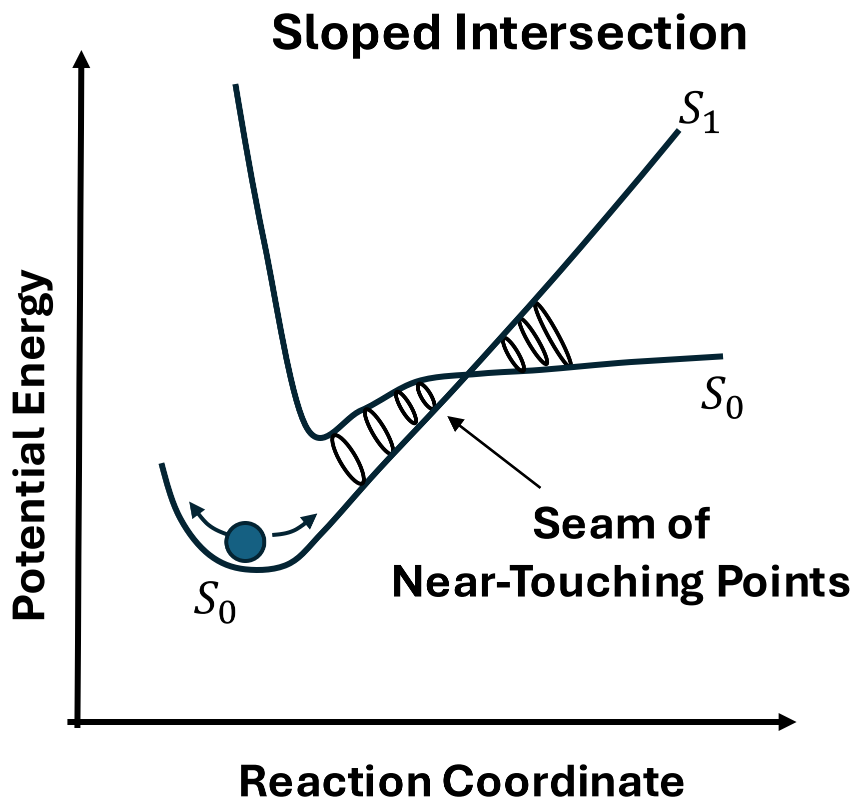

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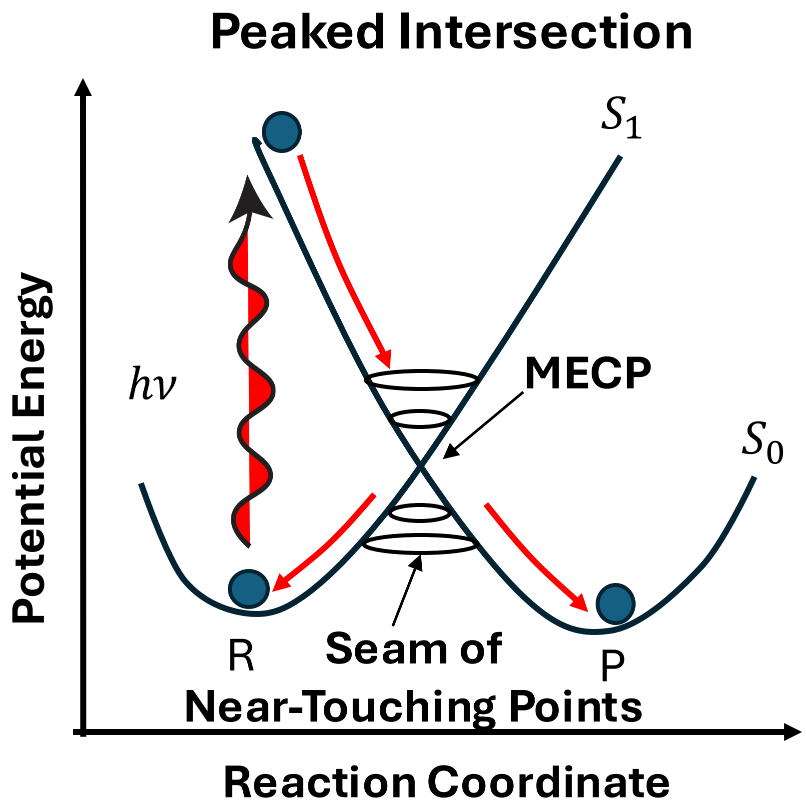

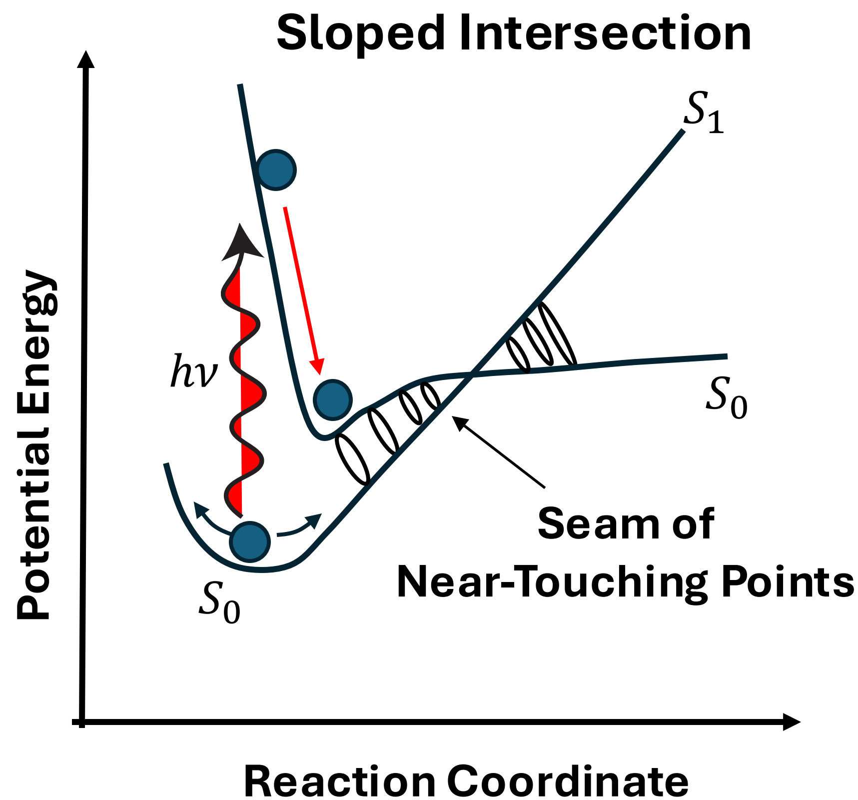

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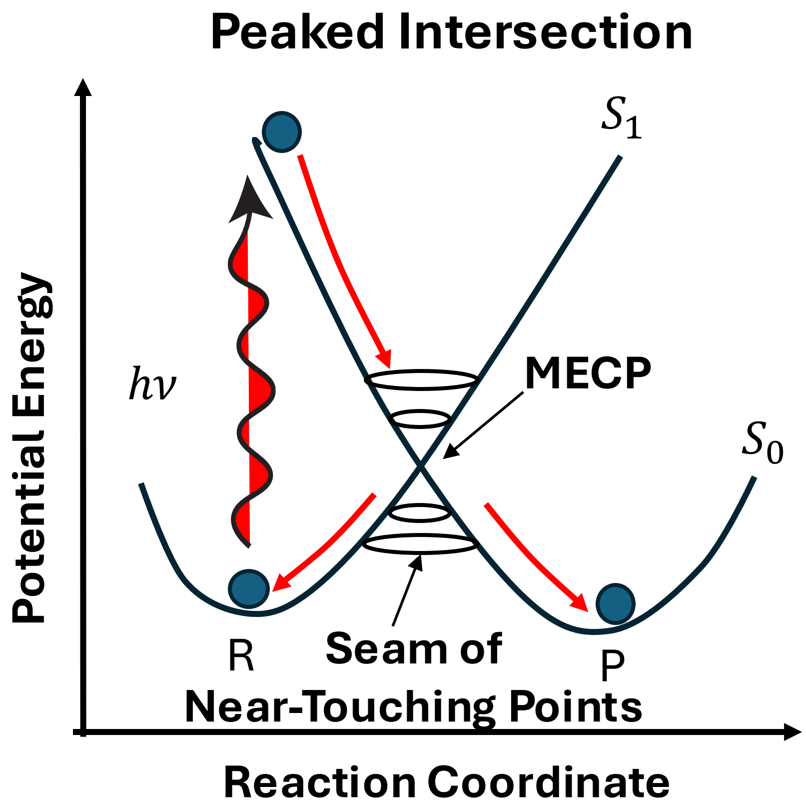

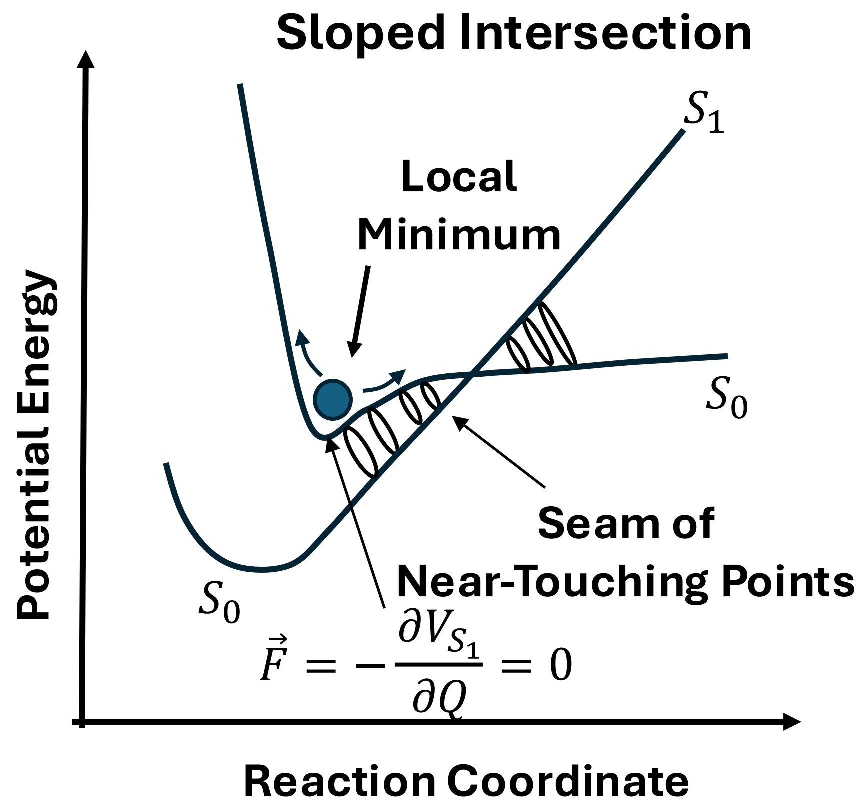

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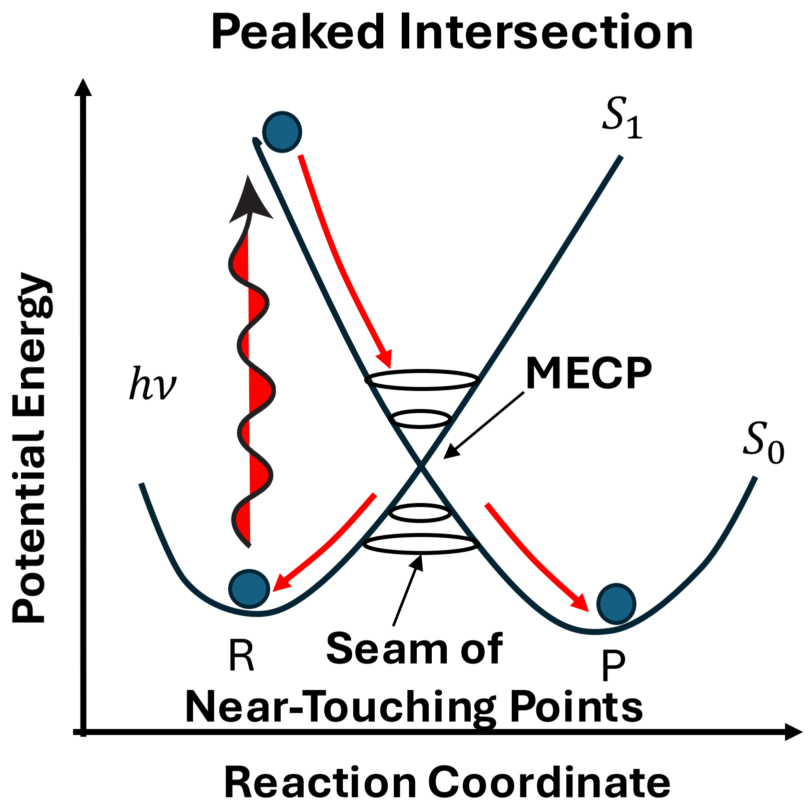

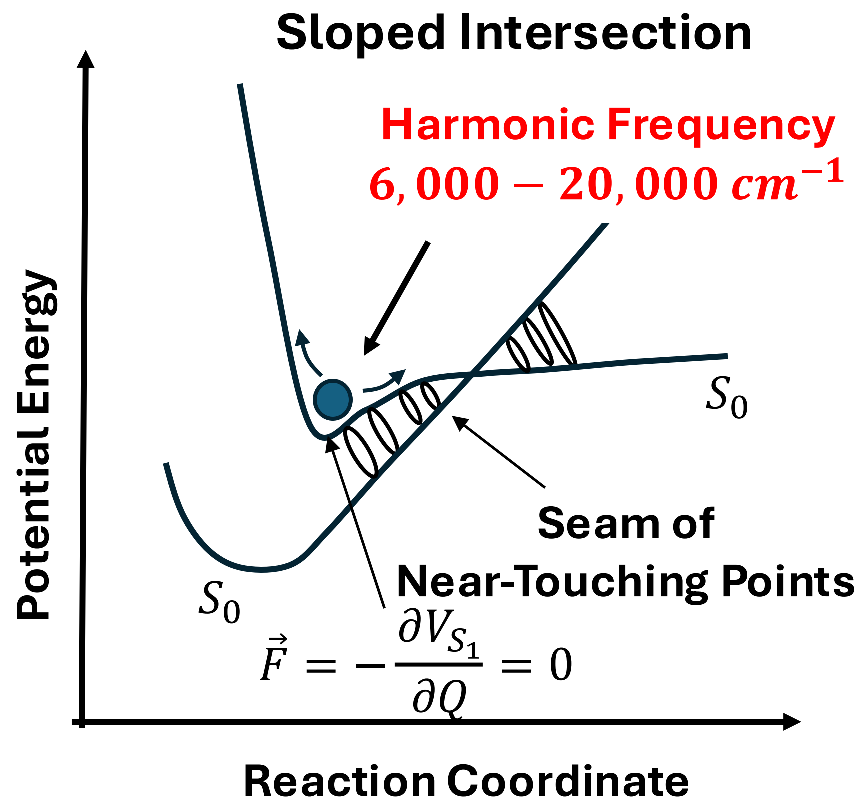

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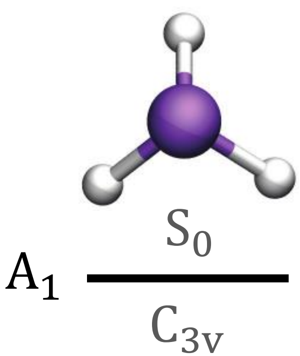
Phosphine (PH_3)



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EOM-EE-CCSD/aug-cc-pVDZ

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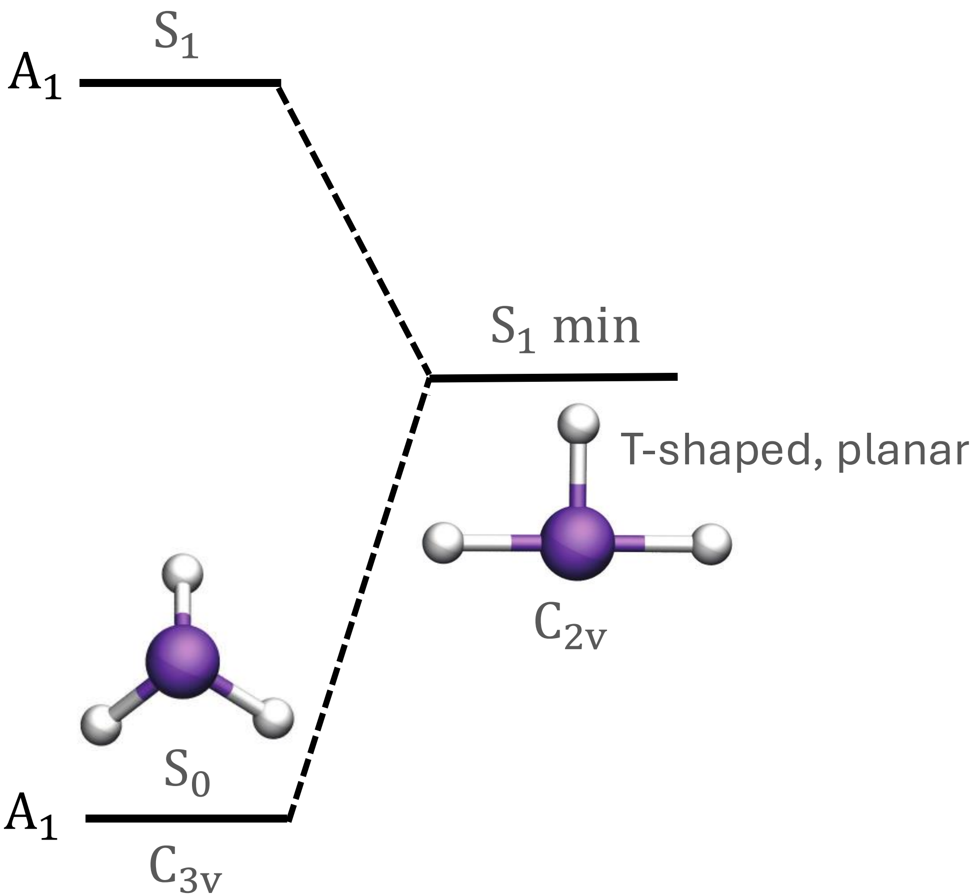

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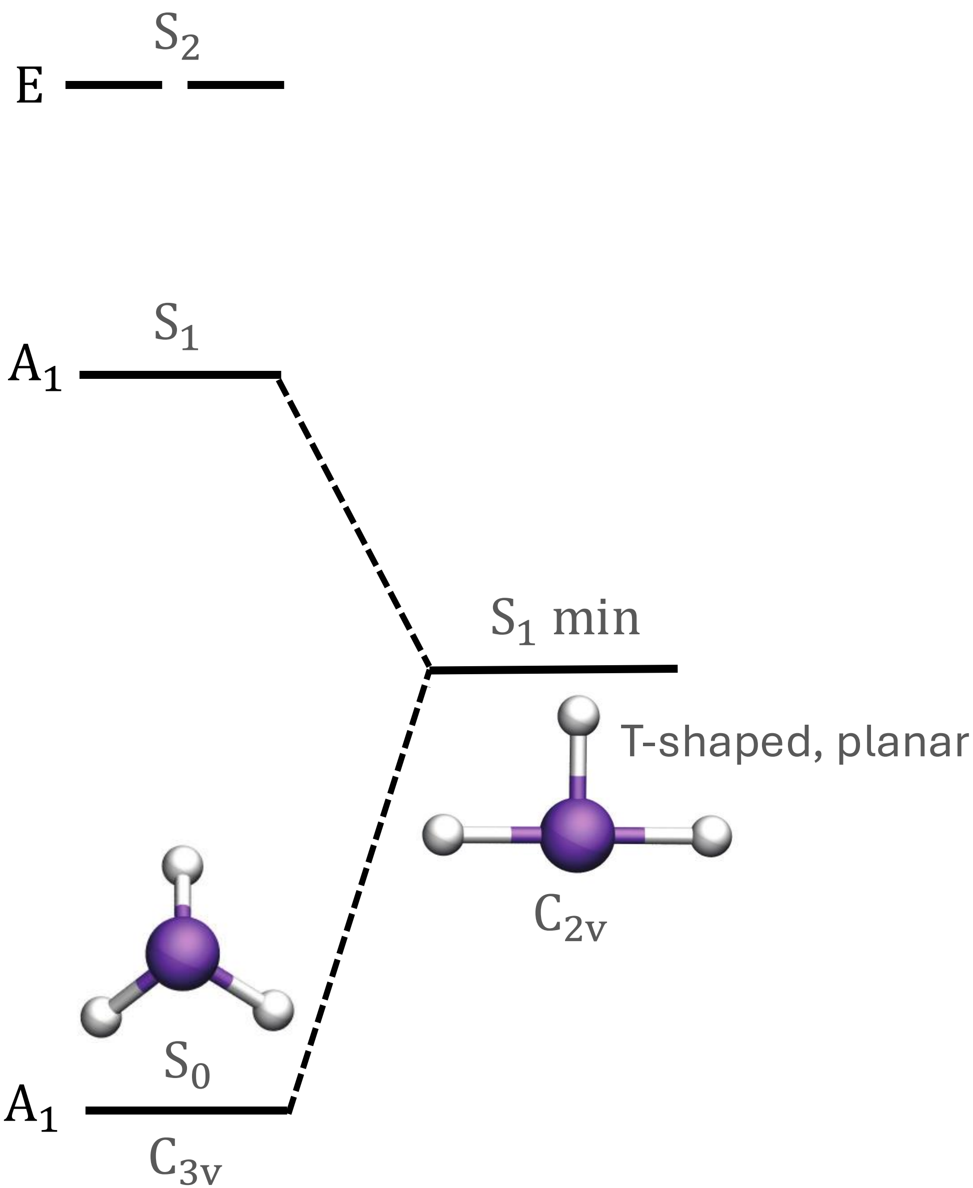

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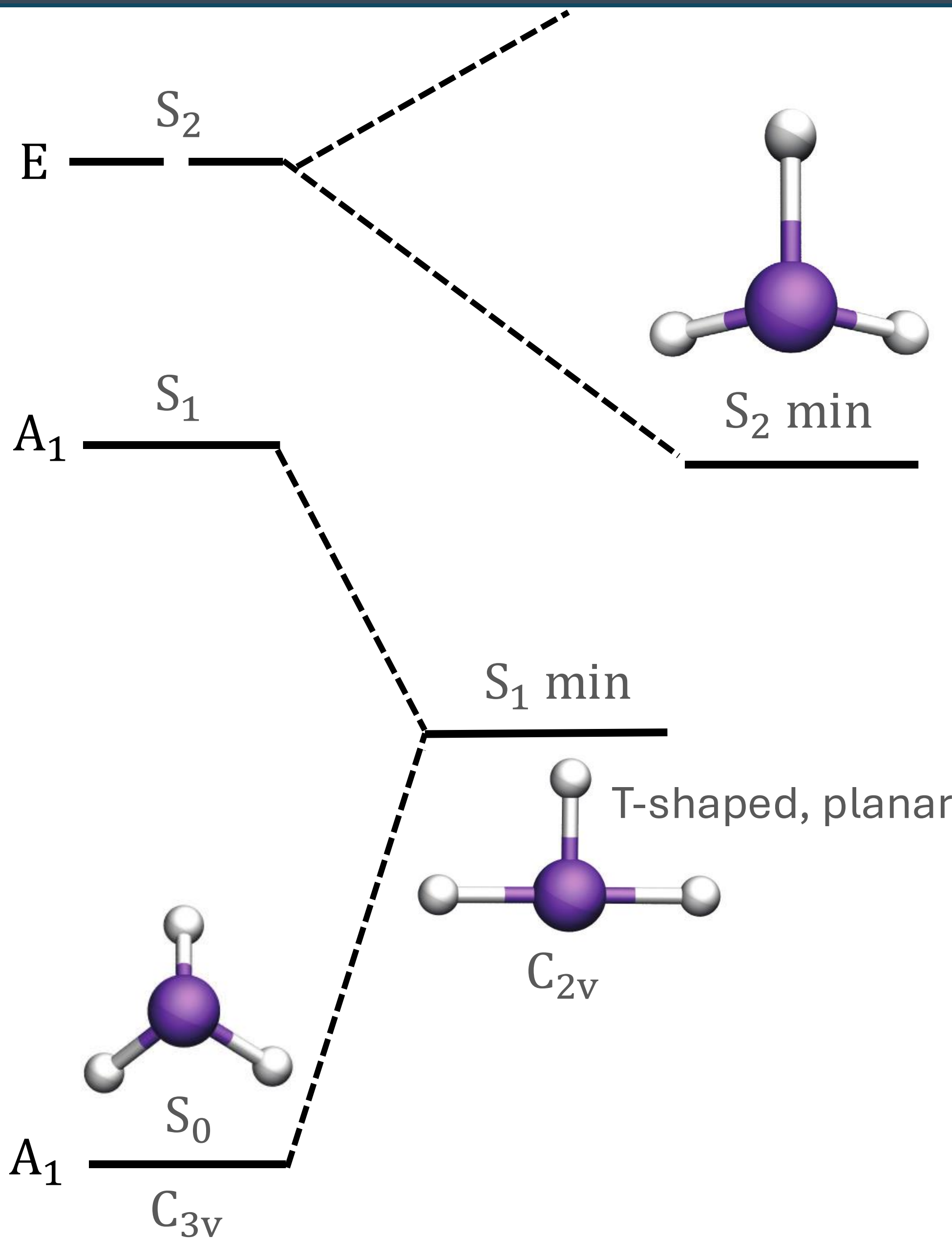

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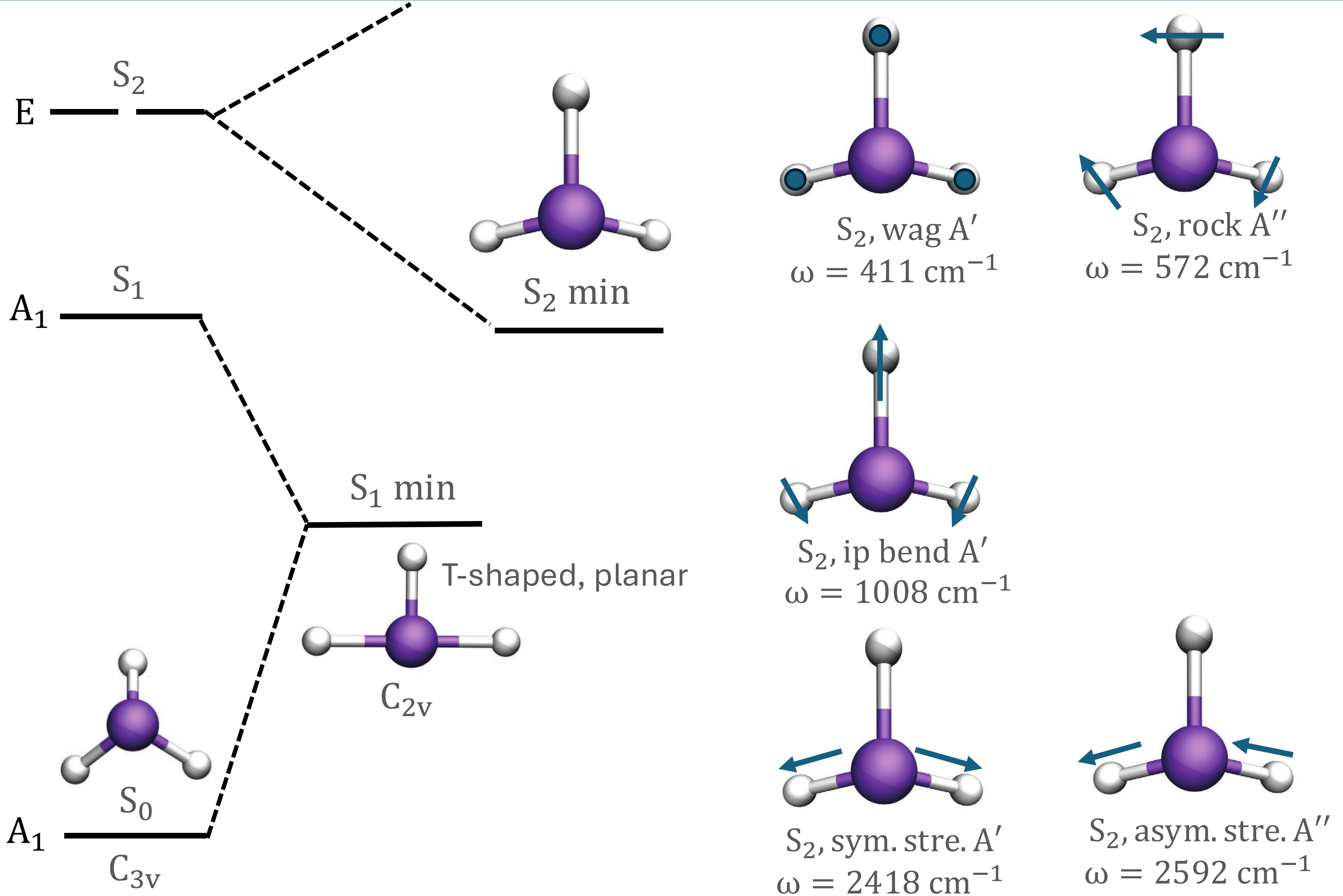

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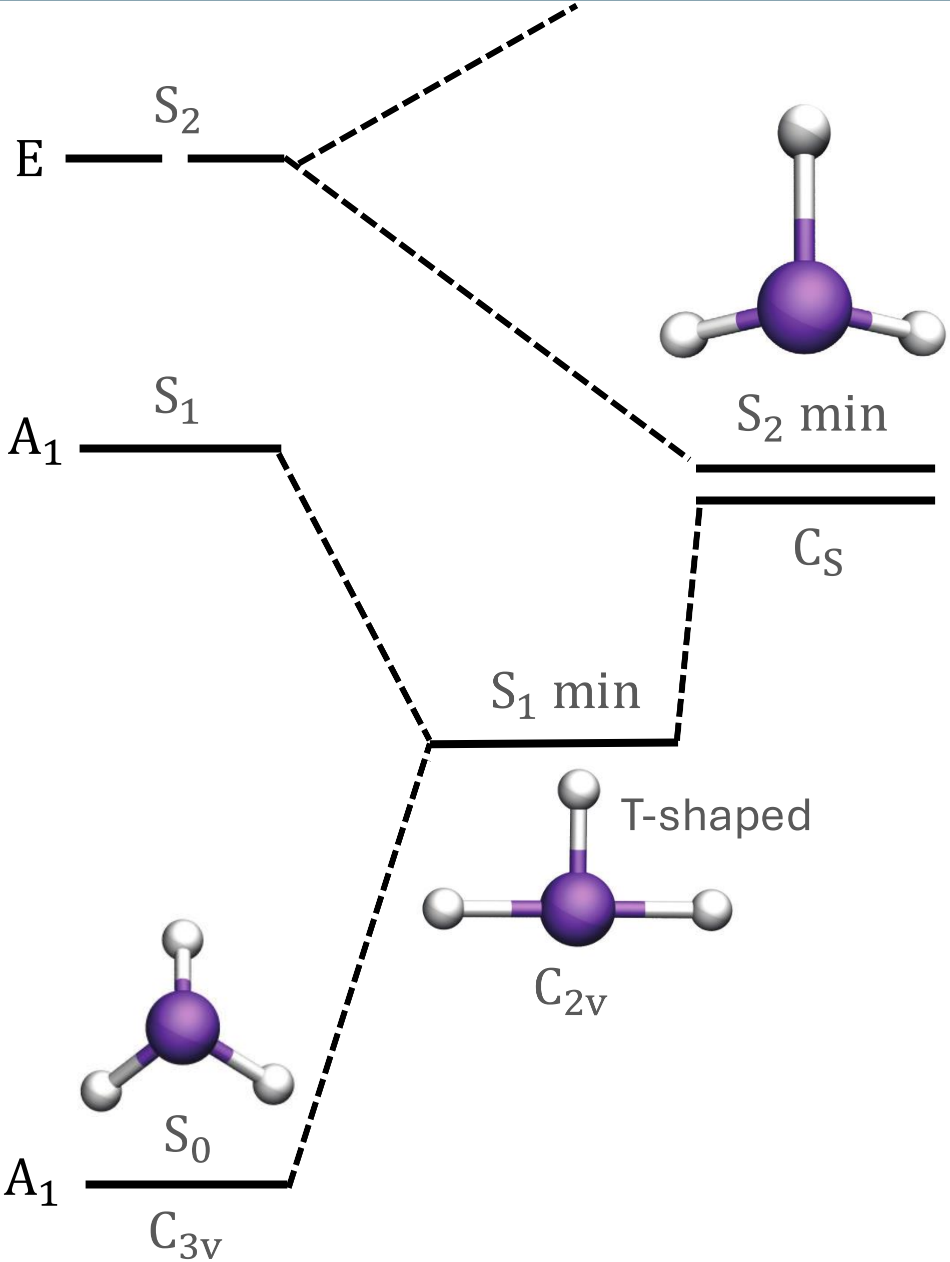
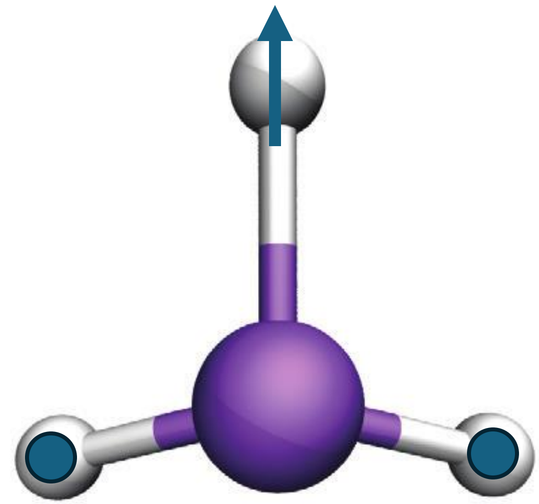


planarizes to form T-shaped configuration



S_2, mega mode A'
$\omega = 6884\ cm^{-1}$

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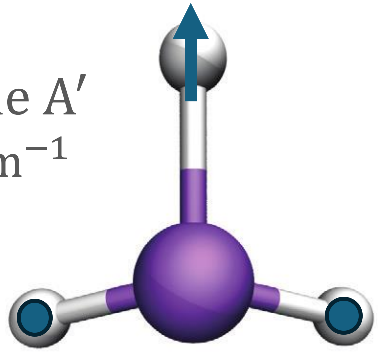

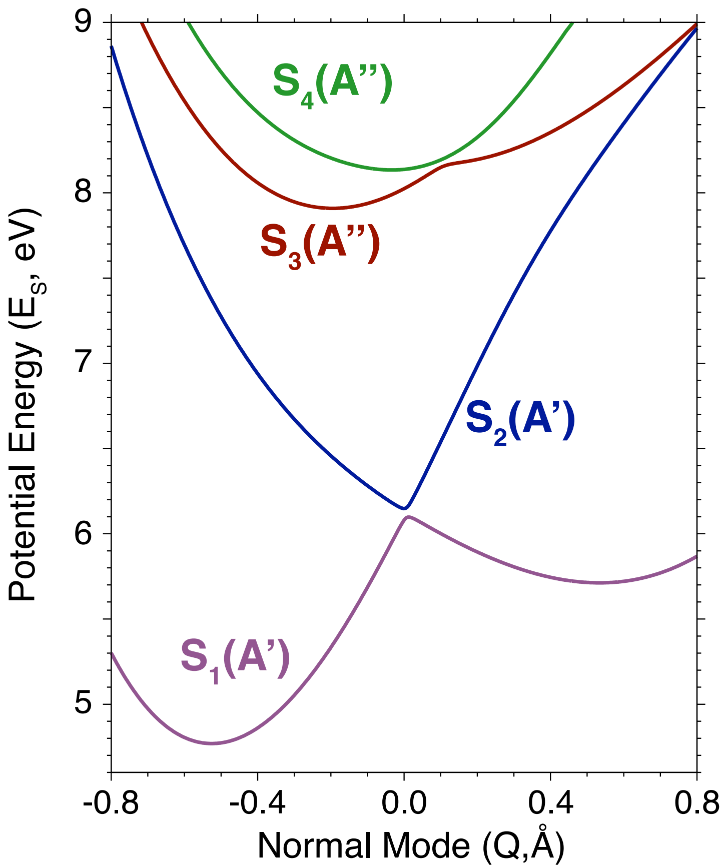

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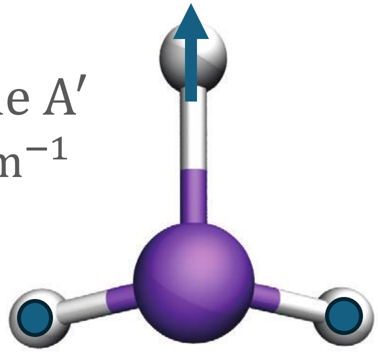

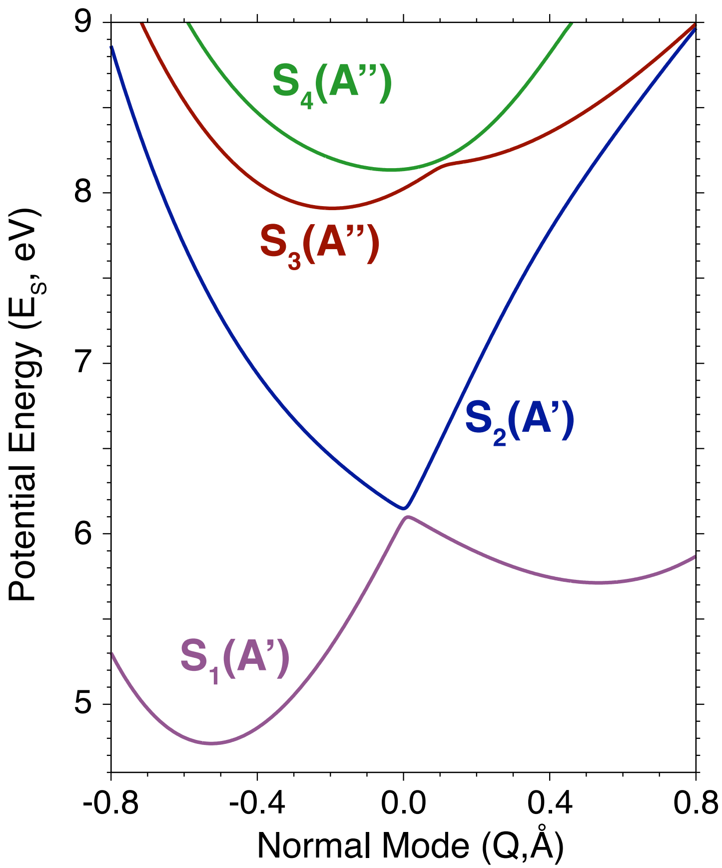

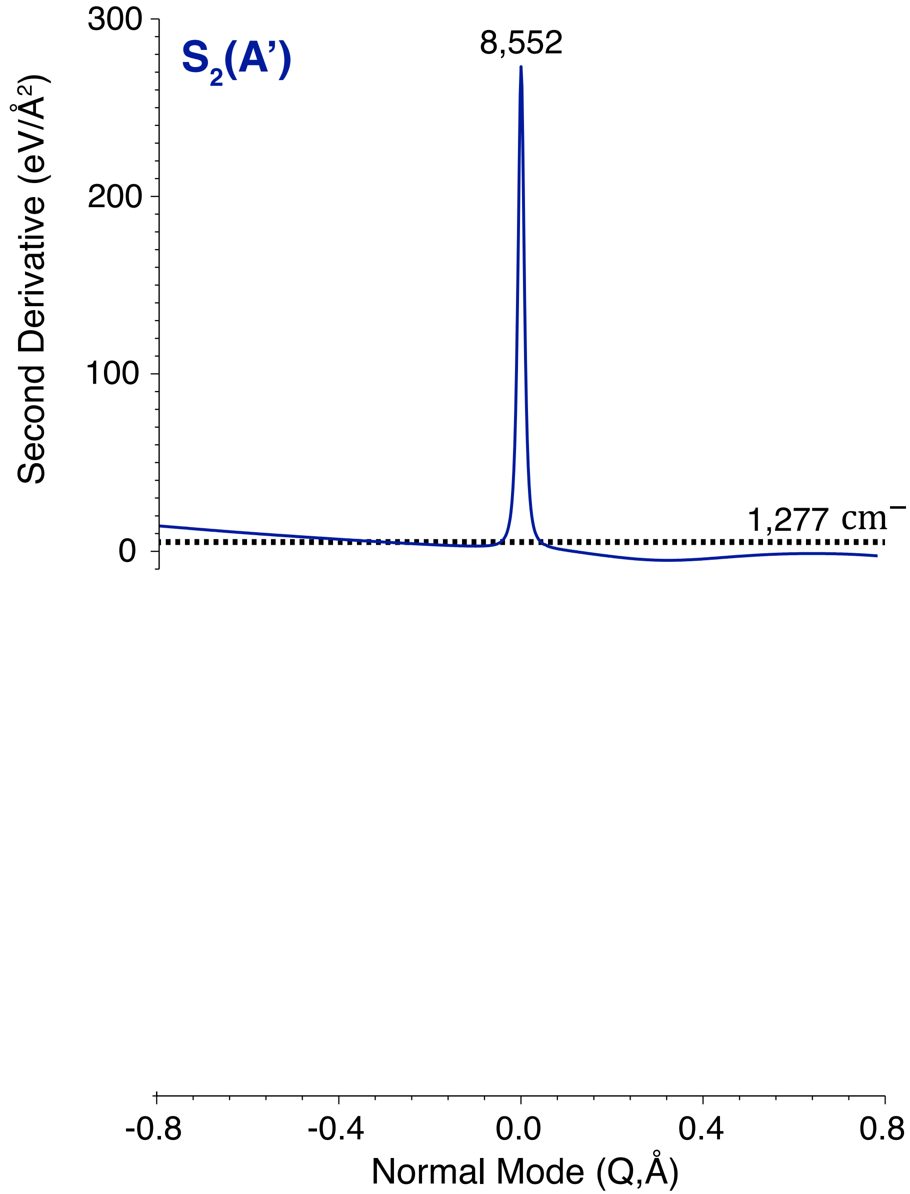

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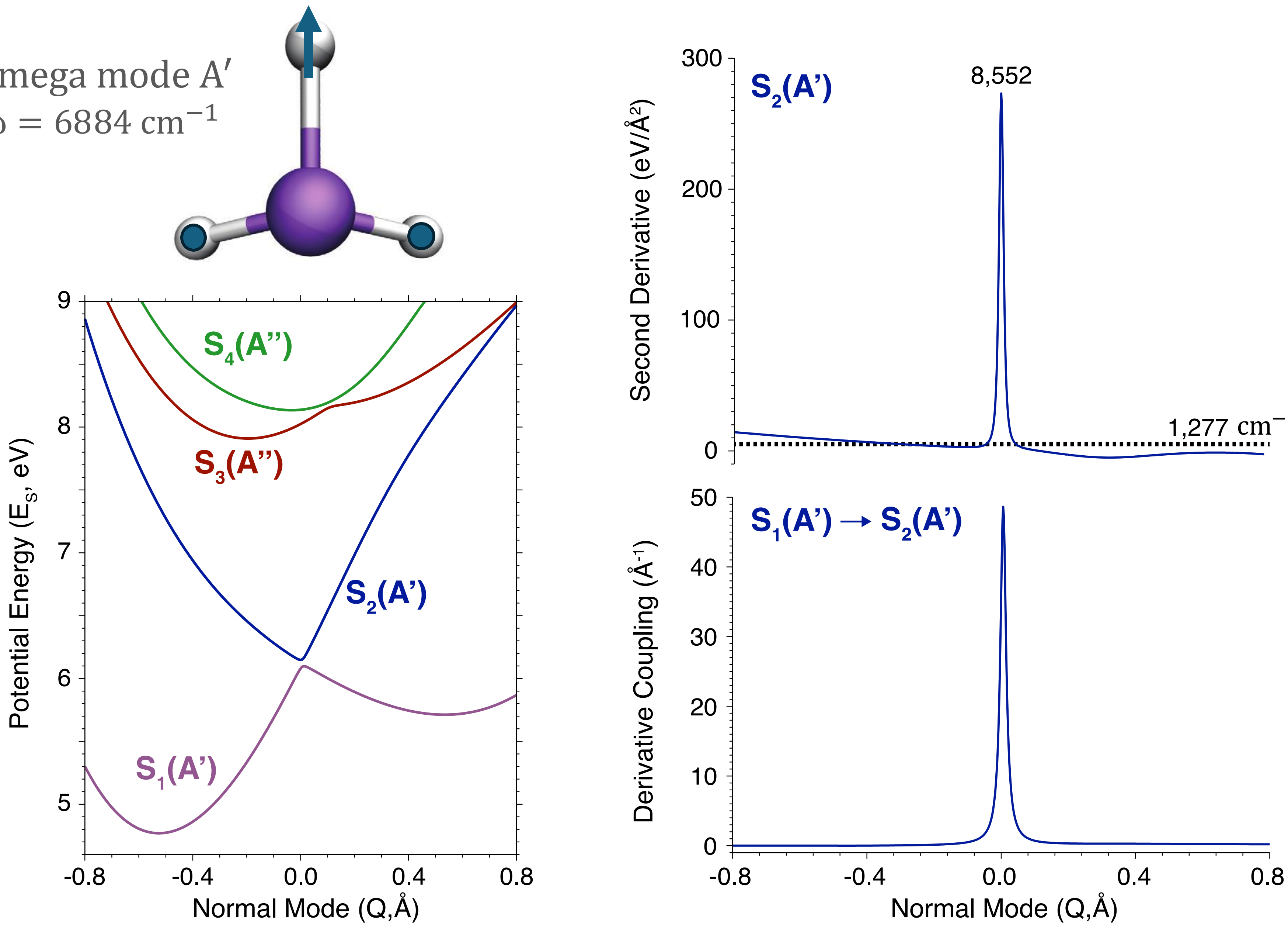

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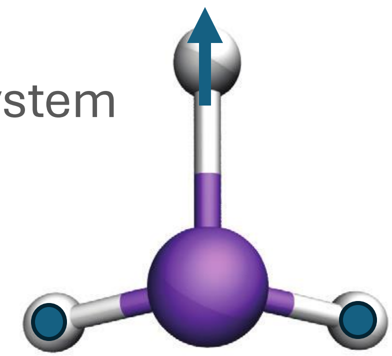
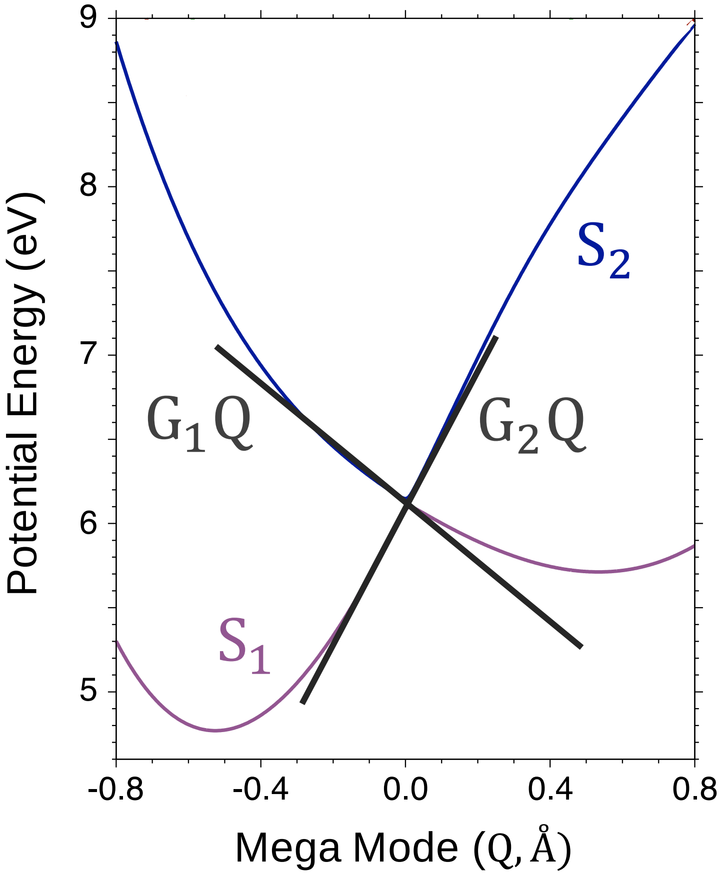
EOM-EE-CCSD/aug-cc-pVDZ

Phosphine (PH_3)

two-level system

S_1 & S_2





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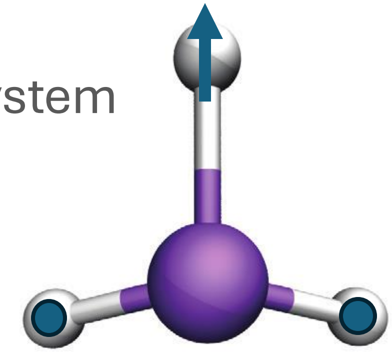

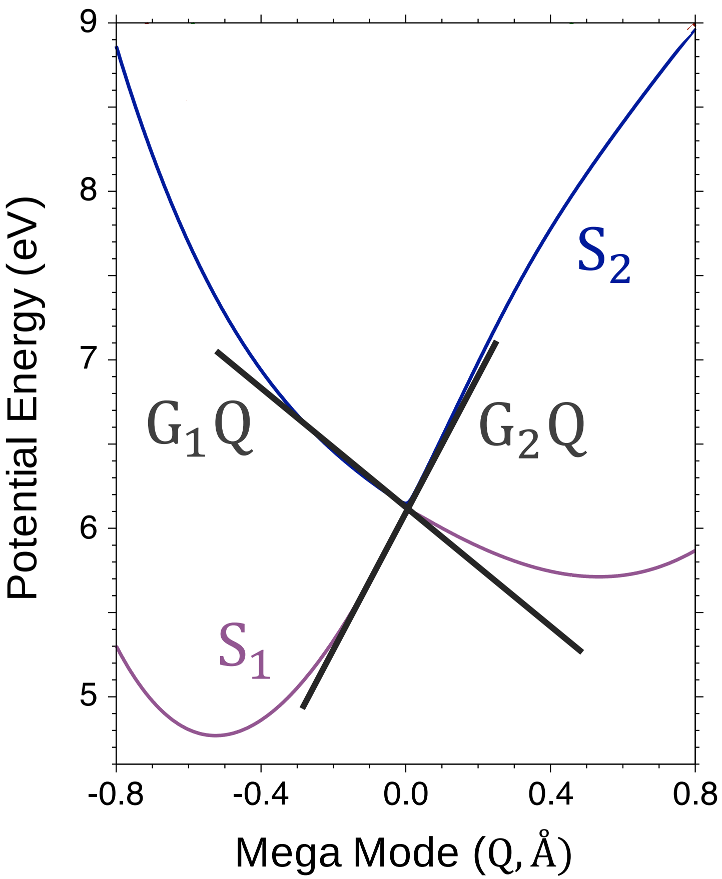

Hamiltonian

$$H_{11}(Q) = G_1 Q$$
$$H_{22}(Q) = G_2 Q$$
$$H_{12}(Q) = \Delta$$

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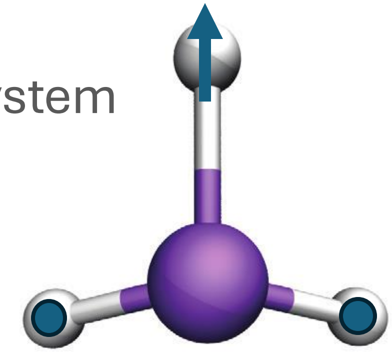

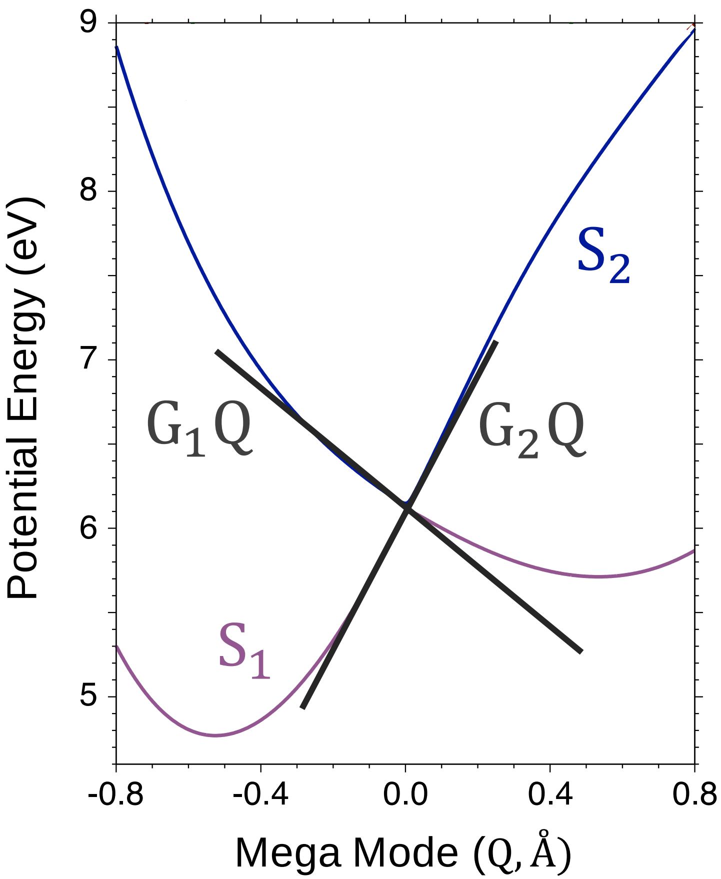

Hamiltonian

$$H_{11}(Q) = G_1 Q$$
$$H_{22}(Q) = G_2 Q$$
$$H_{12}(Q) = \Delta$$

Eigenvalues

$$E_{\pm}(Q) = (G_1 + G_2)Q + \frac{1}{2}\sqrt{Q^2(G_1 - G_2)^2 + 4\Delta^2}$$

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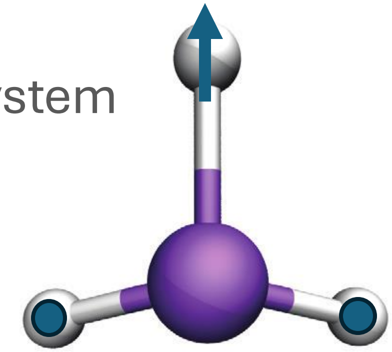
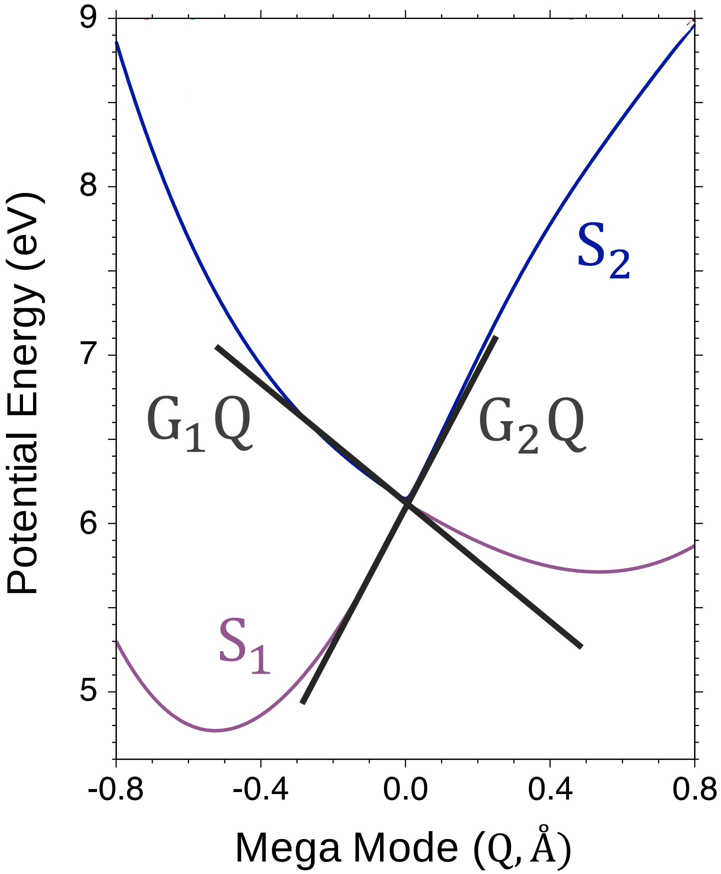
EOM-EE-CCSD/aug-cc-pVDZ

Phosphine (PH_3)

two-level system

S_1 & S_2





Hamiltonian

$$H_{11}(Q) = G_1 Q$$
$$H_{22}(Q) = G_2 Q$$
$$H_{12}(Q) = \Delta$$

Eigenvalues

$$E_{\pm}(Q) = (G_1 + G_2)Q + \frac{1}{2}\sqrt{Q^2(G_1 - G_2)^2 + 4\Delta^2}$$

Second Derivative

$$\left.\frac{\partial^2 E_{+}(Q)}{\partial Q^2}\right|_{Q=0} = \frac{(G_1 - G_2)^2}{4\Delta}$$

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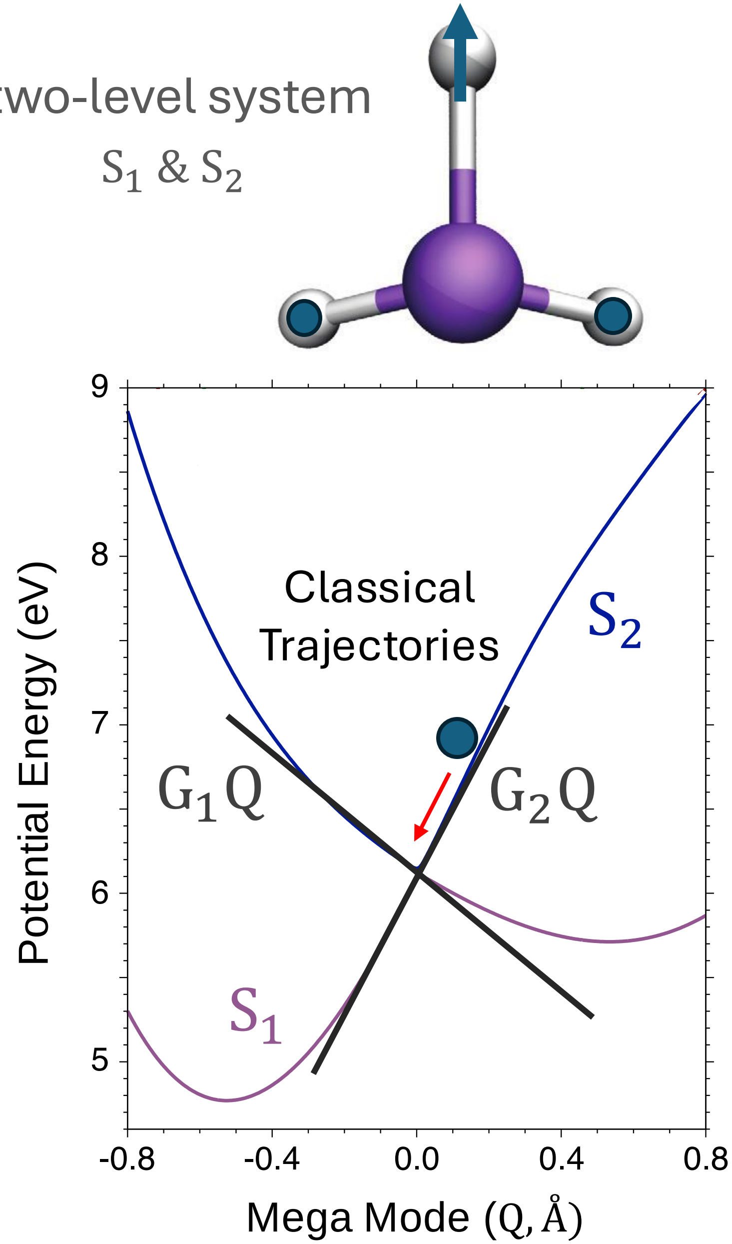

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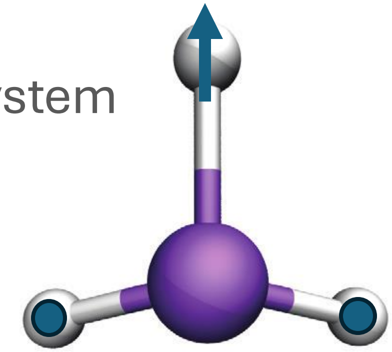

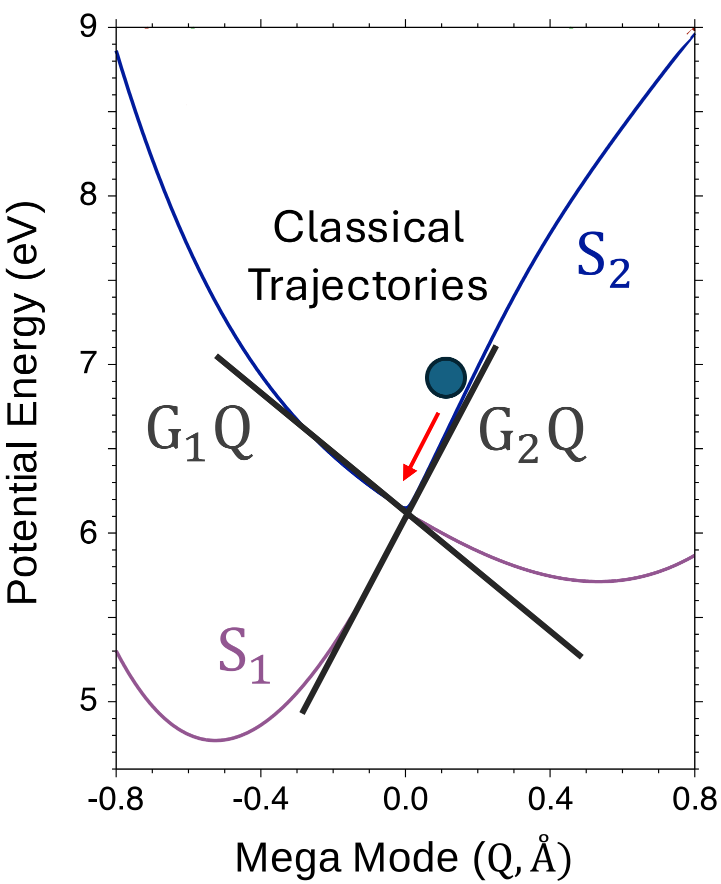

<u>Landau-Zener Transition Probability:</u>

$$P_{LZ} = 1 - \exp\left(-\frac{2\pi\Delta^2}{\hbar\dot{Q}|G_1 - G_2|}\right)$$

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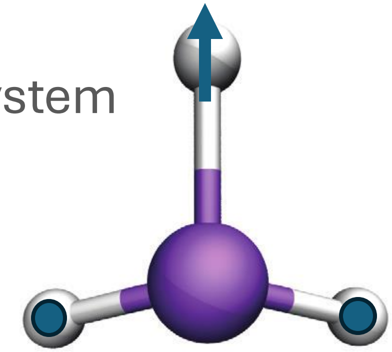

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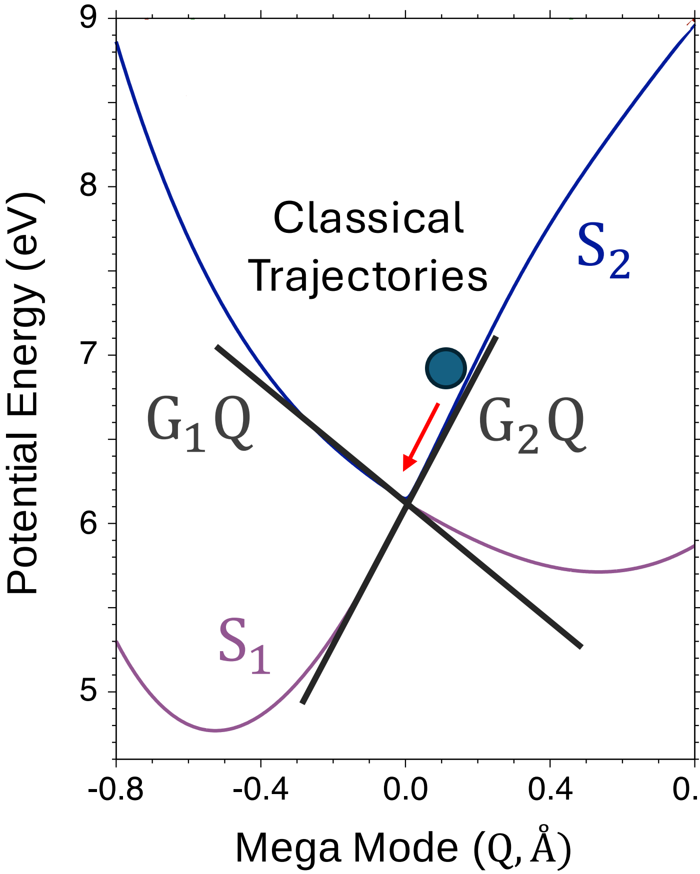

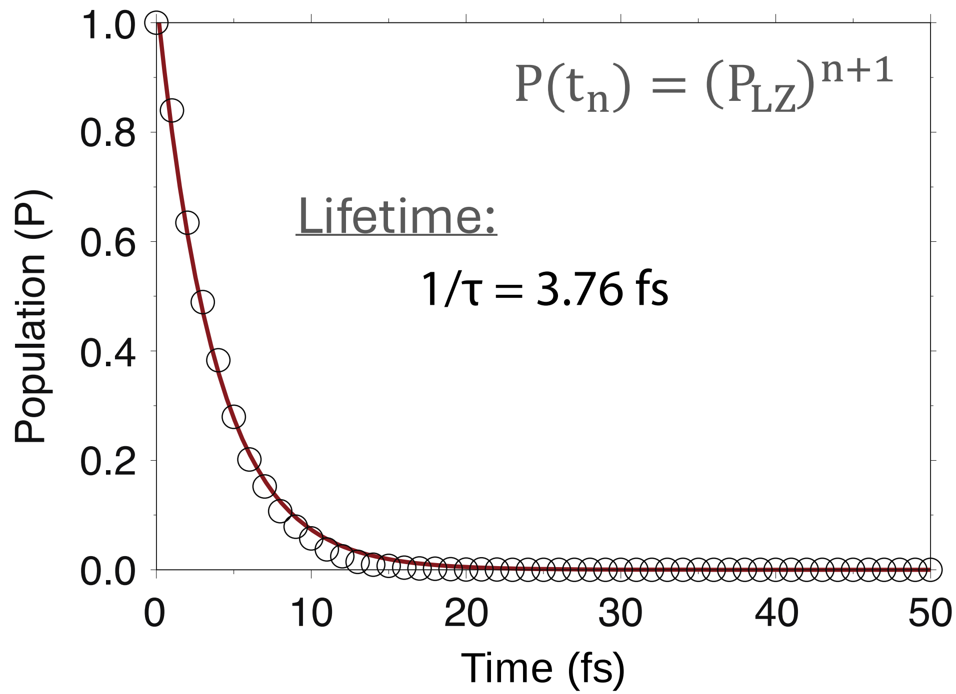

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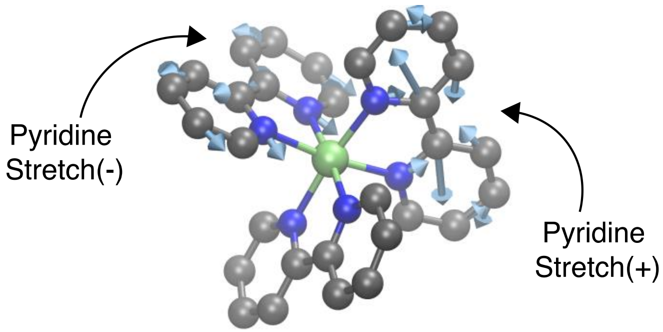
EOM-EE-CCSD/aug-cc-pVDZ

Solar Energy Catalyst

tris(2,2'-bipyridine)ruthenium(2+)



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B3LYP/def2-SVP-PP

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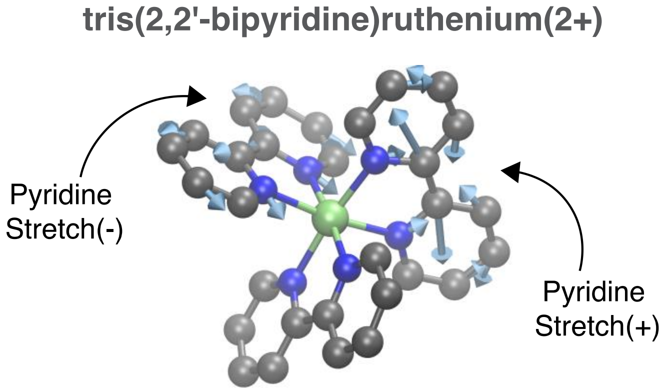

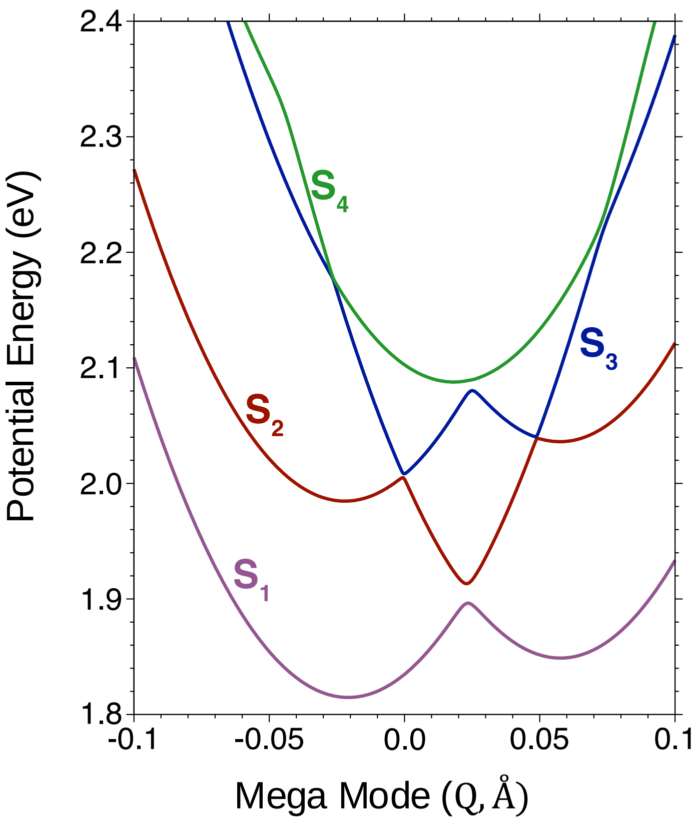

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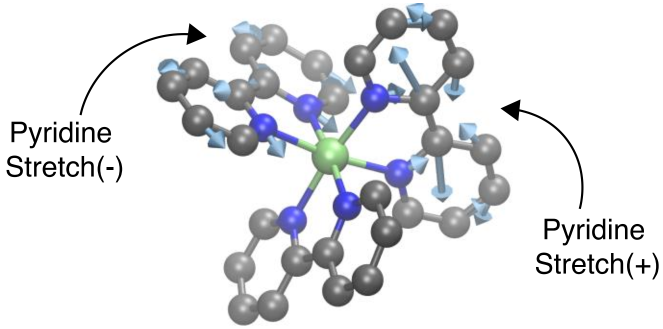

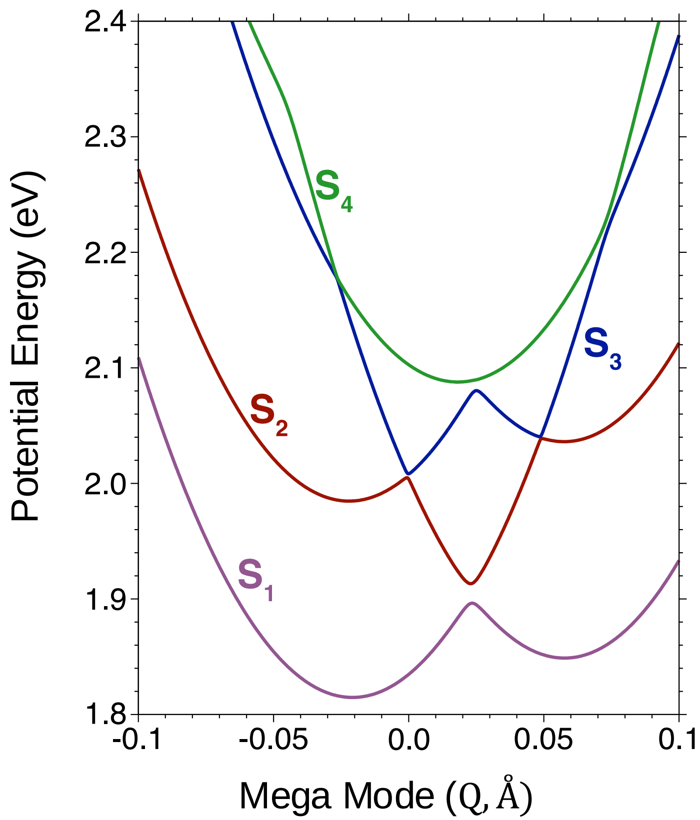

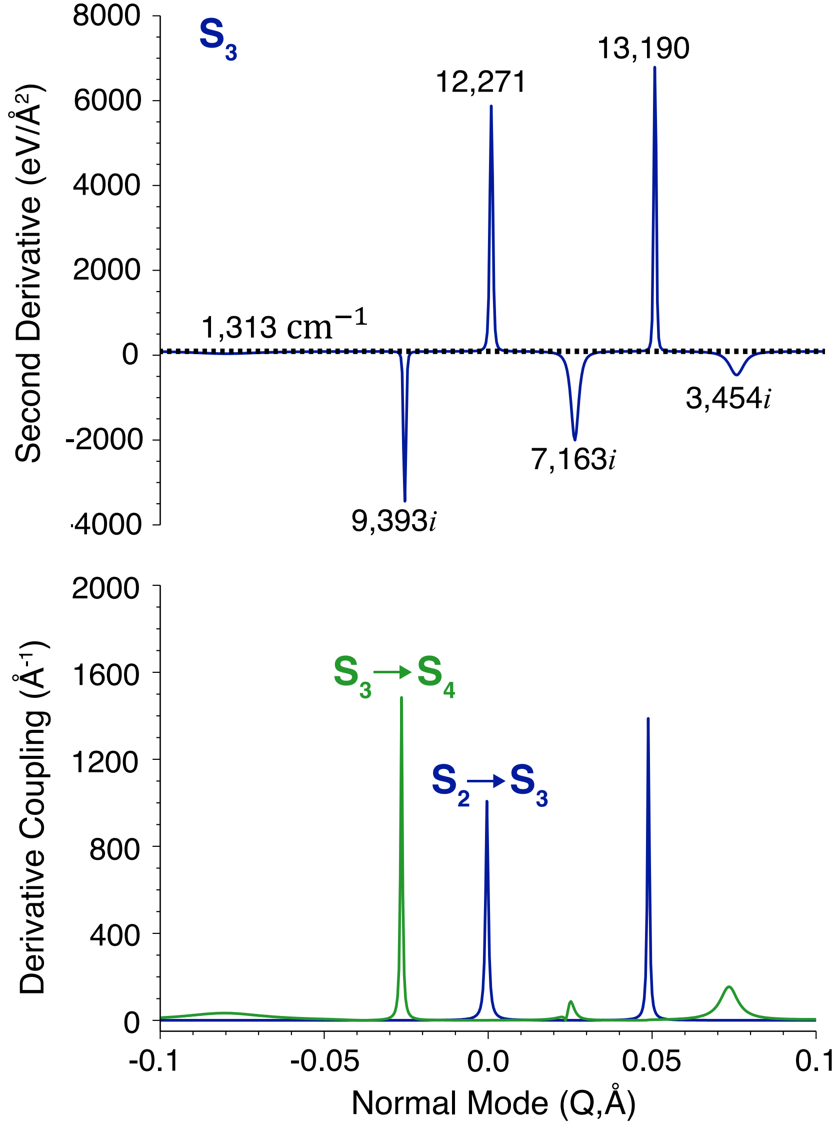

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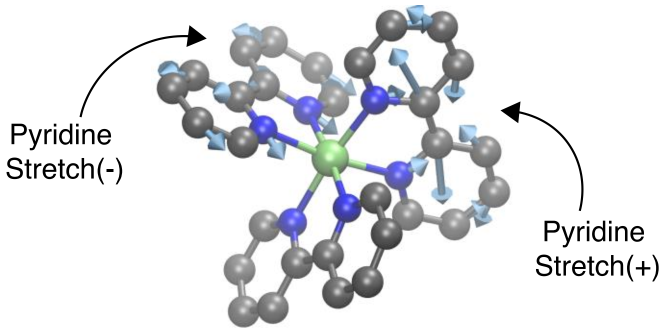

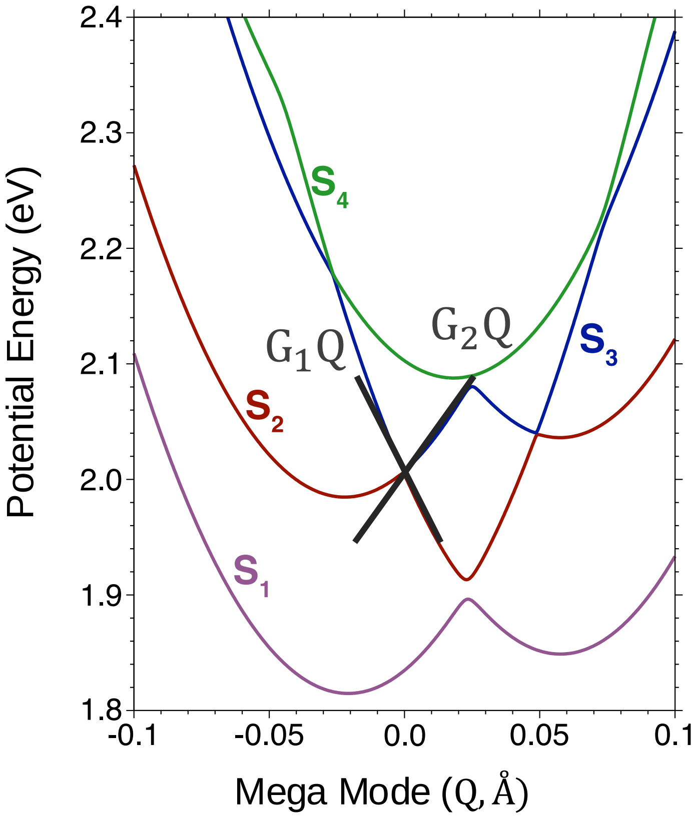

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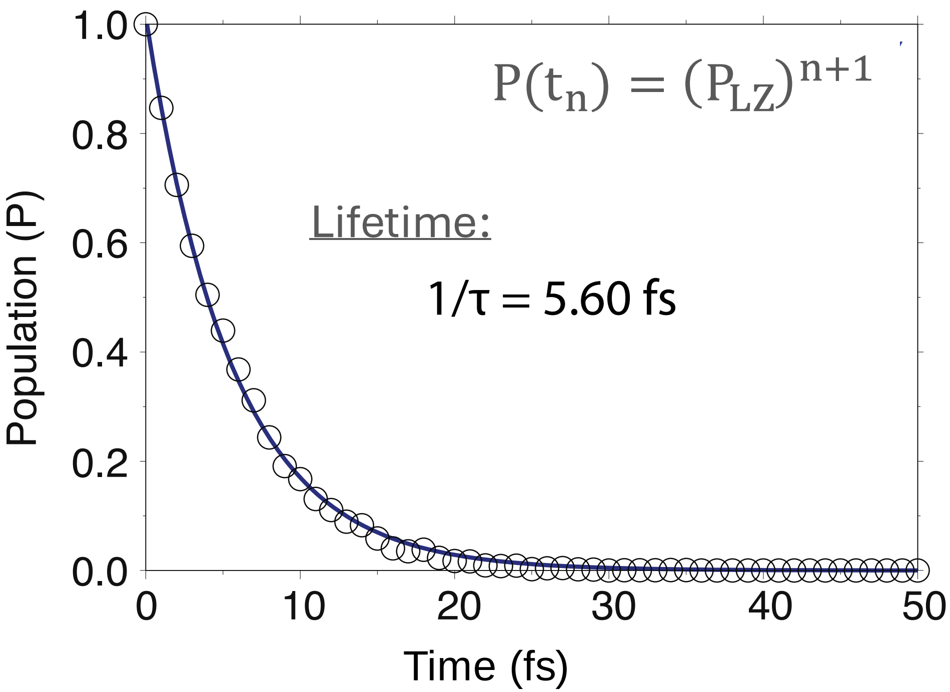

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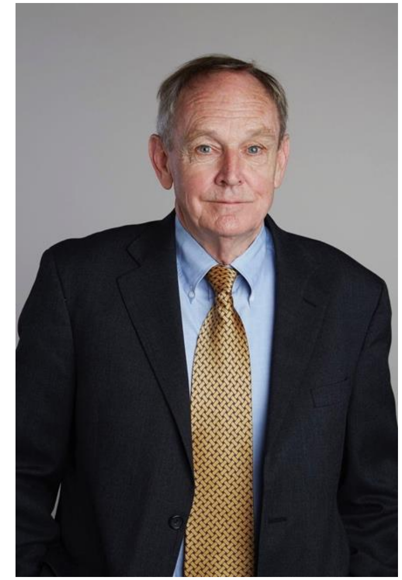
Acknowledgments

Martin Head-Gordon

Stephen J. Cotton

Bill Miller



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Juan E. Arias-Martinez
Sandia National Lab
"Fantastical Excited States"