國立交通大學
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Global switching trajectory surface hopping molecular dynamics simulation on on-the-fly TDDFT potential energy surfaces

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Virtual International Seminar on Theoretical Advancements

Outline

- Global switching algorithm
- Local switching via global switching
- TDDFT potential energy surfaces

1. dMe-OMe-NAIP photoisomerization (41 atoms)

2. Retinal chromophore isomer photoisomerization(63 atoms)

- Conclusions

Global switching algorithm

Mixed quantum-classical electronic coupled equations

$$i\hbar \frac{\partial \Psi(\mathbf{r},\mathbf{R},t)}{\partial t} = (T_N + H_e(\mathbf{r},\mathbf{R}))\Psi(\mathbf{r},\mathbf{R},t)$$

R is from classical trajectory

Nuclear kinetic operator

$$T_N = -\sum_{\alpha=1} \frac{\hbar^2}{2M_\alpha} \nabla^2_{\mathbf{R}_\alpha} = 0$$

Electronic basis expansion

$$\Psi(\mathbf{r},\mathbf{R},t) = \sum_j c_j(\mathbf{R},t)\Psi_j^{BO}(\mathbf{r},\mathbf{R})$$

Electronic time-dependent Schrödinger equations

$$i\hbar \dot{c}_k(t) = \sum_j c_j(t)\left[U_{kj}(\mathbf{R}) - i\hbar \dot{\mathbf{R}} \cdot \mathbf{d}_{kj}\right]$$

$$P_{2\to 1}(t) = \max\left(0, -\frac{\dot{\rho}_{22}(t)dt}{\rho_{22}(t)}\right)$$

Local switching (Tully fewest)

Mixed quantum-classical dynamics (Laudau-Zener model)

$T_N = 0$

$$\begin{pmatrix}\begin{bmatrix} V_{11}(\mathbf{R}) & V_{12}(\mathbf{R}) \\ V_{21}(\mathbf{R}) & V_{22}(\mathbf{R}) \end{bmatrix}\end{pmatrix}\begin{bmatrix} c_1(\mathbf{R}) \\ c_2(\mathbf{R}) \end{bmatrix} = i\hbar \frac{\partial}{\partial t}\begin{bmatrix} c_1(\mathbf{R}) \\ c_2(\mathbf{R}) \end{bmatrix}$$

Linear crossing model

$$V_{11}(x) = -F_1 x \quad V_{22}(x) = -F_2 x \quad V_{12}(x) = V_{21}(x) = V_0$$

Classical trajectory $x = vt$

Scattering matrix

$$\begin{pmatrix} c_1(\infty) \\ c_2(\infty) \end{pmatrix} = \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix}\begin{pmatrix} c_1(-\infty) \\ c_2(-\infty) \end{pmatrix}$$

$$S^R(dia)=\begin{pmatrix} \sqrt{p} & -\sqrt{1-p}e^{i\Phi} \\ \sqrt{1-p}e^{-i\Phi} & \sqrt{p} \end{pmatrix}$$

$$p = e^{-2\delta}$$

$$\delta = \frac{\pi}{8\sqrt{a^2 b^2}}$$

This is an exact solution under $T_N = 0$

Adiabatic switching probability

Nonadiabatic switching probability expressed in terms of

Two unitless parameters

$$a^2 = \frac{\hbar^2}{2\mu}\frac{\sqrt{|F_1F_2|}(|F_2 - F_1|)}{8V_0^3} \longrightarrow \textbf{Effective coupling}$$

$$b^2 = (E_{//} - E_0)\frac{(|F_2 - F_1|)}{2\sqrt{|F_1F_2|}V_0} \longrightarrow \textbf{Effective collision energy}$$

M. S. Child, Molecular Collision Theory (Academic, London, New York, 1974)

Semiclassical solution in time-independent framework

Coupled Schrödinger equation

$$T_N \neq 0 \qquad \left(-\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2}+\begin{bmatrix} V_{11}(R) & V_{12}(R) \\ V_{12}(R) & V_{22}(R)\end{bmatrix}\right)\begin{bmatrix} c_1(R) \\ c_2(R)\end{bmatrix} = E\begin{bmatrix} c_1(R) \\ c_2(R)\end{bmatrix}$$

$$p = \exp\left[-\frac{\pi}{4a}\left(\frac{2}{b^2+\sqrt{b^4 \pm 1}}\right)^{1/2}\right] \xrightarrow{b^2 >> 1} p = \exp\left[-\frac{\pi}{4ab}\right]$$

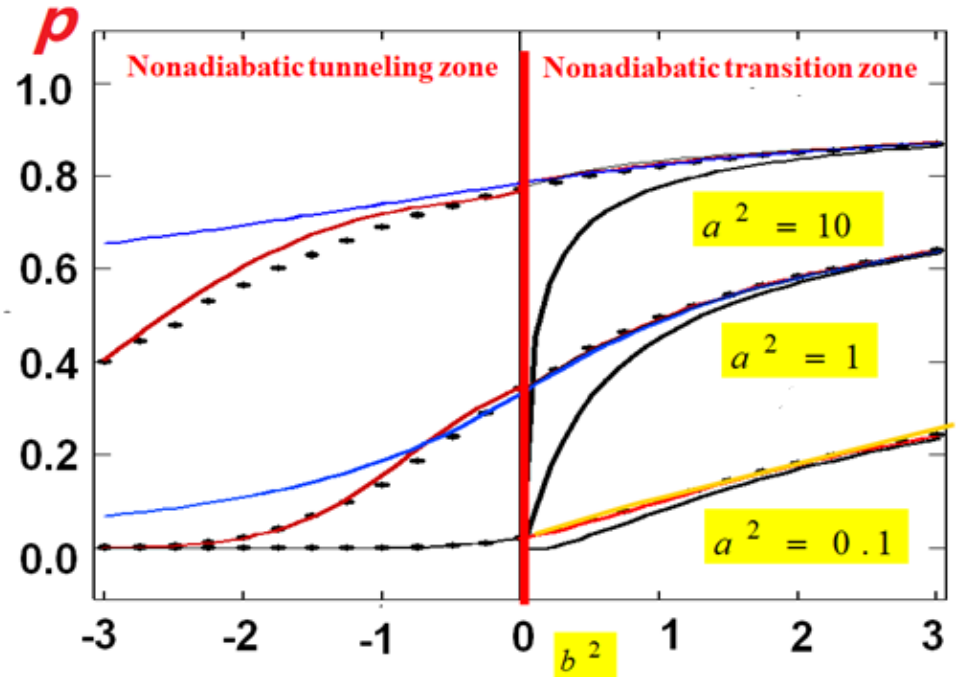
Zhu-Nakamura (work at Ex) **Landau-Zener (not work at Ex)**

C. Zhu and H. Nakamura, J. Chem. Phys. 101, 10630 (1994); 102, 7448(1995)

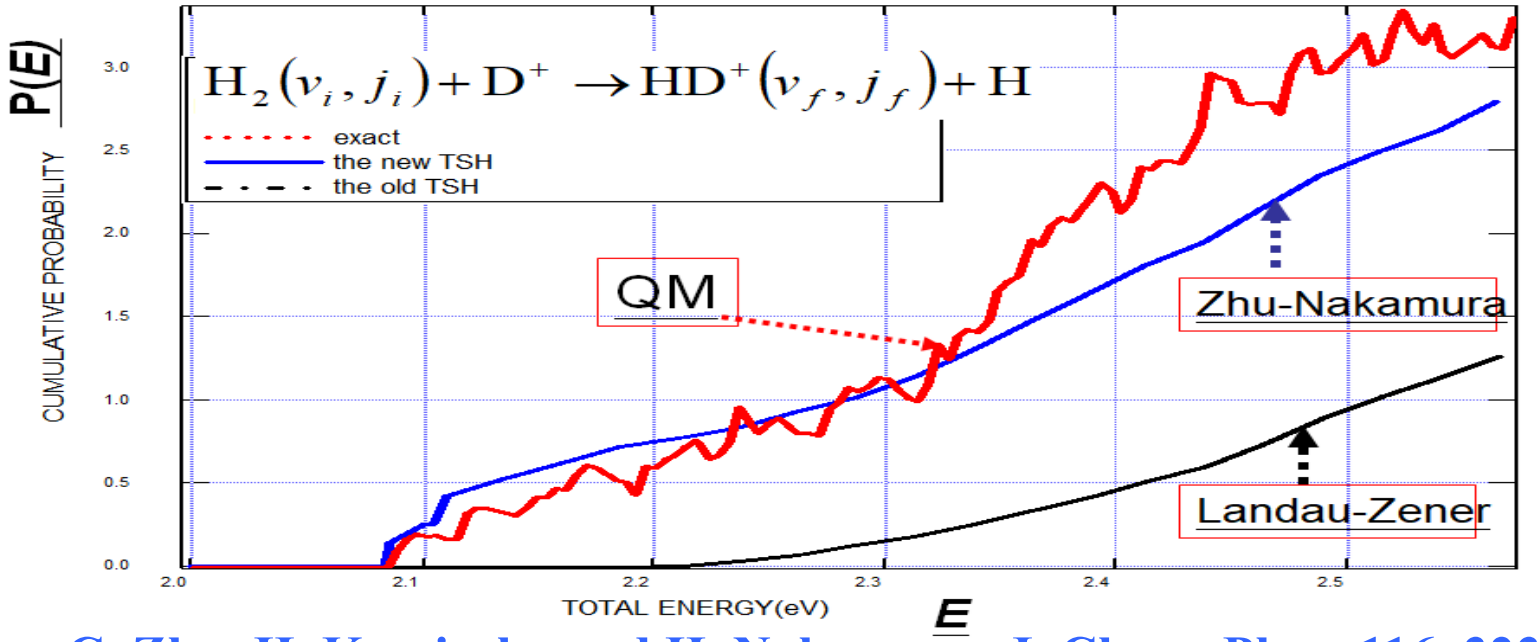
Exact

Zhu-Nakamura

Landau-Zener



Reactive charge transfer



C. Zhu, H. Kamisaka and H. Nakamura, J. Chem. Phys. 116, 3234 (2002)

Re-expressed in terms of Cartesian coordinates $\mathbf{R}_1 \quad \mathbf{R}_2$

For diatom

$$\frac{|F_2 - F_1|}{\sqrt{\mu}} = \sqrt{\sum_{i=1}^{N=2} \frac{1}{m_i} \sum_{\alpha=x,y,z} \left(F_2^{i\alpha} - F_1^{i\alpha}\right)^2}$$

$$\frac{\sqrt{|F_2 F_1|}}{\sqrt{\mu}} = \sqrt{\left|\sum_{i=1}^{N=2} \frac{1}{m_i} \sum_{\alpha=x,y,z} F_2^{i\alpha} F_1^{i\alpha}\right|}$$

$$a^2 = \frac{\hbar^2}{2\mu} \frac{\sqrt{|F_1 F_2|}(|F_2 - F_1|)}{8V_0^3}$$

$$b^2 = (E_{//} - E_0) \frac{(|F_2 - F_1|)}{2\sqrt{|F_1 F_2|}V_0}$$

$$F_1^{i\alpha} = -\frac{\partial V_1}{\partial R_{i\alpha}} \qquad F_2^{i\alpha} = -\frac{\partial V_2}{\partial R_{i\alpha}}$$

Directly extending to multi-dimensional for N atoms

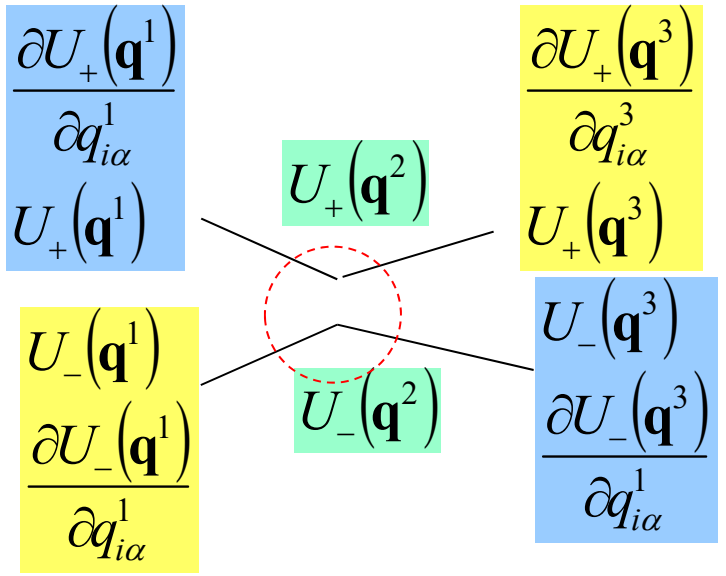
$$2 \rightarrow N$$

Multi-dimensional forces along a trajectory at avoided crossing

Linear connection for each i-component

$$R \rightarrow \mathbf{q}$$

$$\mathbf{q} \equiv (q_1, q_2, \cdots, q_N)$$



$$F_1^{i\alpha}(\mathbf{q}) = \frac{1}{q^3_{i\alpha} - q^1_{i\alpha}} \left[\frac{\partial U_-}{\partial q^3_{i\alpha}} \left(q_{i\alpha} - q^1_{i\alpha} \right) - \frac{\partial U_+}{\partial q^1_{i\alpha}} \left(q_{i\alpha} - q^3_{i\alpha} \right) \right]$$

$$F_2^{i\alpha}(\mathbf{q}) = \frac{1}{q^3_{i\alpha} - q^1_{i\alpha}} \left[\frac{\partial U_+}{\partial q^3_{i\alpha}} \left(q_{i\alpha} - q^1_{i\alpha} \right) - \frac{\partial U_-}{\partial q^1_{i\alpha}} \left(q_{i\alpha} - q^3_{i\alpha} \right) \right]$$

Linear diabatization along a trajectory at avoided crossing

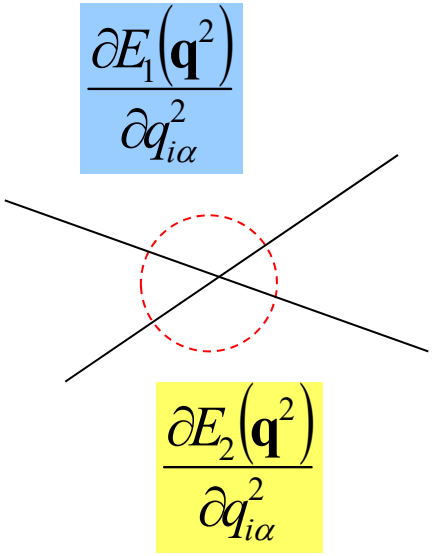
Between different spin states

Linear connection for each i-component

$$\mathbf{q} \equiv (\mathbf{q}_1, \mathbf{q}_2, \cdots, \mathbf{q}_N)$$

$$F_1^{i\alpha}(\mathbf{q}) = \frac{\partial E_1(\mathbf{q}^2)}{\partial q_{i\alpha}^2}$$

$$F_2^{i\alpha}(\mathbf{q}) = \frac{\partial E_2(\mathbf{q}^2)}{\partial q_{i\alpha}^2}$$



Directly given for different spin states

Define hopping direction

$$s_{i\alpha} = \left[F_2^{i\alpha}\left(\mathbf{q}^2\right) - F_1^{i\alpha}\left(\mathbf{q}^2\right)\right]\frac{1}{\sqrt{m_i}}$$

Normalization

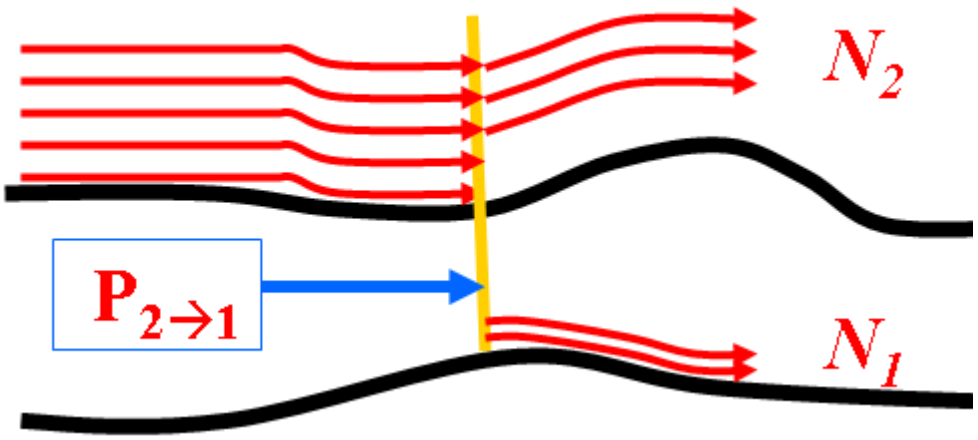
$$\sum_{\alpha=1}^{N}\dot{\mathbf{R}}_\alpha \cdot \mathbf{d}_{12}^{\alpha} \leftarrow \mathbf{n}_i$$

$$\mathbf{n}_i = \frac{1}{\sqrt{s_{ix}^2 + s_{iy}^2 + s_{iz}^2}}\left(s_{ix}, s_{iy}, s_{iz}\right)$$

$$\mathbf{n}_i^2 = 1$$

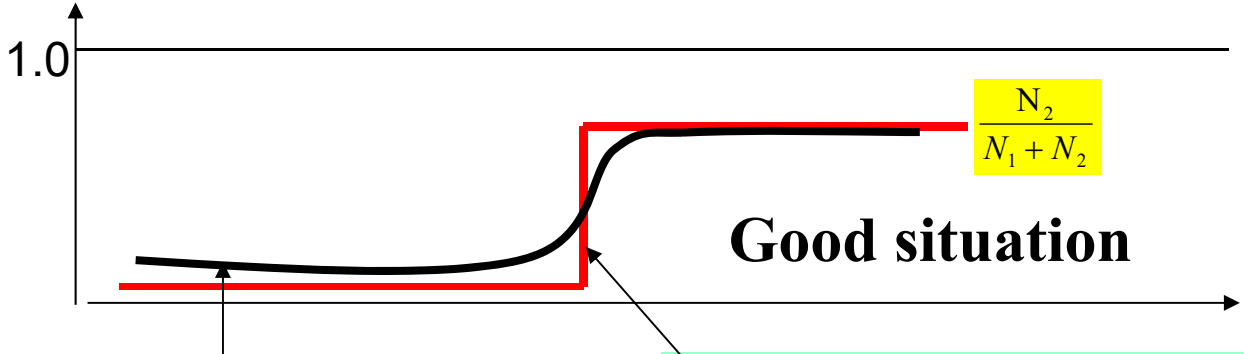
Provide the maximum switching probability at avoided crossing

Trajectory surface hopping



Nonadiabatic switching probability

Population distribution



$$P_{2\to1}(t) = \max\left(0, \; -\frac{\dot{\rho}_{22}(t)dt}{\rho_{22}(t)}\right)$$

$$p_{ZN} = \exp\left[-\frac{\pi}{4a}\left(\frac{2}{b^2+\sqrt{b^4\pm1}}\right)^{1/2}\right]$$

Local switching (Tully fewest)

$T_N = 0$

Global switching (ZN formula)

$T_N \neq 0$

Global nonadiabatic switching algorithm

Only need

Potential energy surfaces **Gradient of potential energy surfaces**

$$U_+(\mathbf{R}) = U_+(q_1, q_2, \cdots, q_{3N})$$
$$U_-(\mathbf{R}) = U_-(q_1, q_2, \cdots, q_{3N})$$

$$\left(\frac{\partial U_+(\mathbf{q})}{\partial q_i}\right) \qquad \left(\frac{\partial U_-(\mathbf{q})}{\partial q_i}\right)$$

Run nonadiabatic molecular dynamics simulation

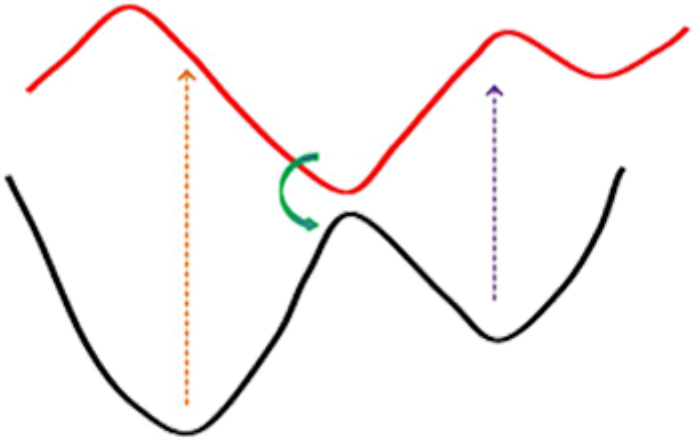
Searching conical intersections

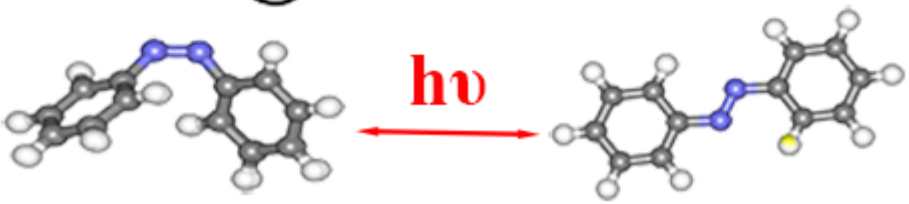
L. Yu, C. Xu, Y. Lei, C. Zhu, and Z. Wen, PCCP 16, 25883 (2014)

Local switching via global switching

Azobenzene photoisomerization

n→π* excitation



Cis  Trans

Cis-to-trans and trans-to-cis

Summary:

Exactly same initial conditions and the same

Potential energy surfaces: OM2/MR-CISD(10,10)

Sampling trajectories:

Starting from cis-azobenzene(800)

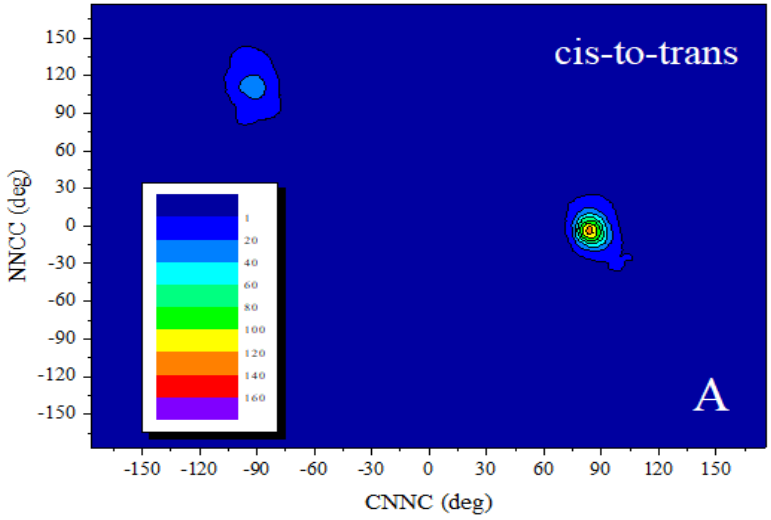
Starting from trans-azobenzene(600),

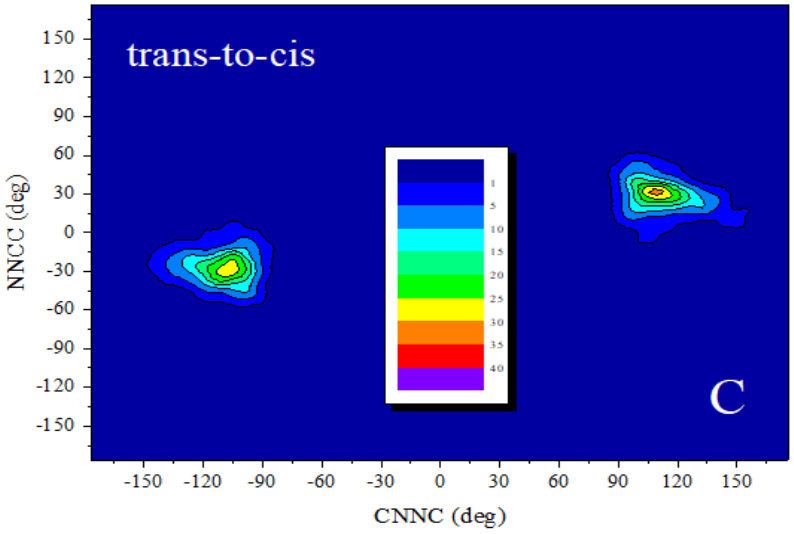
Time step for trajectory propagation is 0.1fs.

	Quantum yield	lifetimes
Cis-to-trans	**Global: 0.57** **Local : 0.58**	**Global: 72fs** **Local : 82fs**
Trans-to-cis	**Global: 0.16** **Local : 0.20**	**Global: 280fs** **Local : 310fs**

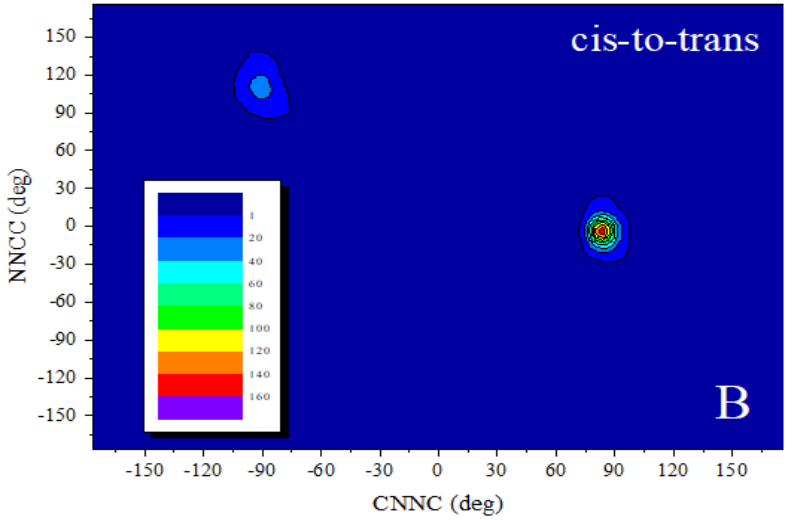
Hopping spot distributions in terms of CNNC dihedral angle

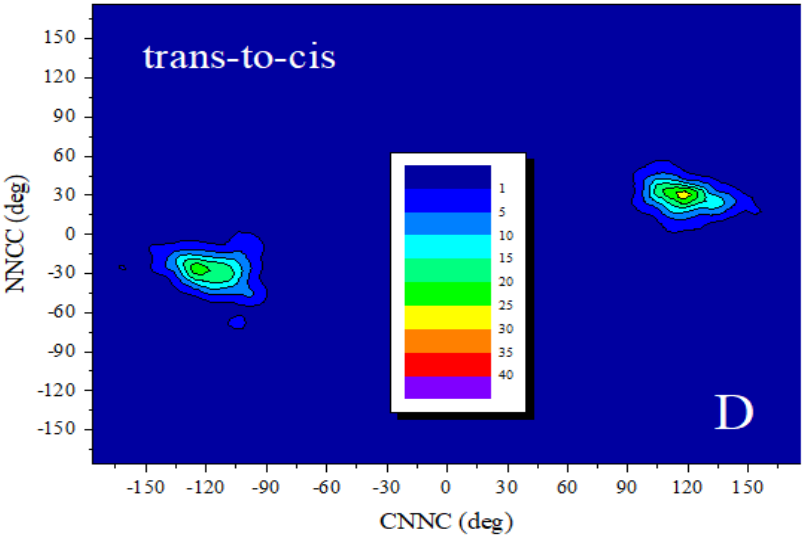
Local





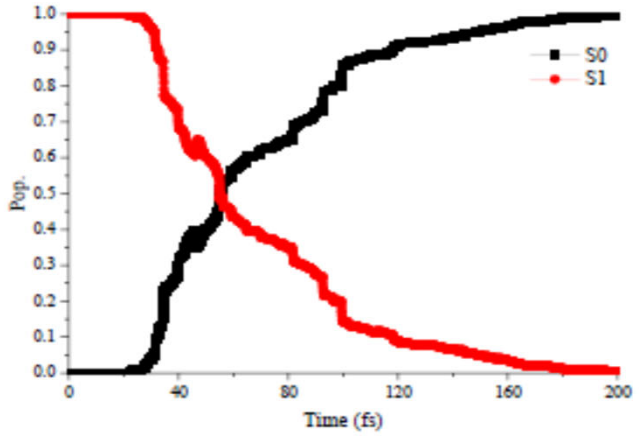
Global



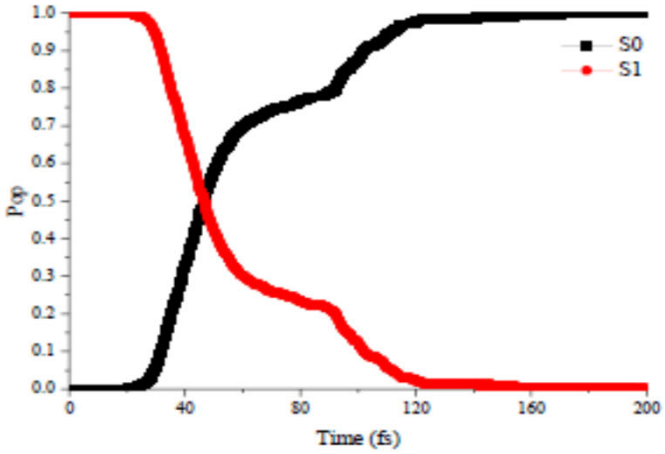


Average population distributions as function of time

Local

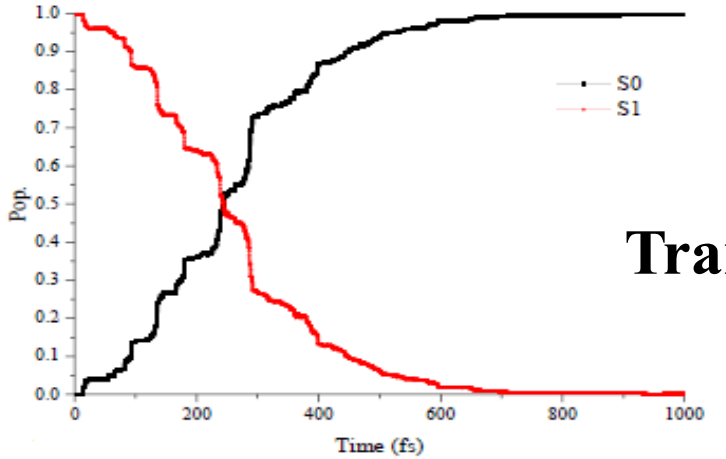


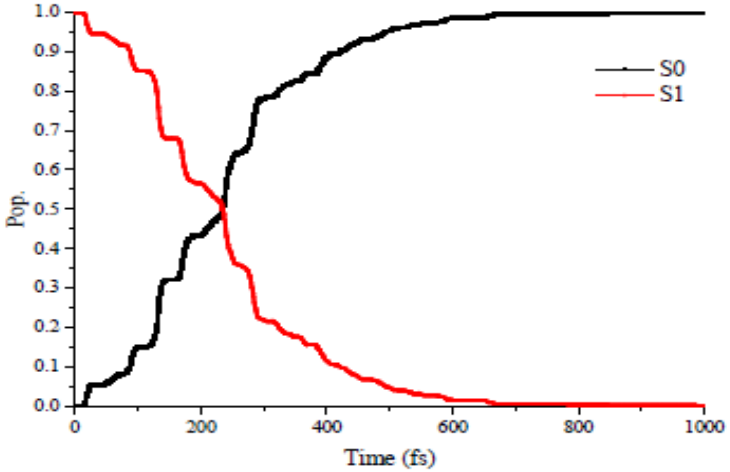
Global



Cis-to-trans

Trans-to-cis





Local switching (Tully fewest)

$$P_{2\to 1}(t) = \max\left(0, -\frac{\dot{\rho}_{22}(t)dt}{\rho_{22}(t)}\right)$$

Global switching)

$$p_{ZN} = \exp\left[-\frac{\pi}{4a}\left(\frac{2}{b^2+\sqrt{b^4\pm 1}}\right)^{1/2}\right]$$

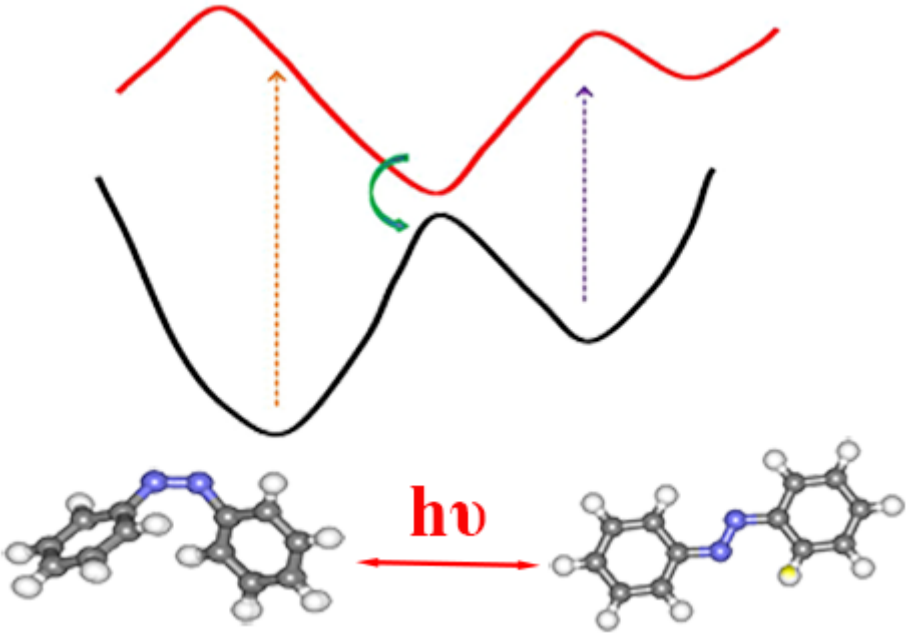
Equally good

L. Yue, L. Yu, C. Xu,Y. Lei, Y. Liu, C. Zhu, ChemPhysChem 18,1274 (2017)

TDDFT potential energy surfaces

Azobenzene photoisomerization

$n \rightarrow \pi^*$ excitation



Cis-to-trans and trans-to-cis

Comparison among SF-TDDFT, TDDFT, CASSCF

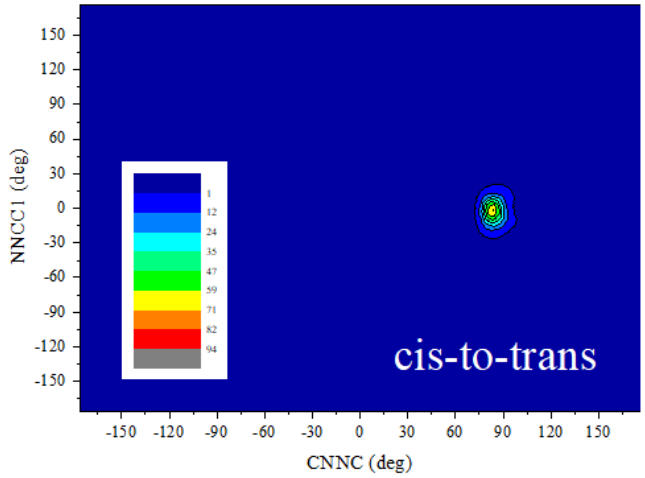
Method	N_{traj} (cis/trans)	cis- to-trans		trans-to-cis	
		QY	Lifetime(fs)	QY	Lifetime(ps)
SF-TDDFT	300/226	0.43±0.07	63.1±1.1	0.11~0.16	2.218±0.010
LR-TDDFT	259/268	0.34±0.09	62.0±0.9	0.13±0.16	1.039±0.009
SA2-CASSCF(6,6)	800/600	0.39±0.04	53.1±3.0	0.33±0.05	0.81±0.10

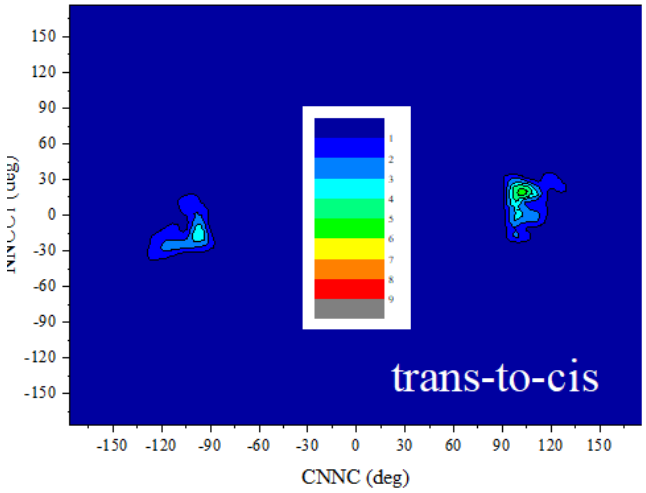
Quantum yield and lifetime all from global switching

L. Yue, Y. Liu and C. Zhu, PCCP 20, 24123 (2018)

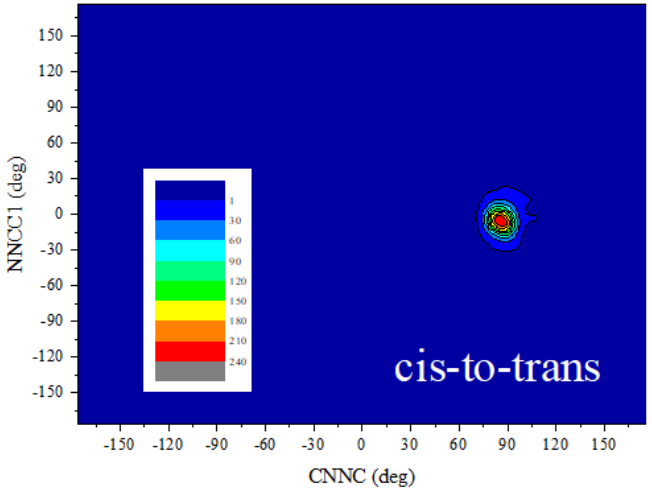
Hopping spot distributions in terms of CNNC dihedral angle

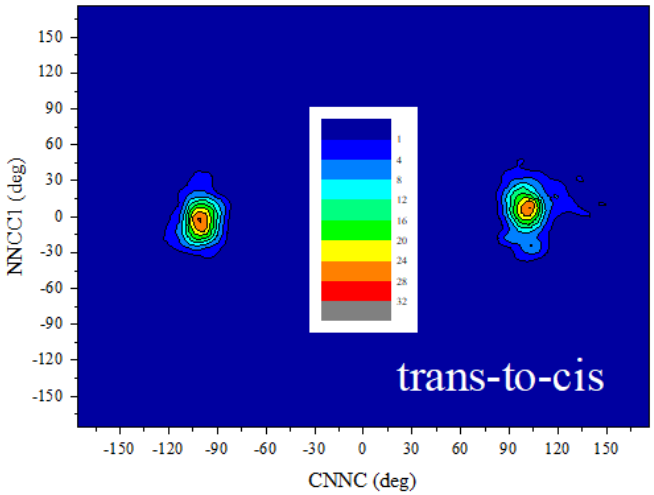
SF-TDDFT





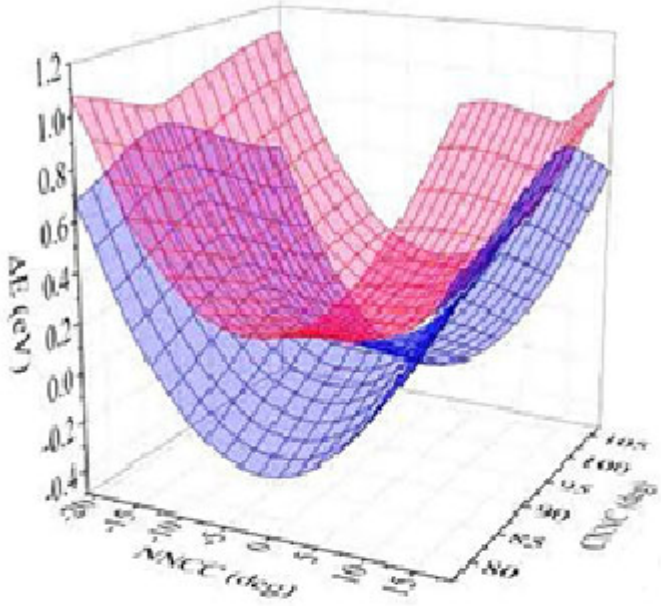
LR-TDDFT



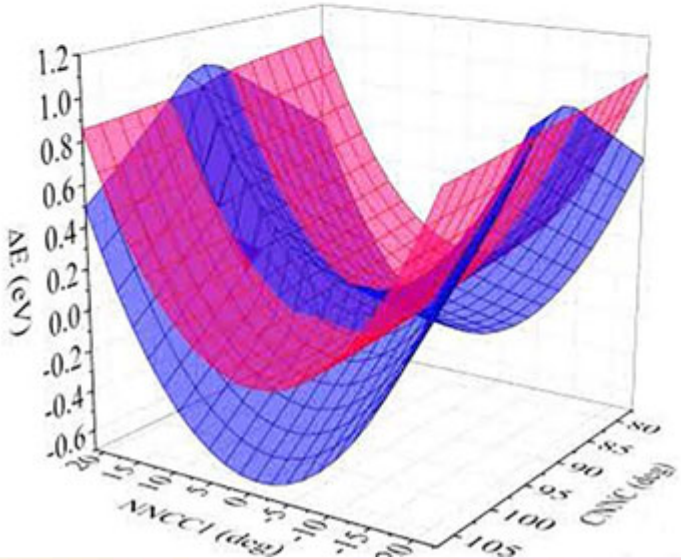


Conical intersections In SF-TDDFT and TDDFT

SF-TDDFT: Correctly single-cone structure

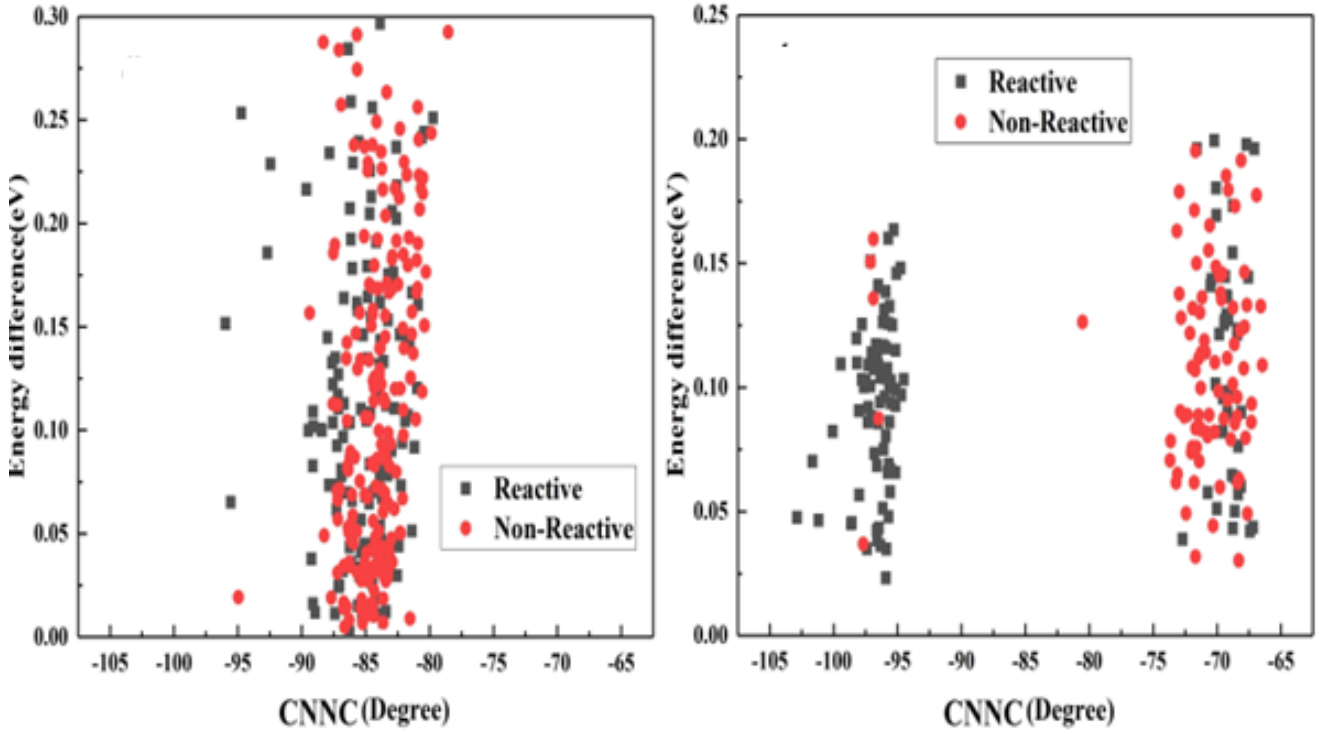


TDDFT: Artificial double-cone structure



The negative excitation energy around CI

Hopping spot distribution in terms of energy gap



SF-TDDFT **TDDFT**

Functional and basis set dependence of TDDFT

TDDFT (Gaussian 16) Dynamics (Our own code)

QY(lifetime)	B3lyp	BHandHLYP	CAM-B3LYP
3-21g	0.51 (35.3)	0.21(36.4)	0.10(36.8)
6-31g	0.57 (37.3)	0.40(36.8)	0.40(37.3)
6-31g(d)	0.63 (47)	0.59(34.6)	0.49(34.4)
cc-pvdz	0.60(37.2)	0.52(34.4)	0.42(33.9)

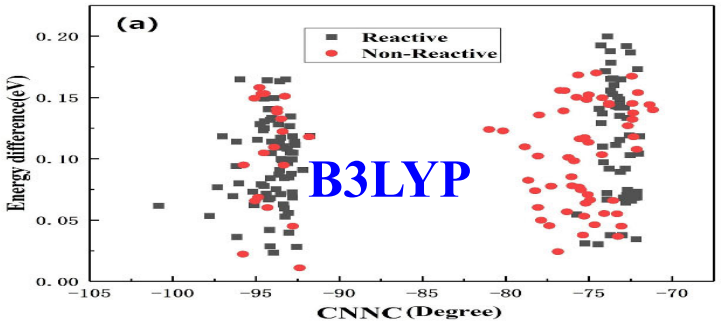
Average	quantum yield	lifetime
B3LYP	0.6 (±5%)	40.5fs (±10%)
BHandHLY	0.5 (±10%)	35.5fs (±4%)
CAM-B3LYP	0.44 (±9%)	35.2fs (±10%)

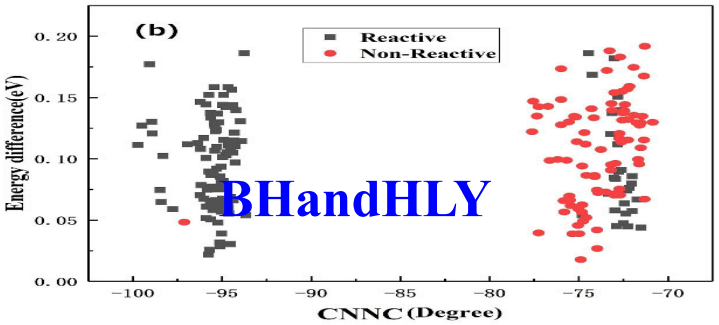
Cis-to-trans

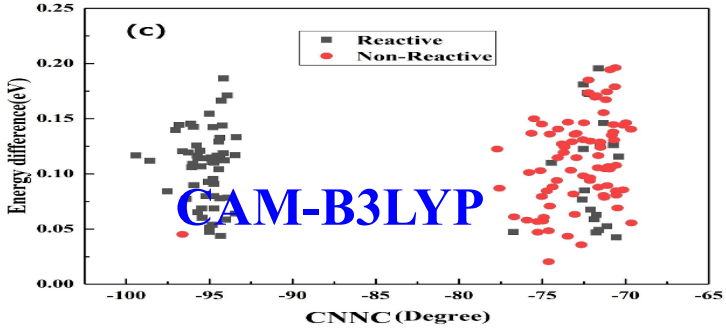
L. Ye, C. Xu, F. L. Gu and C. Zhu, J. Comput. Chem. 41,635 (2020)

The hopping spot distributions for energy gap

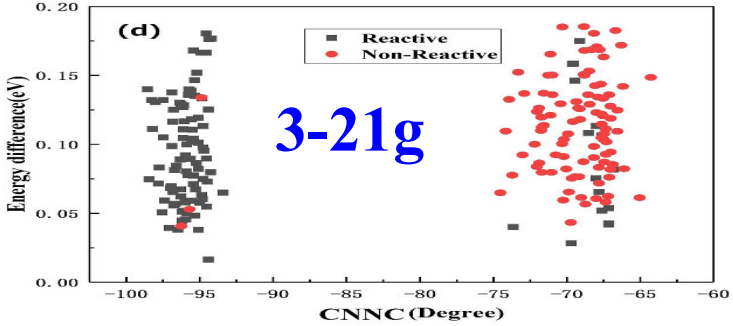
The same 6-31g(d)

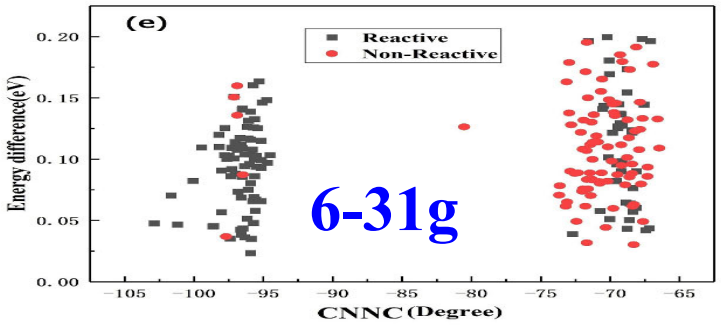


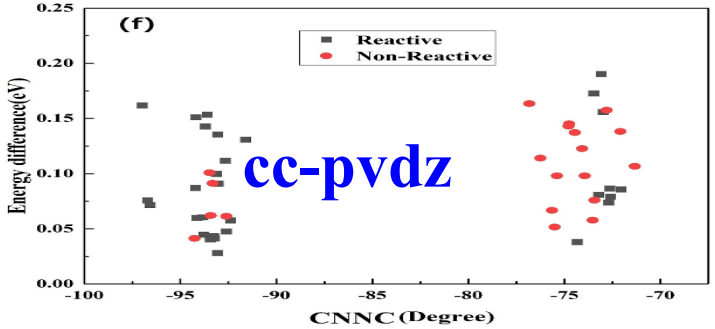




The same B3LYP

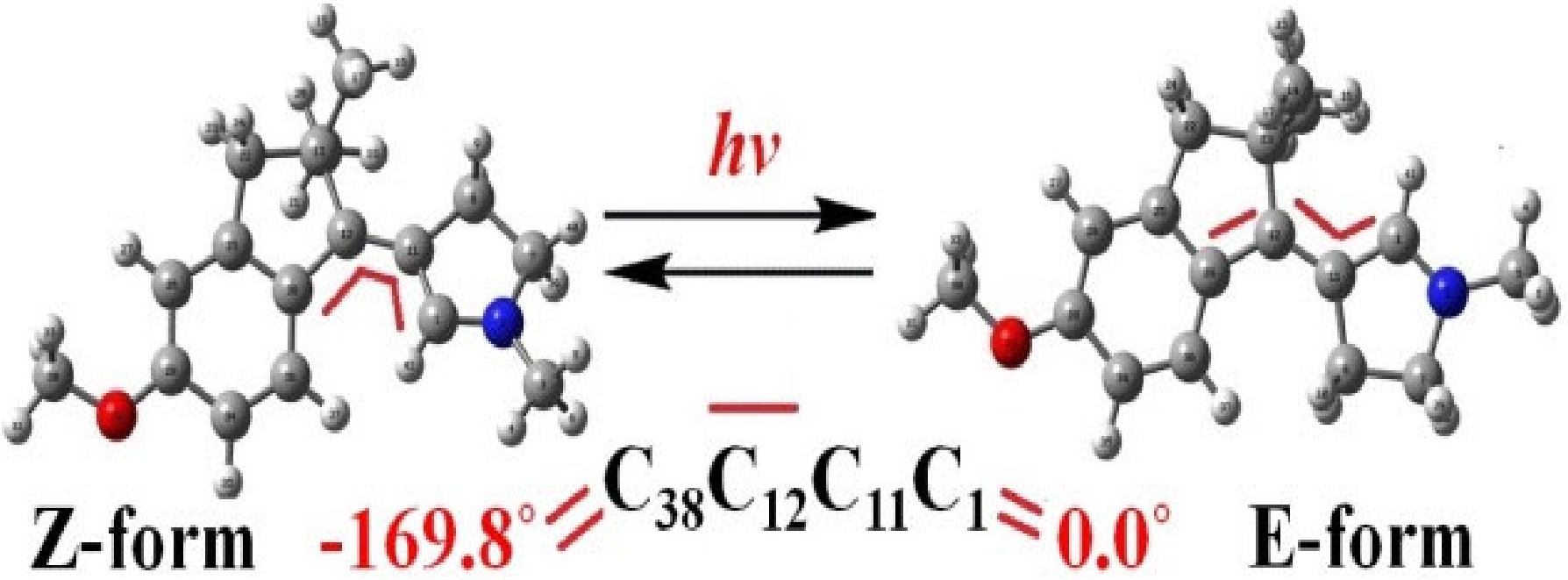






L. Ye, C. Xu, F. L. Gu and C. Zhu, J. Comput. Chem. 41,635 (2020)

1.dMe-OMe-NAIP photoisomerization



Photoisomerization of dMe-OMe-NAIP (41 atoms)

- Too big for applying CSSCF method
- Not work with semiempirical method
- The first time with TDDFT

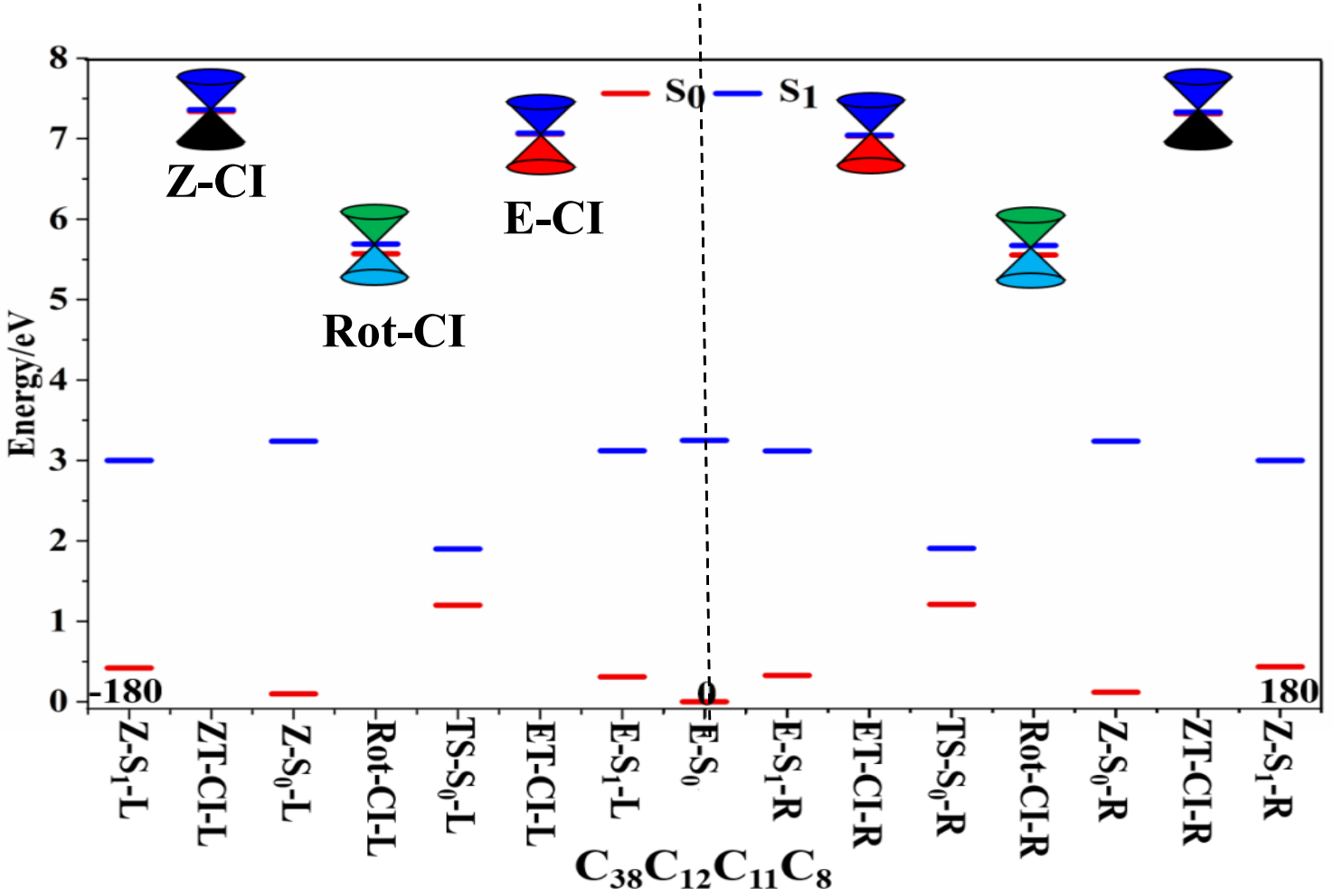
Unique choice for TDDFT method

All hopping points are well behaviors,

No problem at all for CI between S0 and S1

TD-B3LYP/6-31G*

Potential energy surface profiles



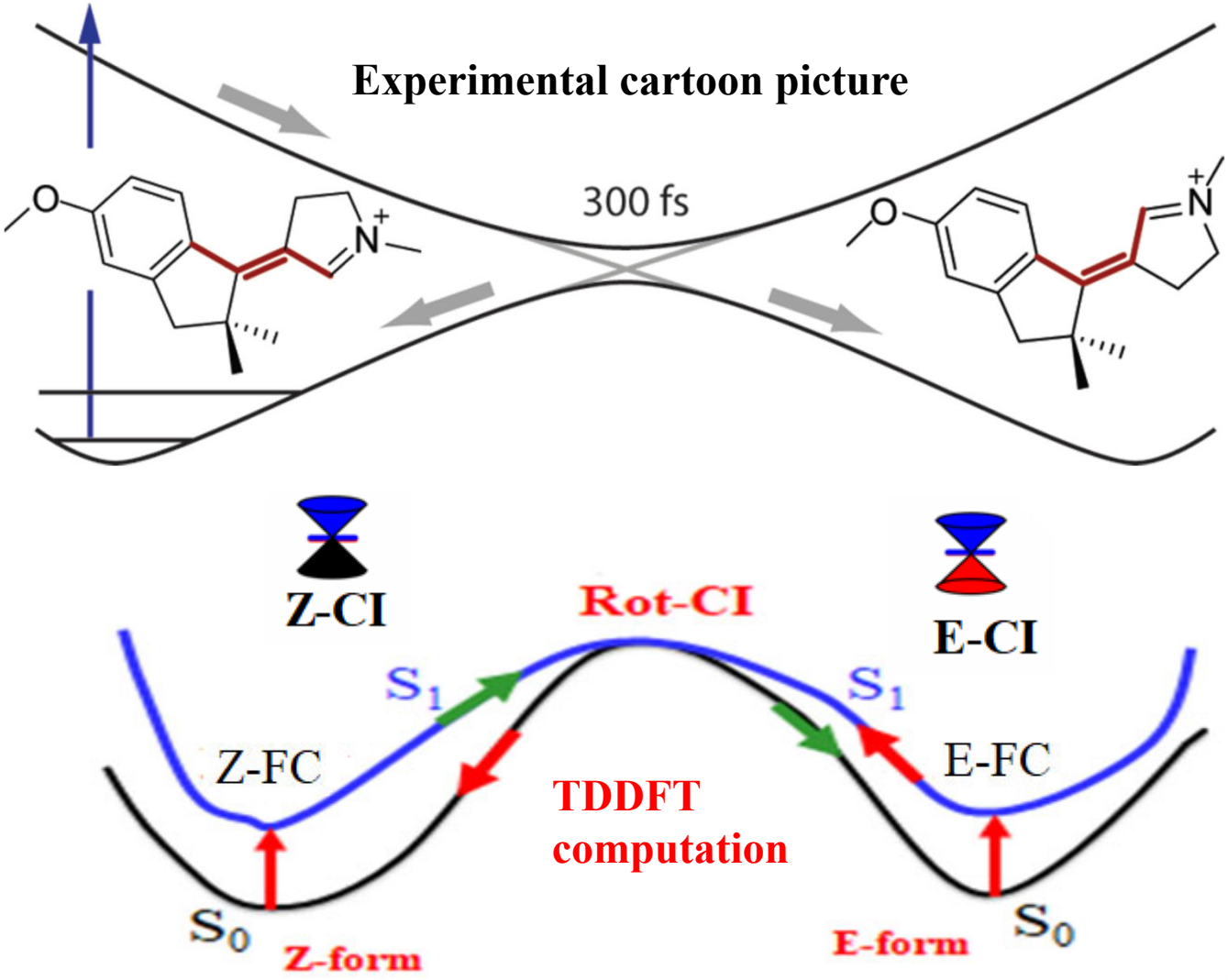
Simulation results

From E-isomer		
Quantum yield		Lifetime (fs)
0.23	Theory	620
0.25	Exp	~480
0.26	Exp	~480

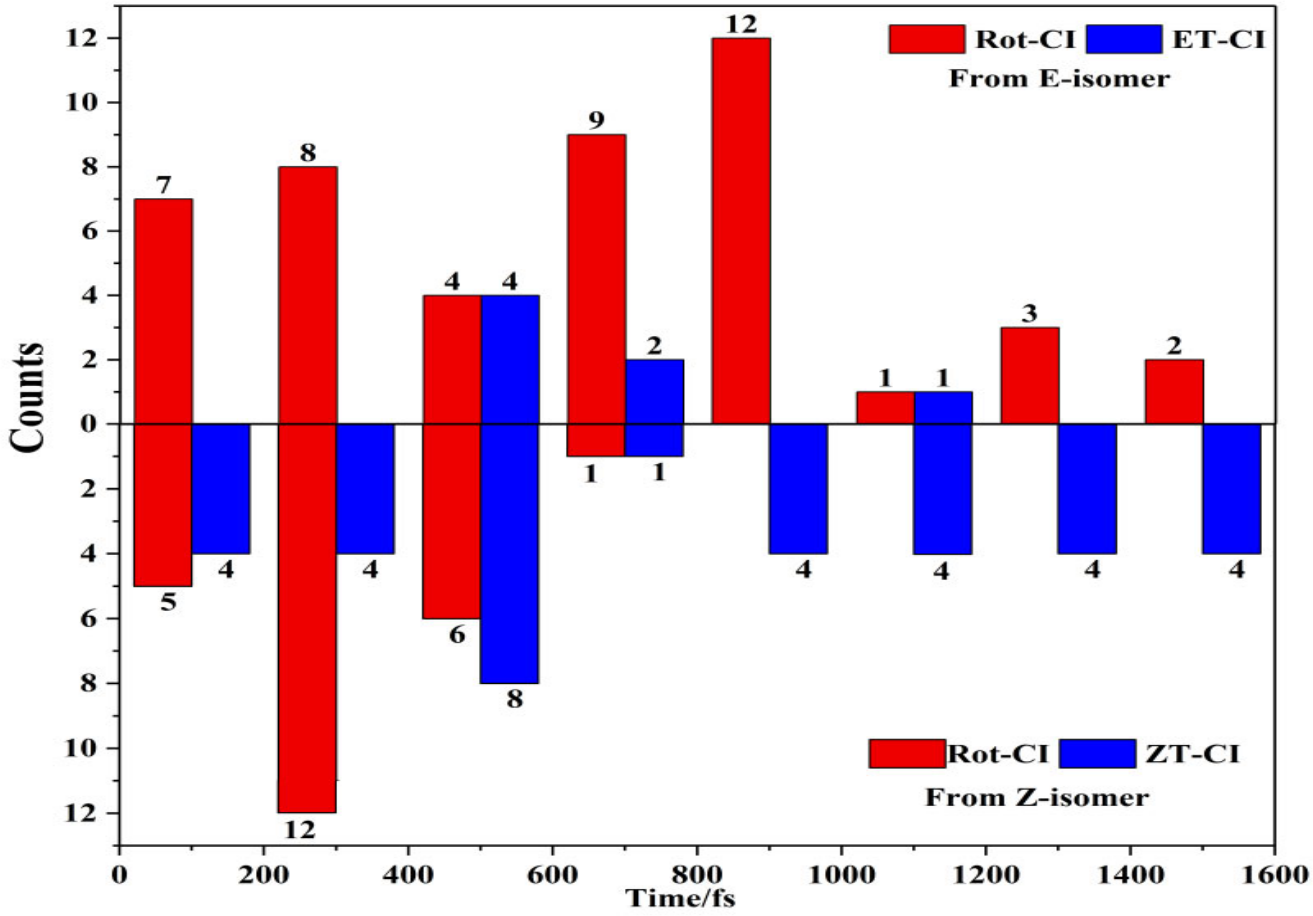
From Z-isomer		
Quantum yield		Lifetime (fs)
0.15	Theory	600
0.24	Exp	430

Y. Hu, C. Xu, L. Ye, F. Gu and C. Zhu, Phys. Chem. Chem. Phys., 23, 5236 (2021)

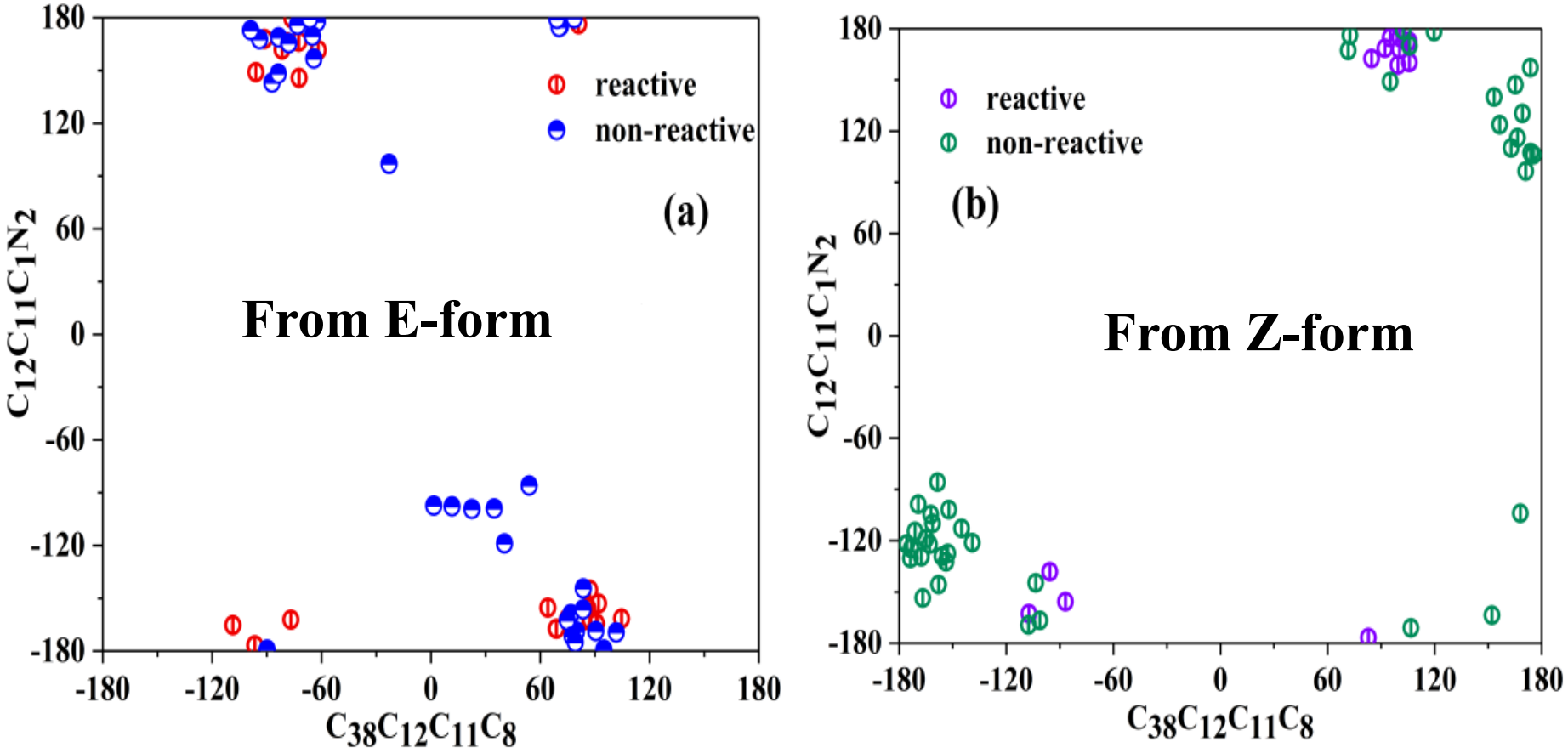
Photoisomerization mechanism from conical intersection



The number of hopping trajectories via CIs as function of time

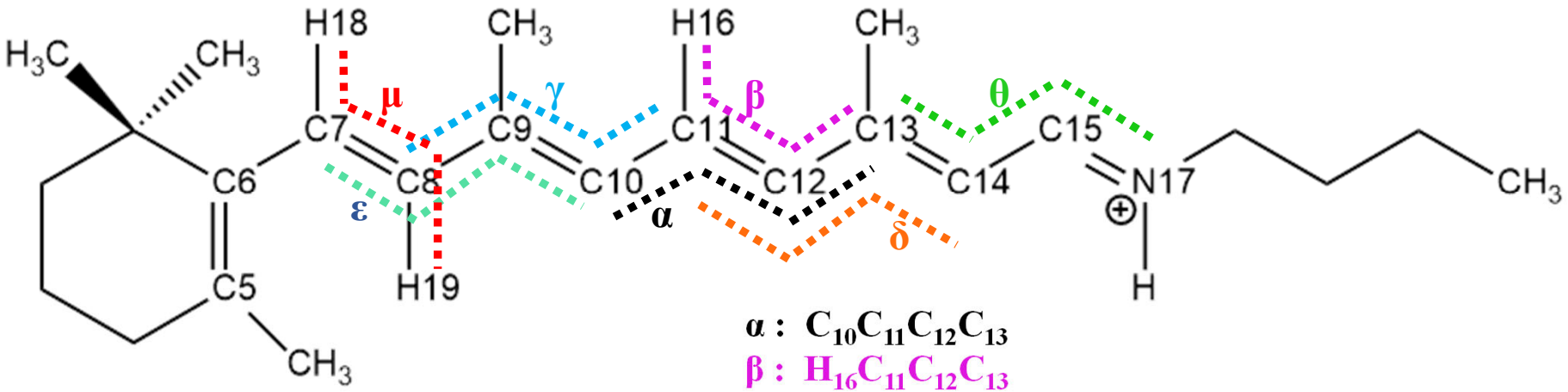


Hopping spot distributions in terms of CCCC and CCCN



No problem at all hopping points between S0 and S1

2.Retinal chromophore isomer photoisomerization



α : $C_{10}C_{11}C_{12}C_{13}$
β : $H_{16}C_{11}C_{12}C_{13}$
γ : $C_8C_9C_{10}C_{11}$
δ : $C_{11}C_{12}C_{13}C_{14}$
ε : $C_7C_8C_9C_{10}$
θ : $C_{13}C_{14}C_{15}N_{17}$
μ : $H_{18}C_7C_8H_{19}$

Photoisomerization of retinal chromophore isomer (63atoms

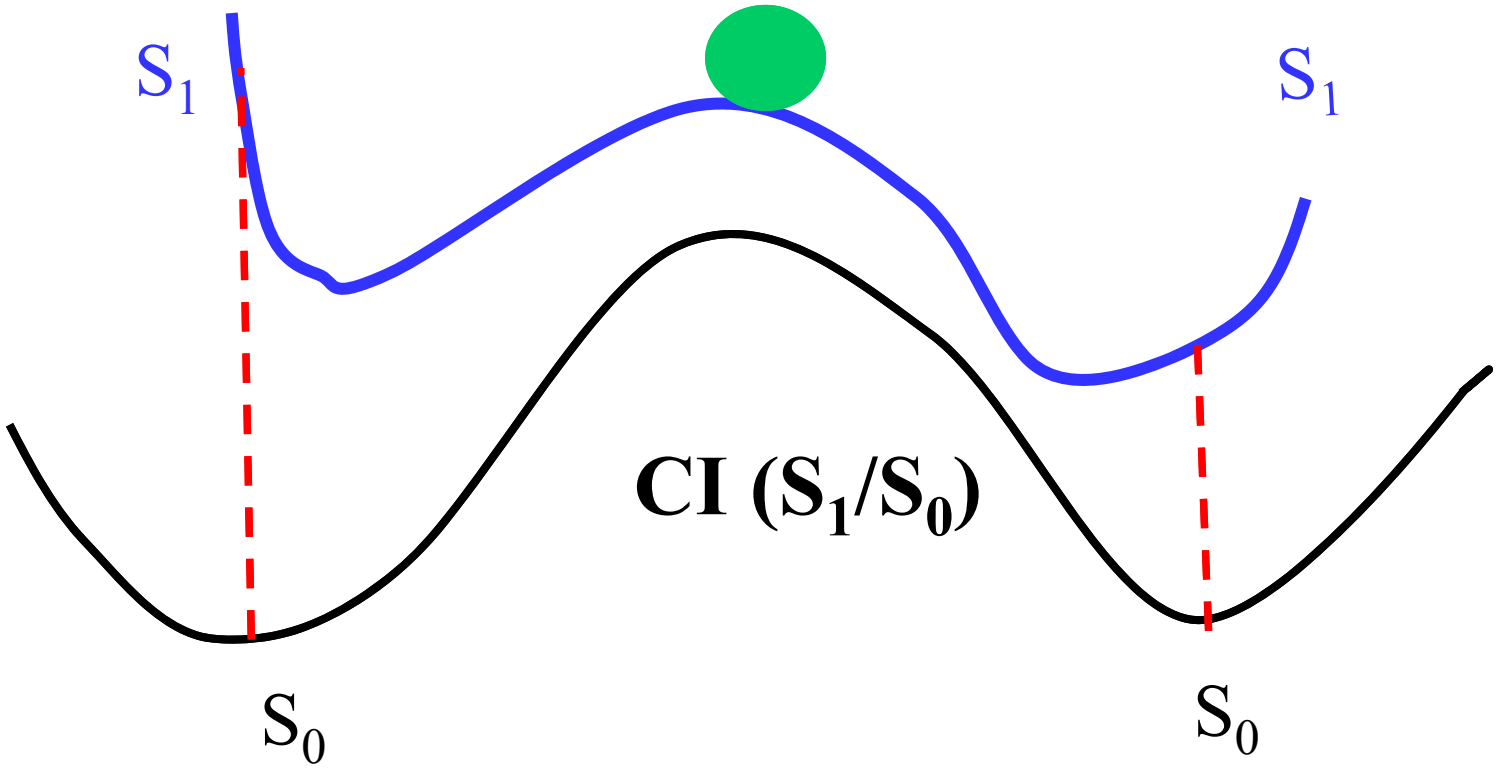
Unique choice for TDDFT method

All hopping points are well behaviors,

No problem at all for CI between S0 and S1 again

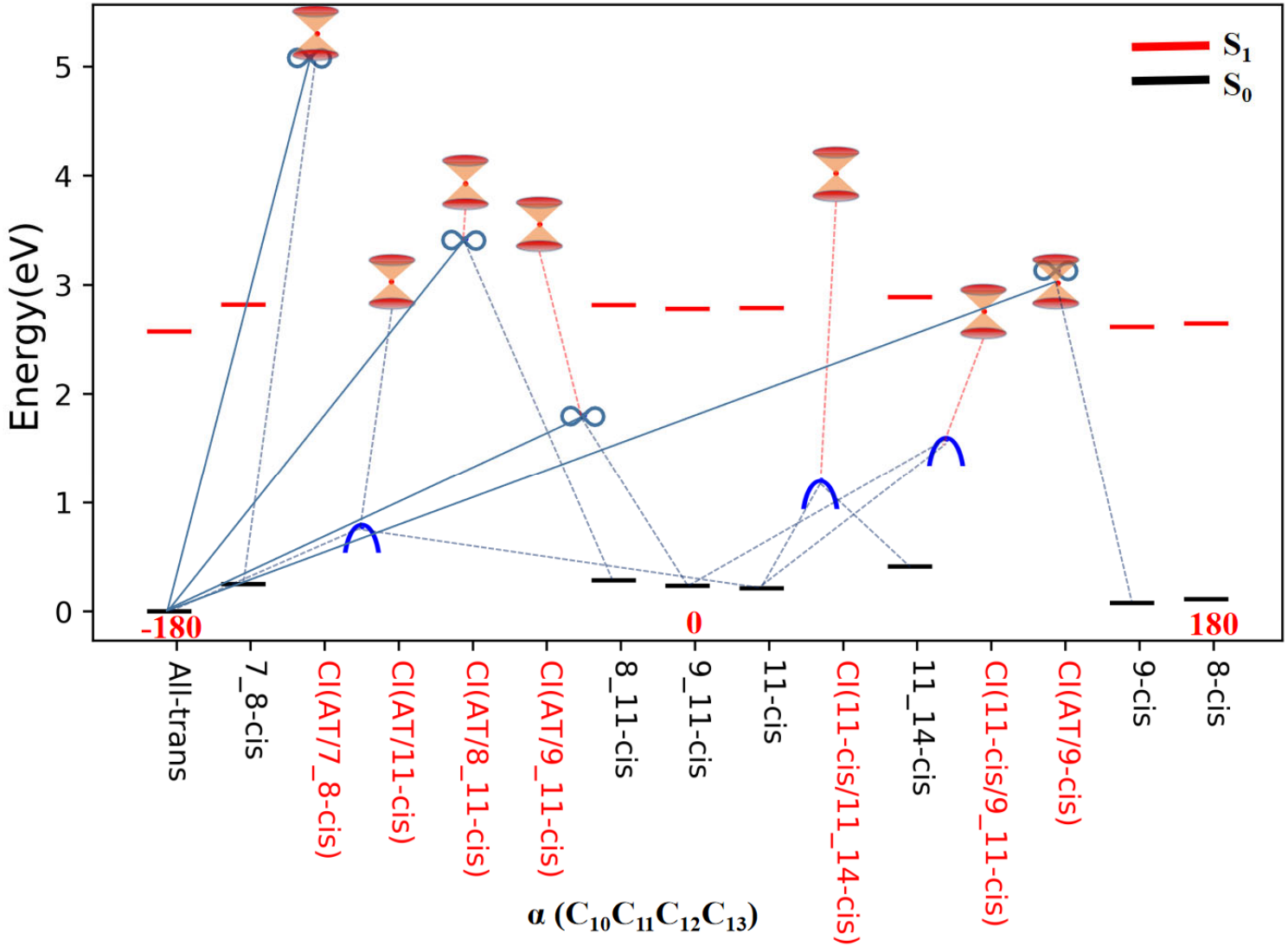
TD-CAM-B3LYP/6-31G

Trajectory starts at anywhere on potential energy surface



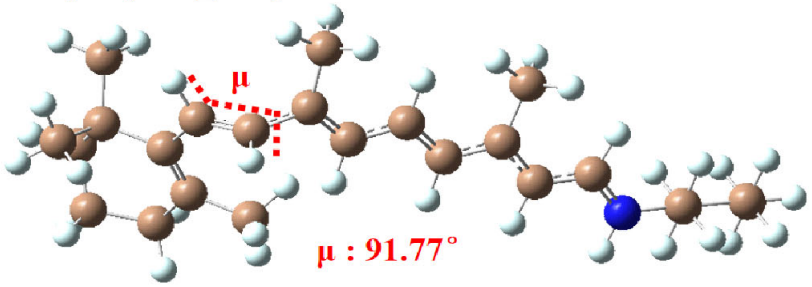
Global switching with TDDFT in Gaussian

Potential energy surface profiles (7 conical intersections)

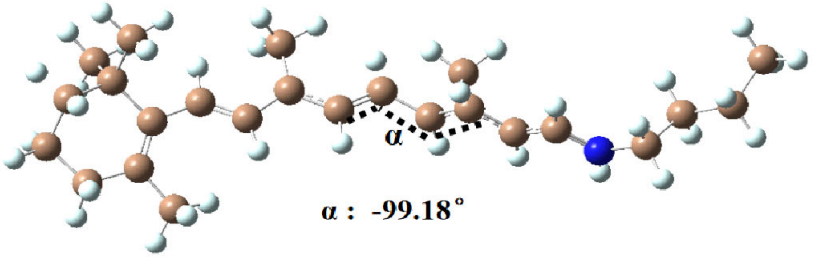


Geometry structures of conical intersections

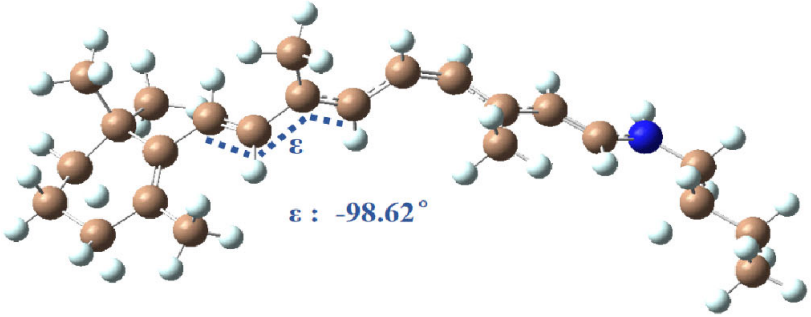
a) CI(AT/7_8-cis) α: -179.86°



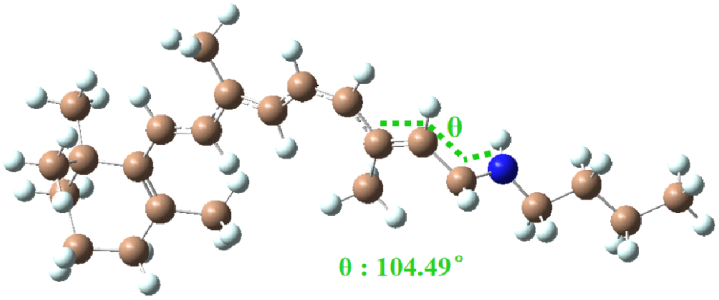
b) CI(AT/11-cis)



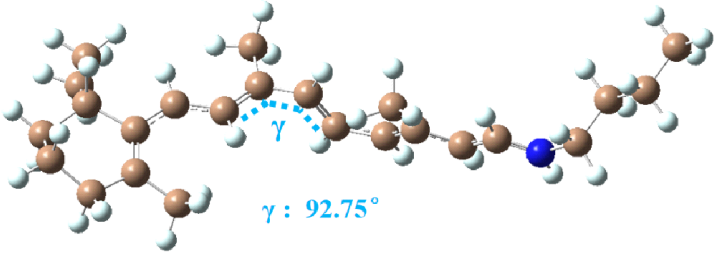
c) CI(AT/8_11-cis) α: -88.74°



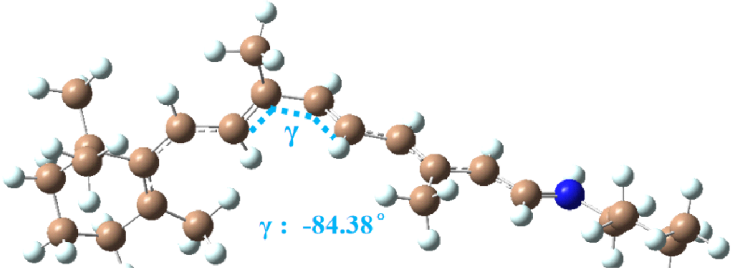
e) CI(11-cis/11_14-cis) α: 1.97°



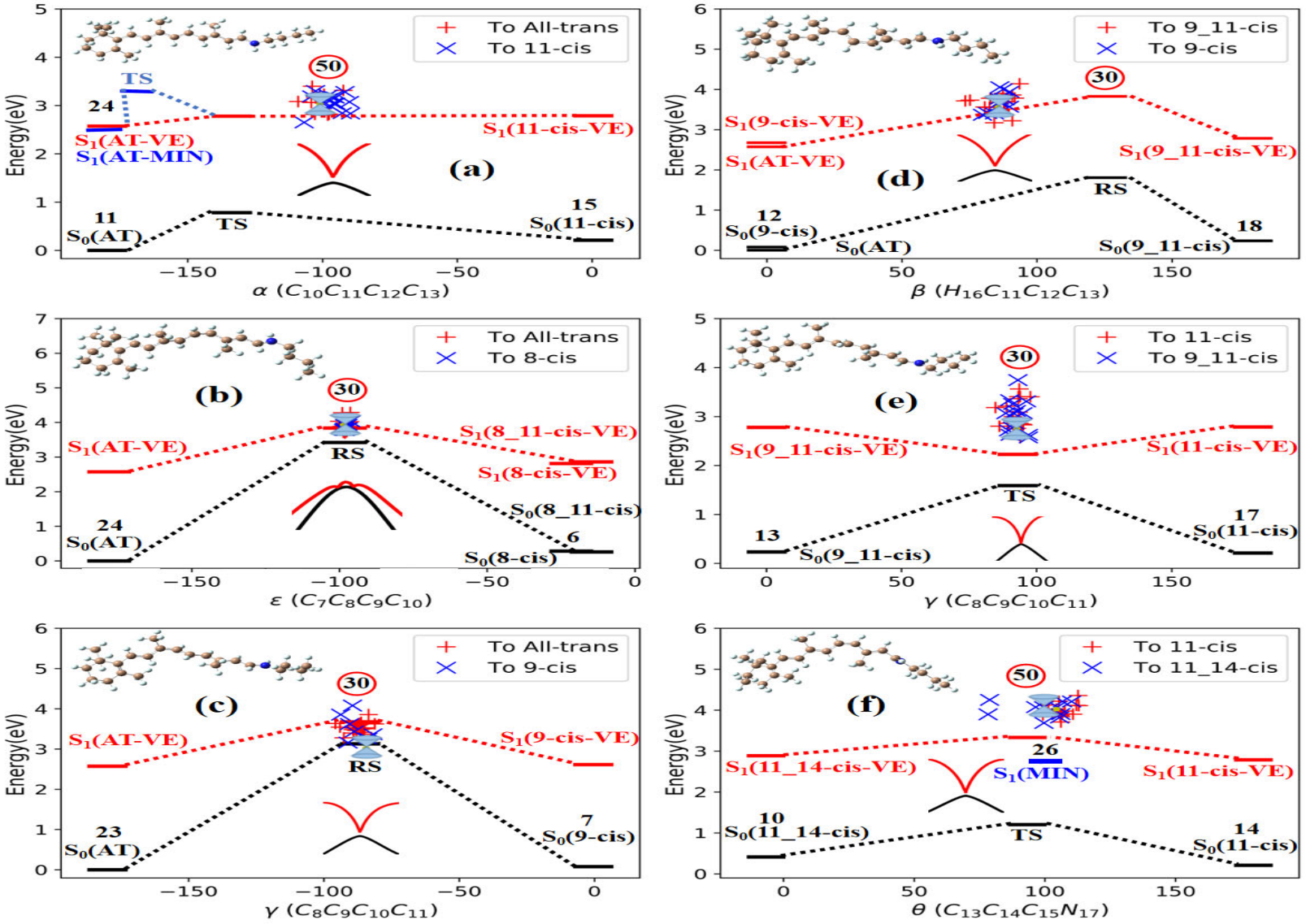
f) CI(11-cis/9_11-cis) α: 23.55°



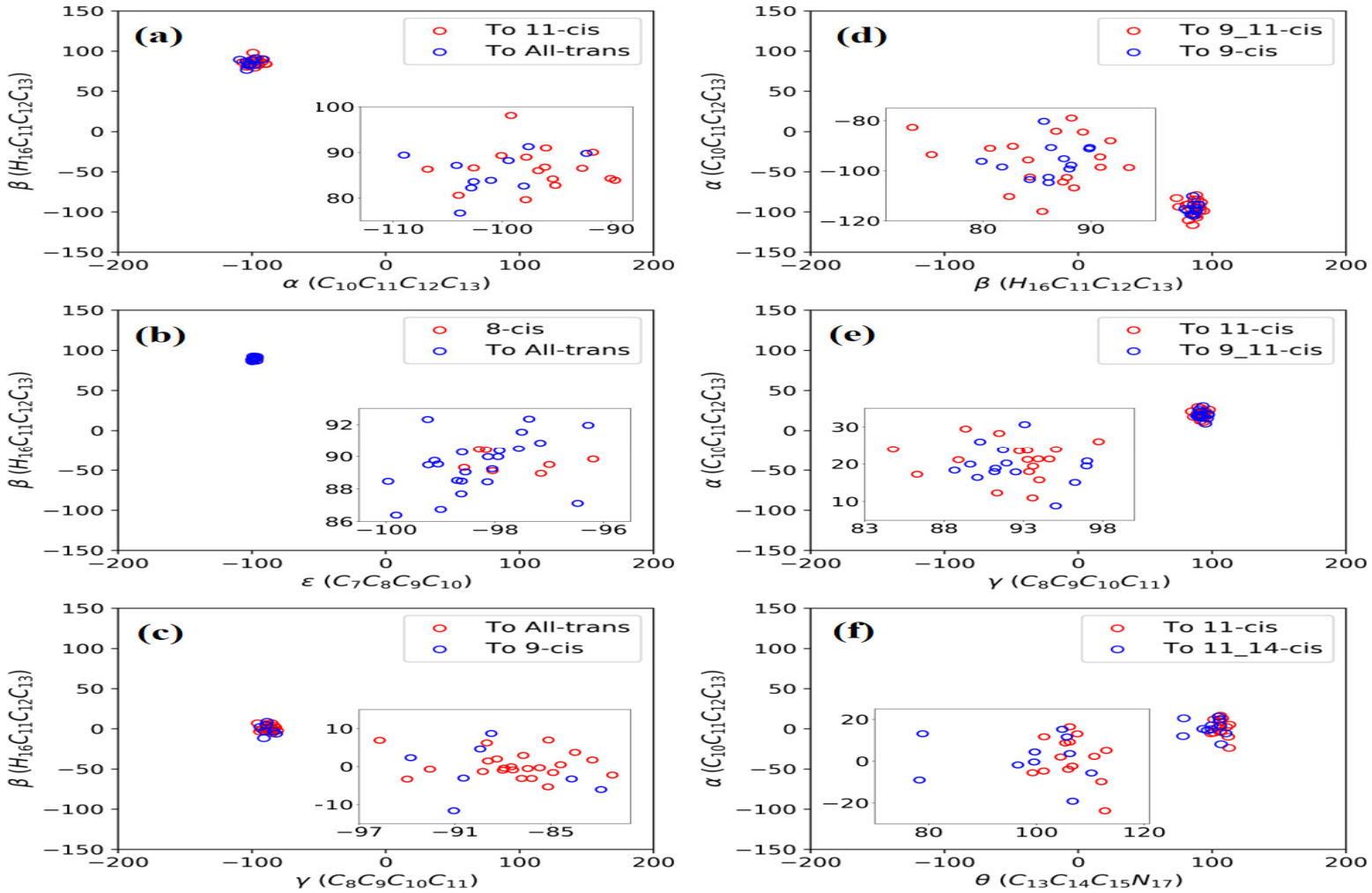
g) CI(AT/9-cis) α: 178.61°



Hopping points connect to reactants and products



Hopping spot distributions in terms of dihedral angles



Simulation results

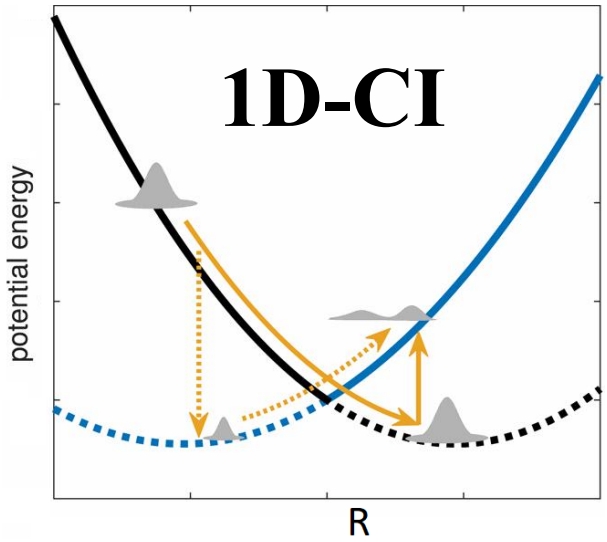
Product	From all-trans (140)		From 11-cis (130)	
	N_{traj}	QY	N_{traj}	QY
All-trans	58	0.41	11	0.08(0.2[b], 0.65[c])
11-cis	15	0.11(0.09[a])	46	0.35
8-cis	6	0.04		
9-cis	19	0.14(0.02)[a]		
9_11-cis	18	0.13	13	0.1
11_14-cis			10	0.08

[a]Ref. 2 and [b]Ref. 11 in methanol solution, and [c]Ref. 8 in Rhodopsin protein.

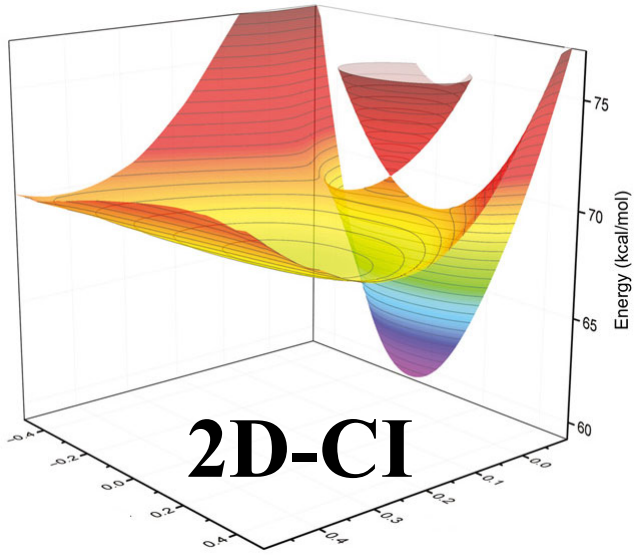
Y. Liu and C. Zhu, Phys. Chem. Chem. Phys., 23, 23861 (2021)

Conclusions

TD-DFT searching intersection between S0 and S1



Cannot avoid CI (singular point)



Trajectory gets less chance to CI

1. As dimension increases for large system, so that TD-DFT gets better and better

2. As far as trajectory runs not right at CI, TD-DFT OK

3. Energy gap where TD-DFT breaks (system dependent)

Conclusions

Global switching TSH methodfor nonadiabatic simulation

No need for calculating nonadiabatic coupling vector
No need for calculating seam surfaces
Only need calculating potential energy surfaces and its gradients

Global switching TSH can also use to search conical intersections

Very good to treat CI (S_1/S_0) with TDDFT method

For large and complicated systems

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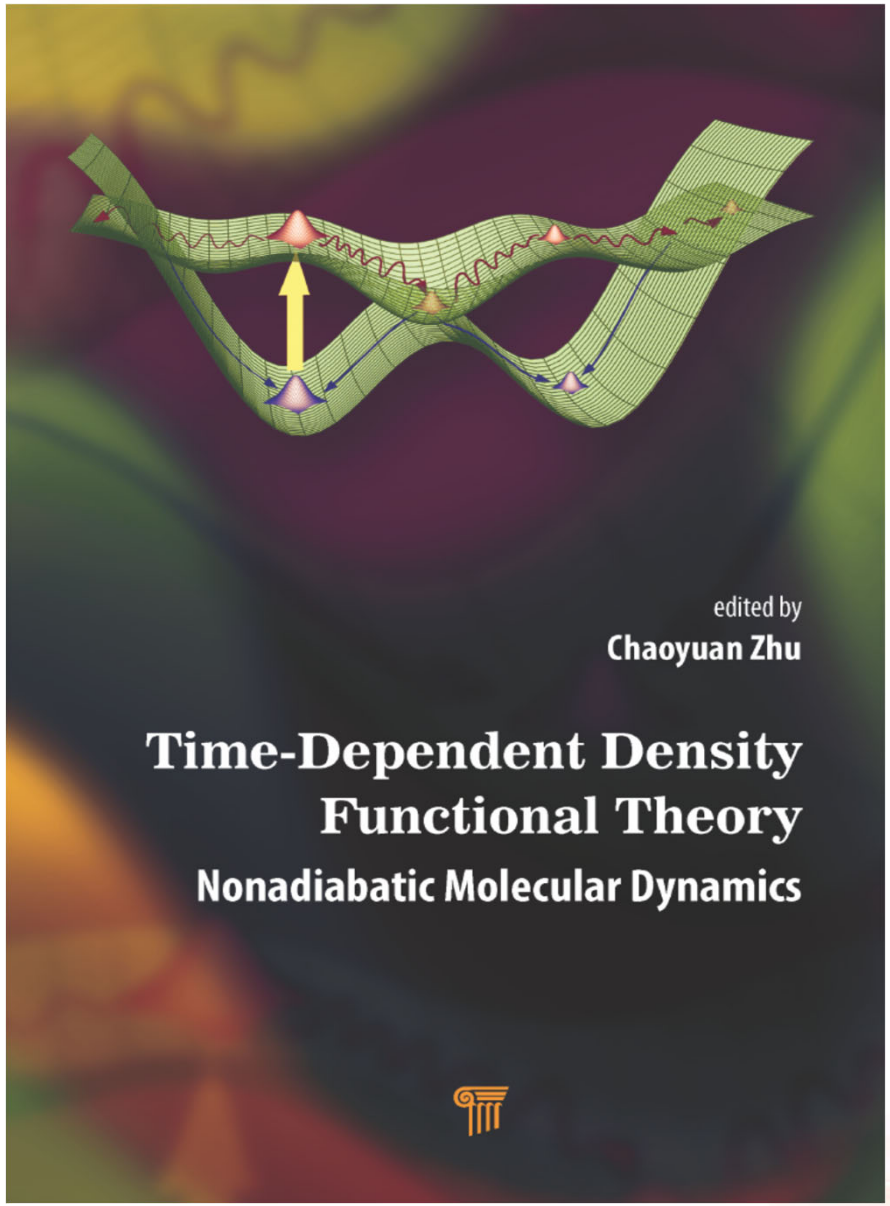
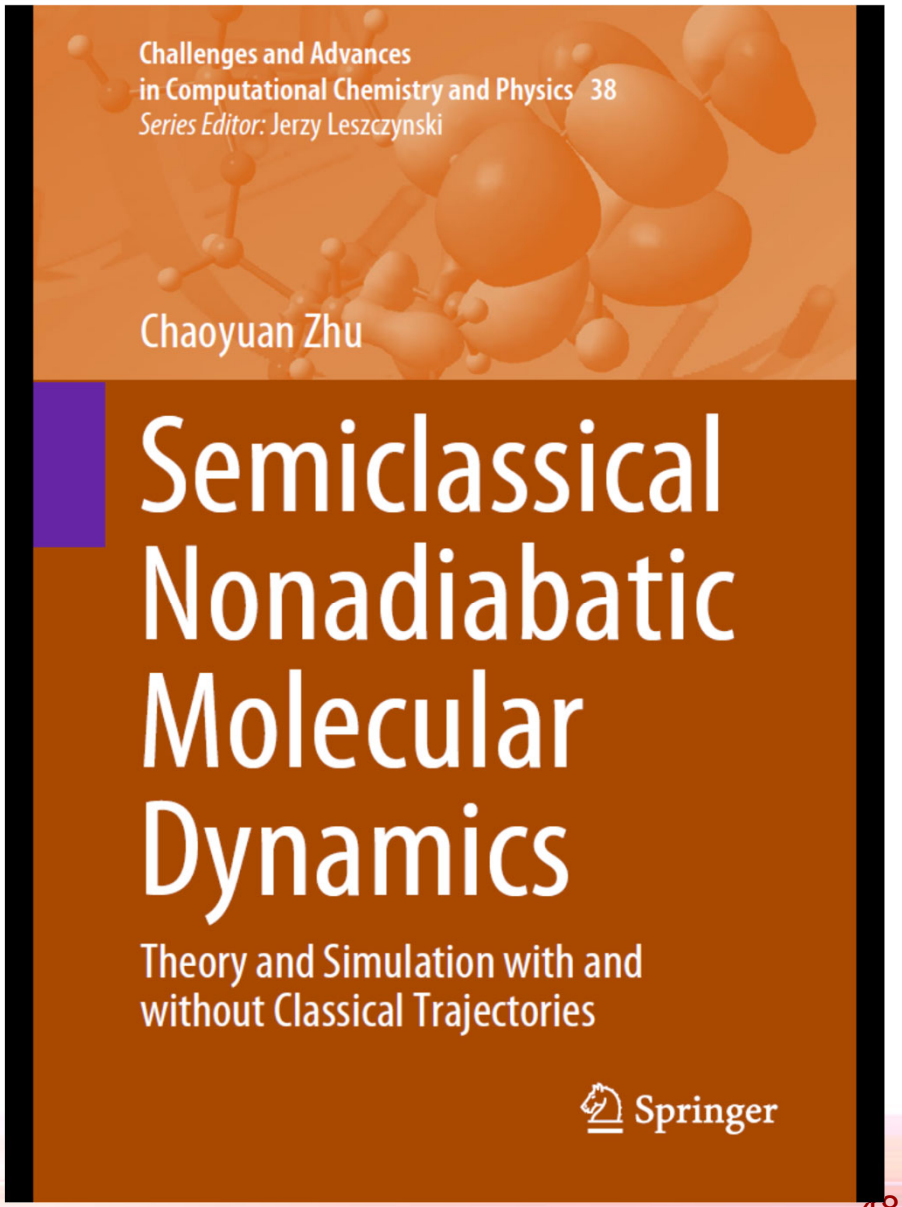

edited by
Chaoyuan Zhu
Time-Dependent Density Functional Theory
Nonadiabatic Molecular Dynamics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Semiclassical Nonadiabatic Molecular Dynamics
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