Application of NEXMD for Modeling Photolytic Decomposition of Explosives

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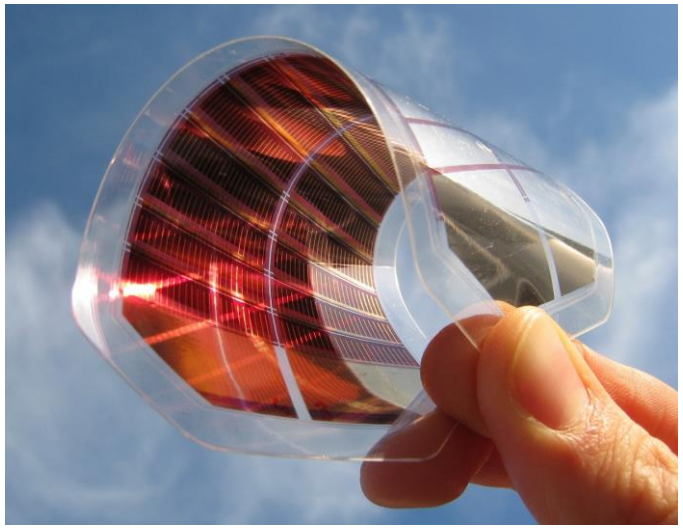
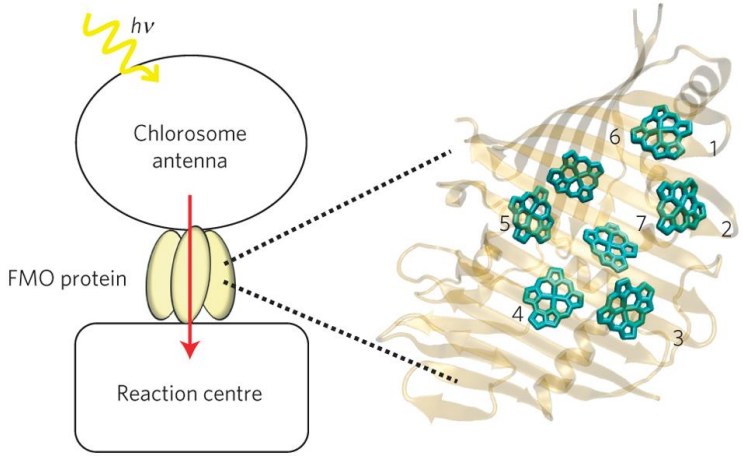
Outline

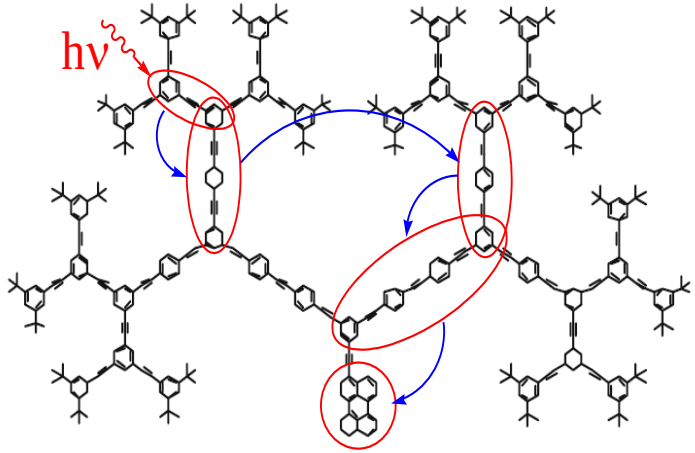
1. Nonadiabatic molecular dynamics in NEXMD
2. Open-shell electronic structure implementation
3. Applications to photochemistry and photophysics
4. Photolysis in energetic materials case study

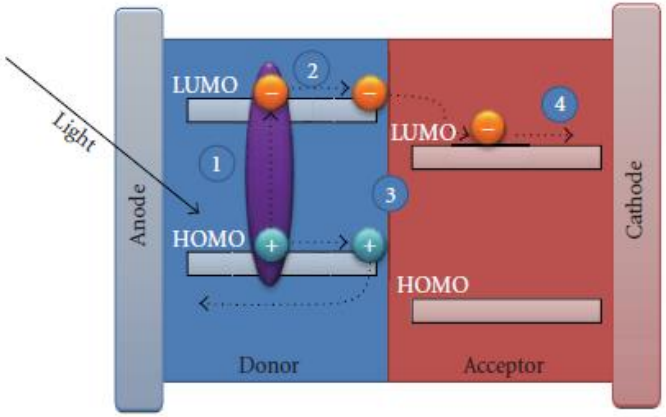
Photodynamics in action

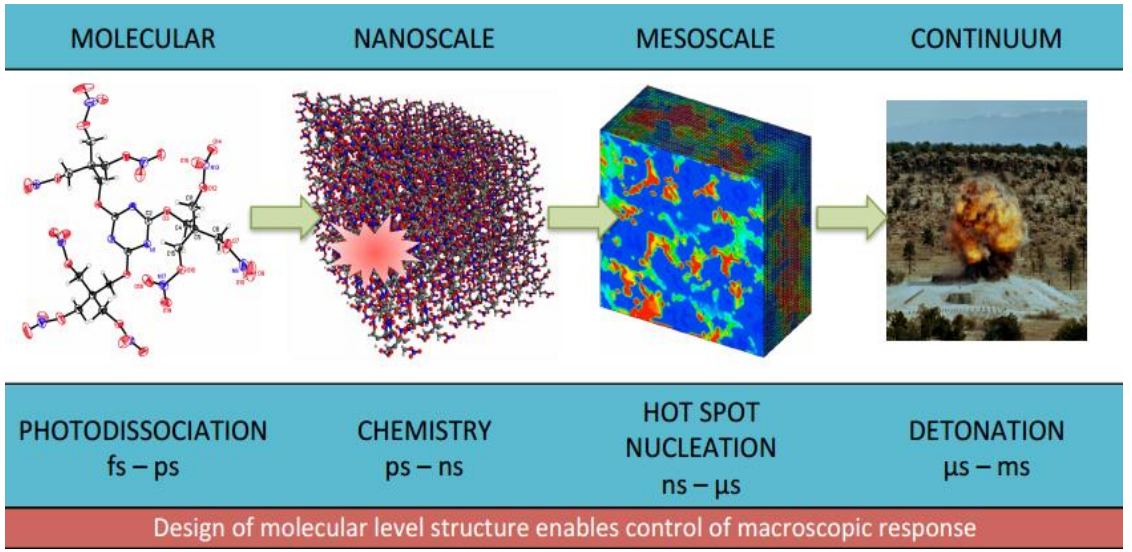




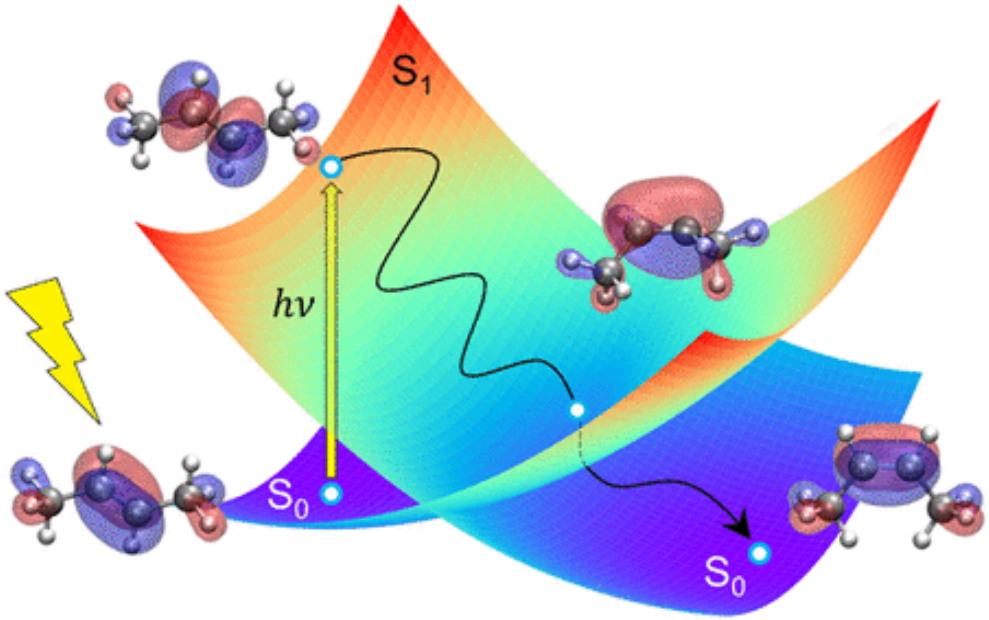
M. Sarovar et al. Nature Physics, **6**, 462 (2010).

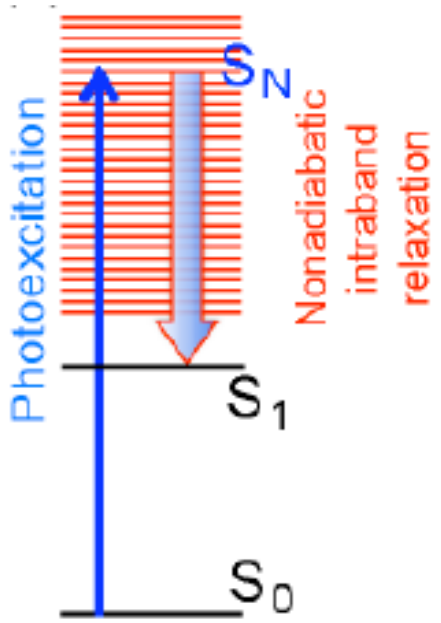


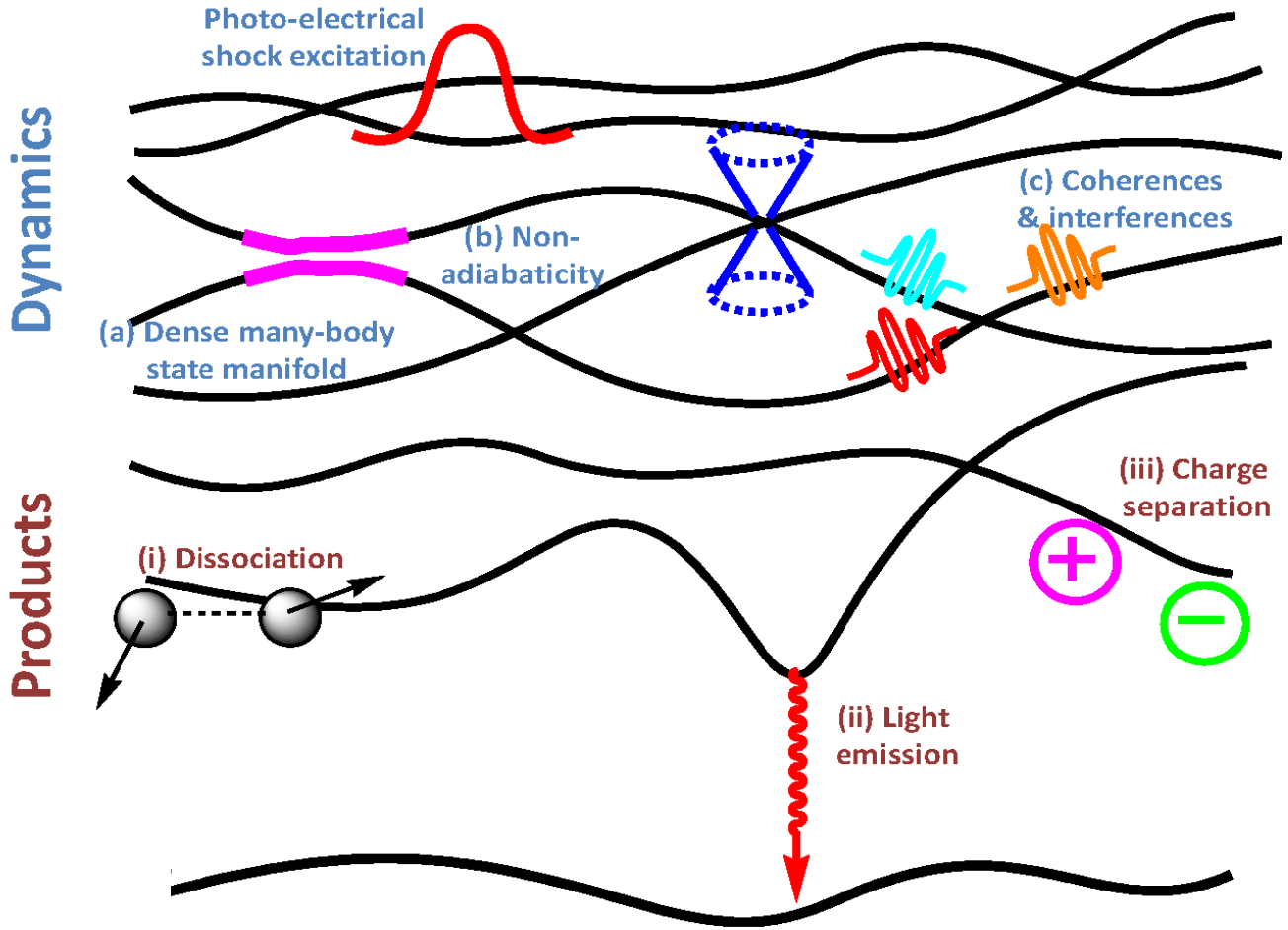




Modeling Photodynamics with Nonadiabatic Molecular Dynamics (NAMD)



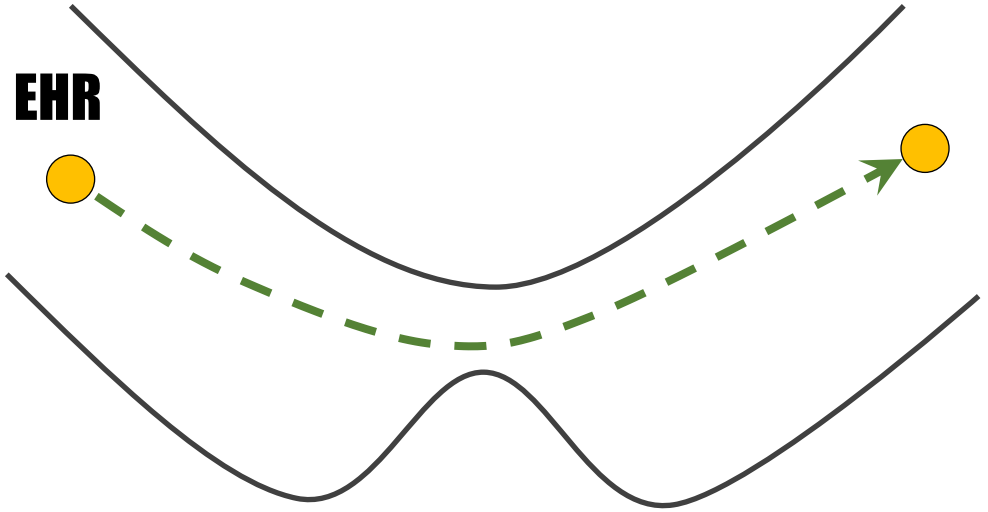


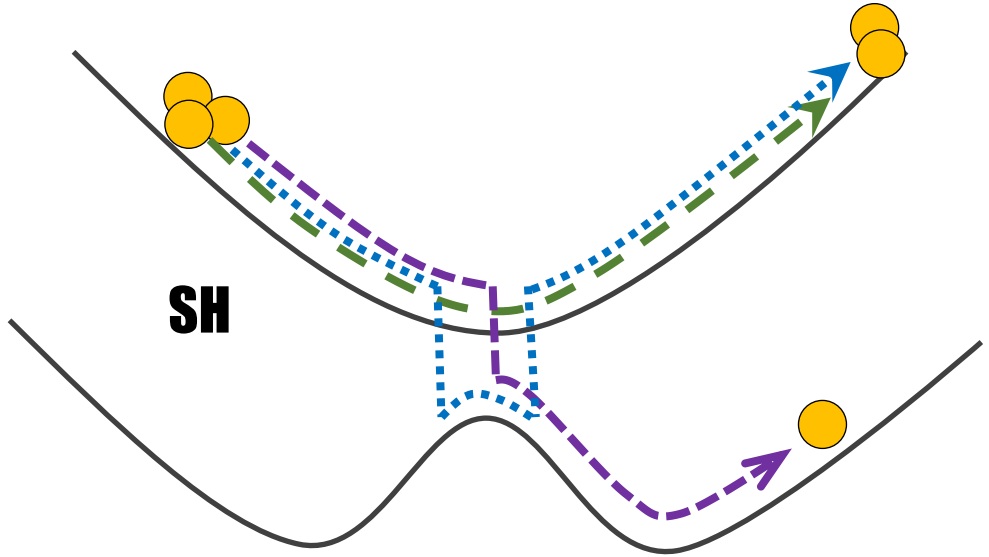


SH & EHR: most popular NAMD methods

Ehrenfest

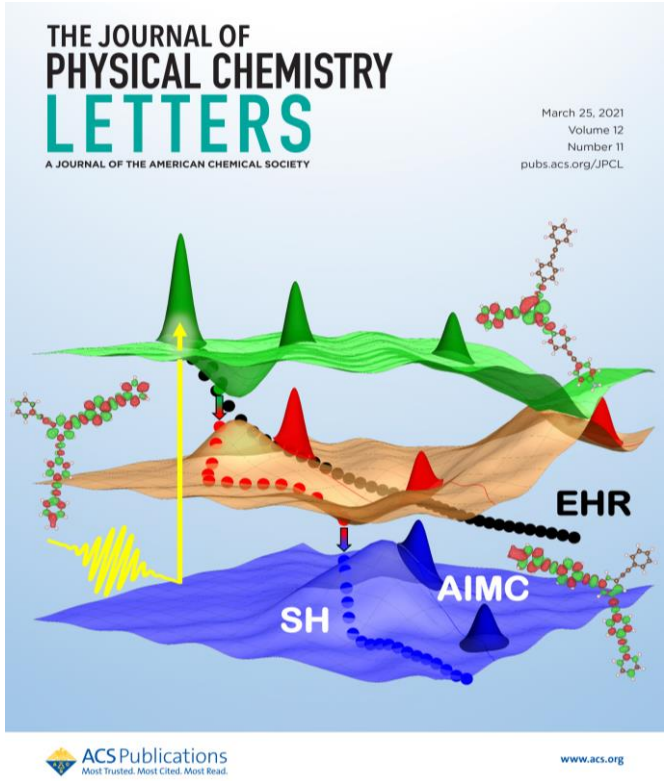
- Nuclei move classically on mean-field potential
- Accurate when PESs remain coupled and dynamics without branching
- Cannot identify branching pathways
- Lack of detailed balance
- Neglects electron-nuclear correlations



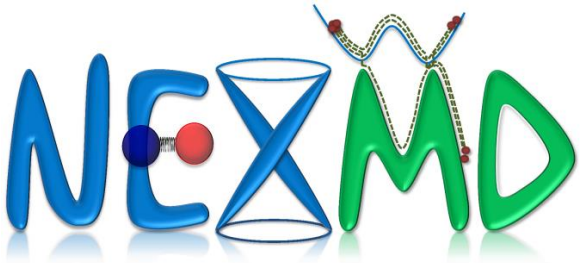


Surface Hopping

- Nuclei move on single PES
- Achieves detailed balance
- Can identify multiple branching pathways
- Requires more trajectories than EHR
- Not accurate when PESs remain coupled
- Frustrated hops, energy redistribution, electronic coherence
- Cannot easily incorporate nuclear quantum effects

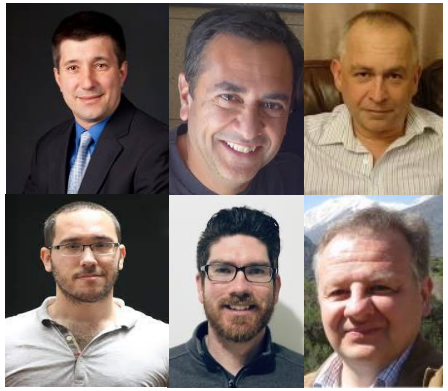


Multiconfigurational Ehrenfest (MCE) and Ab Initio Multiple Cloning (AIMC)



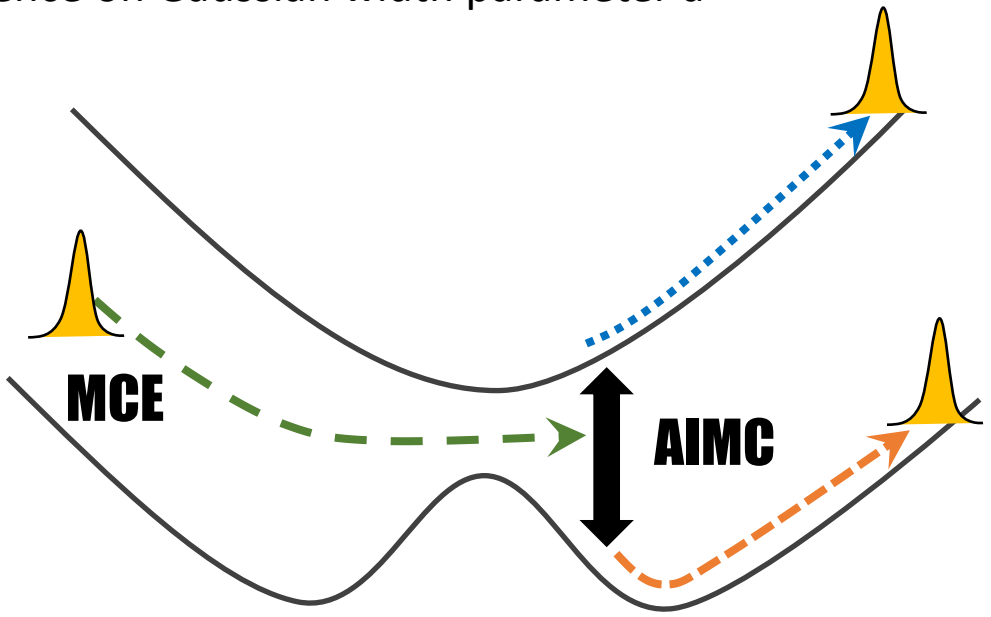
Multiconfigurational Ehrenfest

- Ensembles of EHR trajectories form trajectory-guided Gaussian basis functions (TBFs)
- Time-dependent diabatic basis (TDDB) – no NAC approximations related to WF 2nd derivative
- Naturally accounts for geometric phase effects
- Unknown dependence on Gaussian width parameter a



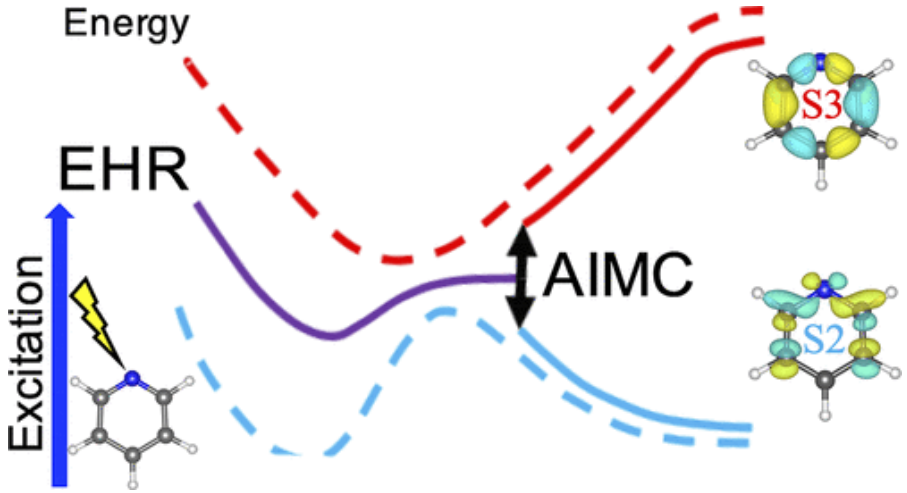
Ab Initio Multiple Cloning

- Basis sampling technique – each EHR trajectory can clone into two copies at level crossing
- Naturally account for decoherence and bifurcating relaxation pathways
- Rapidly increases computational cost



AIMC Three Cloning Criteria

1. At least two adiabatic electronic states are sufficiently populated
2. Breakdown of mean-field approximation
3. Electron



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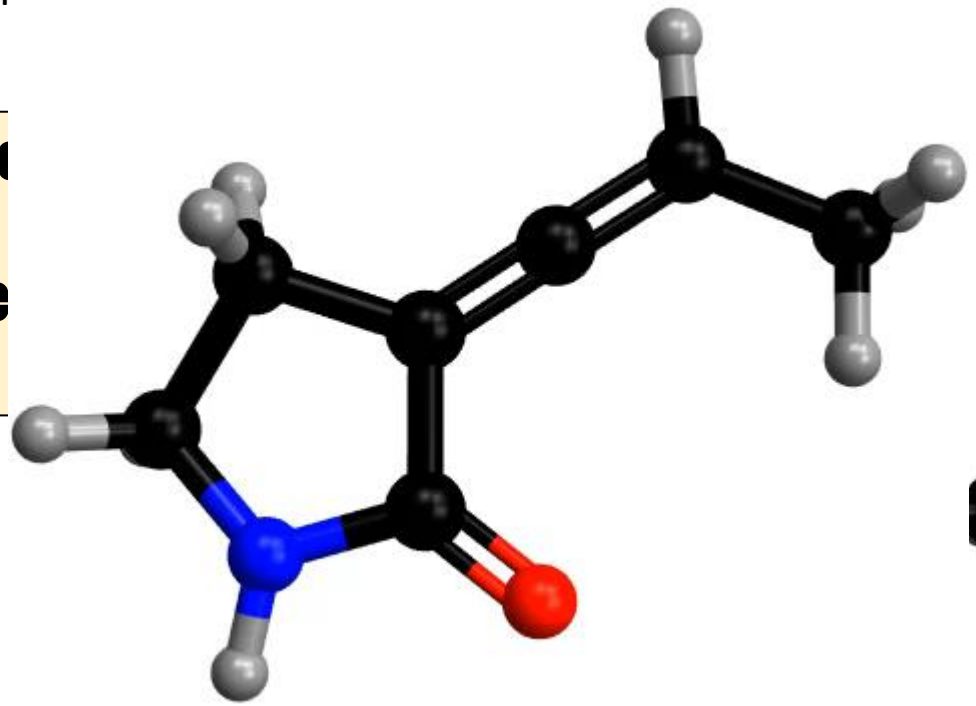
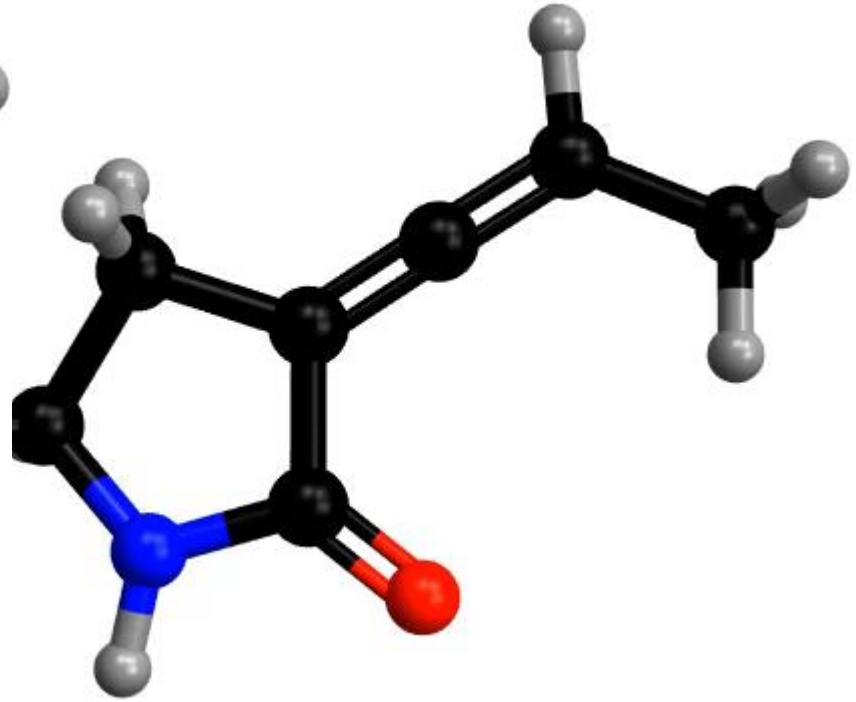
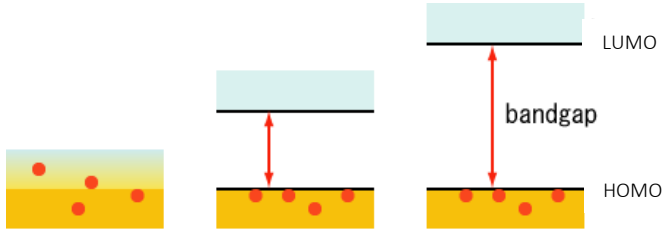


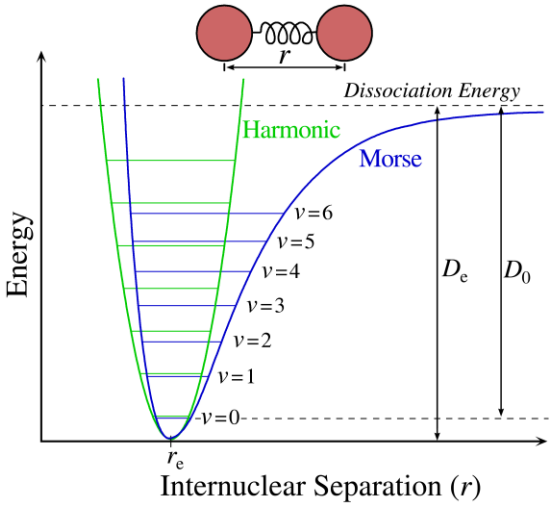


Consistent Electronic Structure Implementation

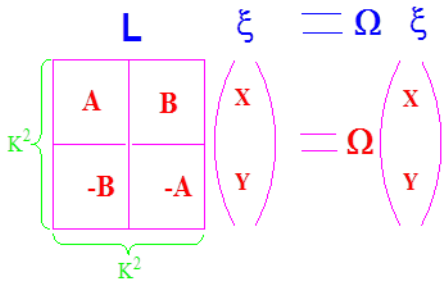
All methods depend on accurate description of PES (forces) and energy gaps (NAC)

- Semiempirical Hamiltonian AM1/PM3/PM6
  - ground state geometry
  - ionization potentials
  - dipole moments…





- Collective electron oscillator (CEO) method using CIS provides transition energies and oscillator strengths



A, X - CIS (particle-hole) part

$$E_\alpha(\mathbf{R}) = E_g(\mathbf{R}) + \Omega_\alpha(\mathbf{R})$$

ρ_{jj}

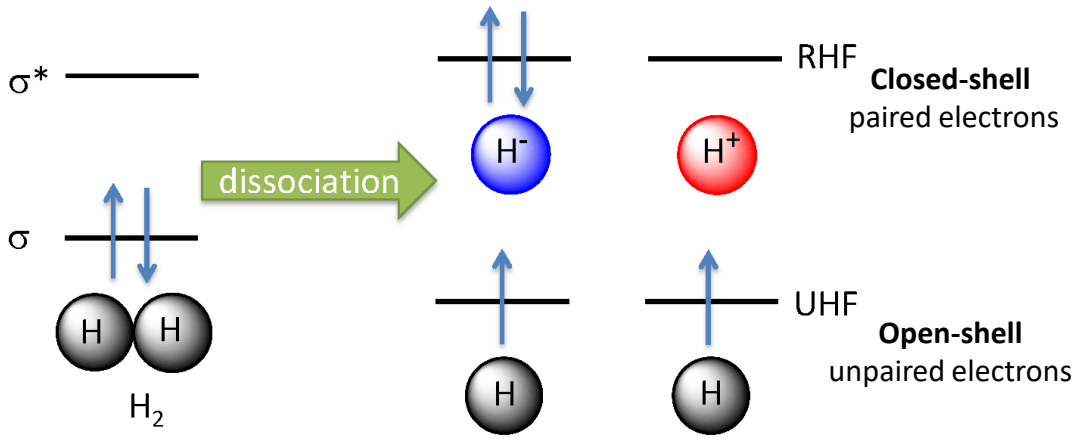
ρ_{ij}

ρ_{ii}

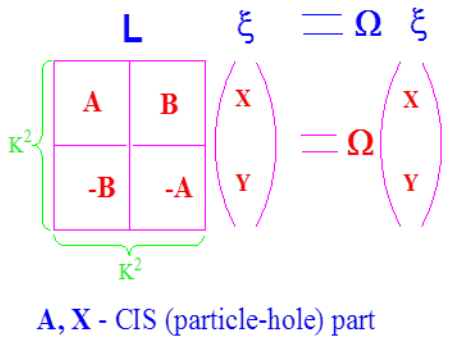
ρ_{0i}

ρ_{00}

Open-Shell Implementations

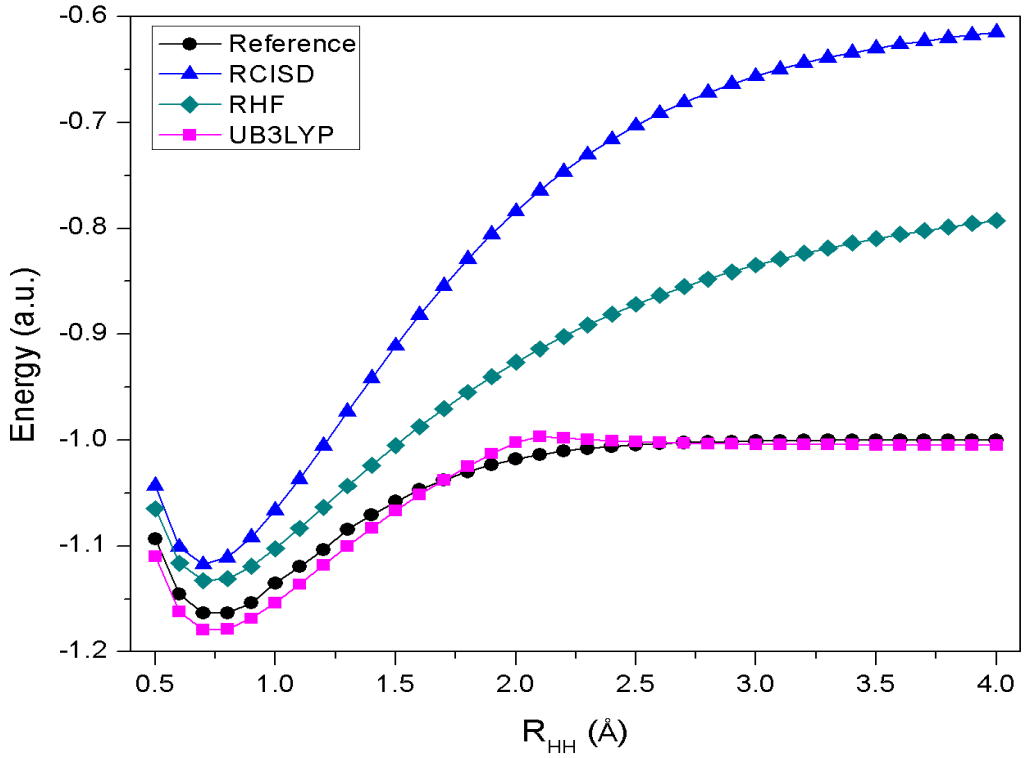


Introduce spin components in RPA/CIS



$$\rho(t) = \bar{\rho} + \xi(t) + T(\xi(t))$$

$$\xi = \begin{pmatrix} \xi^{\alpha} \\ \xi^{\beta} \end{pmatrix}, \text{and,} \quad \xi^{\alpha} = \begin{pmatrix} X^{\alpha} \\ Y^{\beta} \end{pmatrix}$$

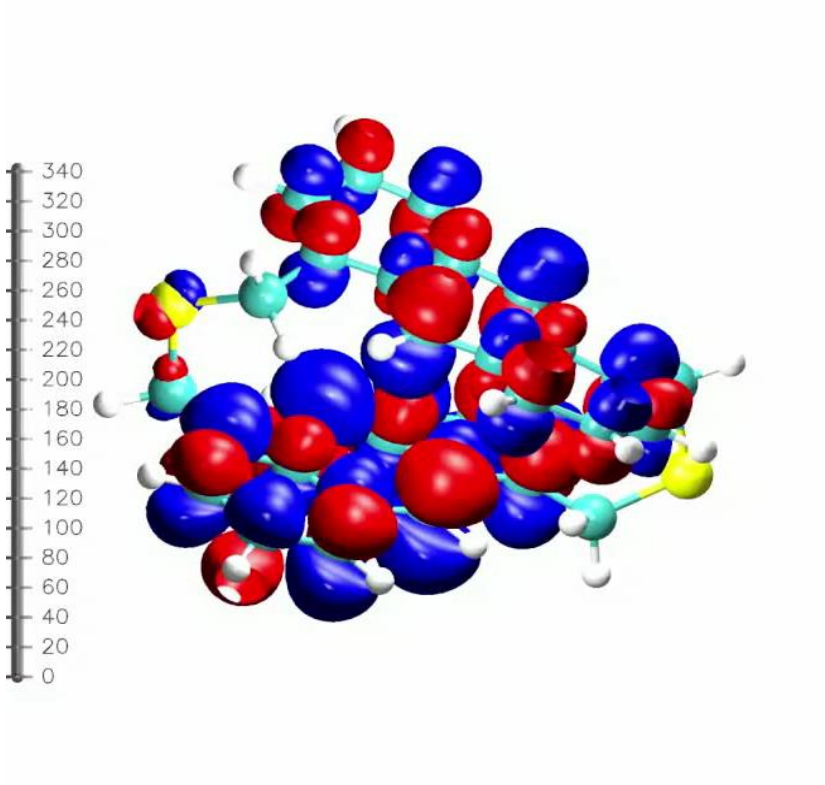


- Dissociation barrier too large
- Photochemical quantum yield too small
- Open-shell intermediates can be present even for closed-shell reactants and products

Y. Zhang, et al. Nonadiabatic Excited-State Molecular Dynamics for Open-Shell Systems. J. Chem. Theory Comput. 2020, 16, 2053–2064.

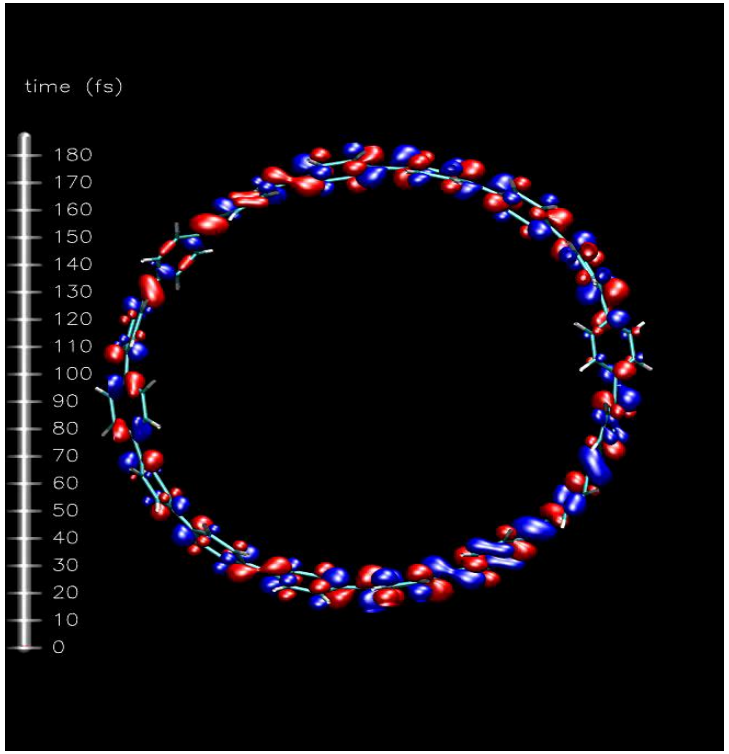
Applications of NEXMD for Photophysics

Photophysics Physical processes (energy transfer, charge transfer) that happen in a molecule as a result of absorbing a photon



Dithia-anthracenophane

Alfonso-Hernandez, et al. JPCB. 2015, 119, 7242.



[16] Cyclo-paraphenylene (CPP)

Adamska, et al. Nano Let. 2014, 14, 6539.

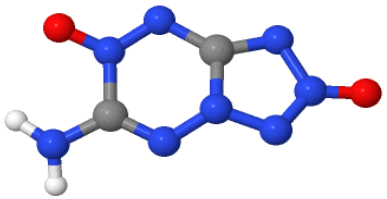
Applications of NEXMD for Photochemistry

Photochemistry Chemical reactions (bond breaking, isomerization, etc.) that result from photon absorption. Light provides the energy to overcome the reaction barrier.

Reaction pathways and quantum yields require accurate barrier heights

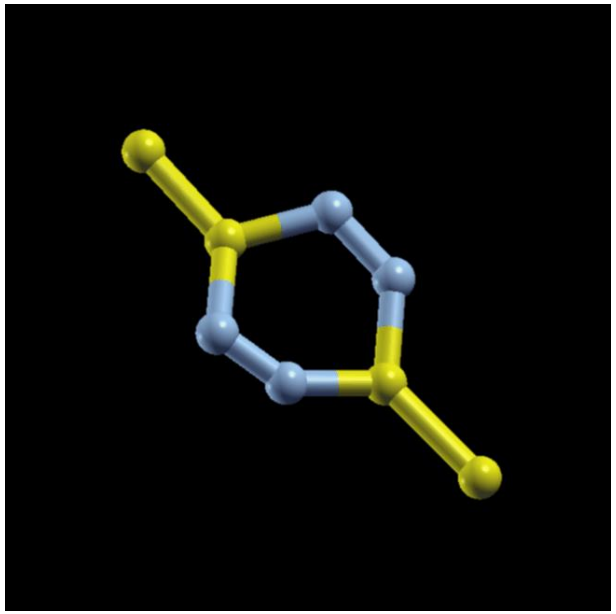
$ATTO_2$

Time = 0000fs



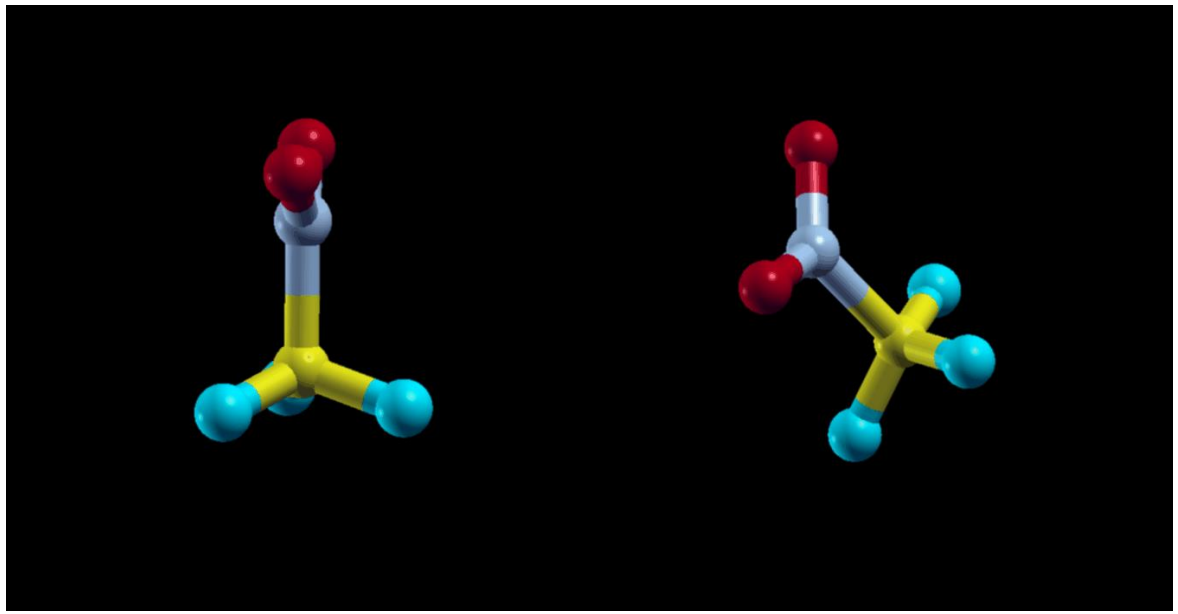
Lystrom, et al. JPCA, 2018, 122, 6055.

Tetrazine dichloride ($TzCl_2$)



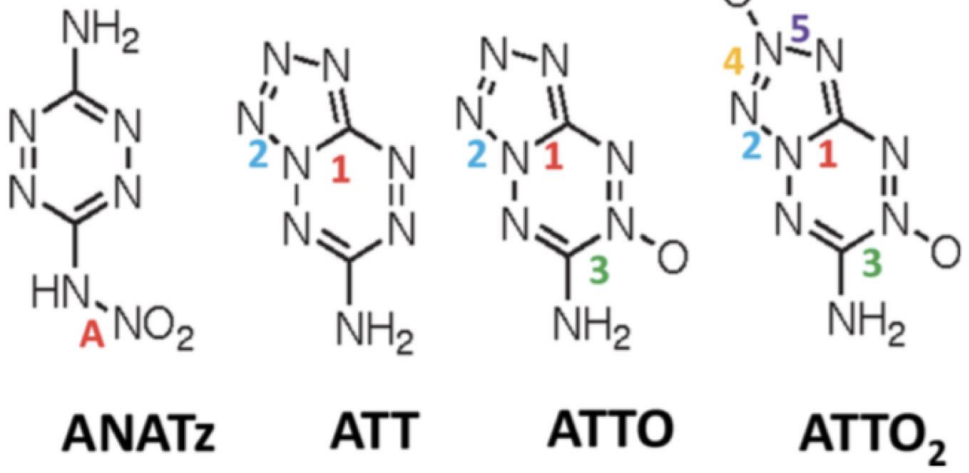
Greenfield, et al. JPCA. 2015, 119, 4846.

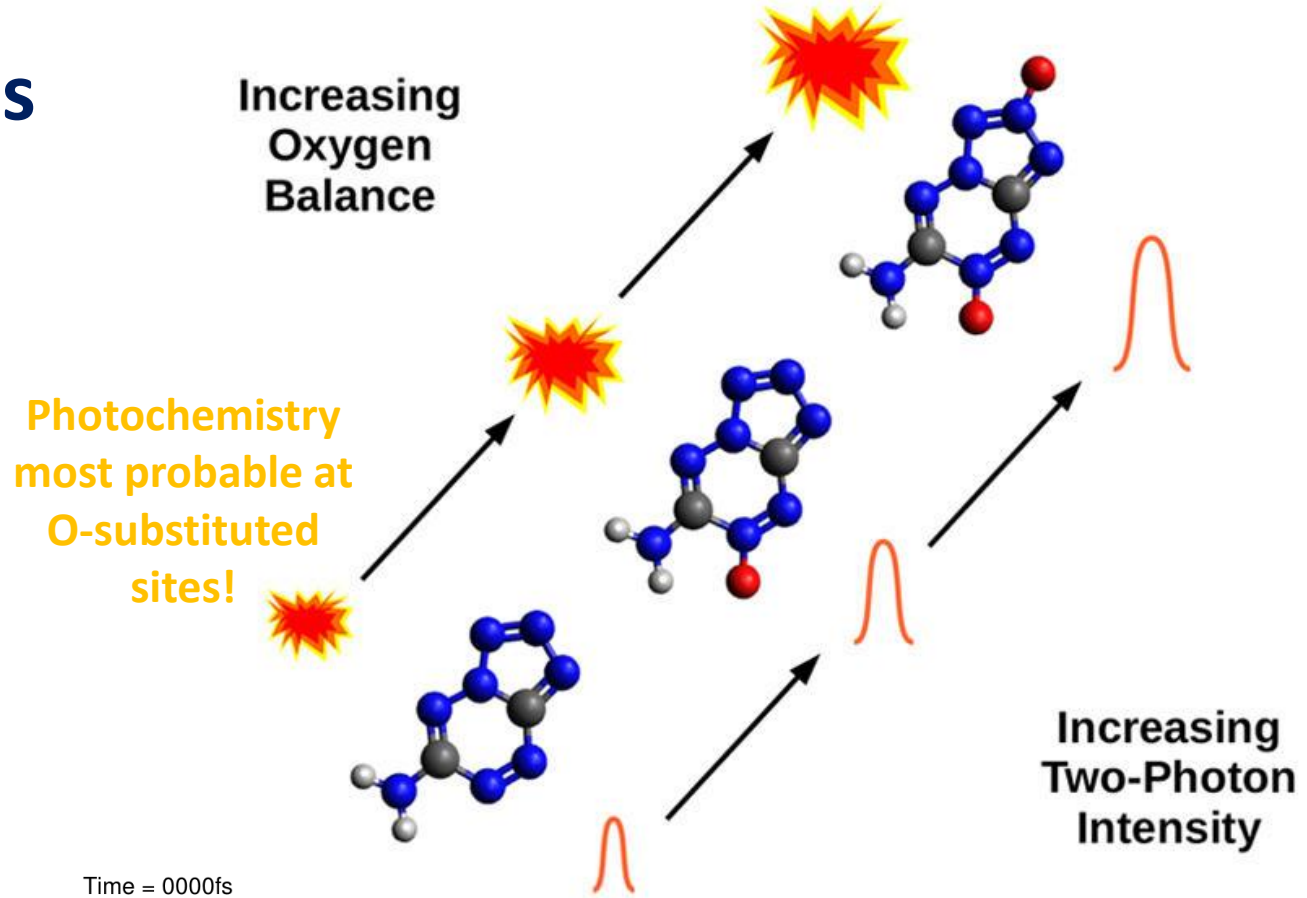
Nitromethane (CH_3NO_2)

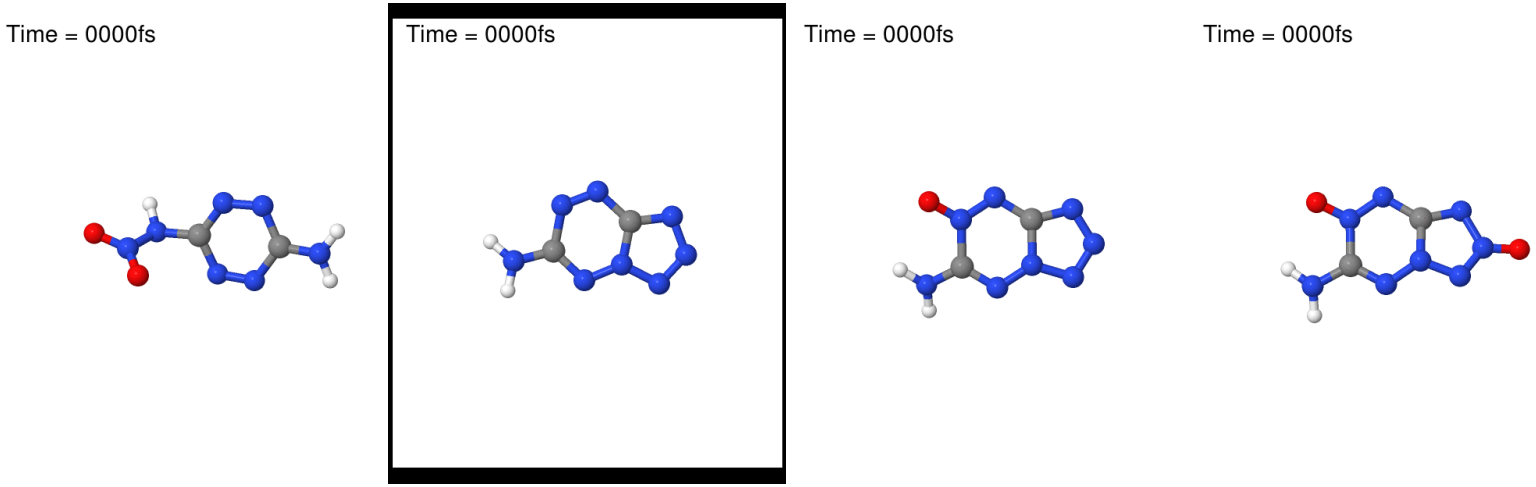


Nelson, et al. JPCA. 2016, 120, 519.

Conjugated Energetic Materials





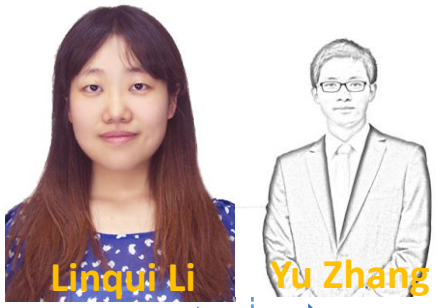


Bjorgaard, et al. *JPCA* 2016, 120, 4455.

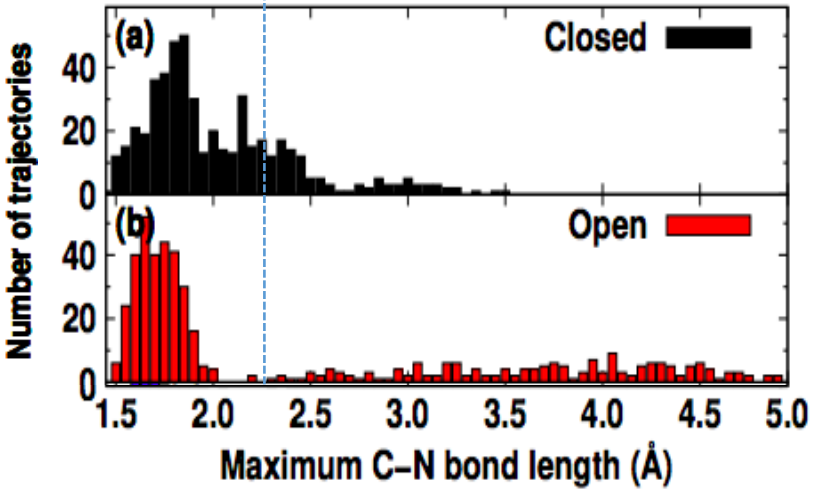
Lystrom, et al. *JPCA* 2018, 122, 6055.

Photochemical Pathways, Quantum Yields, Bond-breaking Timescales

- Predict intermediates and photoproducts
- Estimate quantum yields



Bonded ⟷ Broken Bond



[Aci-ion Formation]

$$CH_3NO_2 \xrightarrow{h\nu} CH_2NO_2^- + H^+$$

1 trajectory / 417
QY=0.002

[Nitro-Nitrite Isomerization]

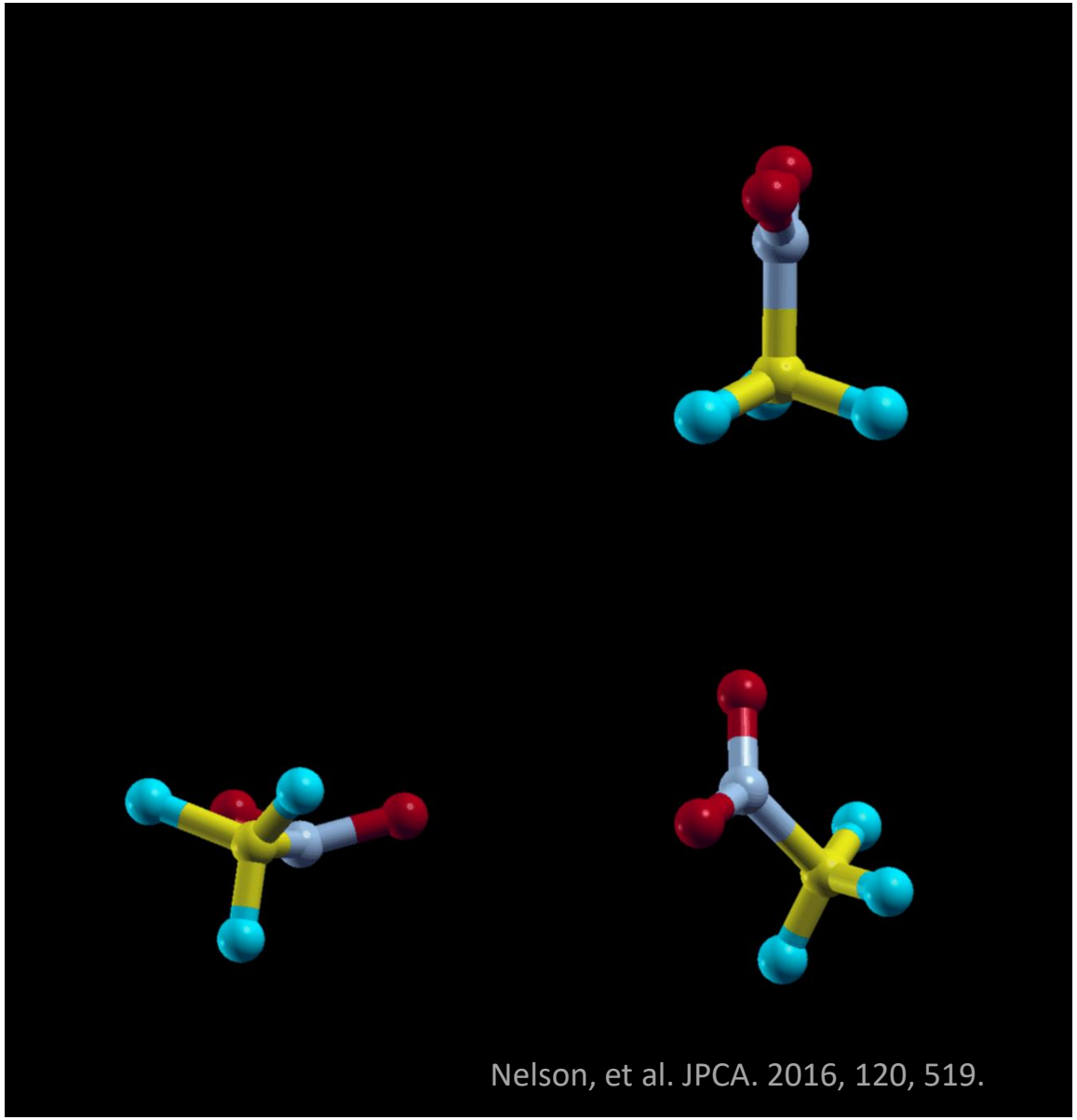
$$CH_3NO_2 \xrightarrow{h\nu} CH_3ONO$$

15 trajectories / 417
QY=0.04

[NO_2 Dissociation]

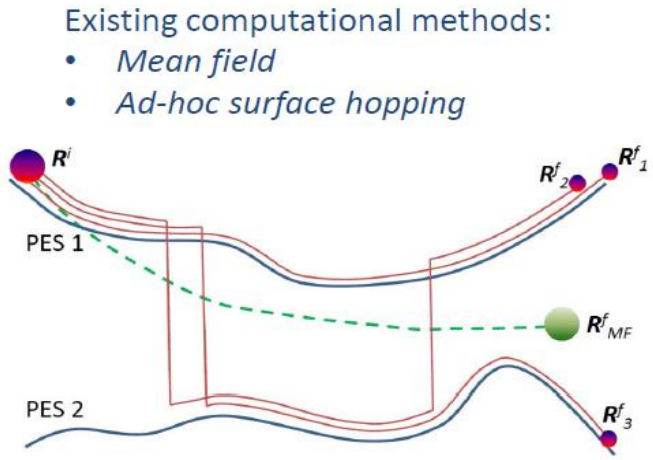
$$CH_3NO_2 \xrightarrow{h\nu} CH_3 + NO_2$$

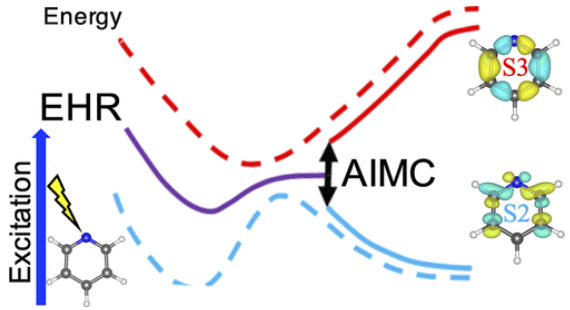
101 trajectories / 417
QY=0.242



Nelson, et al. JPCA. 2016, 120, 519.

NEXMD Conclusions



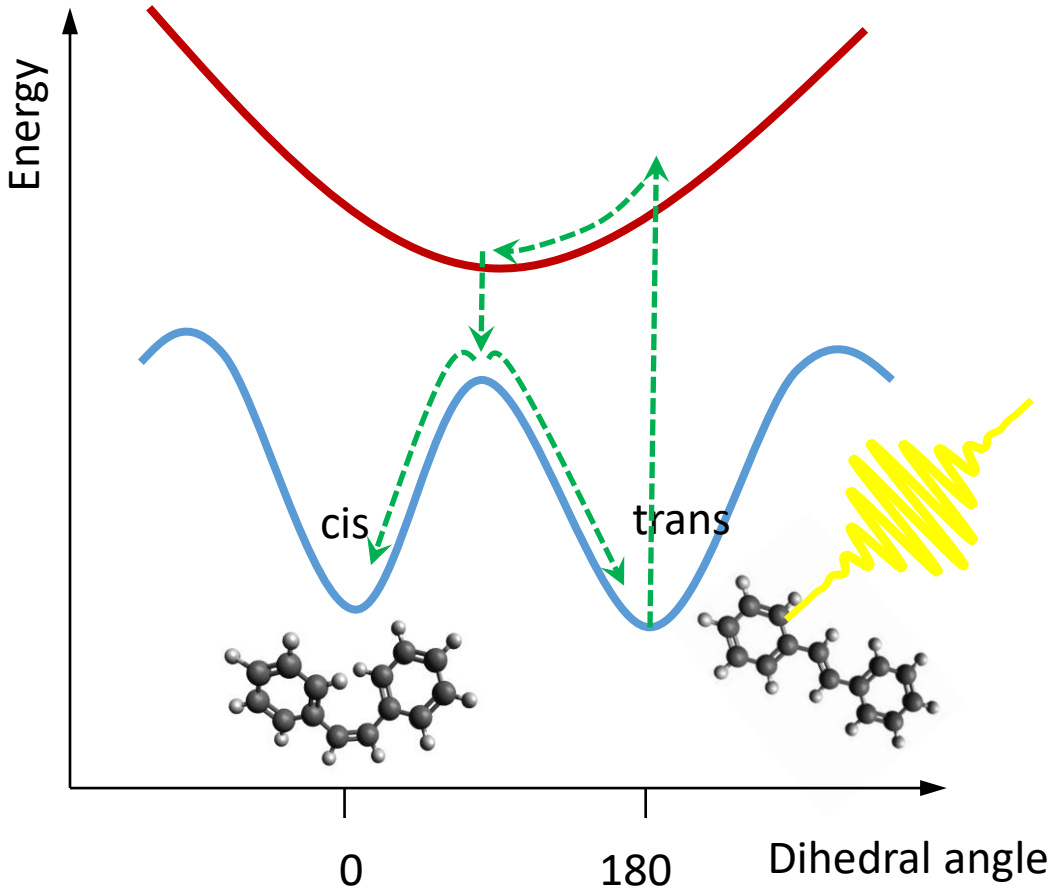


- We now have framework for excited state dynamics
  - NEXMD software package for mixed quantum classical dynamics
  - TSH, Ehrenfest, MCE+AIMC
  - Excited state energies, ES gradients (forces), NACs for NAMD
  - Large molecular systems + long timescales

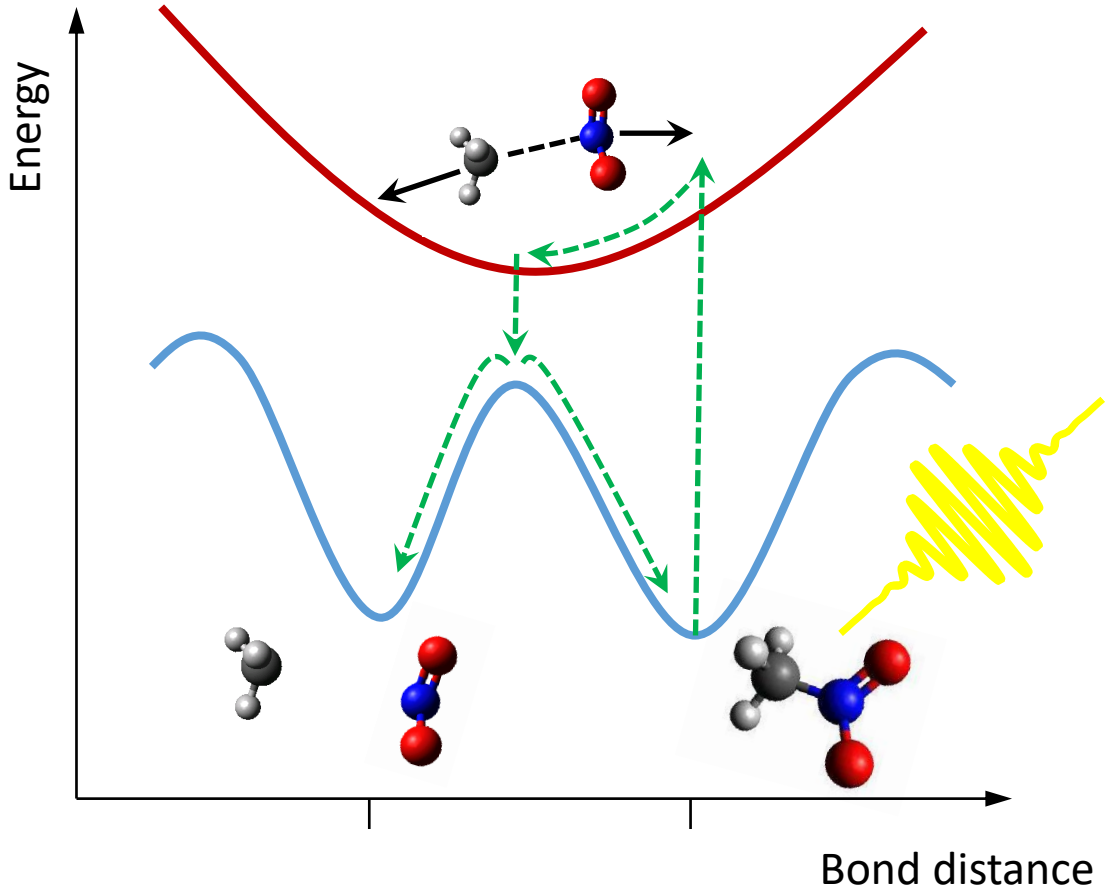
- Promising results for Open-shell NEXMD simulations
  - Now we can model photochemical reactions with bond-breaking
  - Reduced excited state reaction barriers → better description for photochemical QYs
  - Relaxation timescales, bond breaking timescales, dynamics of photofragments

Different Flavors of Photochemistry

Photoisomerization (stilbene)

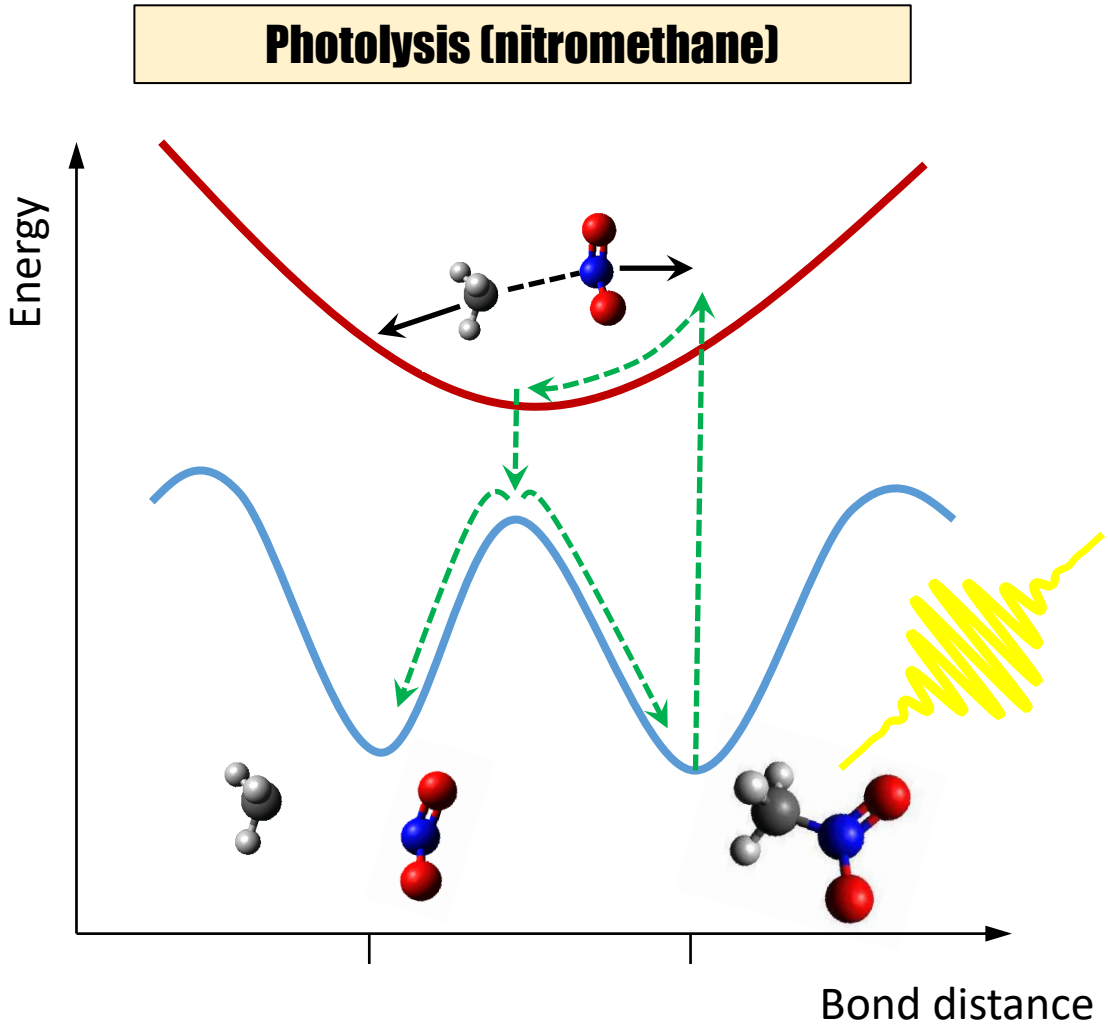


Photolysis (nitromethane)

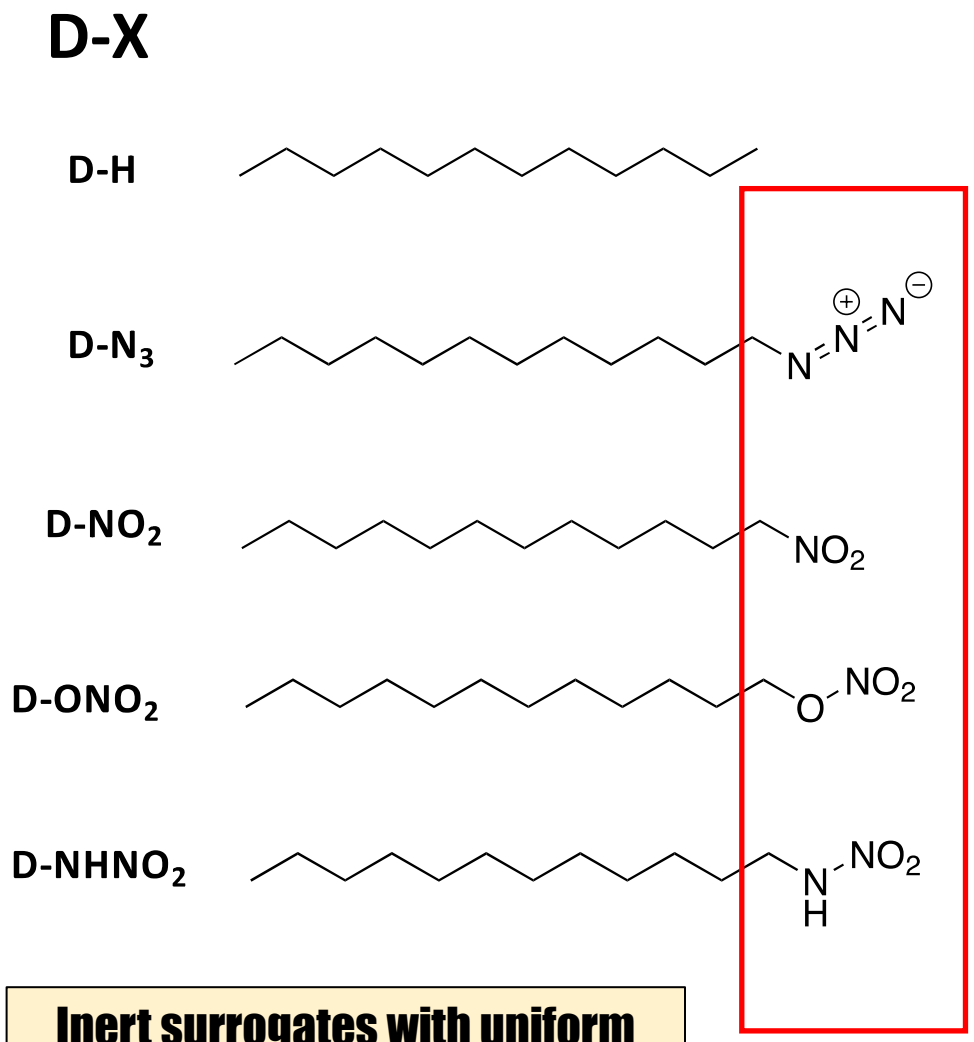


Photolytic degradation of explosives

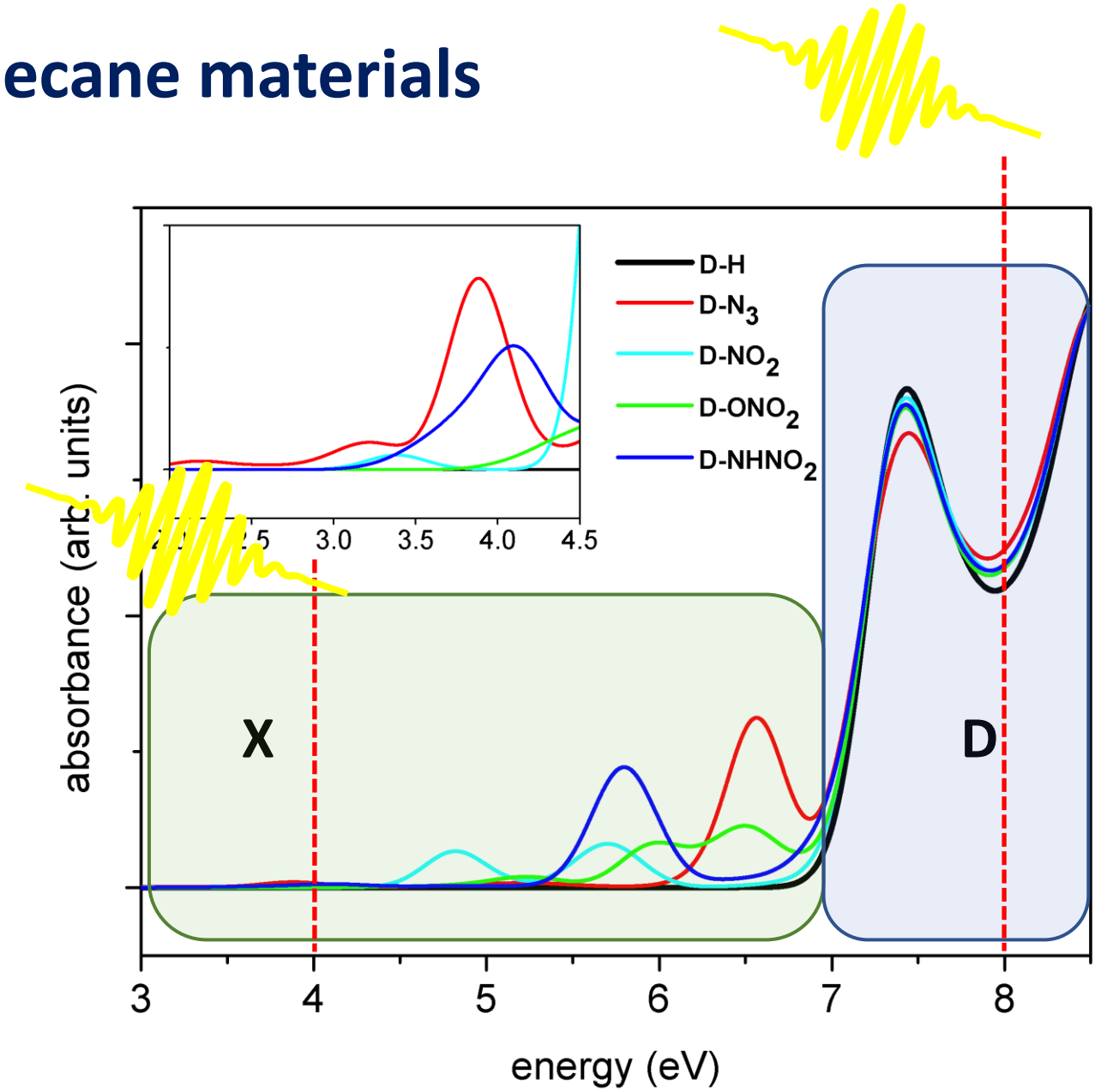
- Sunlight exposure
- Environmental remediation
- Scattering of higher energy radiation
- Photoinitiation
- Aging



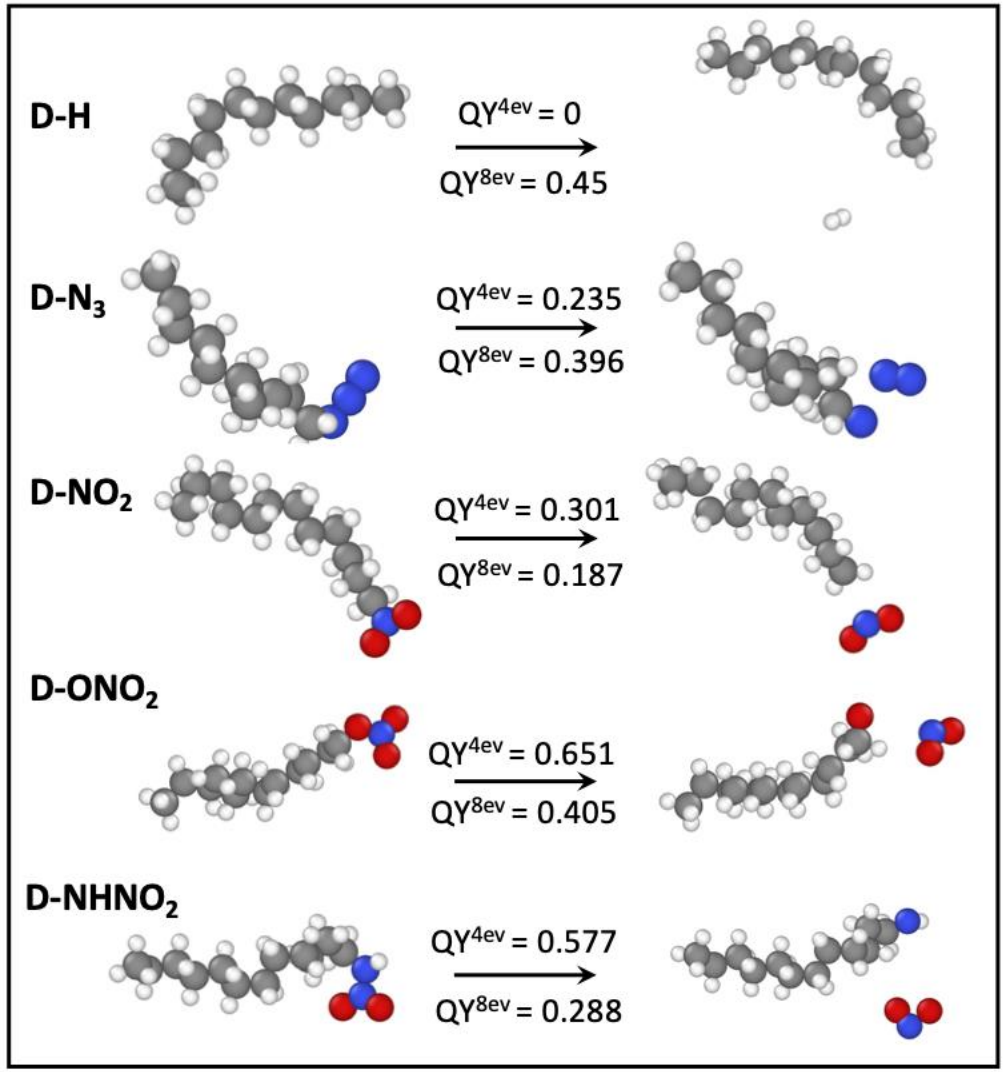
Functionalized Dodecane materials



Inert surrogates with uniform backbone



Photolysis Pathways



$$QY = \frac{number\ of\ trajectories\ with\ bond\ break}{total\ number\ of\ trajectories}$$

molecule	4 eV pathway (QY)	8 eV pathway (QY)
D-H	NA	D-H → D° + H_2 (0.45) D-H → D + $H^{+/-}$ (0.022) D-H → D" + CH_4 (0.002) D-H → D† + CH_3CH_2 (0.002)
D-N_3	D-N_3 → D-N + N_2 (0.235) D-N_3 → D + N_3 (0.002)	D-N_3 → D-N + N_2 (0.396) D-N_3 → D + N_3 (0.01) D-N_3 → D°-N_3 + $H^{+/-}$ (0.018) D-N_3 → D* + CH_2N_3 (0.007)
D-NO_2	D-NO_2 → D + NO_2 (0.301) D-NO_2 → D-NO + O (0.001)	D-NO_2 → D + NO_2 (0.187)
D-ONO_2	D-ONO_2 → D-O + NO_2 (0.651)	D-ONO_2 → D-O + NO_2 (0.405) D-ONO_2 → D°-O + NO_2 + $H^{+/-}$ (0.003)
D-$NHNO_2$	D-$NHNO_2$ → D-NH + NO_2 (0.577) D-$NHNO_2$ → D-N + NO_2 + $H^{+/\cdot/-}$ (0.001)	D-$NHNO_2$ → D-NH + NO_2 (0.288) D-$NHNO_2$ → D-NNO_2 + $H^{+/-}$ (0.007)

[1]D=$C_{12}H_{25}$; D°=$C_{12}H_{24}$; D"=$C_{11}H_{22}$; D†=$C_{10}H_{21}$; D*=$C_{11}H_{23}$

susceptibility to photolytic degradation:

4 eV: D-ONO_2 → D-$NHNO_2$ → D-NO_2 → D-N_3

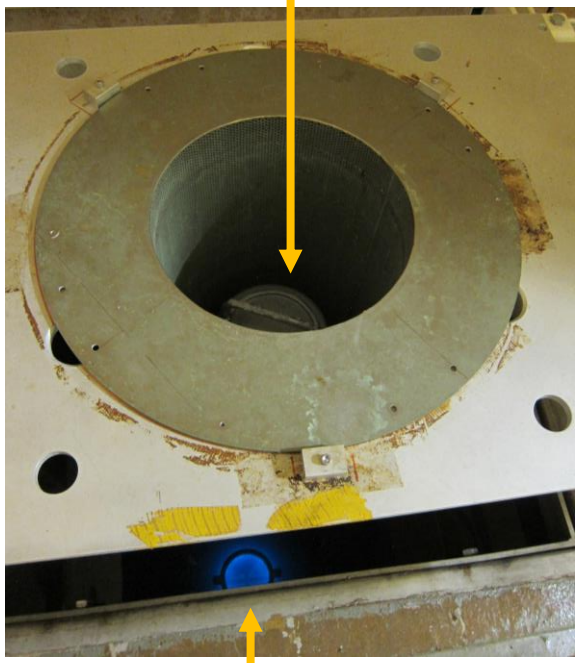
8 eV: D-ONO_2 → D-N_3 → D-$NHNO_2$ → D-NO_2

Decreasing susceptibility

Sub shock impact sensitivity

γ-Irradiation Experiments: Radiolysis products

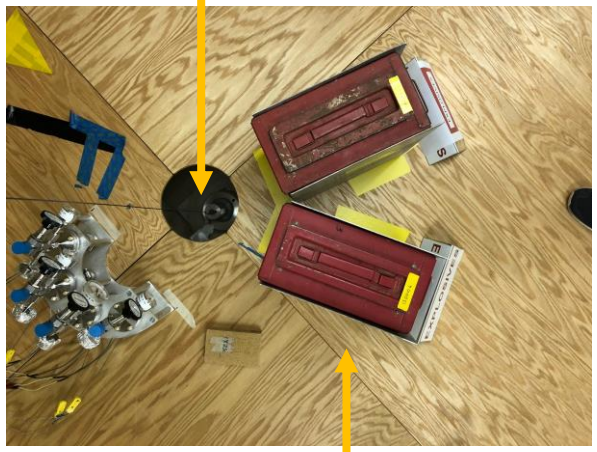
Pipe with explosives



Shutter array. (Blue glow is from the Cherenkov effect. Sources sit ~20 feet below water when not actively irradiating.)

Irradiation vessels containing explosives (inside ammo cans)

Location of ^{137}Cs button source



Ammo cans with explosives

Irradiation

- Gamma Irradiation Facility (GIF) at Sandia National Laboratories (SNL), ^{60}Co source (γ-ray energies 1.17 and 1.33 MeV)
- Irradiated for approximately 84 hours to achieve a total absorbed dose of 300 kGy-CaF2

γ-Irradiation Experiments: Radiolysis products

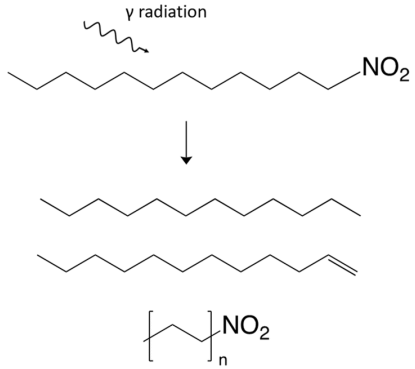
Analysis

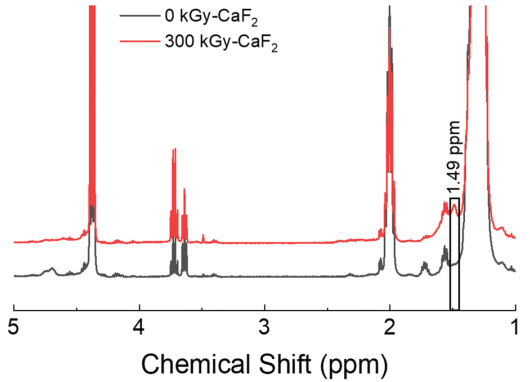
- Condensed phase analysis using gas chromatography time-of-flight mass spectrometry (GC-TOFMS)
- ^{1}H nuclear magnetic resonance (^{1}H-NMR) spectroscopy
- Headspace gas analysis using gas chromatography mass spectrometry (GC-MS)

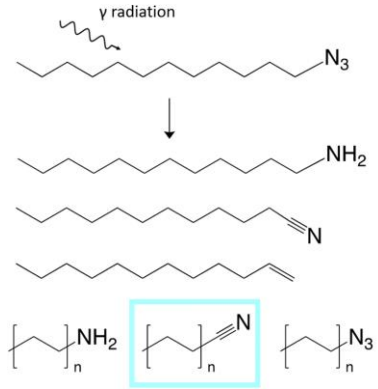
Radiolytic susceptibility

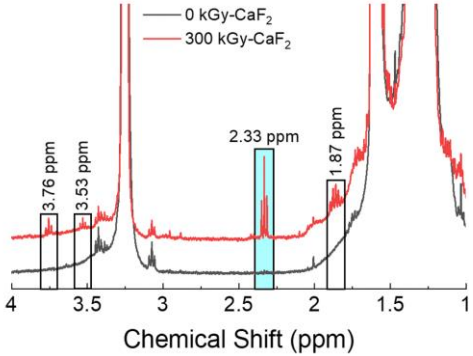
D-ONO2 → D-N3 → D-NHNO2 → D-NO2

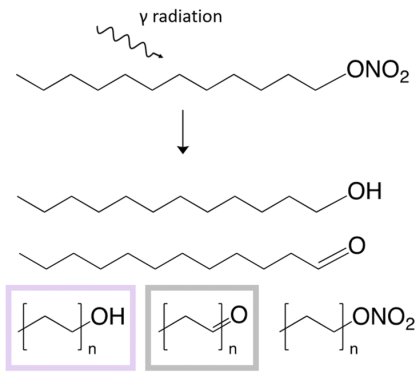
Decreasing susceptibility

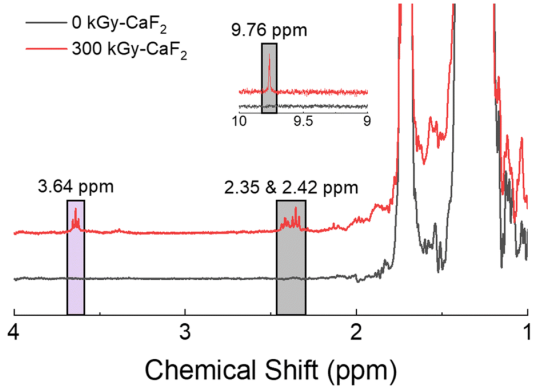




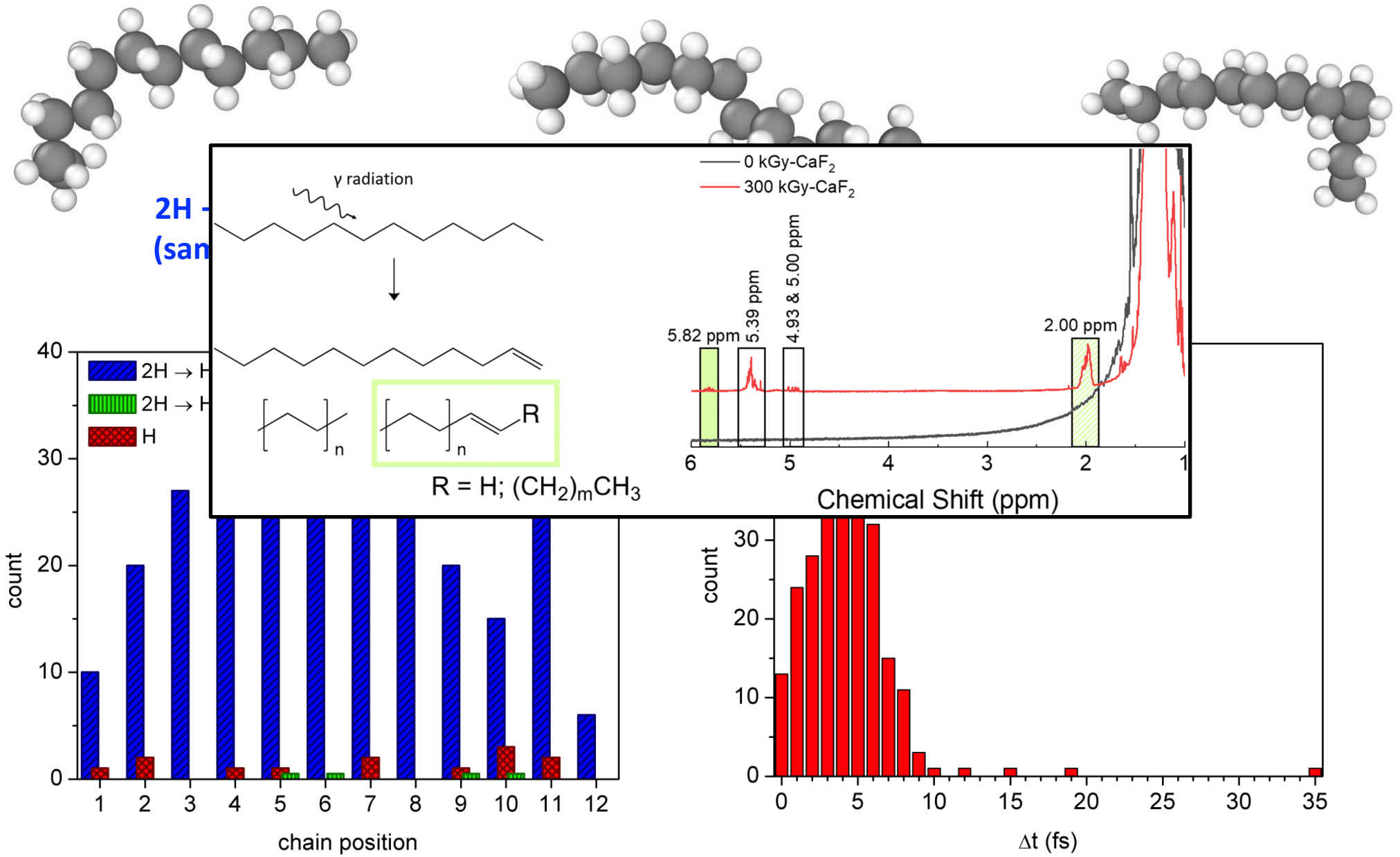




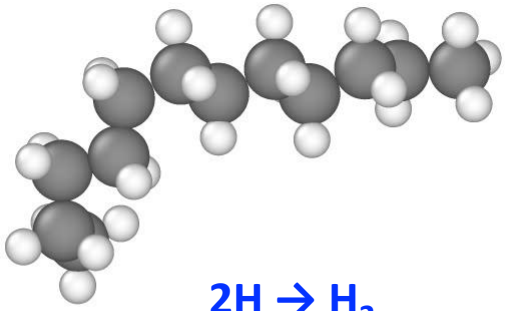




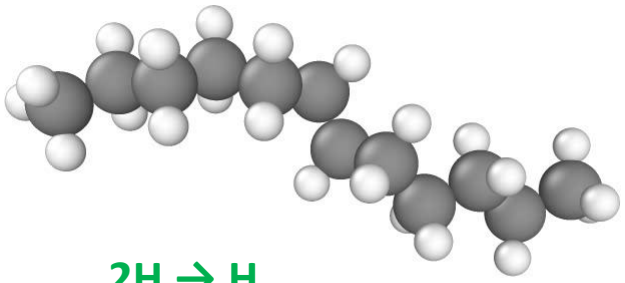
Detailed H Dissociation Mechanisms



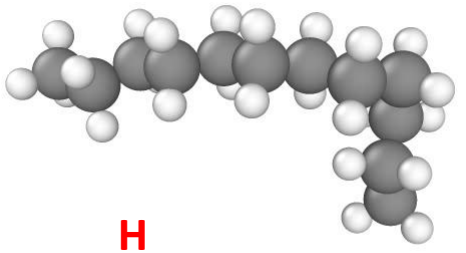
Detailed H Dissociation Mechanisms



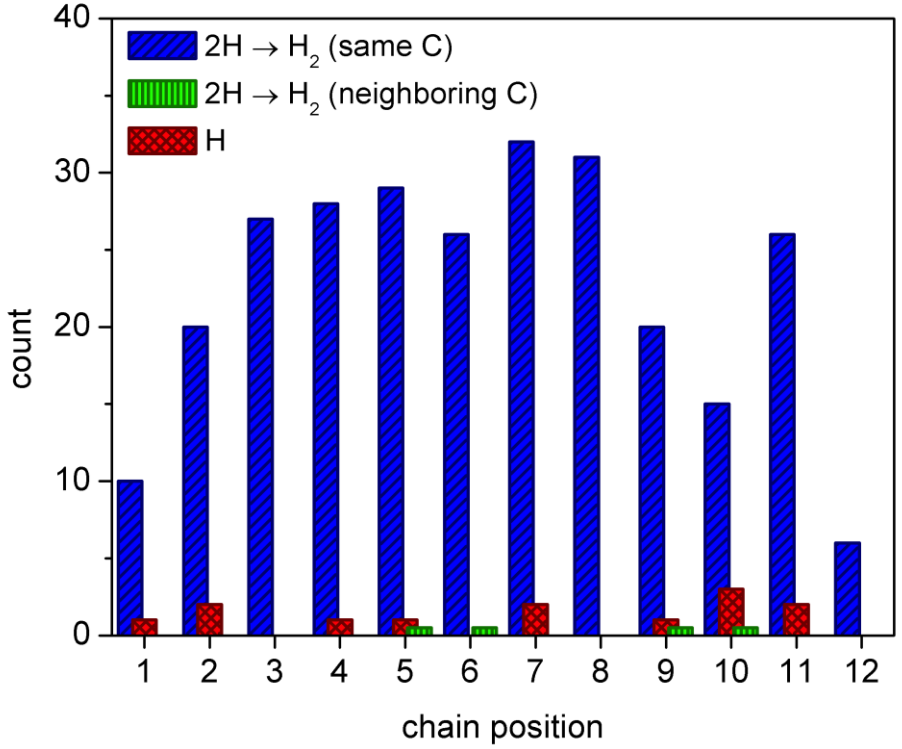
$2H \rightarrow H_2$ (same C)

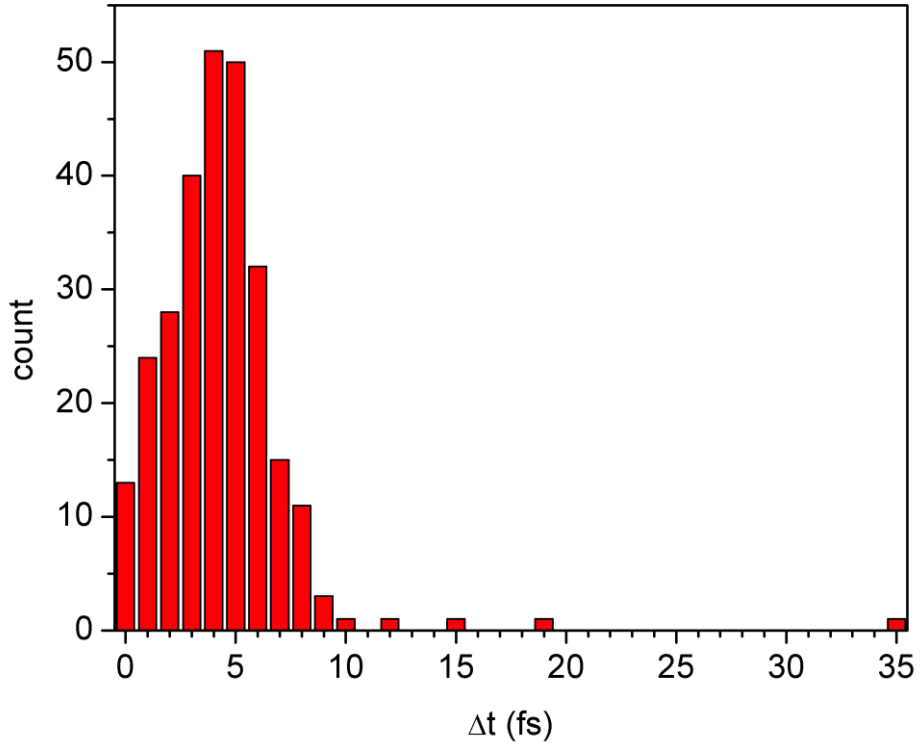


$2H \rightarrow H_2$ (neighboring C)

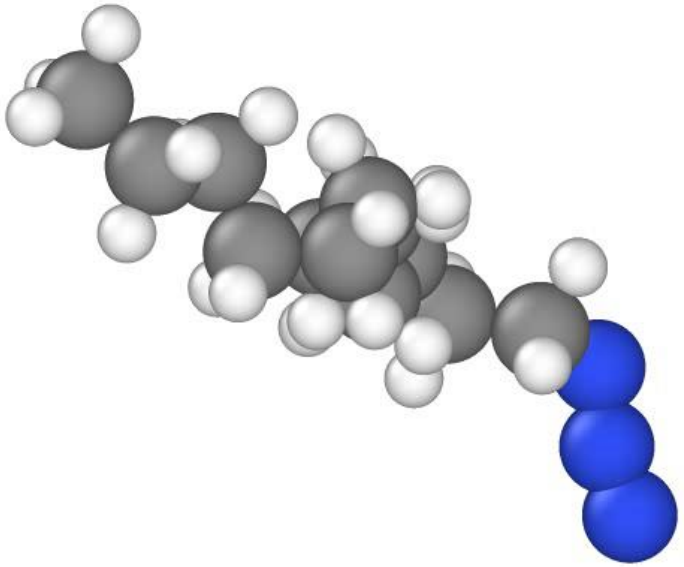


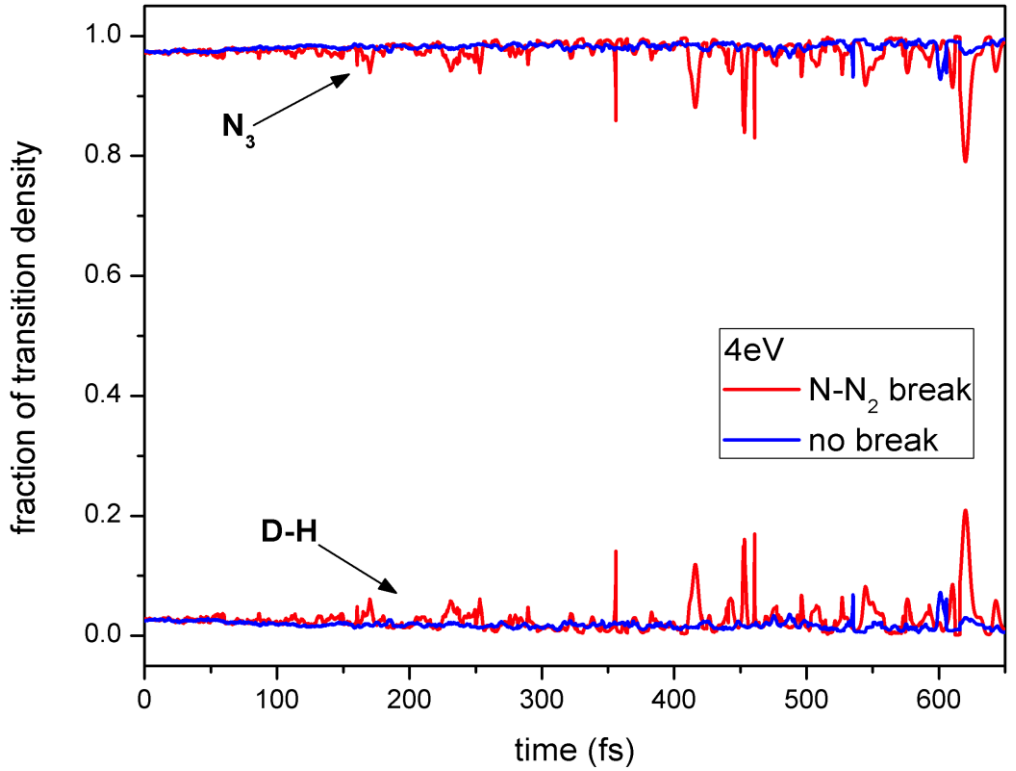
H

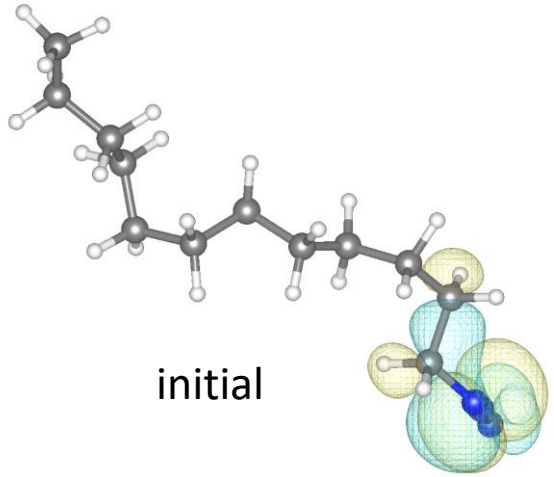




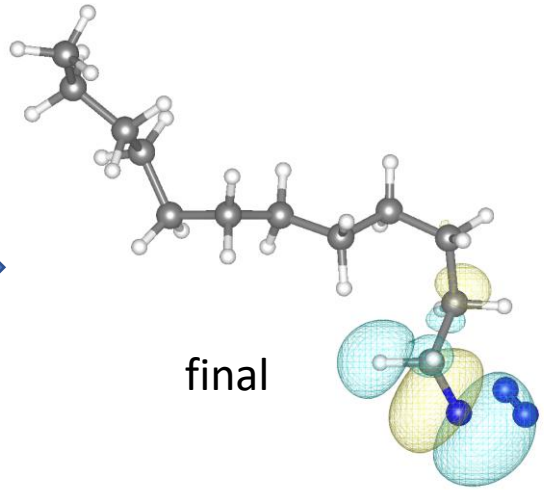
Electron Density Localization (4 eV)





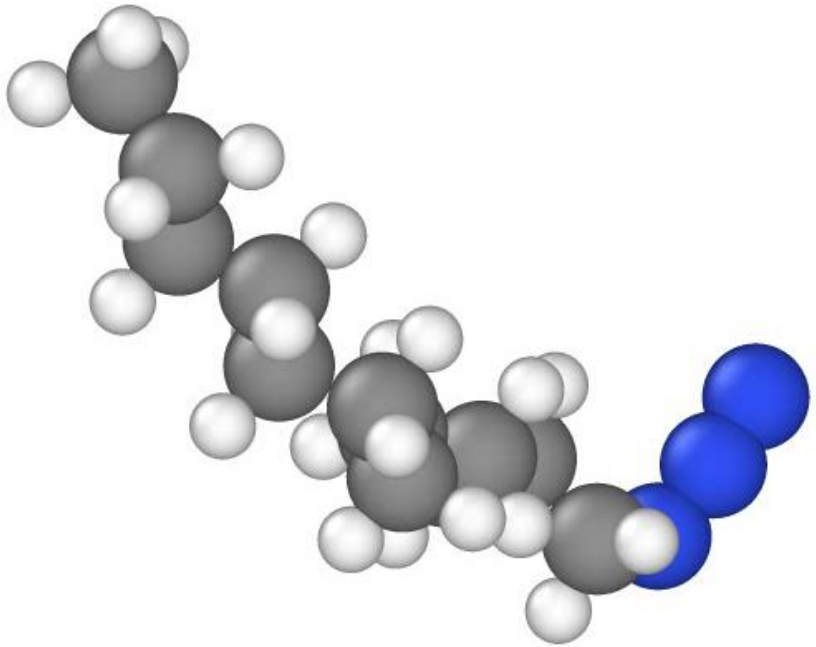


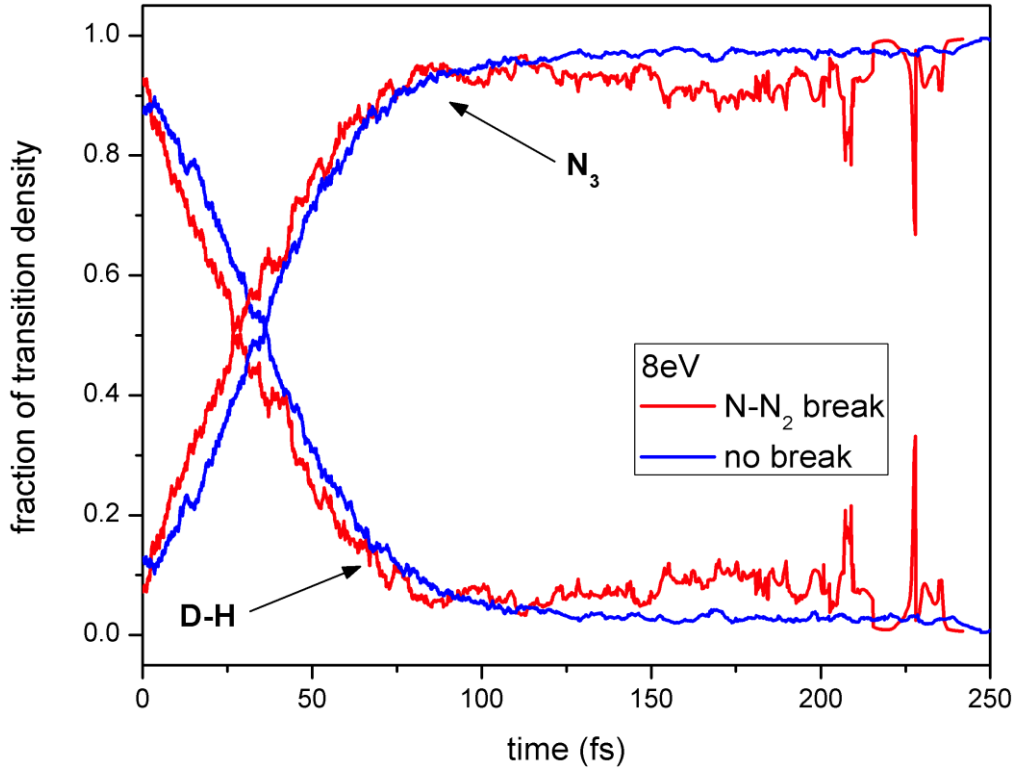
initial

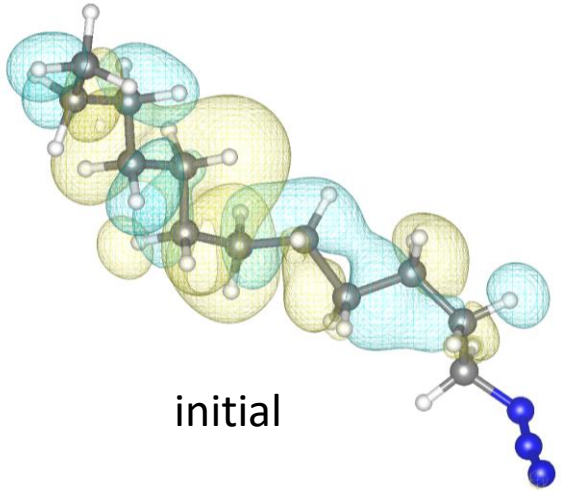


final

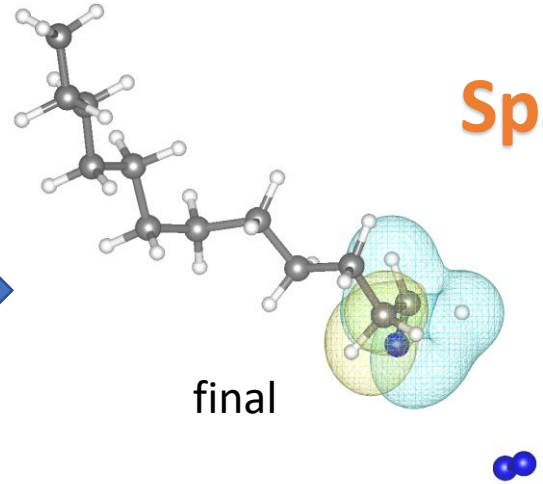
Electron Density Localization (8 eV)





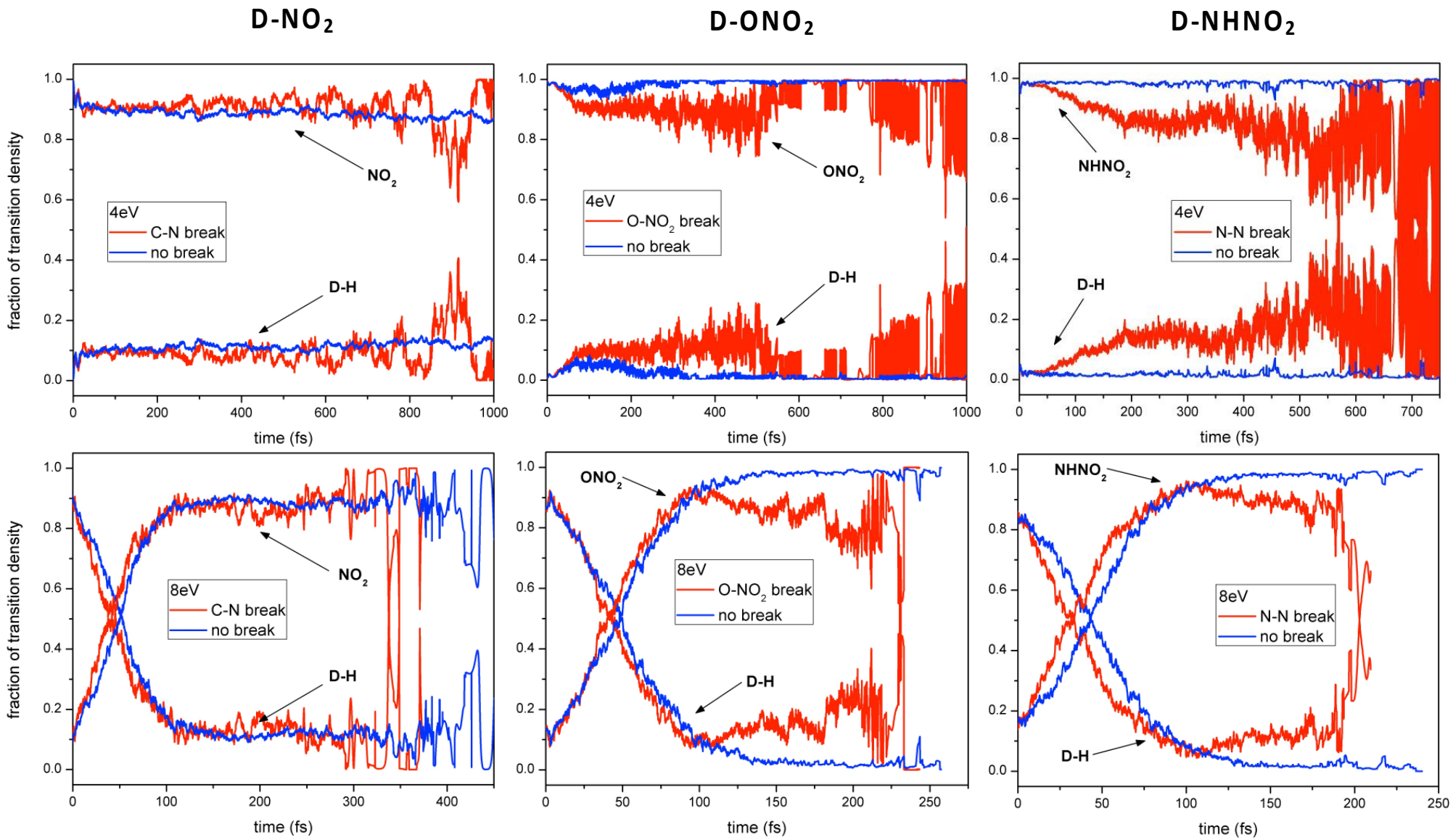


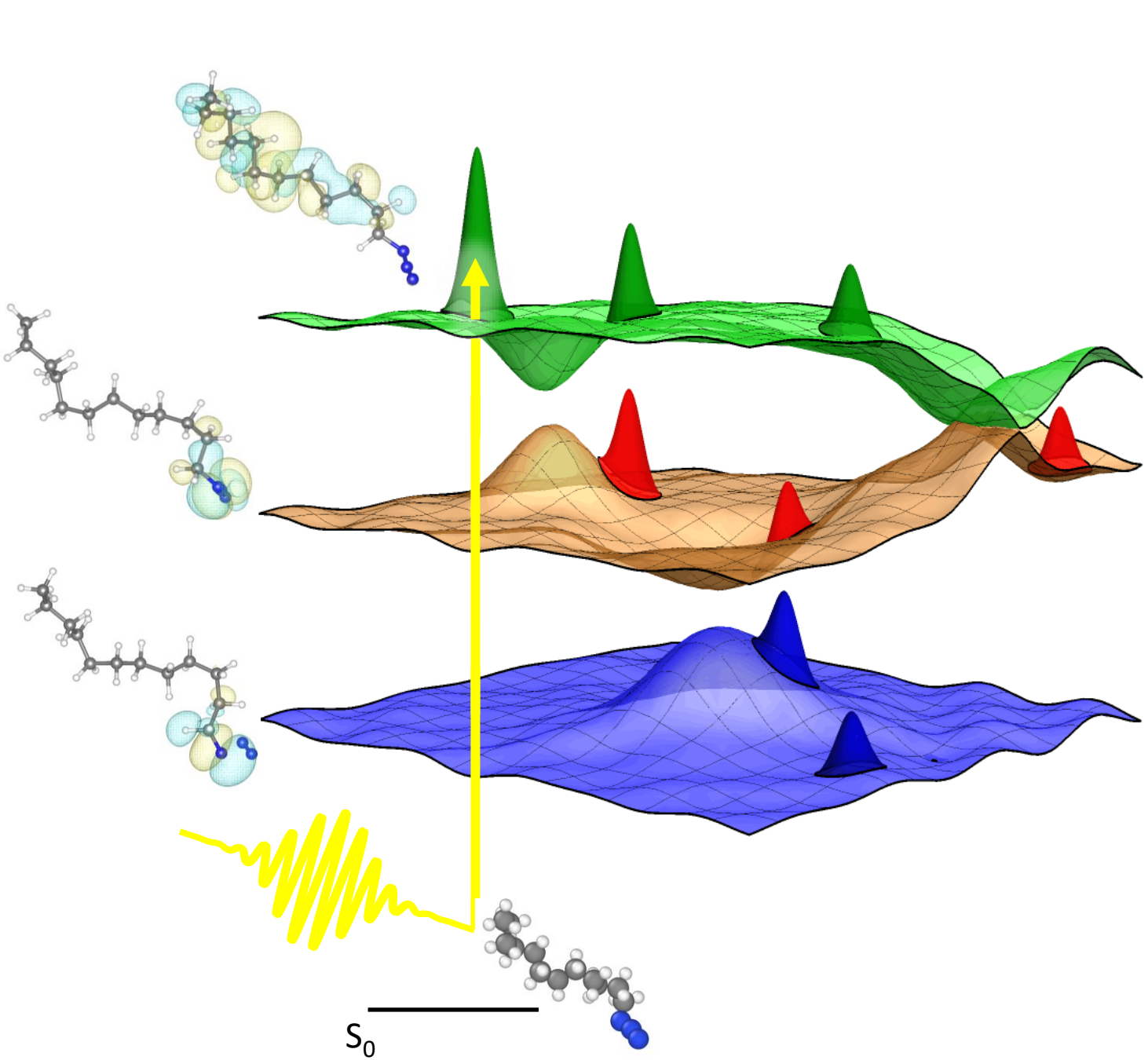
initial

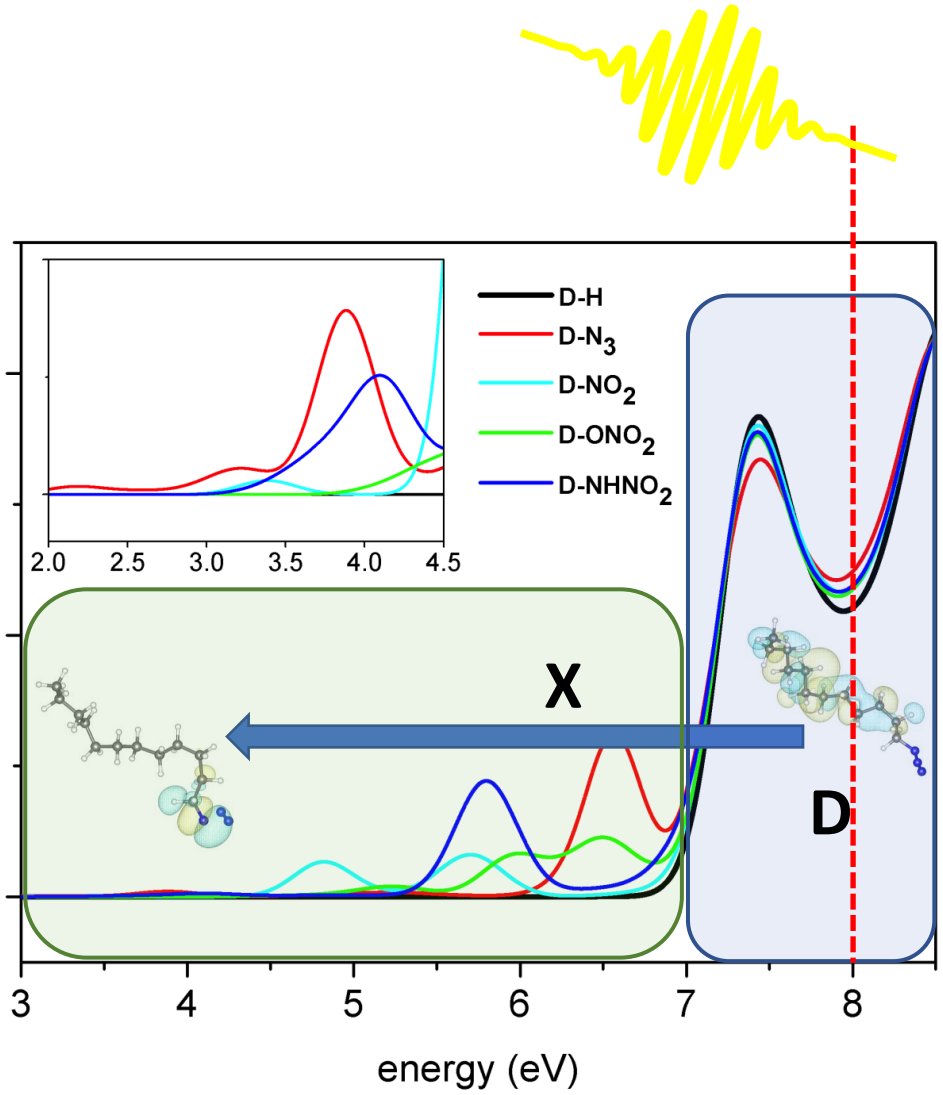


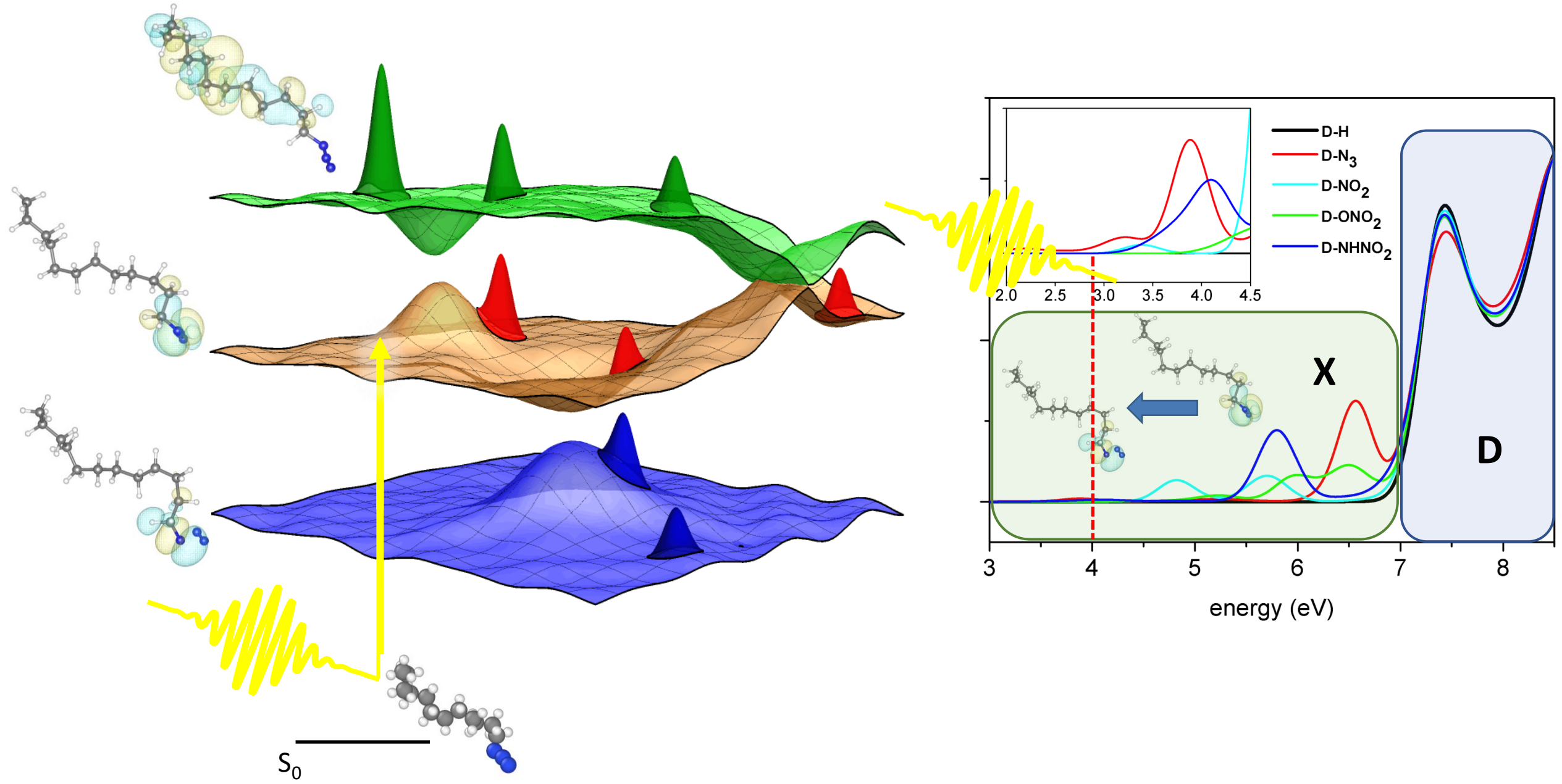
final

Spatial Energy Transfer


D-NO2
D-ONO2
D-NHNO2
fraction of transition density
time (fs)
4eV
C-N break
no break
O-NO2 break
N-N break
8eV
NO2
ONO2
NHNO2
D-H


S0


D-H
D-N3
D-NO2
D-ONO2
D-NHNO2
2.0
2.5
3.0
3.5
4.0
4.5
X
D
3
4
5
6
7
8
energy (eV)


S0
D-H
D-N3
D-NO2
D-ONO2
D-NHNO2
2.0
2.5
3.0
3.5
4.0
4.5
X
D
3
4
5
6
7
8
energy (eV)

Conclusions for photoloysis applications

- First known systematic study comparing photolytic stability of energetic functional groups using consistent backbone structure
- Photolysis degradation pathways and ranking for nitrate esters, nitramines, and nitro groups are comparable between photolysis results and thermal and sub shock degradation
- More degradation pathways become available at 8 eV, the predominant degradation pathway remained the same for the two energies
- Predicted UV degradation products and susceptibility consistent with gamma irradiation degradation products and susceptibility determined by GC, ^{1}H-NMR spectroscopy
- No matter where energy is initially localized, it travels to the energetic functional group
- Azide does not behave as the other functional groups modeled, exact reason for this requires more work to be done

Acknowledgements

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Yu Zhang (LANL)
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Patricia Huestis (LANL)

Photolysis Experiments
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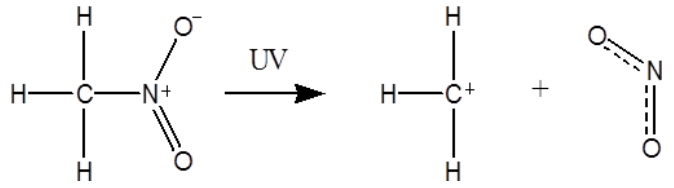
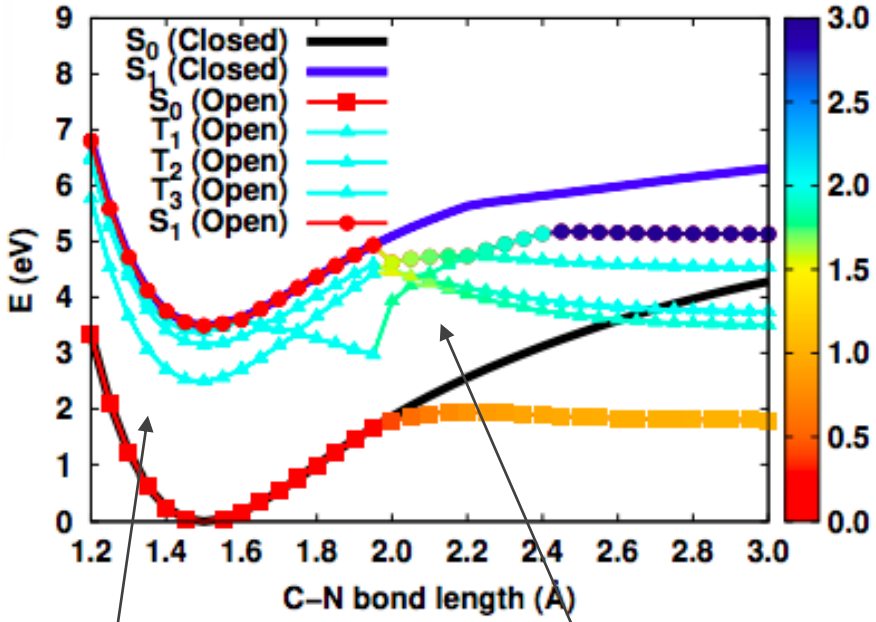
Daniel Huber (LANL)
Geoffrey Brown (LANL)
Daniel McDonald (LANL)
Christopher Snyder (LANL)

Appearance of Triplet-like states in open-shell

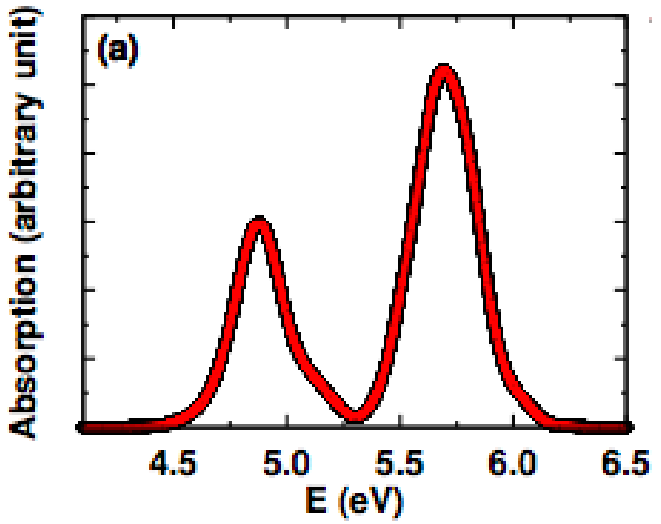




Pure states close to equilibrium

Reduced reaction barriers

- Appearance of Singlet-like $\langle S^2 \rangle = 0$ and Triplet-like states $\langle S^2 \rangle = 2$
- Mixed states near bond breaking region
- Triplets are dark states



$$\xi^{\alpha} = -\xi^{\beta}$$

Closed-shell
10 states

Open-shell
20 states