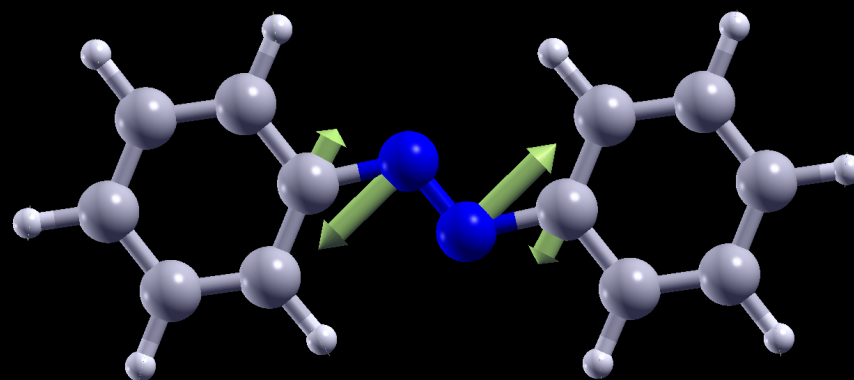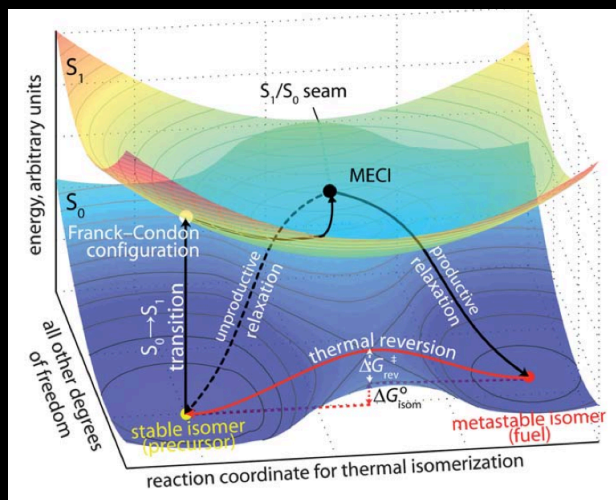# Photoisomerization dynamics of solar thermal fuels with TDDFT excited-state forces

David A. Strubbe and Jeffrey C. Grossman

Department of Materials Science and Engineering
Massachusetts Institute of Technology
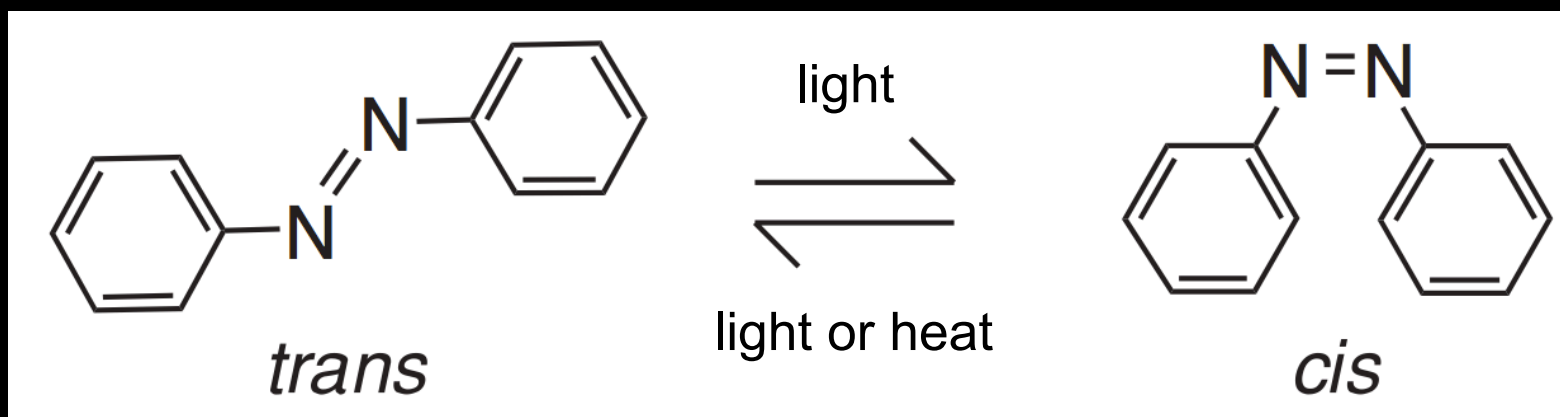
MASSACHUSETTS INSTITUTE OF TECHNOLOGY

Solar thermal fuels

sunlight → chemical energy → heat

solar cell + battery + resistor

Key performance metrics

Absorption cross-section
Quantum yield of photoisomerization
Energy stored per molecule (weight, volume)
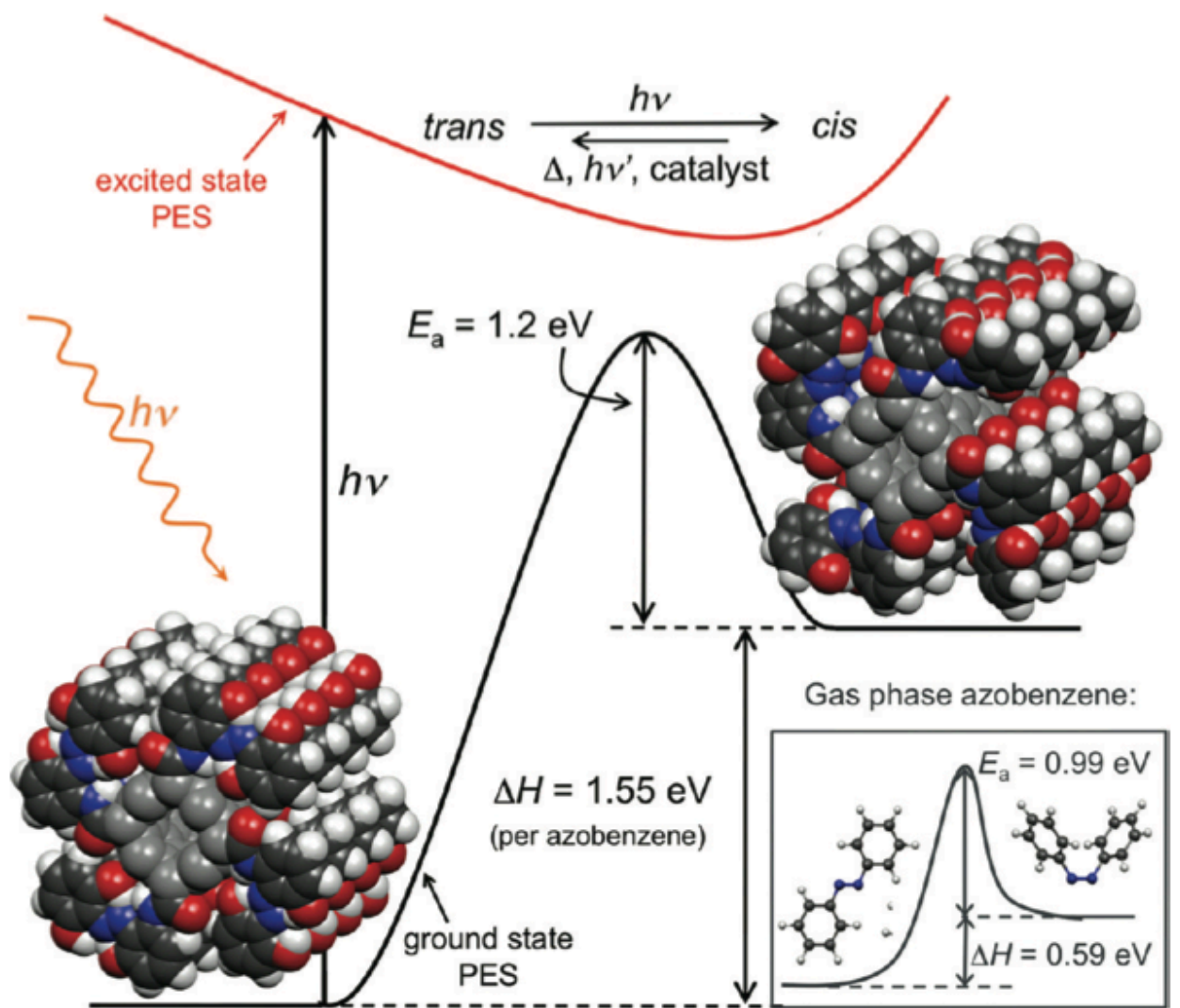Barrier to thermal reversion (lifetime)

Azobenzene:
UV excitation
0.6 eV storage
1.0 eV thermal barrier

Templating and functionalization

trans $\xrightarrow[\Delta,\ h\nu',\ \text{catalyst}]{h\nu}$ cis

excited state PES

$h\nu$

$h\nu$

$E_a = 1.2$ eV

$\Delta H = 1.55$ eV (per azobenzene)

ground state PES

Gas phase azobenzene:
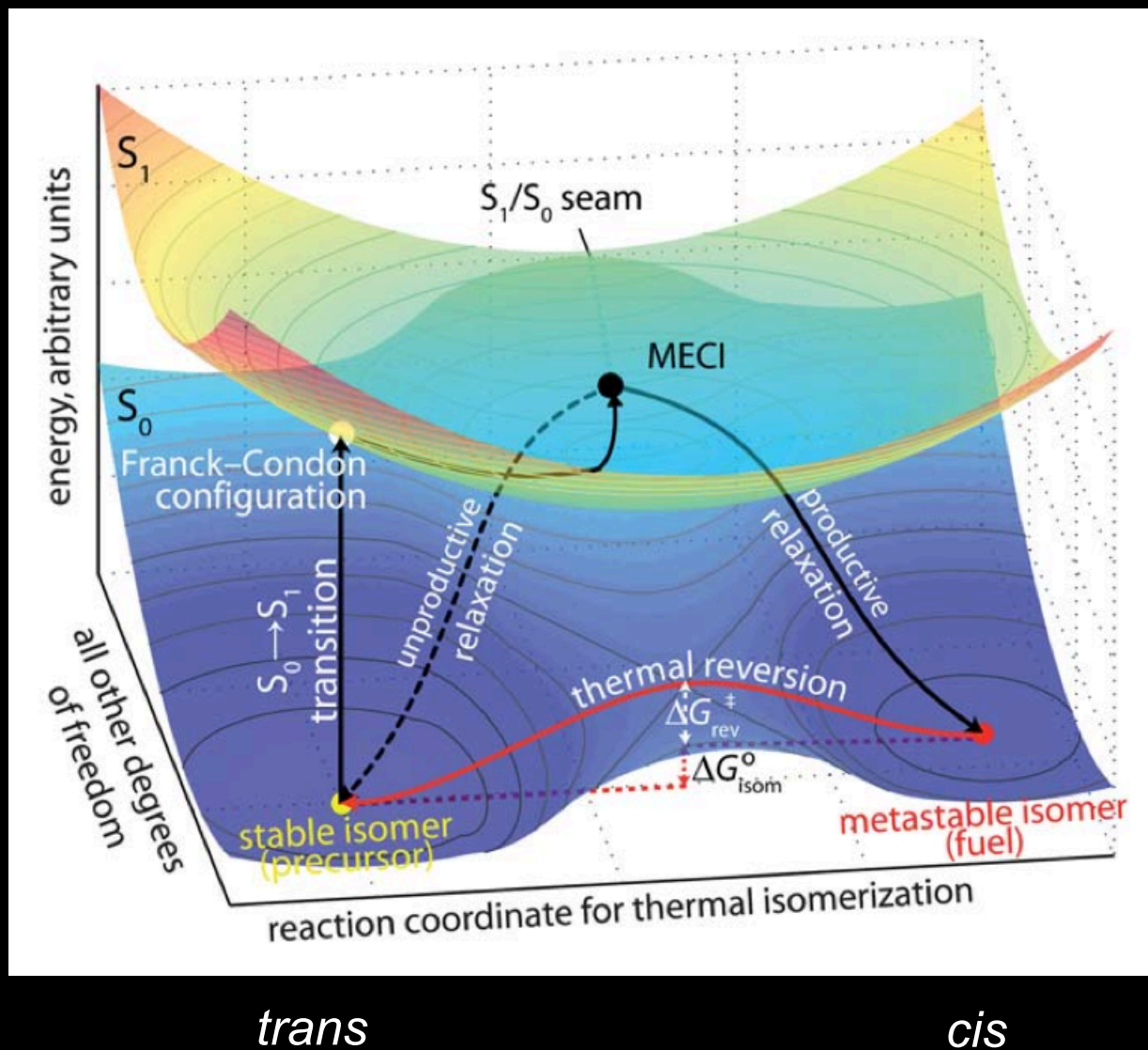
$E_a = 0.99$ eV

$\Delta H = 0.59$ eV

Improved energy storage and thermal barrier (lifetime)

Synthesized and experimentally verified

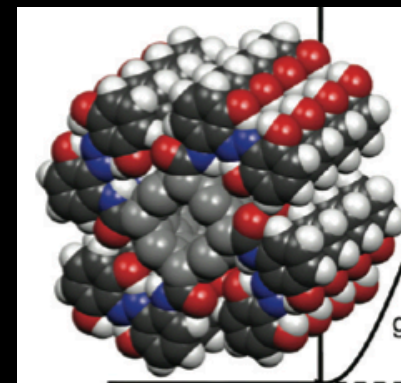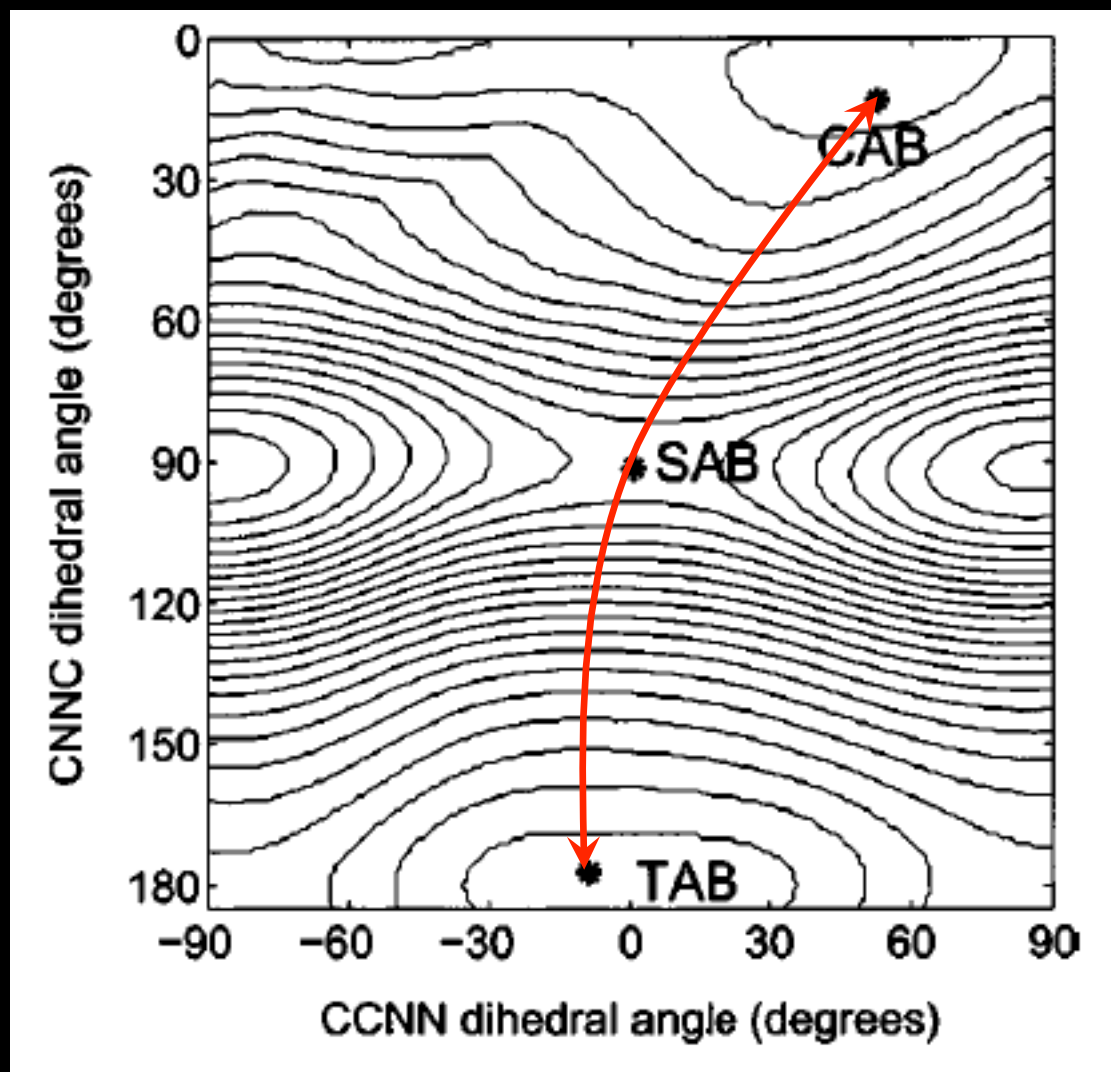What about quantum yield? barriers, quenching, sensitization

A. M. Kolpak and J. C. Grossman, *Nano Lett.* **11**, 3156 (2011)
T. J. Kucharski *et al.*, *Nat. Chem.* **6**, 441-447 (2014)

Potential energy surfaces for photoisomerization

trans

cis

Potential energy surfaces for photoisomerization

Too many degrees of freedom to vary all.

Which are the key ones?

Follow forces.

TDDFT: need efficient method for large system!

constrained DFT for azobenzene

M. L. Tiago, S. Ismail-Beigi, and S. G. Louie, *J. Chem. Phys.* **122**, 094311 (2005)

Excited-state forces in TDDFT

$$E_{\mathrm{S}} = E_0 + \omega$$

$$\partial E_{\mathrm{S}} = \partial E_0 + \partial \omega$$

Derivative of excitation energy with respect to atomic displacements.

Ground-state forces from DFT (= 0 at equilibrium)

Tamm-Dancoff approximation (for simplicity)

$$H^{(2)} |A\rangle = \omega |A\rangle$$

$$\langle cv | H^{(2)} | c'v' \rangle = (\epsilon_c - \epsilon_v)\, \delta_{cc'} \delta_{vv'} + \langle cv | v + f_{\mathrm{xc}} | c'v' \rangle$$

S. Hirata and M. Head-Gordon, *Chem. Phys. Lett.* **314**, 291 (1999)

$$\omega = \langle A | H^{(2)} | A \rangle$$

A = *e-h* state
c = unoccupied
v = occupied

Excited-state forces in TDDFT

Analytic derivative: Hellman-Feynman Theorem

$$\partial\omega = \langle A | \partial H^{(2)} | A \rangle$$

$$\langle cv | \partial H^{(2)} | c'v' \rangle = \langle c' | \partial H | c \rangle \delta_{vv'} - \langle v | \partial H | v' \rangle \delta_{cc'} + \langle cv | K_{\mathrm{xc}} \partial\rho | c'v' \rangle$$

Hartree derivative is zero,
so would be exact exchange

Density-functional perturbation theory

$$(H - \epsilon_v) | \partial v \rangle = -\partial H | v \rangle$$

Implemented in Octopus real-space TDDFT code

Using adiabatic LDA functional (VWN parameterization)

www.tddft.org/programs/octopus

X. Andrade, J. Alberdi-Rodriguez, D. A. Strubbe, *et al.*,
J. Phys.: Condens. Matter **24**, 233202 (2012)

Comparison to other approaches for excited-state forces

Standard approaches use sum over states instead of DFPT

e.g. J. Hütter, *J. Chem. Phys.* **118**, 3928 (2003)

Based on earlier work on TDDFT Casida equation forces with DFPT

A. Sitt, L. Kronik, S. Ismail-Beigi, and J. R. Chelikowsky, *Phys. Rev. A* **76**, 054501 (2007)
T. Tsukagoshi, and O. Sugino, Phys. Rev. A **86**, 064501 (2012)

Now, no further expansion in unoccupied states required.

Inspired by corresponding approach to Bethe-Salpeter equation

$$\epsilon_{ck}^{KS} - \epsilon_{vk}^{KS} \rightarrow \epsilon_{ck}^{GW} - \epsilon_{vk}^{GW}$$
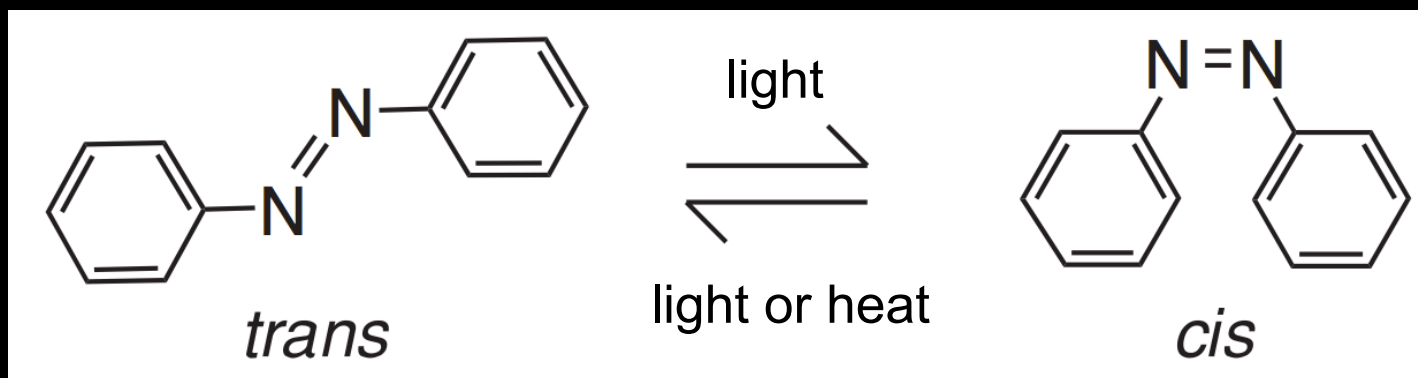
$$f_{xc}(r, r') \rightarrow \langle c'k', ck | \epsilon^{-1}\hat{v} | v'k'vk \rangle + \langle vck | \hat{v} | v'c'k' \rangle$$

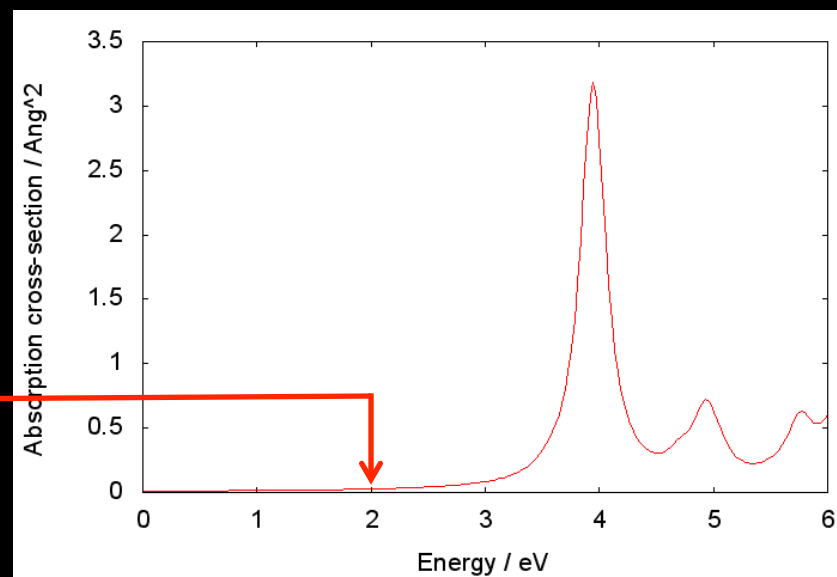S. Ismail-Beigi and S. G. Louie, *Phys. Rev. Lett.* **90**, 076401 (2003)
D. A. Strubbe, PhD thesis, University of California, Berkeley (2012)
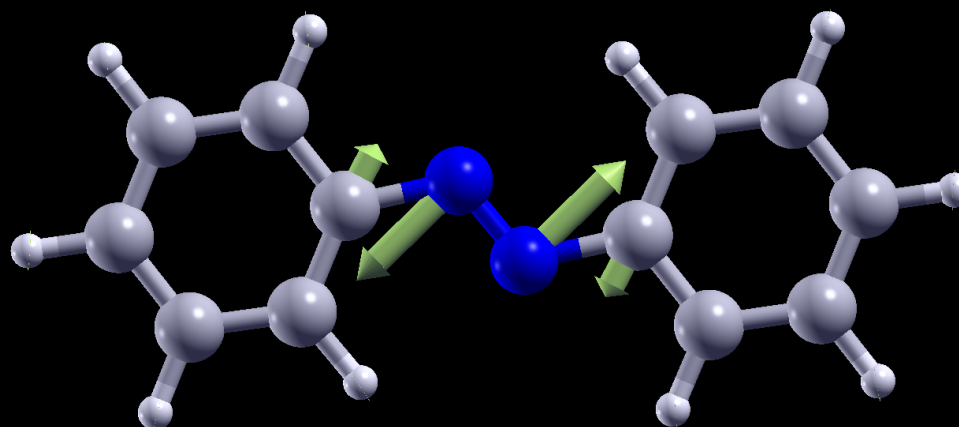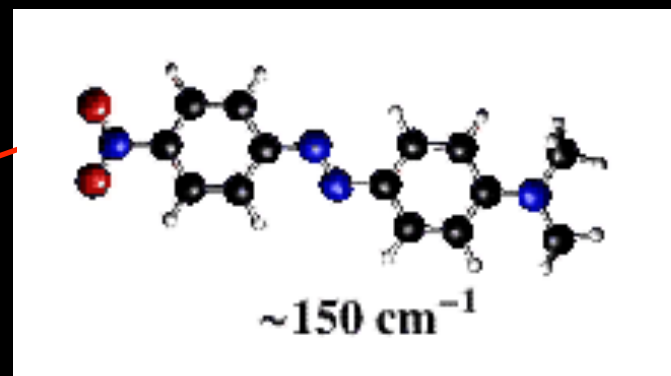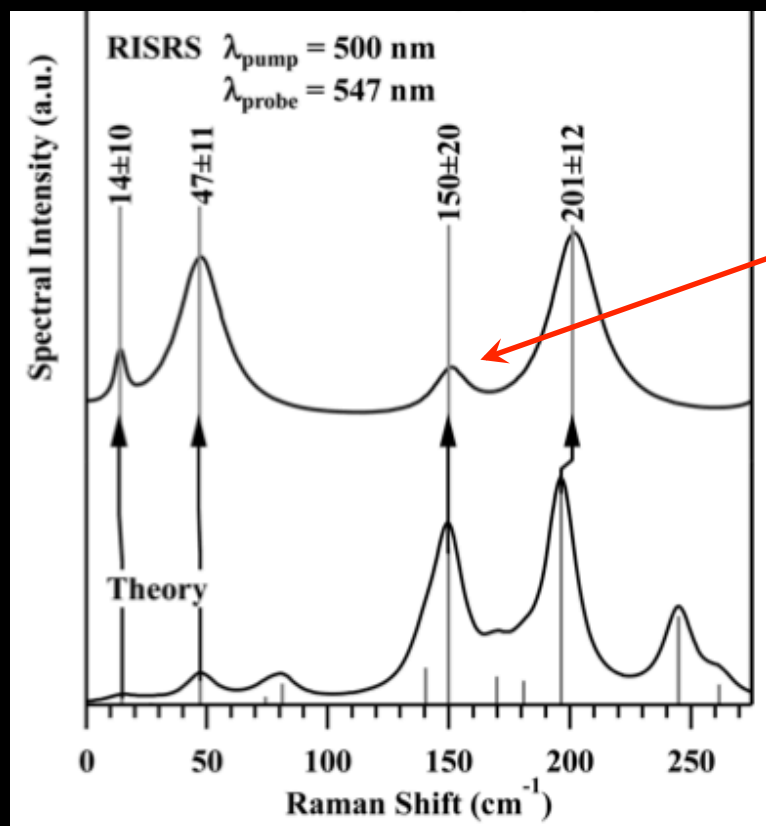
Benchmark adiabatic LDA/TDDFT against more powerful theory

trans-azobenzene: initial forces
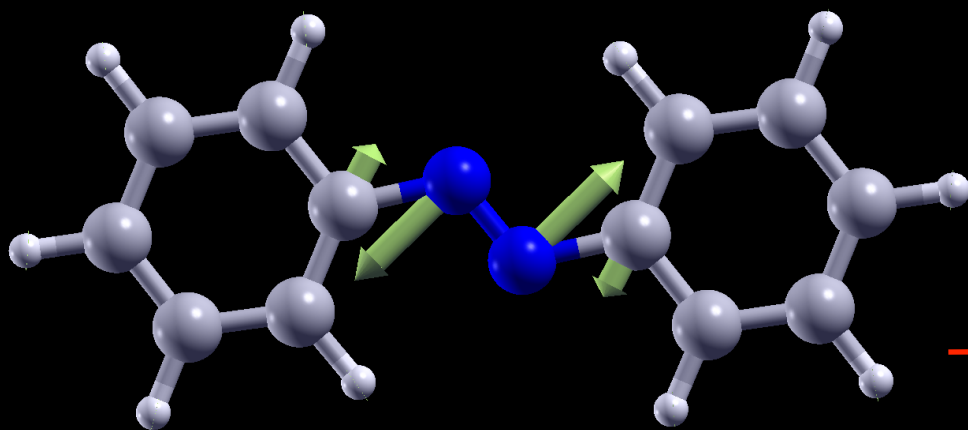
Lowest singlet, 2.0 eV
Forces ~ 0.06 eV/Å

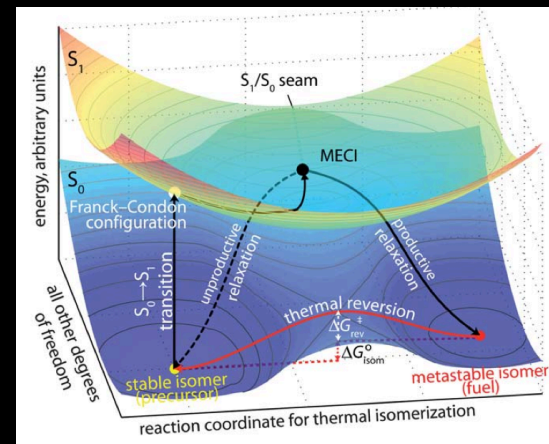# Resonant impulsive stimulated Raman spectroscopy

Modes excited by light

D. P. Hoffman, S. R. Ellis, and R. A. Mathies, *J. Phys. Chem. A* **117**, 11472 (2013)

cis-azobenzene: initial forces
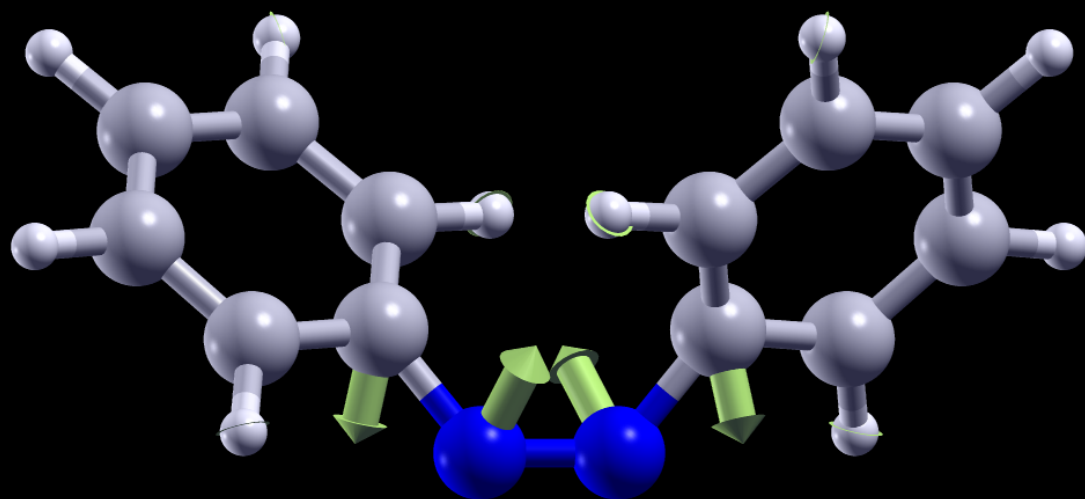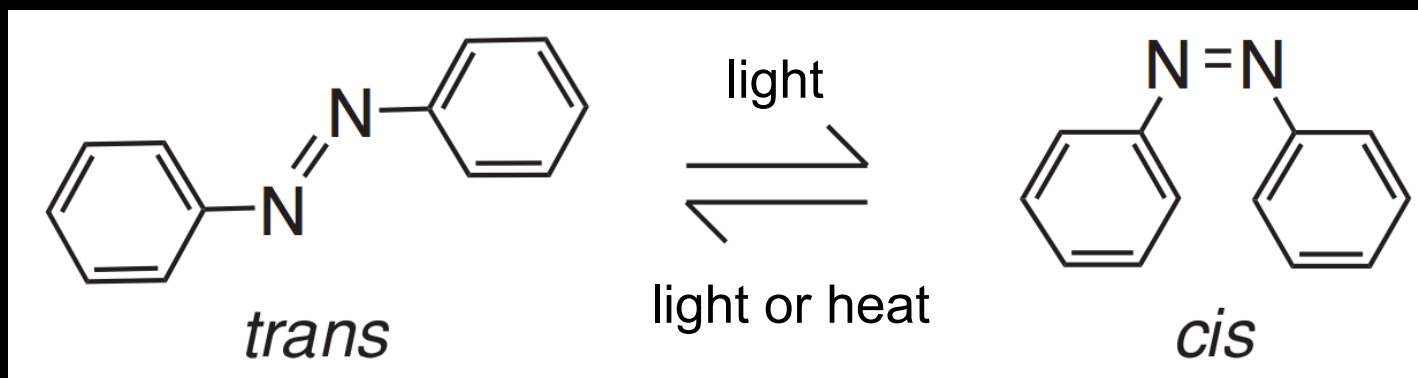
Forces ~ 0.04 eV/Å

norbornadiene   **quadricyclane**

hν

NBD, **1**   *hν* or $k_B T$ QC, **2**
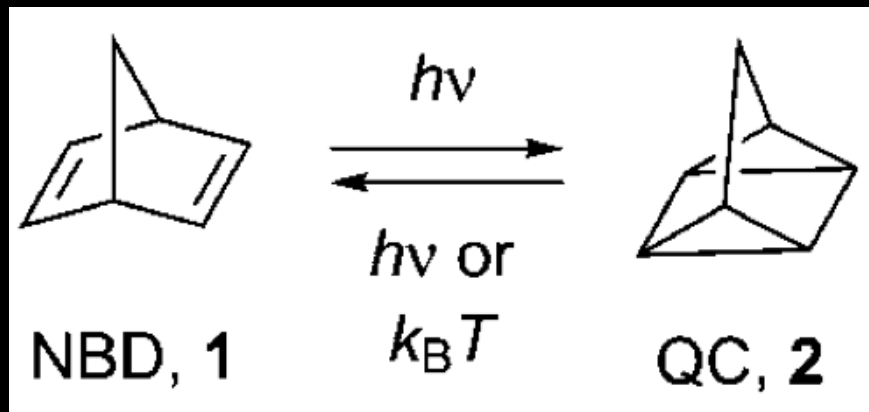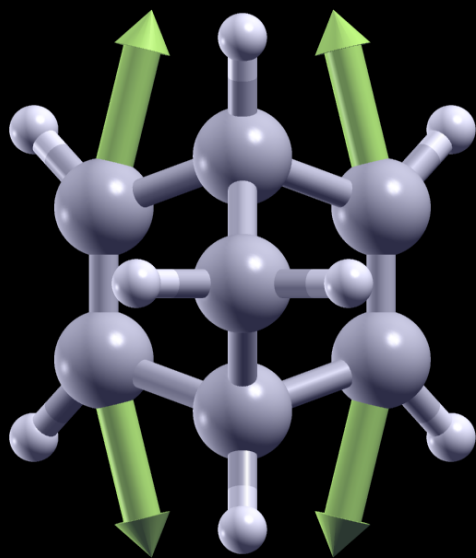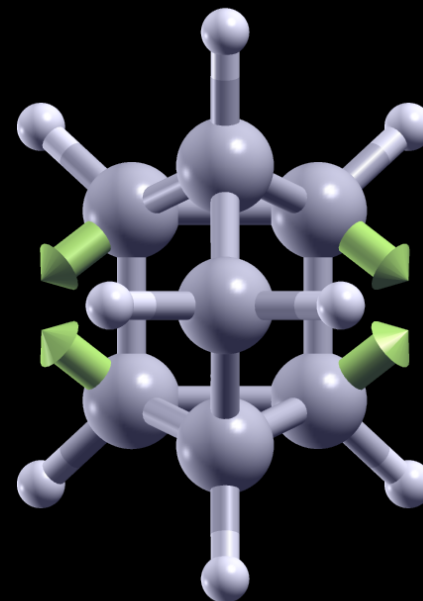
0.9 eV storage
1.4 eV thermal barrier

Lowest singlet, 4.6 eV
Forces ~ 0.03 eV/Å

Lowest singlet, 4.0 eV
Forces ~ 0.03 eV/Å

Conclusions

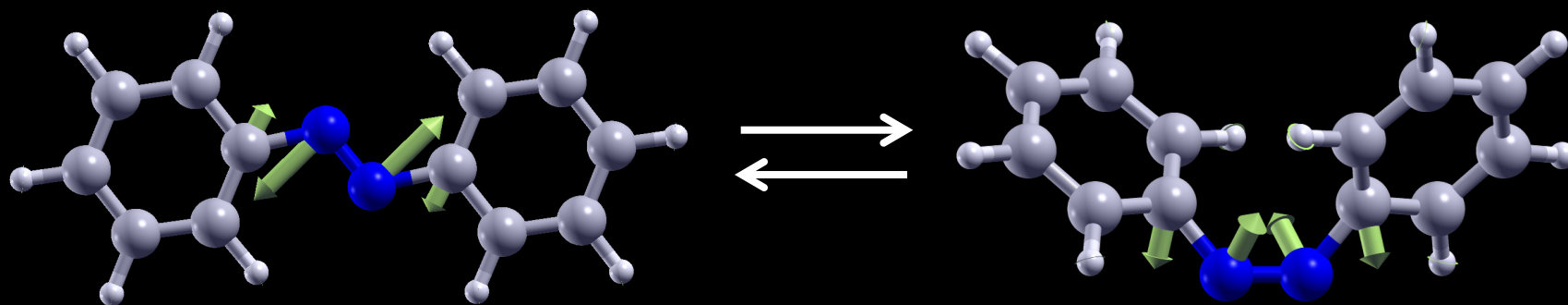Improved formulation of excited-state forces in TDDFT

Implemented in freely available Octopus code

www.tddft.org/programs/octopus

Access to photoisomerization dynamics of large and complex systems

Initial forces on *trans*-azobenzene consistent with spectroscopy

Based on earlier work on TDDFT Casida equation forces

A. Sitt, L. Kronik, S. Ismail-Beigi, and J. R. Chelikowsky, *Phys. Rev. A* **76**, 054501 (2007)
T. Tsukagoshi, and O. Sugino, Phys. Rev. A **86**, 064501 (2012)

Now, no further expansion in unoccupied states required.

No calculation of expensive Hartree ("exchange") terms

Degenerate perturbation theory

Correct derivative of Casida S^1/2 matrices possible

show Casida here, or QC approaches?

Extended Lagrangian for Tamm-Dancoff approximation
(as in Rothlisberger talk)

F. Furche and R. Ahlrichs, *J. Chem. Phys.* **117**, 7433 (2002)
J. Hütter, *J. Chem. Phys.* **118**, 3928 (2003)