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Title: Non-adiabatic Excited State Molecule Dynamics Modeling of Photochemistry and Photophysics of Materials

Author(s): Nelson, Tammie Renee
Tretiak, Sergei

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Project Title & Participants

Non-adiabatic Excited State Molecule Dynamics Modeling of Photochemistry and Photophysics of Materials

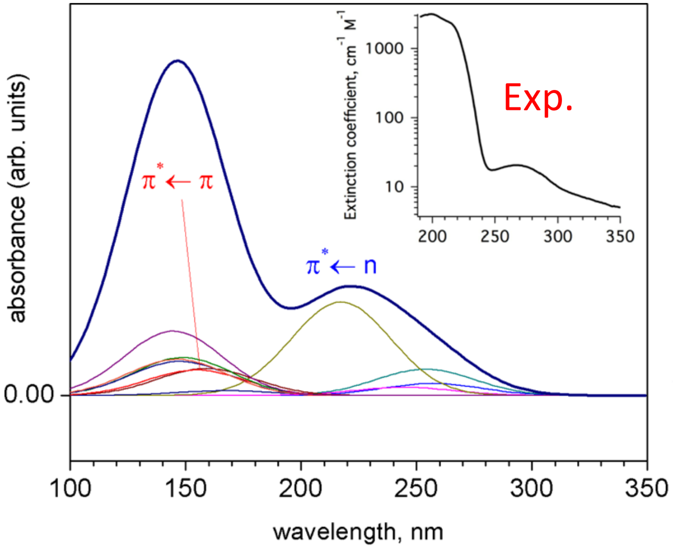
PI: Sergei Tretiak, Theoretical Division, T-1/MPA-CINT, serg@lanl.gov, 505-667-8351
Tammie Nelson, Theoretical Division, T-1, tammien@lanl.gov, 5-6828

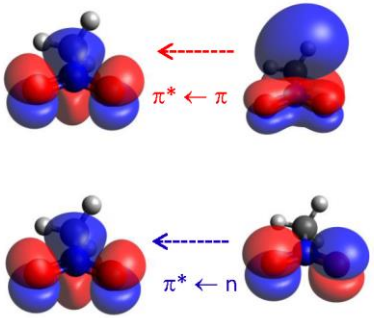
Project: W15_naesmd

Abstract:

Understanding and controlling excited state dynamics lies at the heart of all our efforts to design photoactive materials with desired functionality. This tailor-design approach has become the standard for many technological applications (e.g., solar energy harvesting) including the design of organic conjugated electronic materials with applications in photovoltaic and light-emitting devices. Over the years, our team has developed efficient LANL-based codes to model the relevant photophysical processes following photoexcitation (spatial energy transfer, excitation localization/delocalization, and/or charge separation). The developed approach allows the non-radiative relaxation to be followed on up to ~10 ps timescales for large realistic molecules (hundreds of atoms in size) in the realistic solvent dielectric environment. The Collective Electronic Oscillator (CEO) code is used to compute electronic excited states, and the Non-adiabatic Excited State Molecular Dynamics (NA-ESMD) code is used to follow the non-adiabatic dynamics on multiple coupled Born-Oppenheimer potential energy surfaces. Our preliminary NA-ESMD simulations have revealed key photoinduced mechanisms controlling competing interactions and relaxation pathways in complex materials, including organic conjugated polymer materials, and have provided a detailed understanding of photochemical products and intermediates and the internal conversion process during the initiation of energetic materials. This project will be using LANL-based CEO and NA-ESMD codes to model non-radiative relaxation in organic and energetic materials. The NA-ESMD and CEO codes belong to a class of electronic structure/quantum chemistry codes that require large memory, "long-queue-few-core" distribution of resources in order to make useful progress. The NA-ESMD simulations are trivially parallelizable requiring ~300 processors for up to one week runtime to reach a meaningful restart point.

Non-adiabatic Excited State Molecular Dynamics Modeling of Photochemistry in Energetic Materials



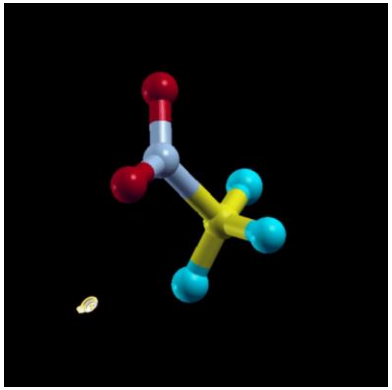


$\tau = 452 \pm 9\,fs$

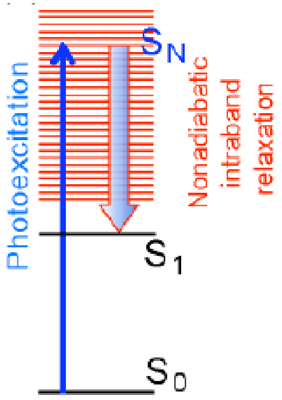
NA-ESMD QY 0.04

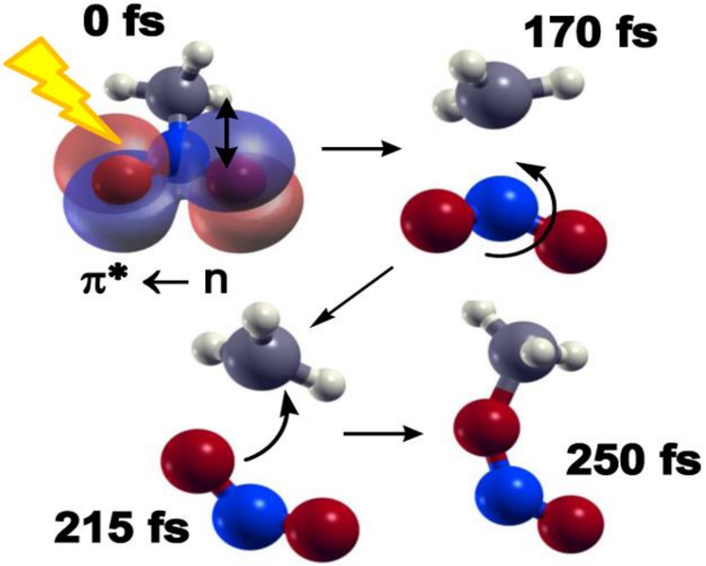
$\tau = 81 \pm 4\,fs$

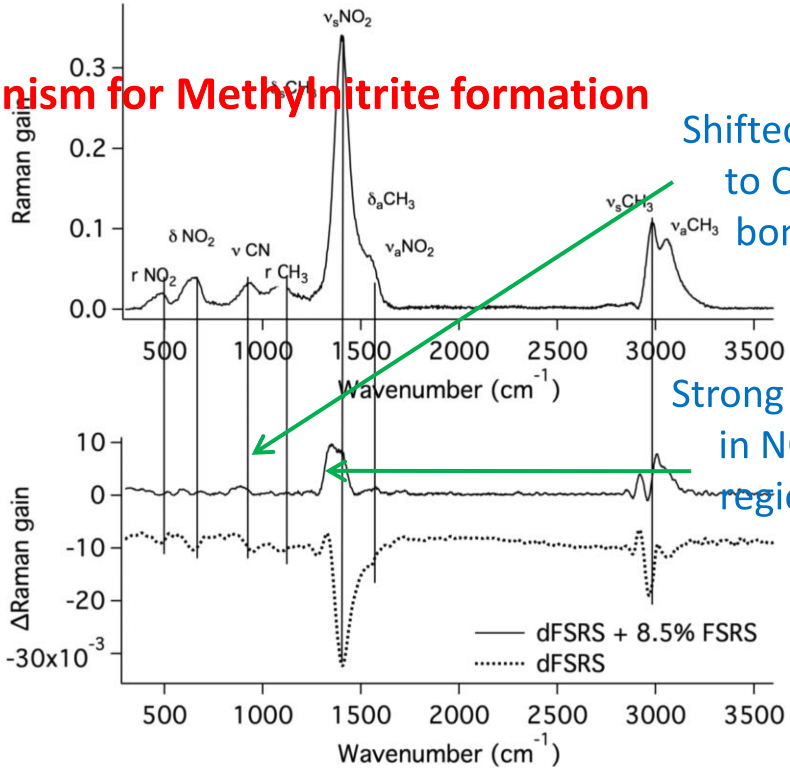
NA-ESMD QY 0.24



Relative timescales support roaming mechanism for Methylnitrite formation





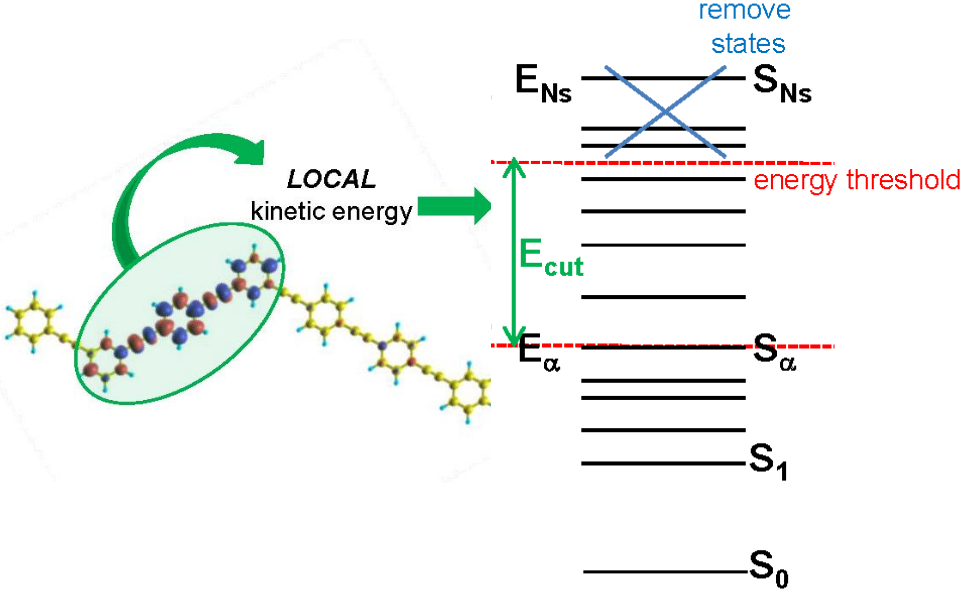


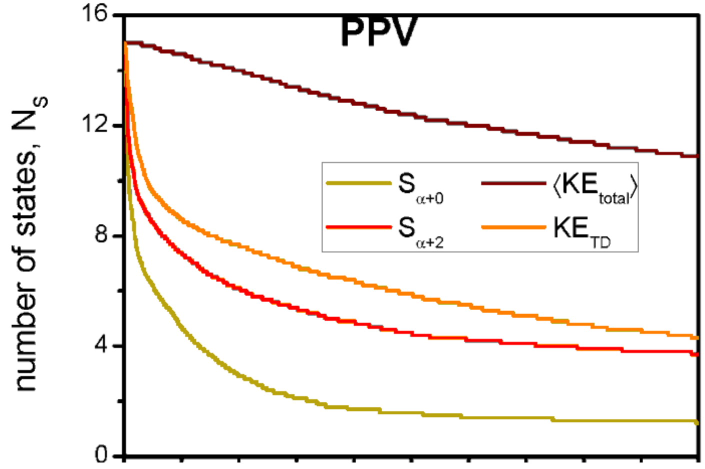
Shifted C-N to C-O bond

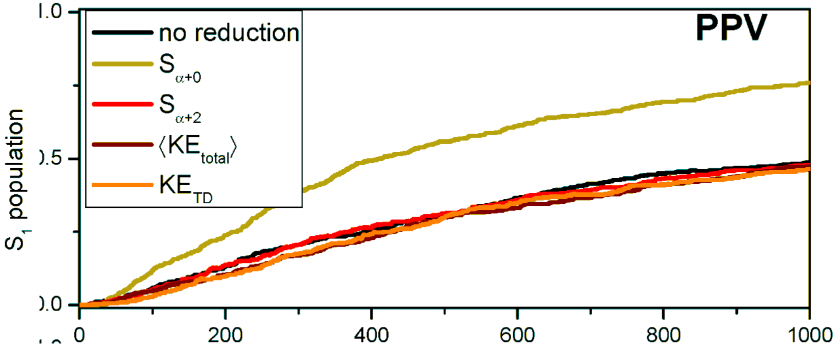
Strong peak in NO_2 region

T. Nelson, et al. *J. Phys. Chem. A.* 119, 4846 (2016).

Efficient Algorithms for Non-adiabatic Excited State Molecular Dynamics in Large Systems







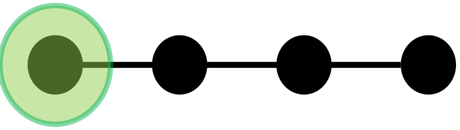
Define an energy threshold:

Participation number per atom

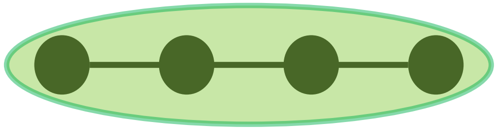
$$P = \left[\sum_A \left(\sum_{n_A} \left(\rho^{g\alpha}\right)^2_{n_A n_A}\right)^2\right]^{-1}$$

Local Kinetic Energy: Sum contributions from first P atoms

$$KE_{TD} = \sum_P \frac{1}{2} m_B v_B^2$$



Localized P=1



Delocalized P=4 (N)

	PPV	PPE
# Atoms	40	84
Initial State	8-12	4-7
Full Sim.	1	1
KE_{total}	1.2	1.0
KE_{TD}	2.3	1.7

More than 2x computational speed-up for model systems

T. Nelson, et al. *Chem. Phys.*, 481, 84-90 (2016).