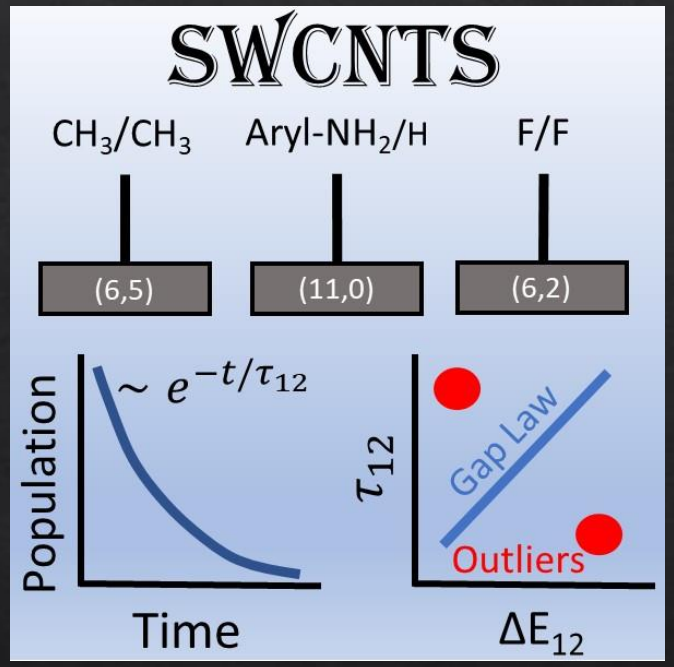
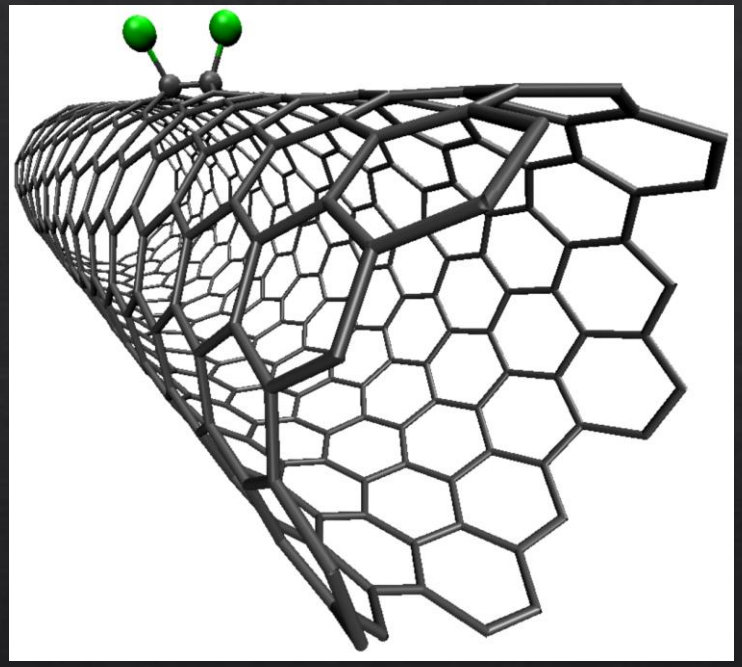
Non-adiabatic Dynamics Simulations of Single-Walled Carbon Nanotubes with Topological sp3-defects: An On-the-fly NEXMD Study





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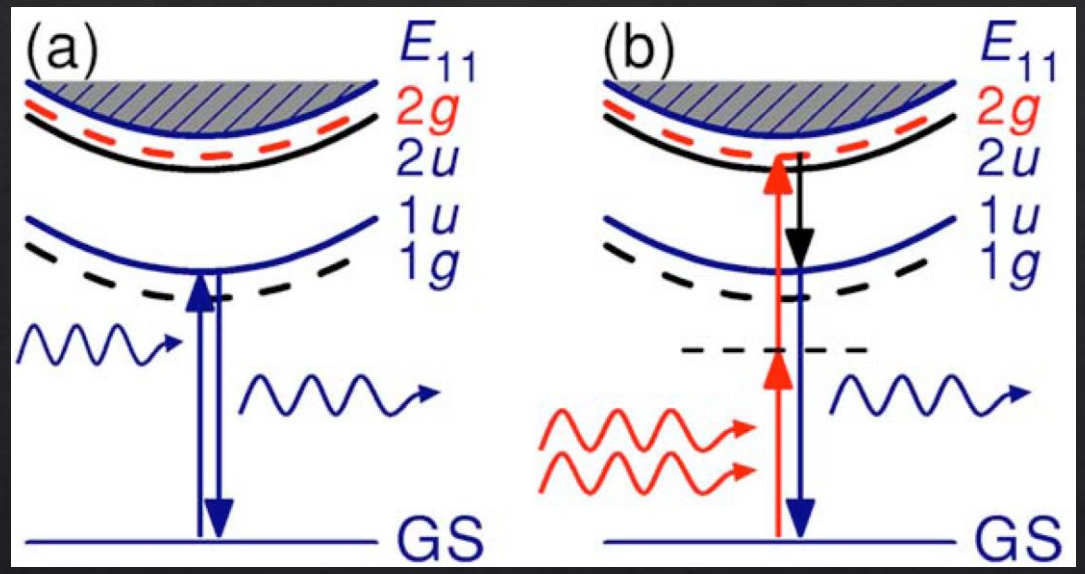
Outline

- Background / Open Questions
  - Thermally activated dynamical exciton trapping/de-trapping
  - Dynamical coupling of pristine and defect-localized excitonic manifold
  - Chemical nature of defects affects excitonic population
- Atomistic Models and Non-adiabatic Evolution
  - # Atoms ~ 400 with excitonic effects
- Results and Discussion
  - Strong dependence on defect orientation and composition
- Further Directions

Carbon Nanotubes – A Brief History

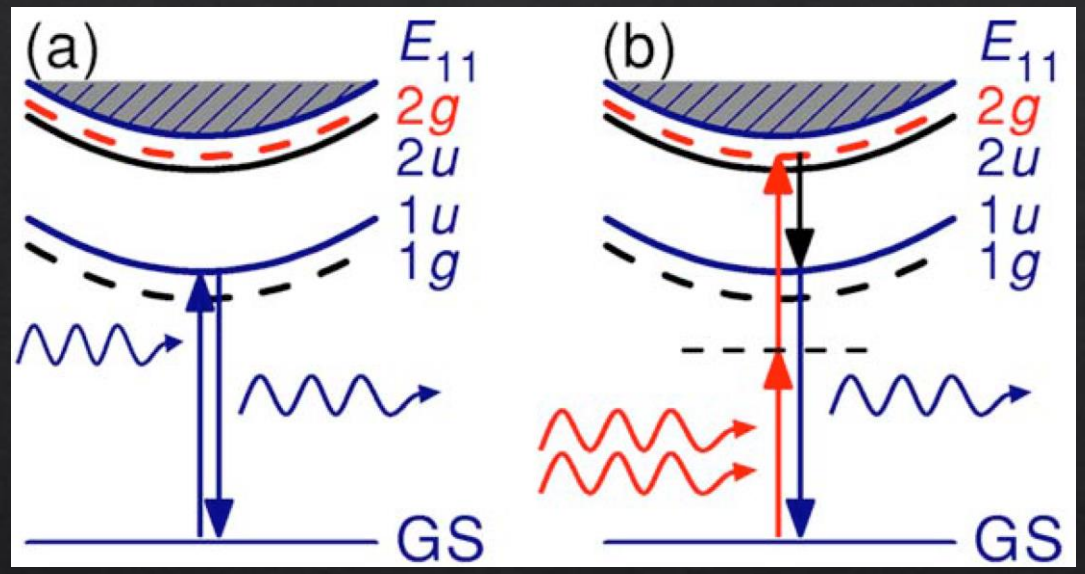
Pristine SWCNTs



- Dipole-forbidden emission from S_1

Carbon Nanotubes – A Brief History

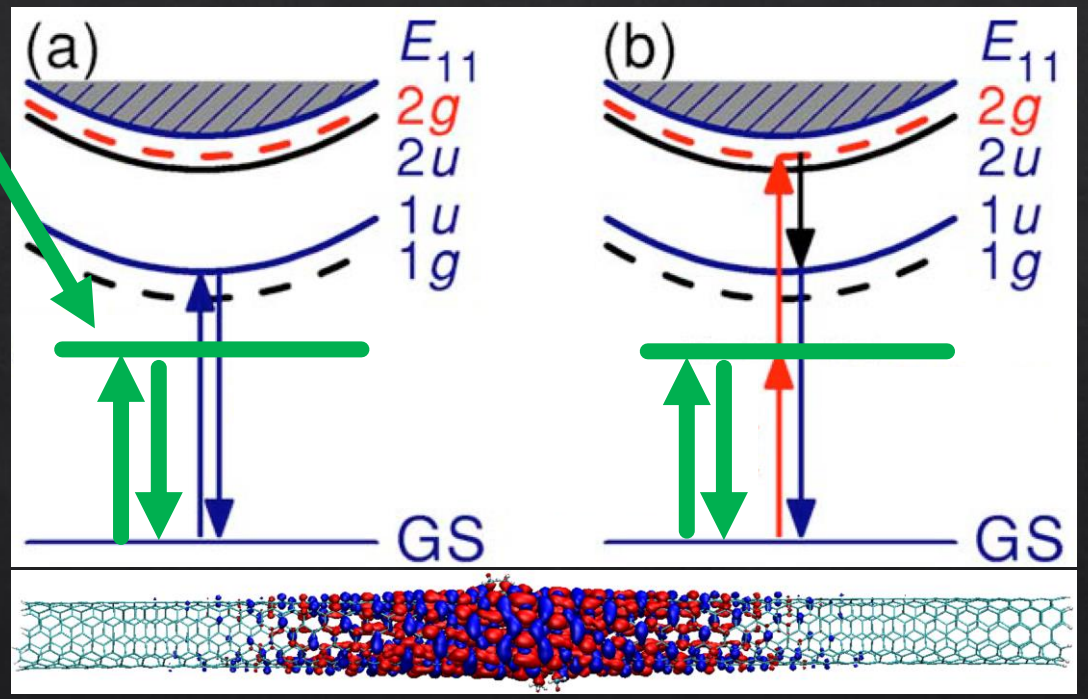
Pristine SWCNTs



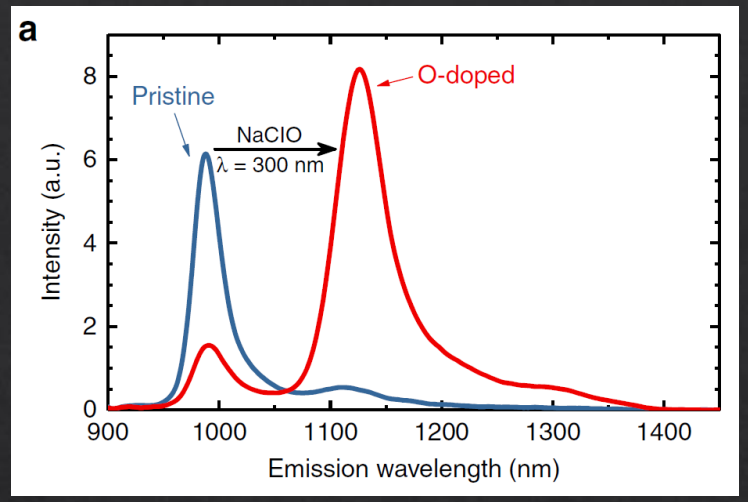
- Dipole-forbidden emission from S_1

SWCNTs with Defect

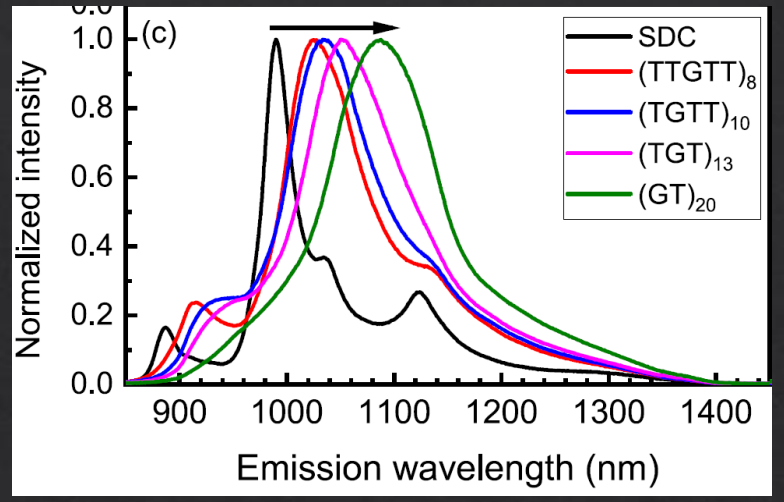
New Defect State



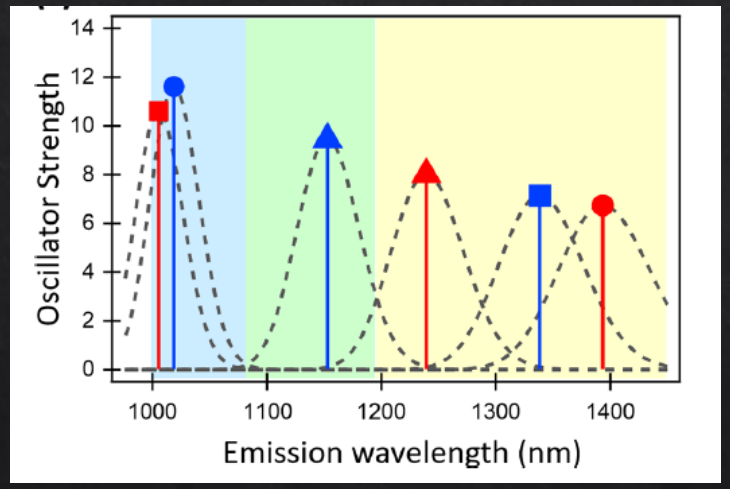
- Allowed S_0/S_1 transition
  - ➢ Symmetry breaking from defect

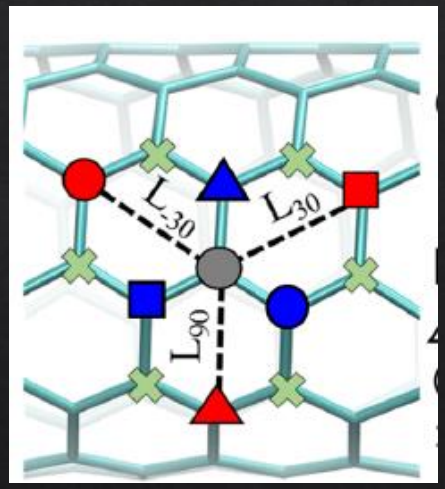


Defect Leads to Redshift in Emission

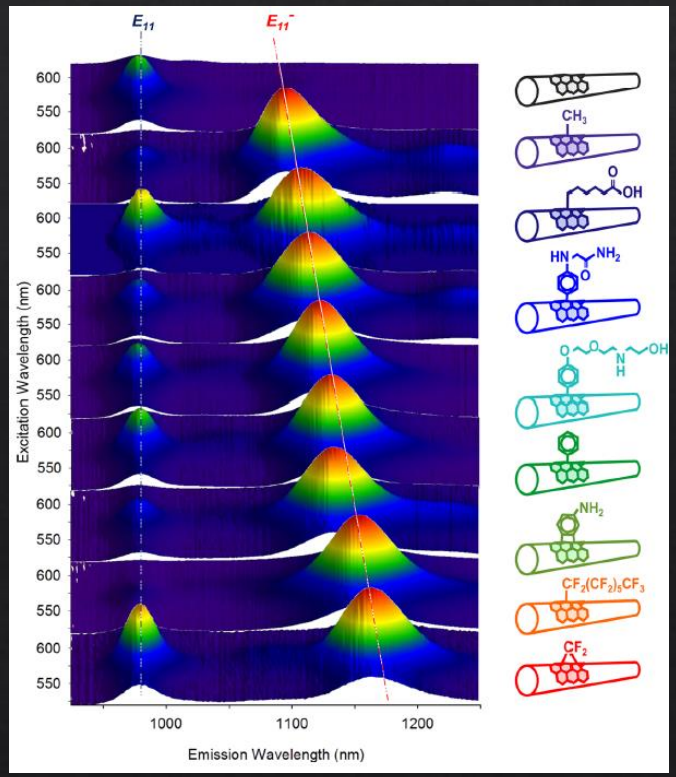


Defect-Defect Coupling





Different Orientations



Chemical Composition

Lin et al. Nat. Comm., 10, 2874 (2019)

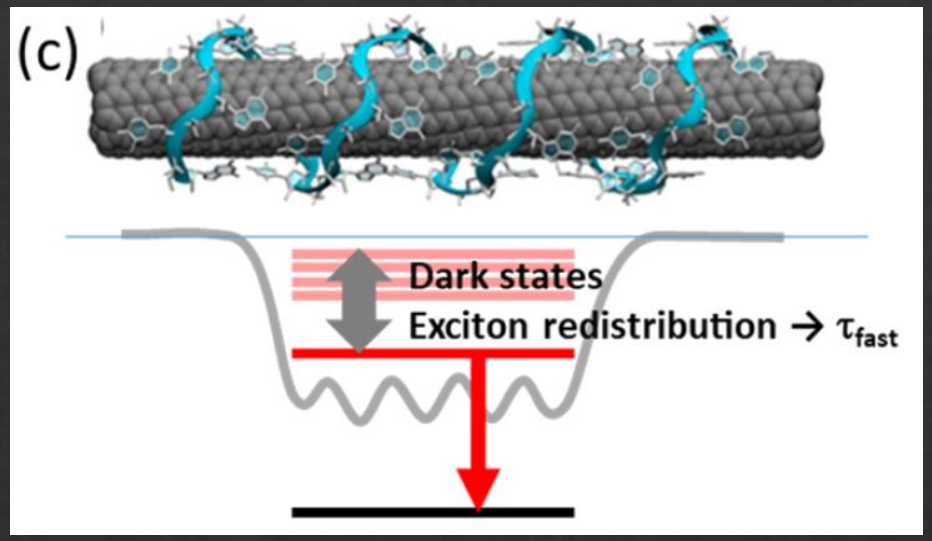
He et al. ACS Nano 2017, 11, 10785−10796

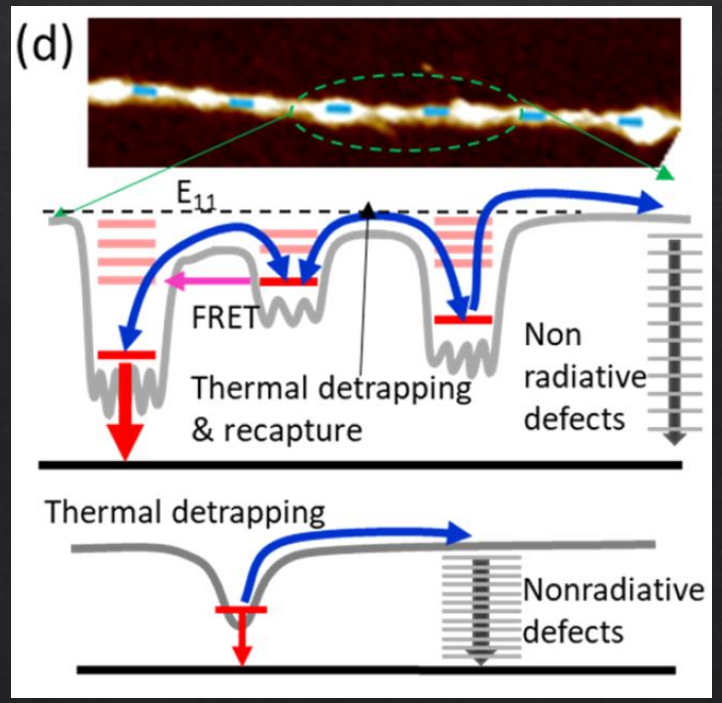
Zheng et al. ACS Nano 2021, 15, 923−933

Kwon et al. J. Am. Chem. Soc. 2016, 138, 6878−6885

Open Questions

- Redistribution among dark defect states
  - ➢ Non-adiabatic coupling between dark states
- Thermally activated dynamical exciton trapping/de-trapping
  - ➢ Non-adiabatic coupling to band-edge exciton
- How do topological changes to the excitonic potential energy landscape (stemming from defect orientation and composition) affect the excitonic populations during relaxation?

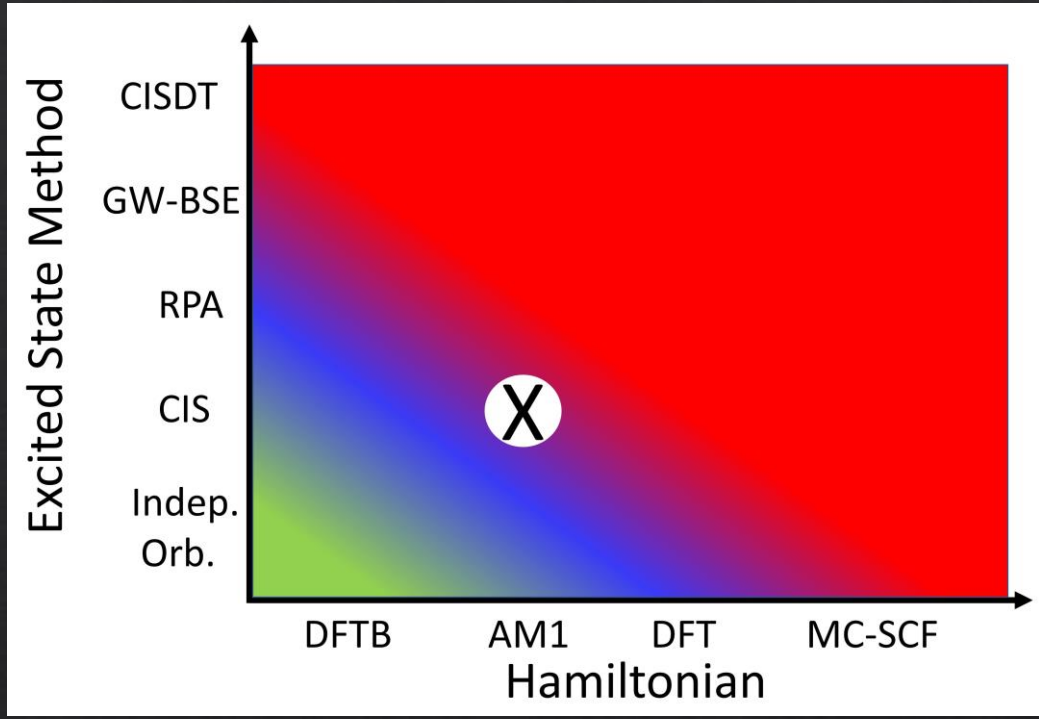


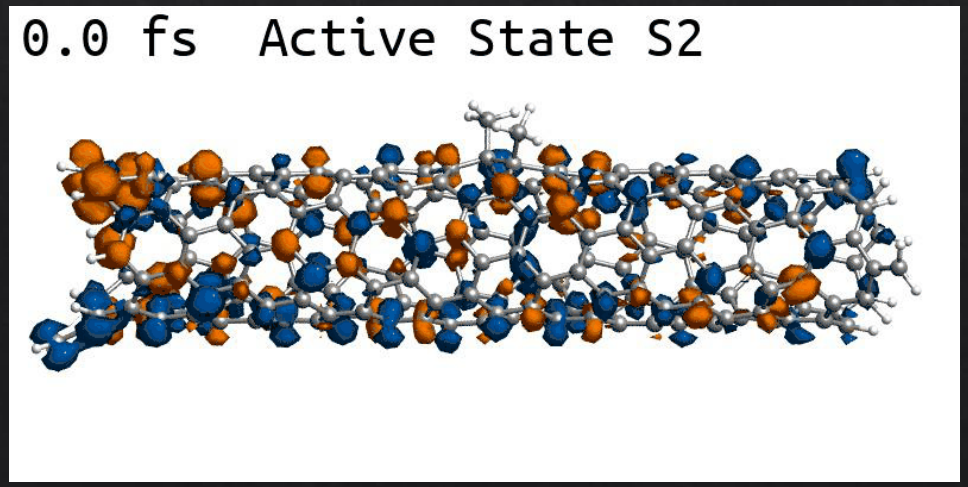


Zheng et al. ACS Nano 2021, 15, 923−933

Model and Methods

- Hamiltonian:
  - Semi-empirical AM1
- Excited States:
  - RPA Equations in CIS Approximation
  - Solutions for transition density matrices provided by the collective oscillator (CEO) method
- Non-adiabatic Molecular Dynamics:
  - NEXMD Package
  - Fewest Switches Surface Hopping (FSSH)
  - Instantaneous Decoherence Corrections
  - Unavoided Crossing Detection
  - Linear Response Solvation
  - Microcanonical Ensemble (NVE)

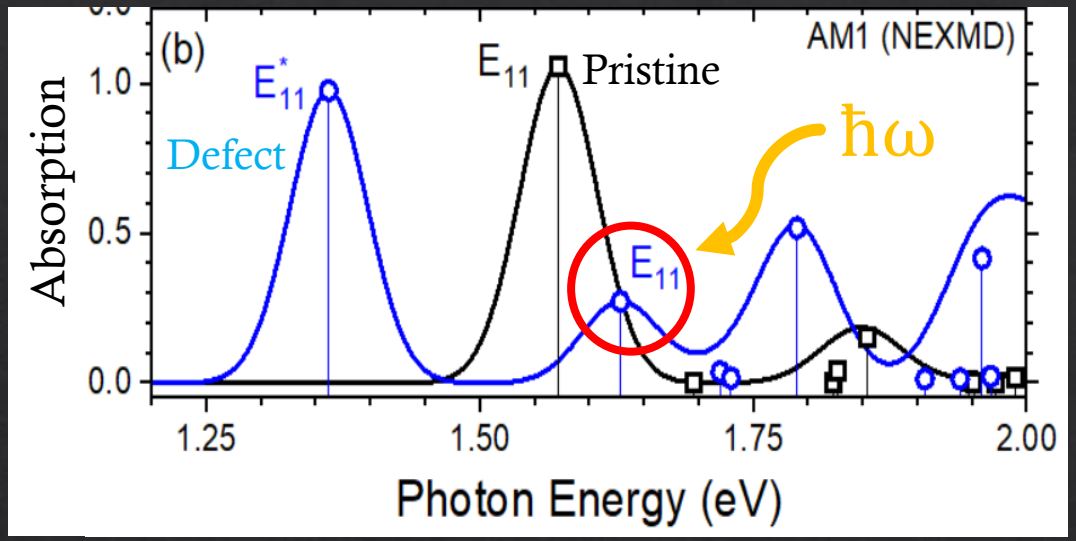




https://github.com/lanl/NEXMD

Initial Conditions

- Ground State Nuclear Wavepacket
  - NVT Ensemble, T = 300 K
  - 300 trajectories
- Initial Electronic Configuration
  - $\hat{\rho}_{el.} = |S_k><S_k|$, k = 2 (E_{11} Exciton)
- Initial Wavefunction
  - $\hat{\rho}_o = \hat{\rho}_R \otimes \hat{\rho}_{el.}$

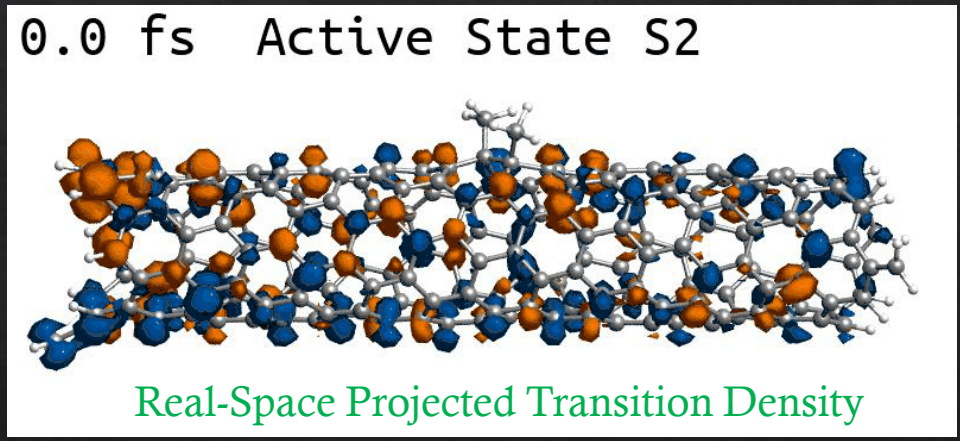


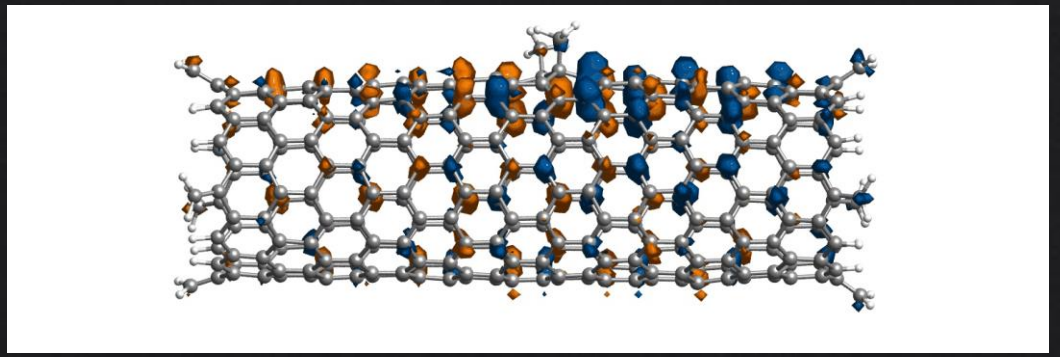
Fewest Switches Surface Hopping (FSSH)

$$|\Psi(\mathbf{R}(t))\rangle = \sum_{\alpha} c_{\alpha}(t)|\alpha(\mathbf{R}(t))\rangle$$

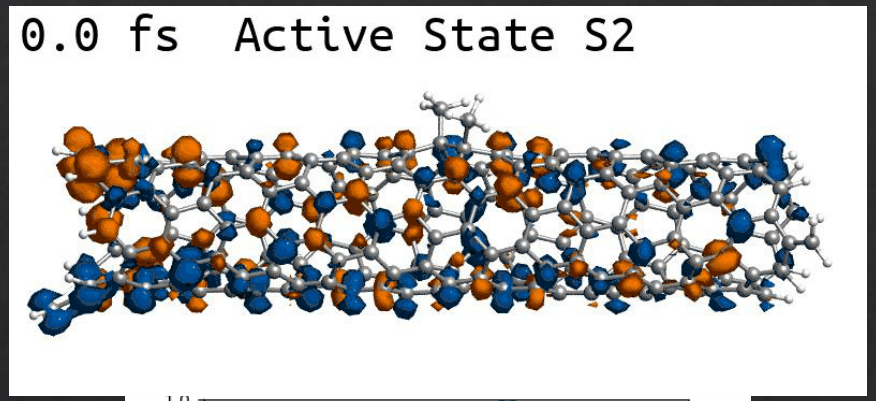
$$\dot{c}_j = -ic_j E_j - \sum_k c_k \dot{\vec{R}} \cdot \vec{d}_{jk}$$

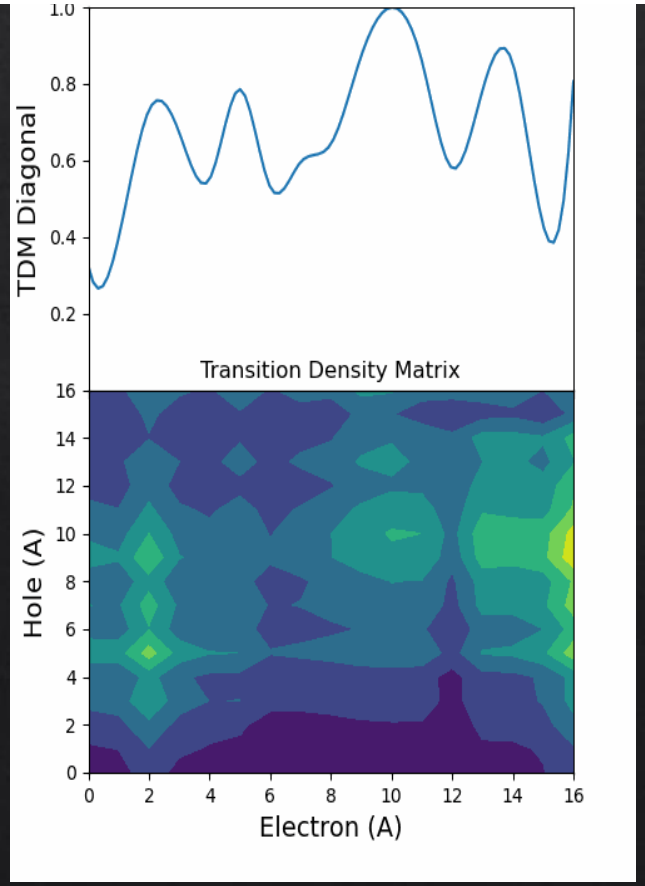
$$\vec{d}_{jk} = \langle j|\vec{\nabla}_{\boldsymbol{R}}|k\rangle \qquad g_{jk} = \Delta t \frac{c_{jk}(t)}{c_{kk}(t)}$$

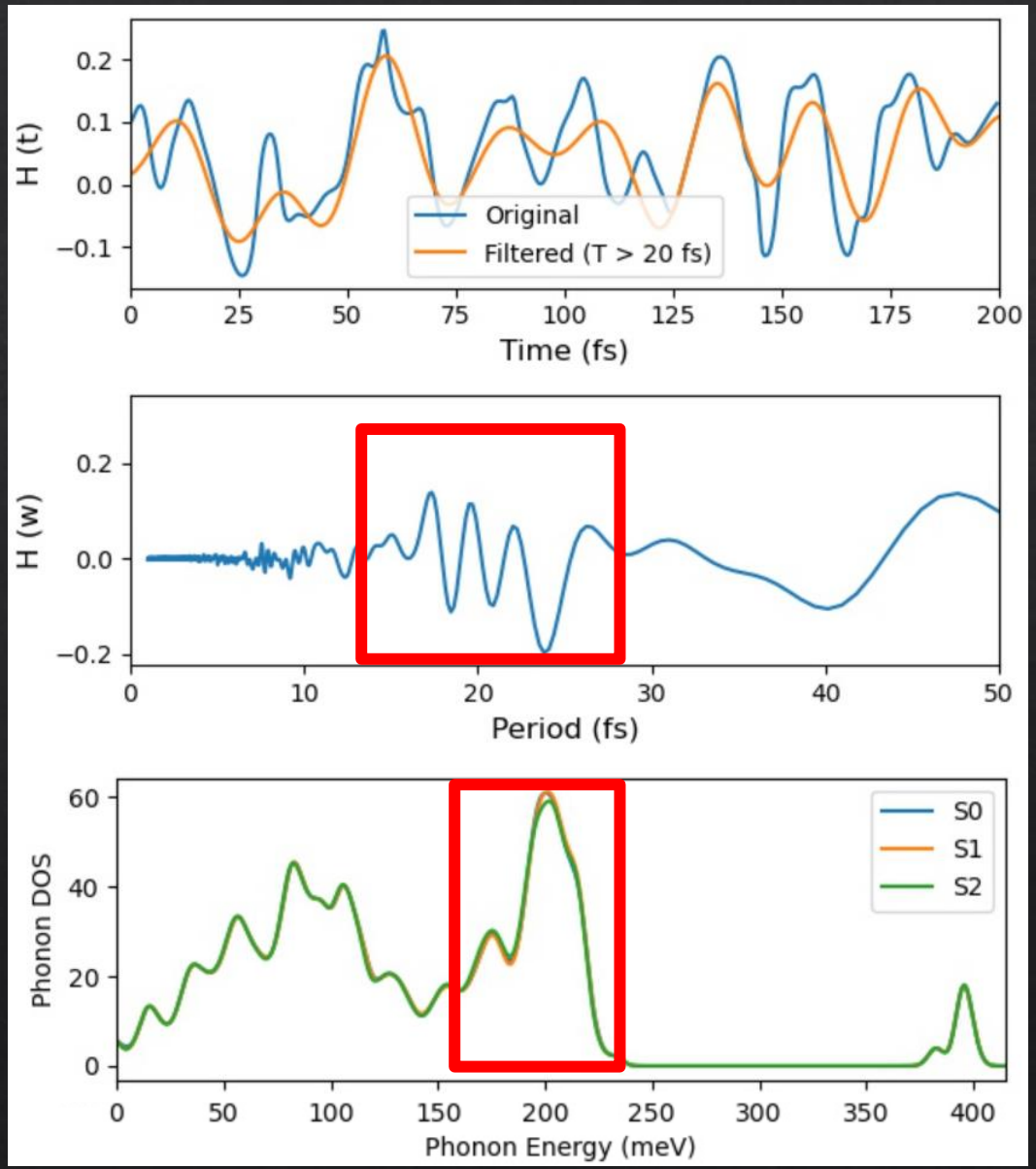




Oscillations In Transition Density Come from C-C Bond Stretching



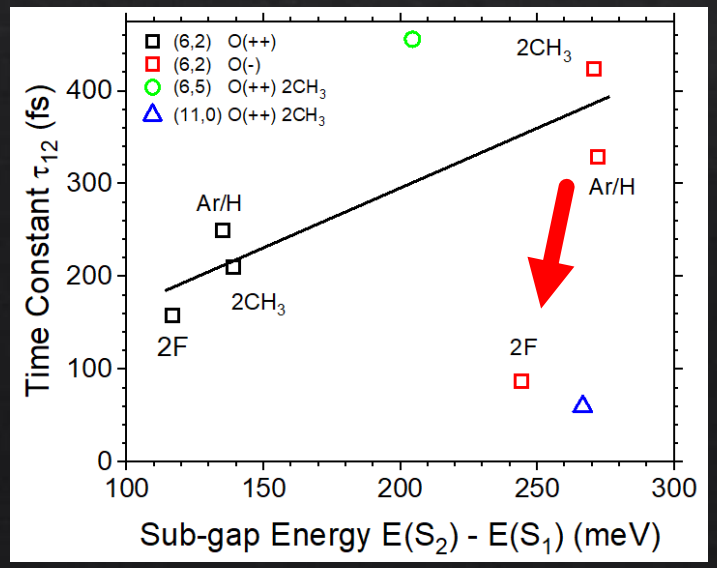




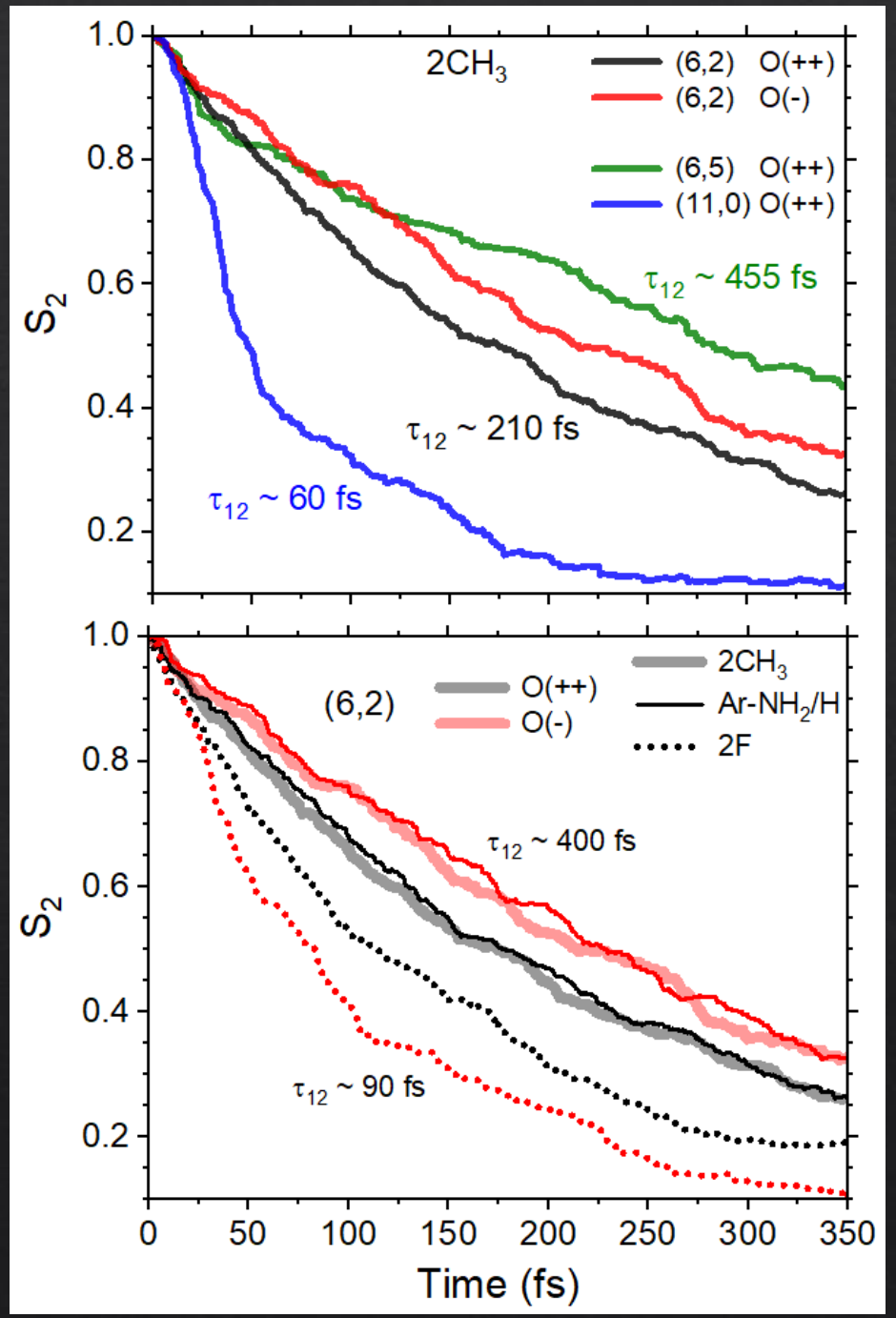
Excitonic Population

Single-exponential Fit: $S_2(t) \sim \exp[- t/\tau_{12}]$

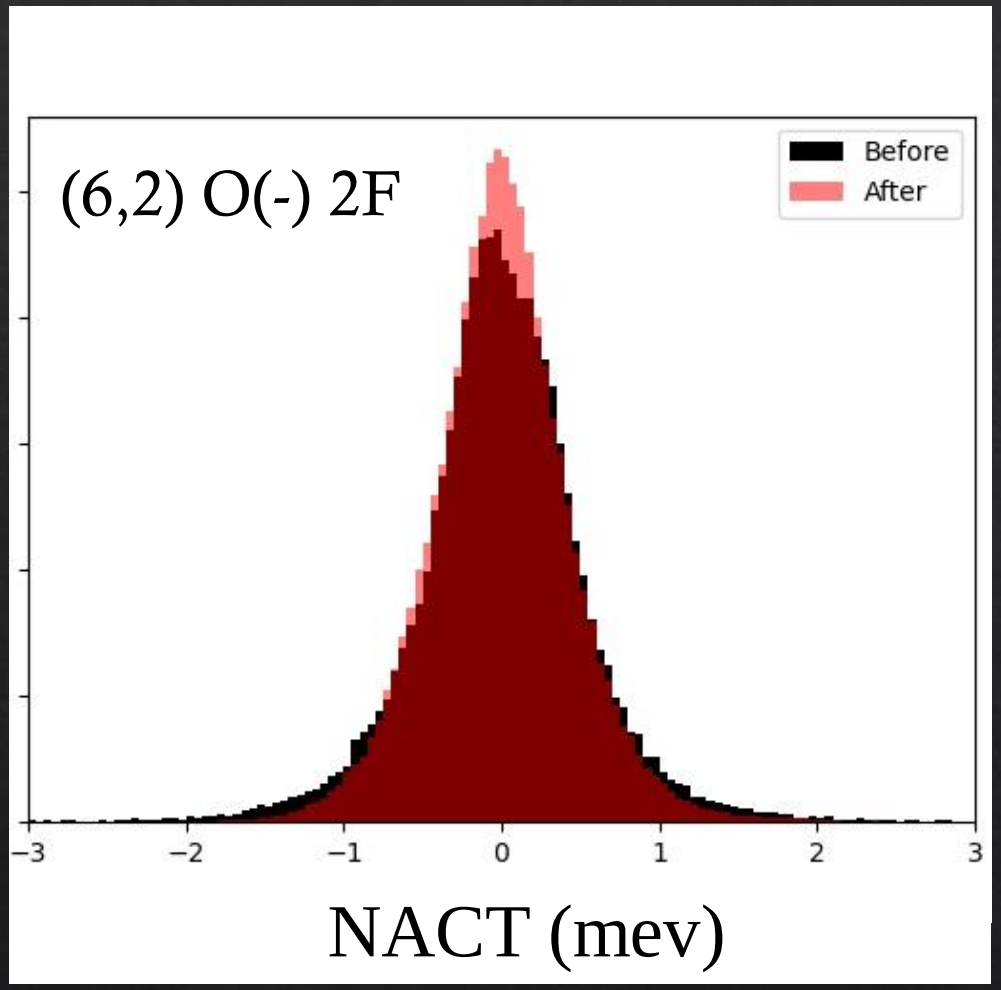
- Strongly chirality-dependent
  - (11,0) shows uniquely fast relaxation (θ = 0°)
- Strongly dependent on chemical composition
  - Alkyl and Aryl defects act similarly
  - Halide attachment produces fast relaxation
  - Ortho(-) coupled with halide produces largest change from alkyl/aryl rate

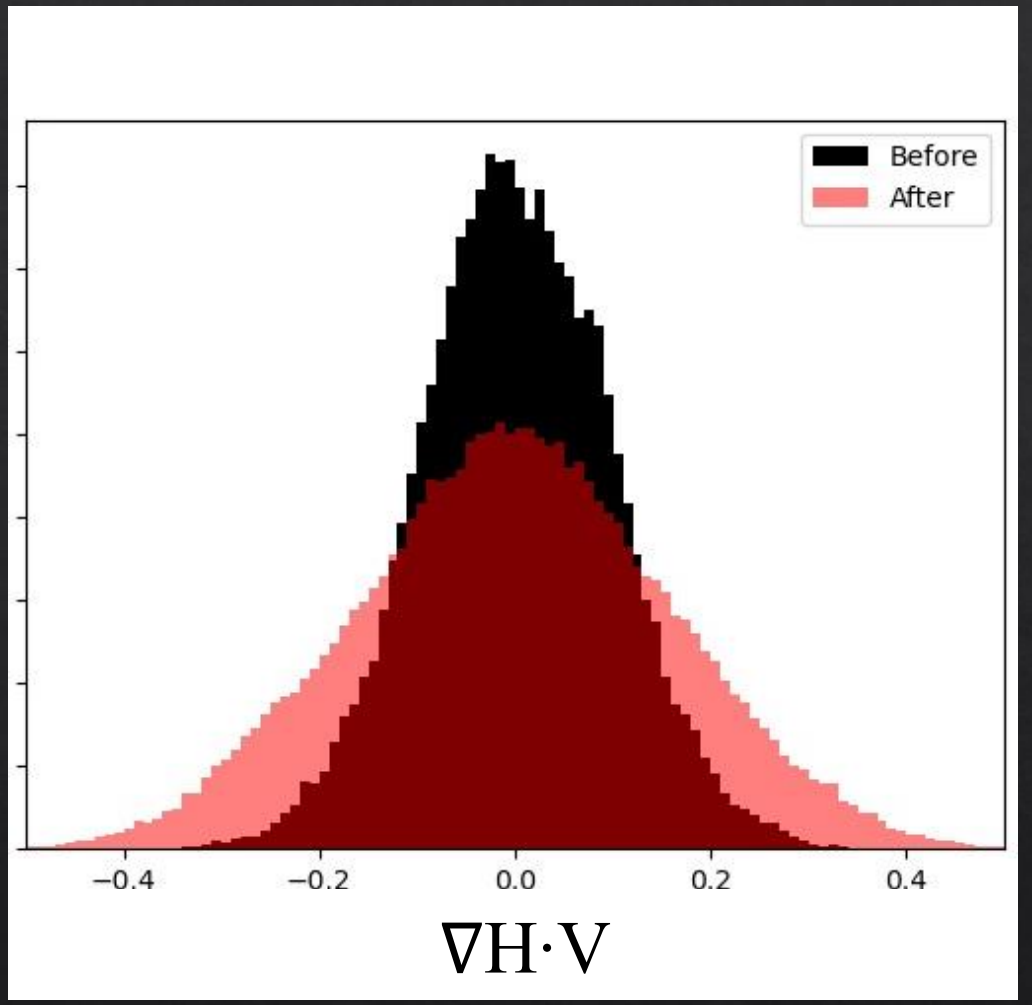


Gap law is broken for fluorine defects



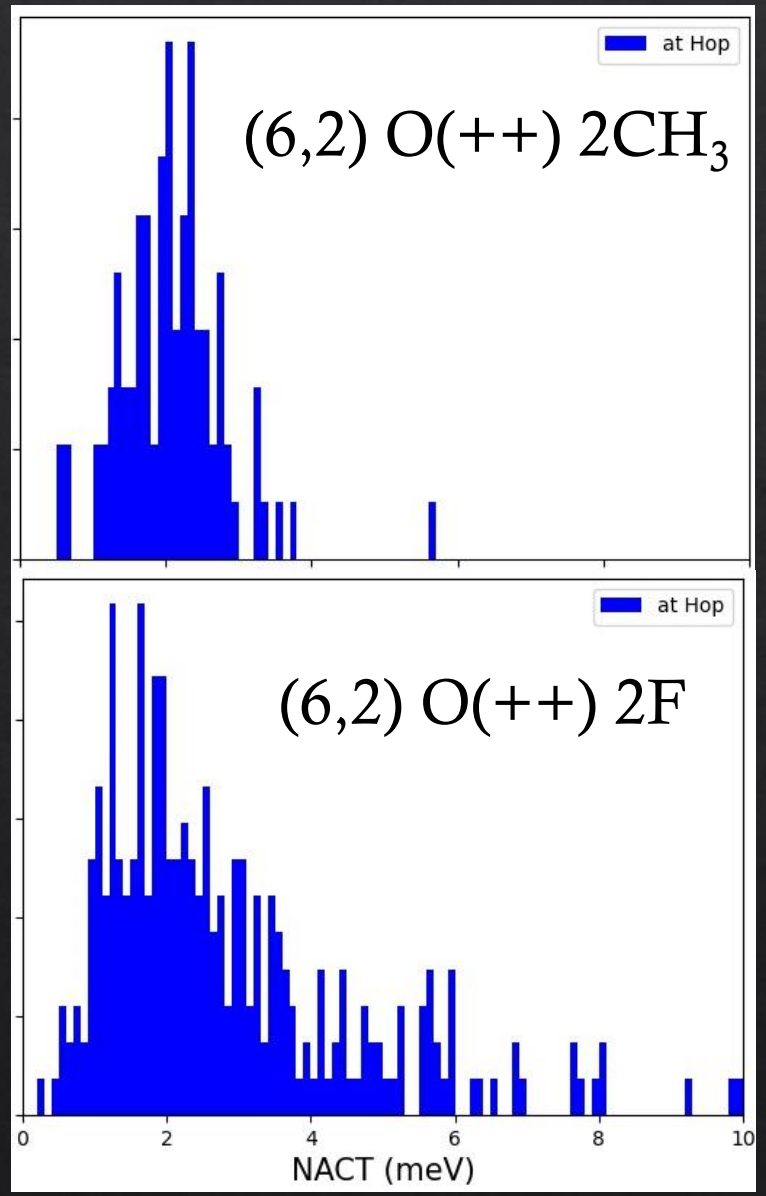
NACT and ∇H·V Probability Distributions



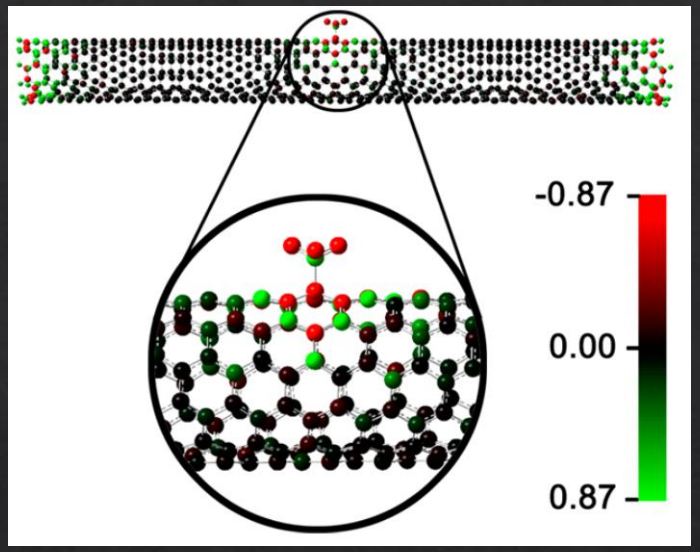


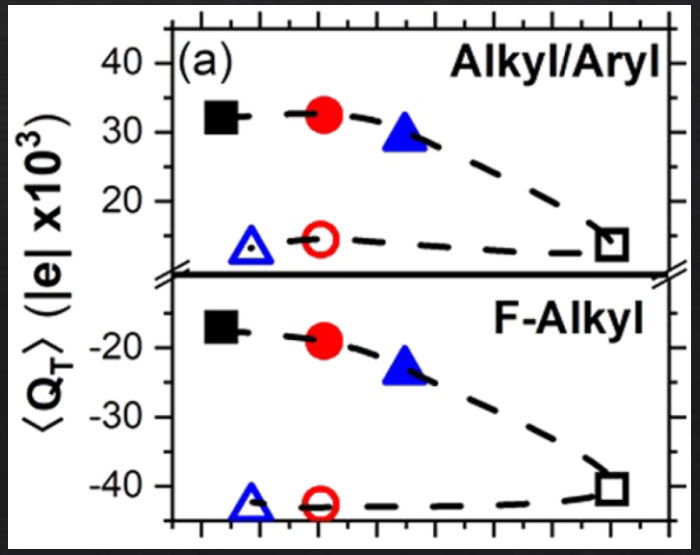
- Before and after the hop, the NACT is nearly equivalent
- ∇H·V shows changes in distribution after transferring to lower adiabatic state
  - Minimum of PES changes

NACT Probability Distribution



Local Charge Distribution Strongly Affected by Direct Fluorine Attachment



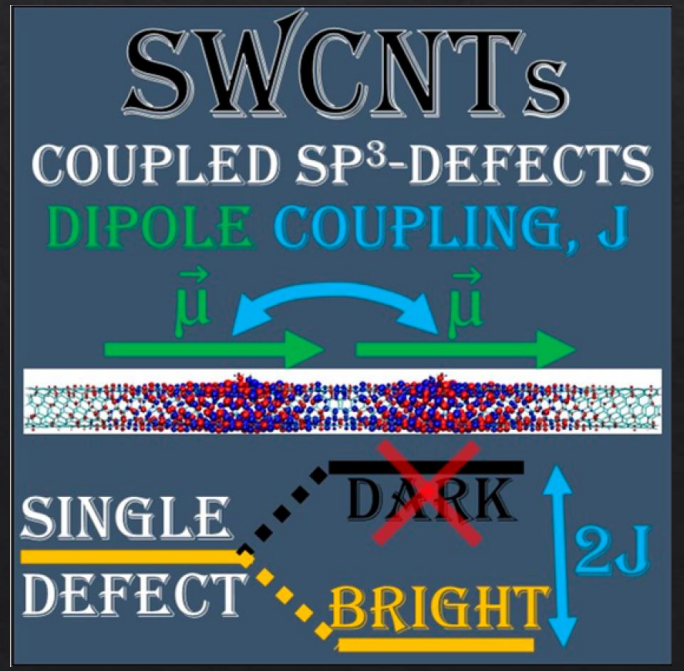


Kwon et al. J. Am. Chem. Soc. 2016, 138, 6878−6885
Weight et al. J. Phys. Chem. C 2021, 125, 4785−4793

Conclusions and Future Work

- Performed on-the-fly non-adiabatic dynamics simulations of large nanostructures
  - # Atoms ~ 400
  - Excitonic Effects
  - AM1 Semi-empirical Hamiltonian

- Extracted population dynamics and made structure – property correspondence
  - Fluorinated defects strongly alter the local charge distribution, allowing for increased NACT
  - Zig-zag SWCNTs may exhibit fast relaxation compared to chiral SWCNTs



Weight et al. *J. Phys. Chem. Lett.* 2021, 12, 7846−7853

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