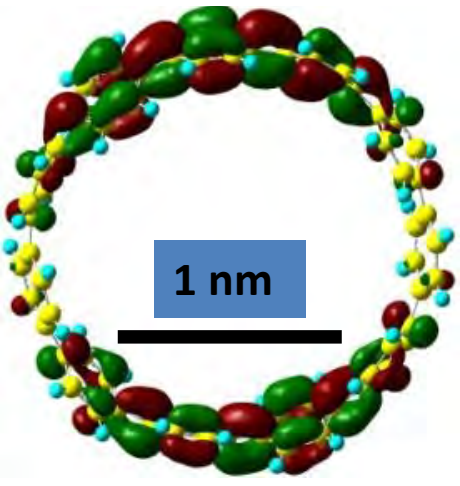
Coherent Photoexcited Dynamics and Intermolecular Conical Intersections

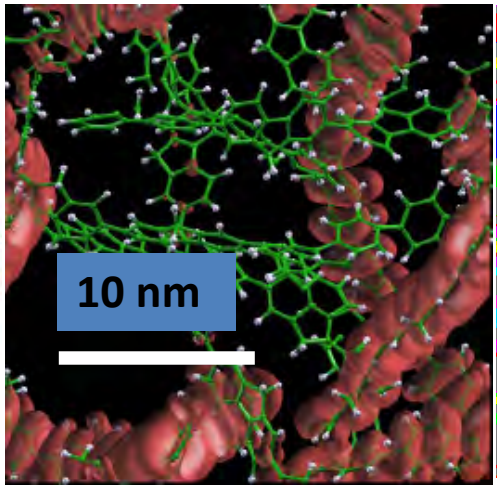
Sergei Tretiak

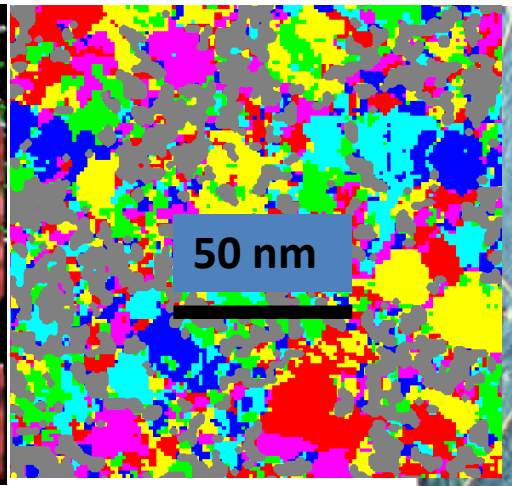
Group homepage: http://cnls.lanl.gov/~serg/ **tretiak@lanl.gov**

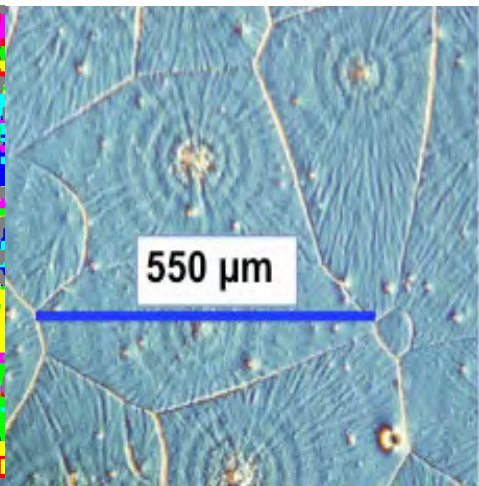
Center for Integrated Nanotechnologies (CINT)
Center for Nonlinear Studies (CNLS)
Theoretical Division

Los Alamos NATIONAL LABORATORY

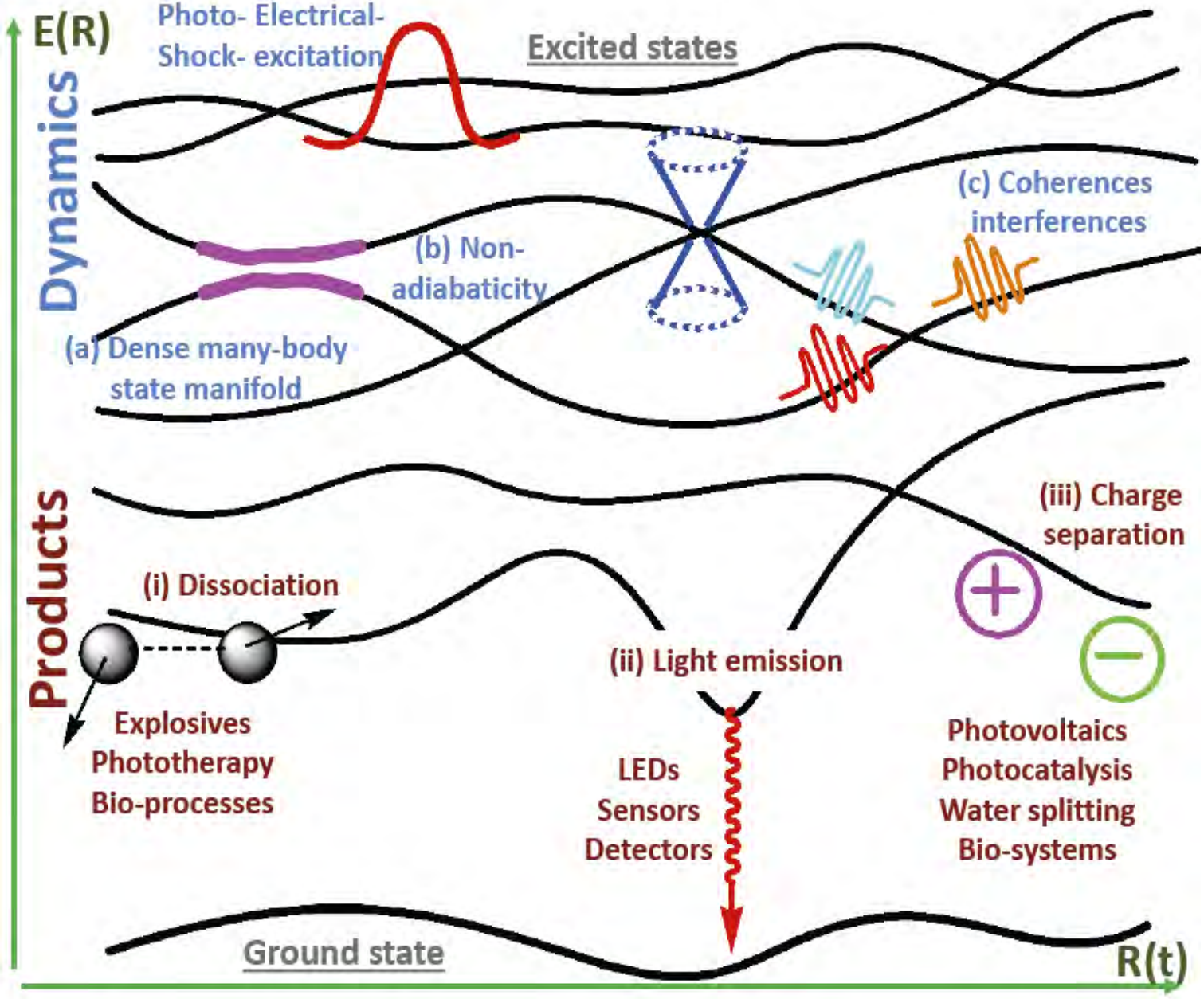








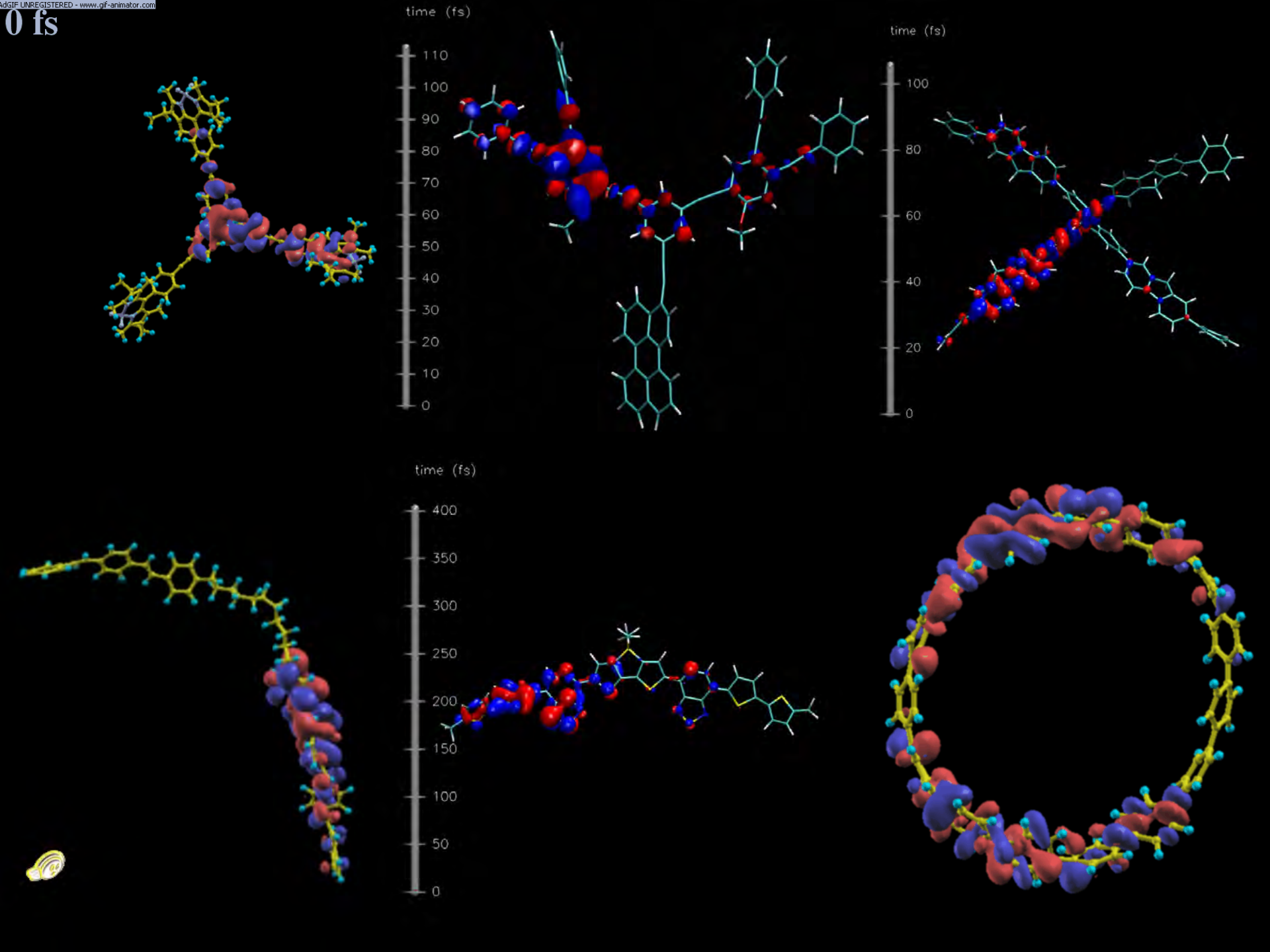
Photoexcited dynamics



Excited state relaxation timescales:

- ❑ Phosphorescence decay ~ 1ms
- ❑ Fluorescence decay ~ 1ns
- ❑ Intersystem crossing ~ 1μs
- ❑ Nonradiative relaxation ~ 10ps
- ❑ Conical inter-section ~ 100fs

0 fs



Outline

- *A brief outline of non-adiabatic excited state molecular dynamics modeling*
- *Side to side comparison of Ehrenfest (Ehr), surface hopping (SH) and Multiconfigurational Ehrenfest-Ab Initio Multiple Cloning (MCE-AIMC) results*
- *Coherent passage through intermolecular conical intersections*
- *XFEL spectroscopy (TRUECARS Raman) for monitoring coherent dynamics*
- *Machine learning of Hamiltonians (time allowed)*

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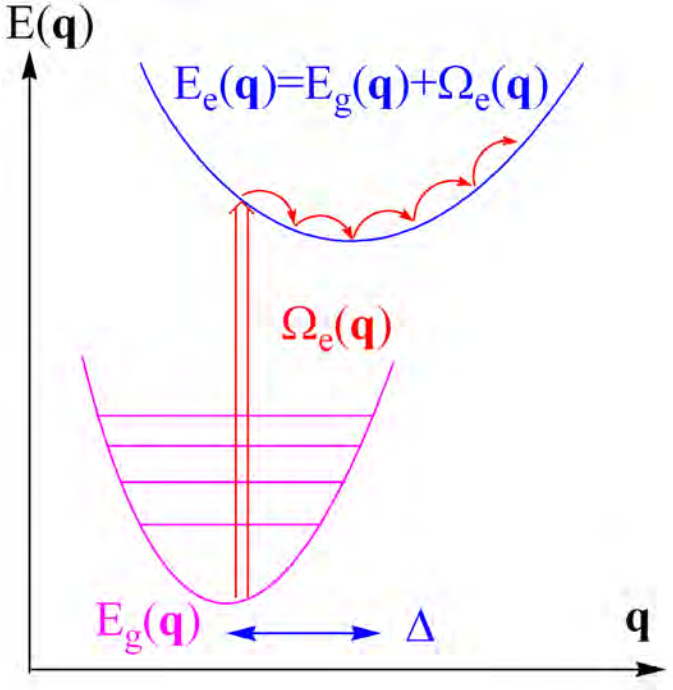
Excited state molecular dynamics

➢ ***Born-Oppenheimer* (mixed Quantum-Classical) Dynamics:**



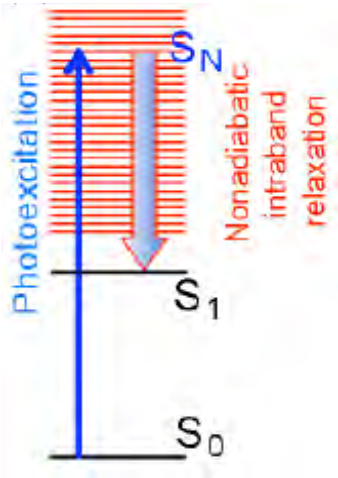
Langevin equation of motion for nuclei

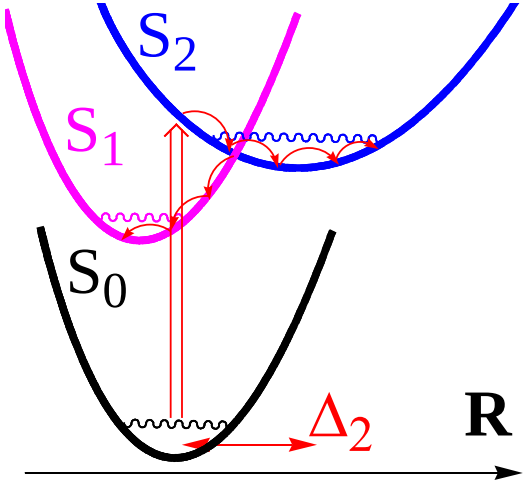
$$M_i\ddot{\mathbf{R}}_i(t) = -\nabla E_\alpha(\mathbf{R}(t)) - \zeta M_i\dot{\mathbf{R}}_i(t) + \mathbf{A}(t)$$

Mass, acceleration ***Force*** ***Viscosity*** ***Stochastic force***

S. Tretiak, A. Saxena, R.L. Martin and A. R. Bishop, Phys. Rev. Lett. 89, 97402 (2002)

➢ ***Non-adiabatic dynamics with Quantum Transitions:***





$$\mathbf{d}_{\alpha\beta} = \langle\phi_\alpha(R)|\nabla_R\phi_\beta(R)\rangle$$

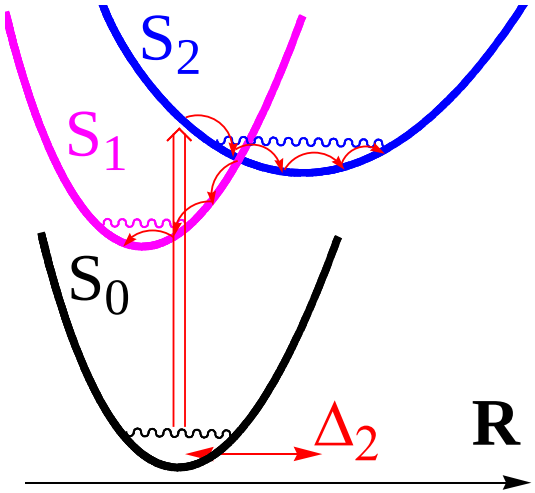
- **Non-adiabatic couplings define transition probability between states**
- **Run ensembles of trajectories (wavepacket) to statistically determine the relaxation rate**

T. Nelson, A. White, J. Bjorgaard, A. Sifain, Y. Zhang, B. Nebgen, S. Fernandez-Alberti, D. Mozyrsky, A. Roitberg and S. Tretiak, Chem. Rev. 120, 2215 (2020)

Overcoming the numerical expense:

- *10 ps excited state dynamics;*
- *0.05 fs time-step for electronic dynamics*
- *500 trajectories*

10^9 calculations of excited states



NEXMD

Software package

https://github.com/lanl/NEXMD

- ***Surface hopping (FSSH), Ehrenfest or ab initio multiple cloning with multiconfigurational Ehrenfest (AIMS-MCE);***
- **Efficient semiempirical calculations of the excited states at TDHF or CIS level (Krylov space algorithms);**
- **Analytic gradients for excited state potential energy surfaces and *non-adiabatic couplings;***
- ***Various types of the excited state MD (Langevin, Anderson thermostats, energy conserving dynamics, etc.);***
- ***Decoherence corrections, treatment of trivial crossings, state-specific solvation (PCE or QM/MM), extended Lagrangian =dynamics, open shells, polaritons, etc.***

NEXMD allows calculations ~1000 atoms molecules and ~10ps timescales

T. Nelson, A. White, J. Bjorgaard, A. Sifain, Y. Zhang, B. Nebgen, S. Fernandez-Alberti, D. Mozyrsky, A. Roitberg and S. Tretiak, Chem. Rev. 120, 2215 (2020); W. Malone, B. Nebgen, A. White, Y. Zhang, H. Song, J. Bjorgaard, A. Sifain, B. Rodriguez-Hernandez, S. Fernandez-Alberti, A. E. Roitberg, T. Nelson and S. Tretiak, J. Chem. Theory Comput. 16, 5771 (2020)

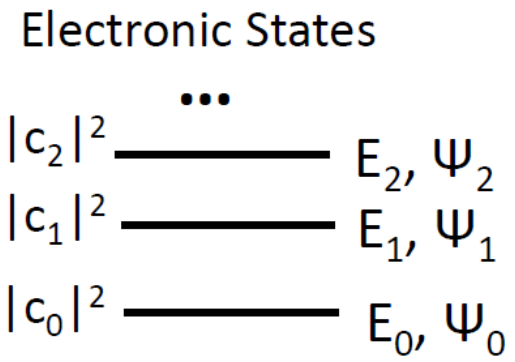
Electronic surface hopping

Main Idea: Monte-Carlo

1) Set electrons in ***one*** of the states (n) and evaluate force according to $F=-\partial E_n/\partial x$ and propagate ions for time Δt

2) Propagate occupation probabilities for electrons according to Schrodinger equation

$$i\hbar\partial_t c_n + \sum_m d_{mn}\dot{x}c_m = E_n c_n$$



3) "Toss a coin" according to probabilities determined in Step 2. If no switch occurs, go to step 1.

4) If switch occurs, make sure energy is satisfied. If not, discard the switch. If yes, set electrons in the new state and proceed with Step 1.

J. Tully, J. Chem. Phys. 93, 1061 (1990)

Multiconfigurational Ehrenfest approach (MCE)

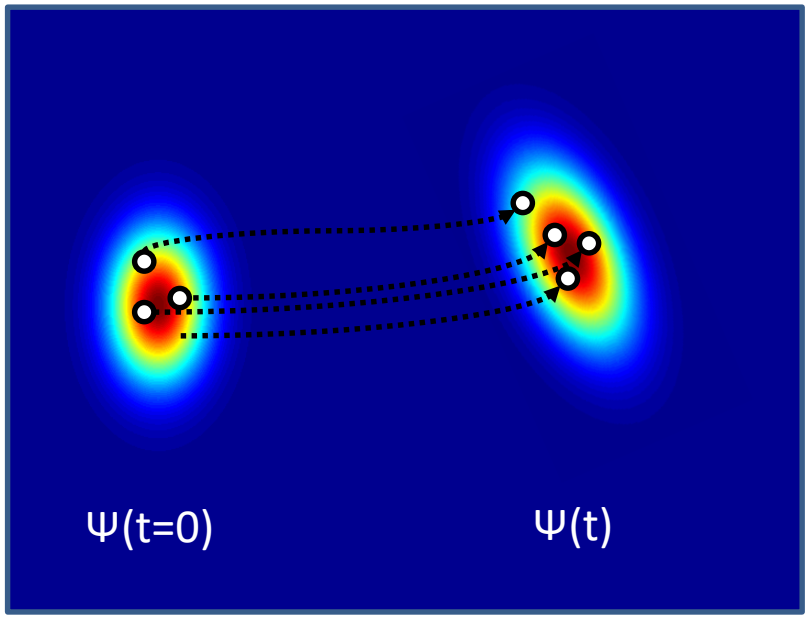
- ***Trajectory guided basis allows to run on the fly dynamics***

The wavefunction in a trajectory-guided basis

$$|\Psi(t)\rangle = \sum_n c_n(t)|\psi_n(t)\rangle .$$

with

$$|\psi_n(t)\rangle = |\chi_n(t)\rangle \left(\sum_I a_I^{(n)}(t) \left| \phi_I^{(n)} \right\rangle \right)$$



Trajectory guided grid

nuclear part: *Gaussian wave-packet moving along an Ehrenfest trajectory*

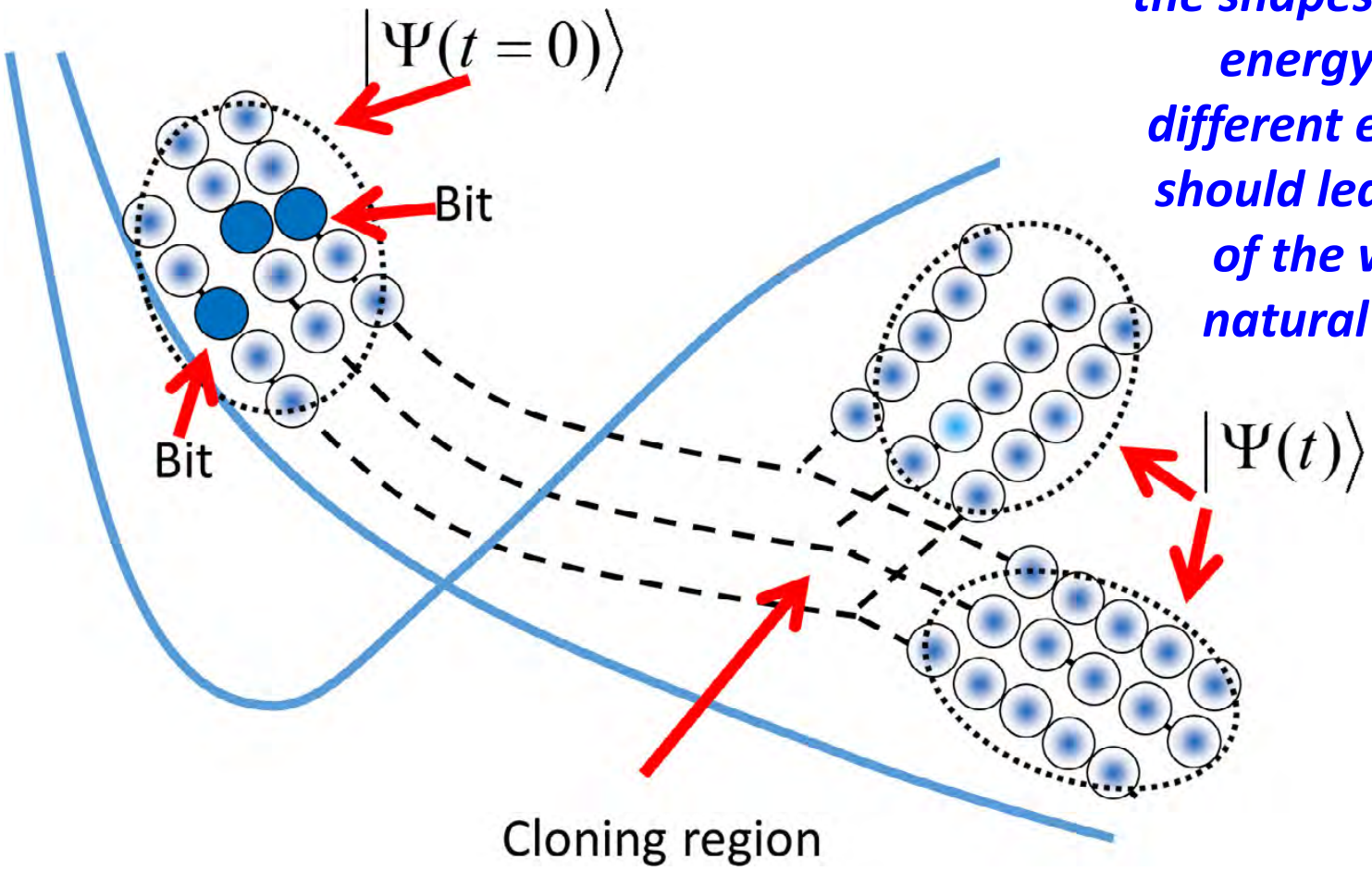
electronic part: *superposition of several electronic eigenstates*

$$\chi_n(\mathbf{R},t) = \left(\frac{2\alpha}{\pi}\right)^{N_{\mathrm{dof}}/4} \exp\left(-\alpha(\mathbf{R}-\bar{\mathbf{R}}_n(t))^2 + \frac{i}{\hbar}\bar{\mathbf{P}}_n(t)(\mathbf{R}-\bar{\mathbf{R}}_n(t)) + \frac{i}{\hbar}\gamma_n(t) \right)$$

D. Shalashilin, Faraday Disc. 153, 105 (2011)

AIMC-MCE: Ab initio multiple cloning

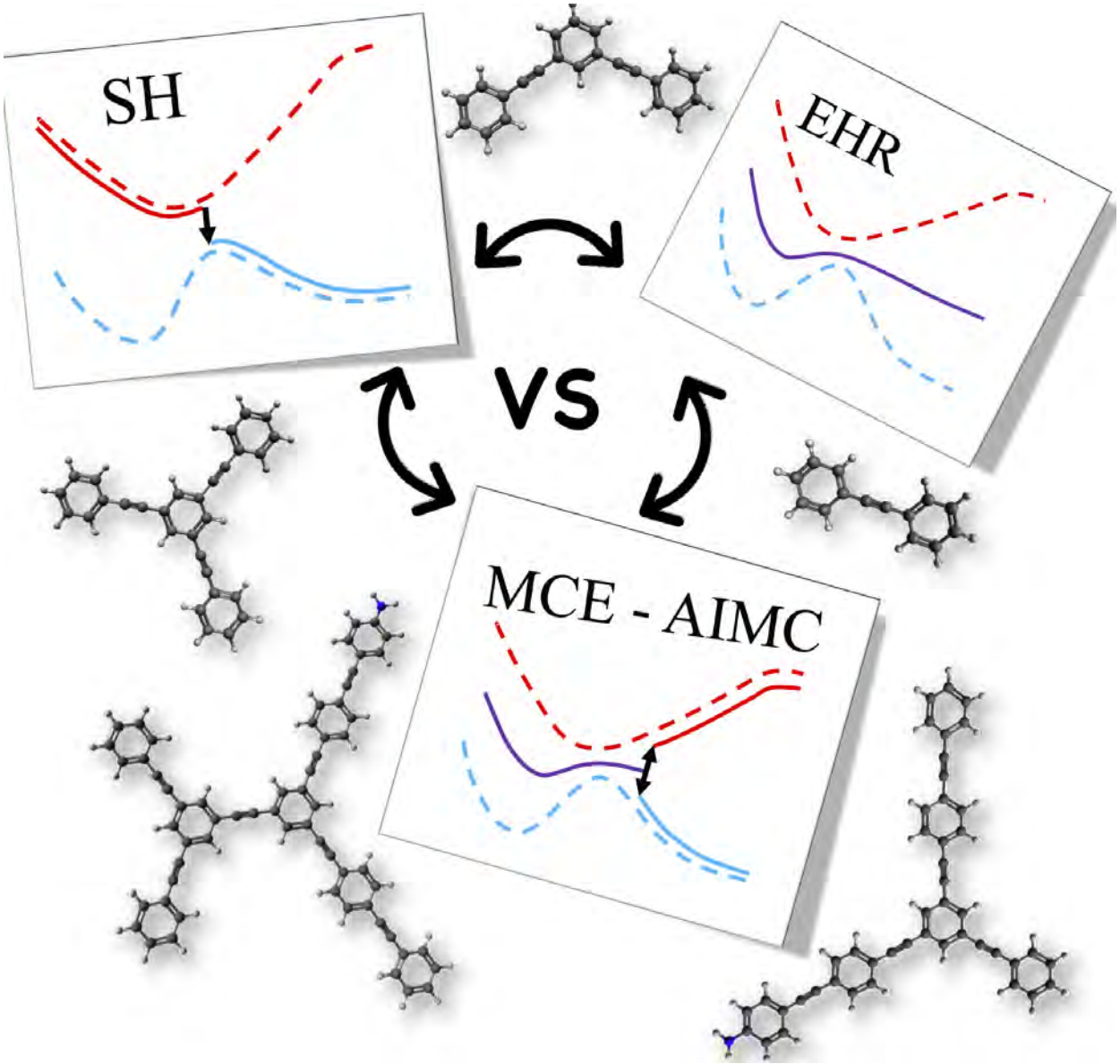
The difference between the shapes of the potential energy surfaces for different electronic states should lead to branching of the wave packet: natural decoherence



D. V. Makhov, W. J. Glover, T. J. Martinez and D. V. Shalashilin, J. Chem. Phys., 141, 054110 (2014)

V. M. Freixas S. Fernandez-Alberti, S. Tretiak, D. Shalashilin, Phys. Chem. Chem. Phys. 20, 17762, (2018)

SH vs Ehr vs AIMC-MCE



V.M. Freixas, A.J. White, T. Nelson, D.V. Makhov, D. Shalashilin, S. Fernandez-Alberti, S. Tretiak, (2020, in preparation)

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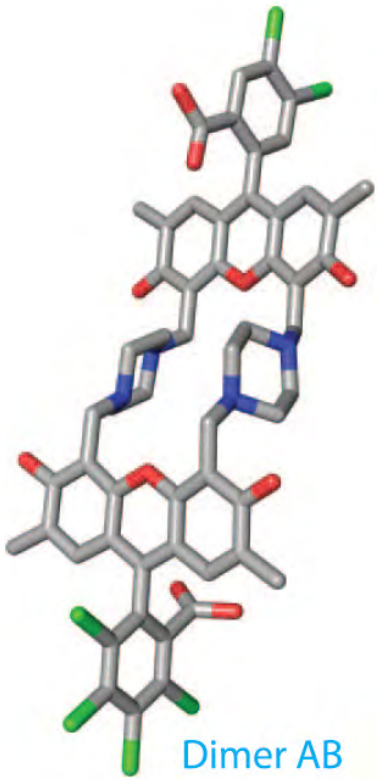
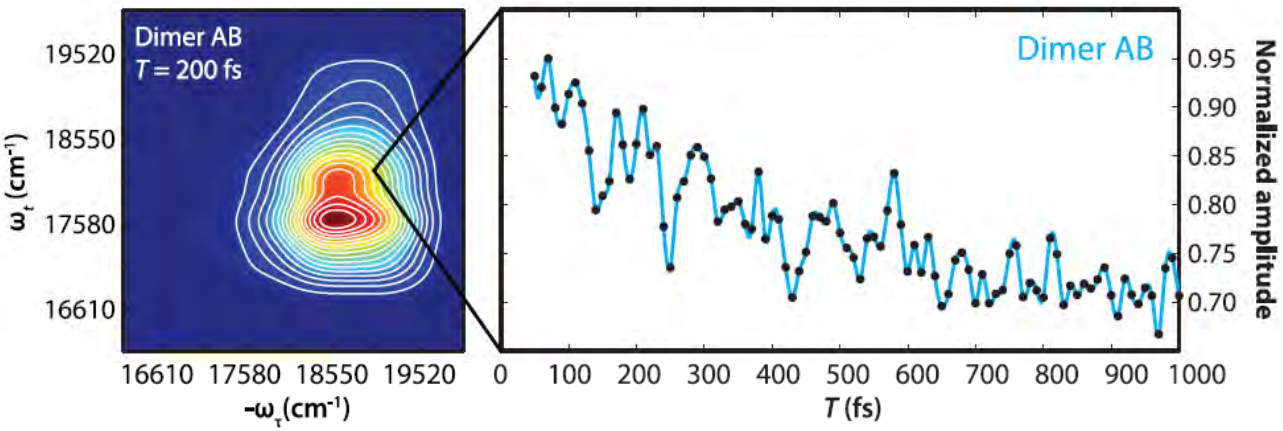
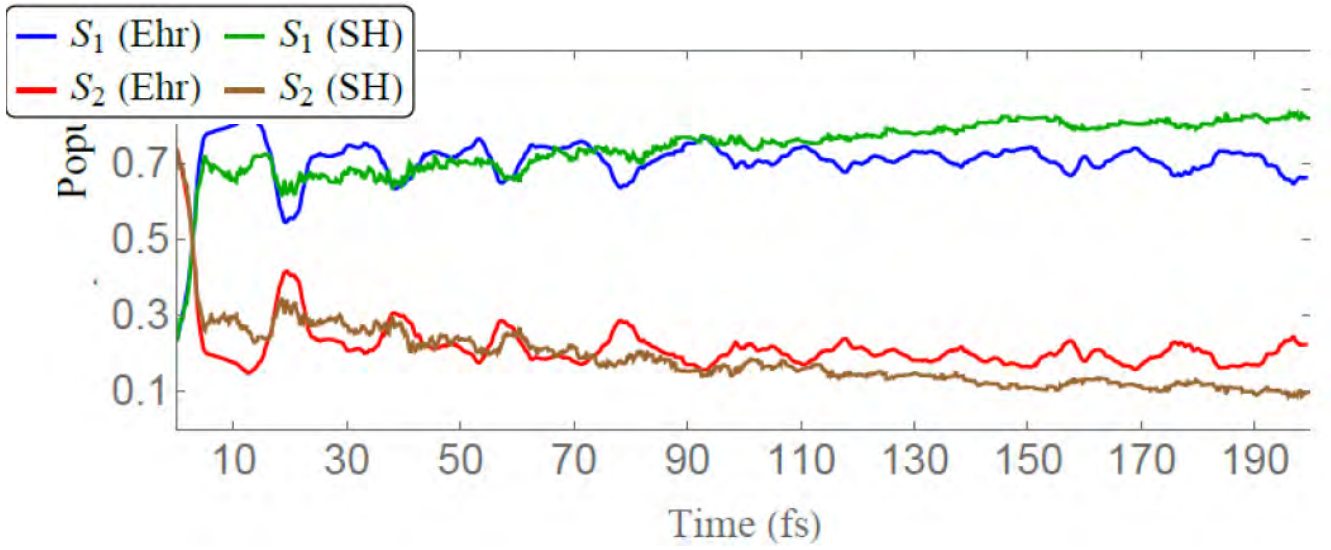




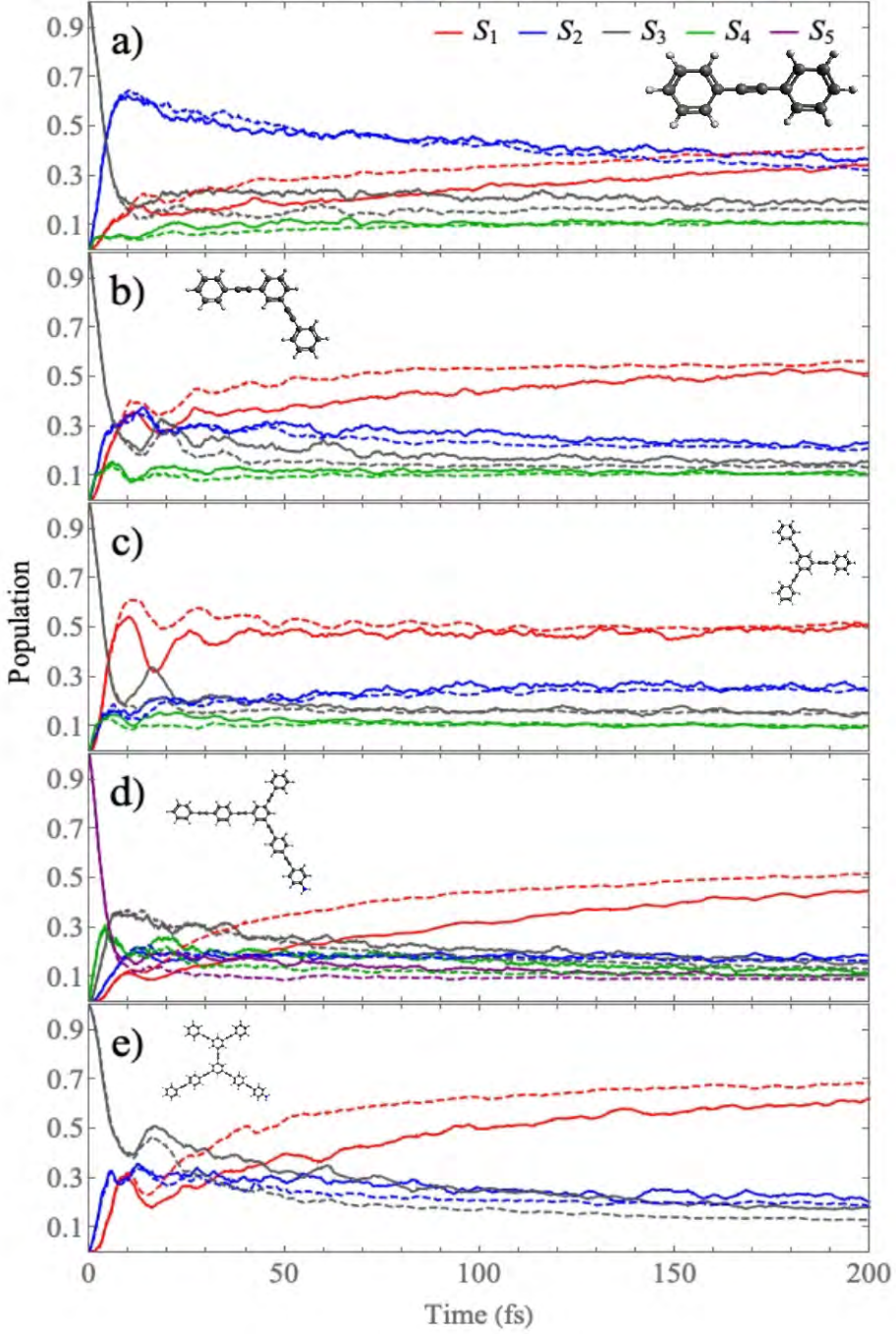
Experimental dephasing time at TR is about 60 fs



D. Hayes, G.B. Griffin, G.S. Engel, Science, 340, 1431 (2013)

Coherent electron-vibrational dynamics is perhaps one place where the Non-Adiabatic Molecular Dynamics (NAMD) methodology can make a difference!

V.M. Freixas, A.J. White, T. Nelson, D.V. Makhov, D. Shalashilin, S. Fernandez-Alberti, S. Tretiak, (2020, in preparation)



SH vs Ehr vs AIMC-MCE

I. Population evolution

Decay rates generally follow $k_{SH} > k_{MCE\text{-}AIC} > k_{Ehr}$

SH rates strongly depend on the type of decoherence corrections

Decay rates are MUCH MORE sensitive to electronic structure methods used (due to gaps)

II. Coherences

As manifested by 'wiggles' in population or gap or other observables:

Ehr - the strongest coherence (vibronic wavepacket cannot decohere in mean field),

SH – the weakest coherence (independent trajectories, no vibronic wavepacket!)

AIMC – in between SH and Ehr

V.M. Freixas, A.J. White, T. Nelson, D.V. Makhov, D. Shalashilin, S. Fernandez-Alberti, S. Tretiak, (2020, in preparation)

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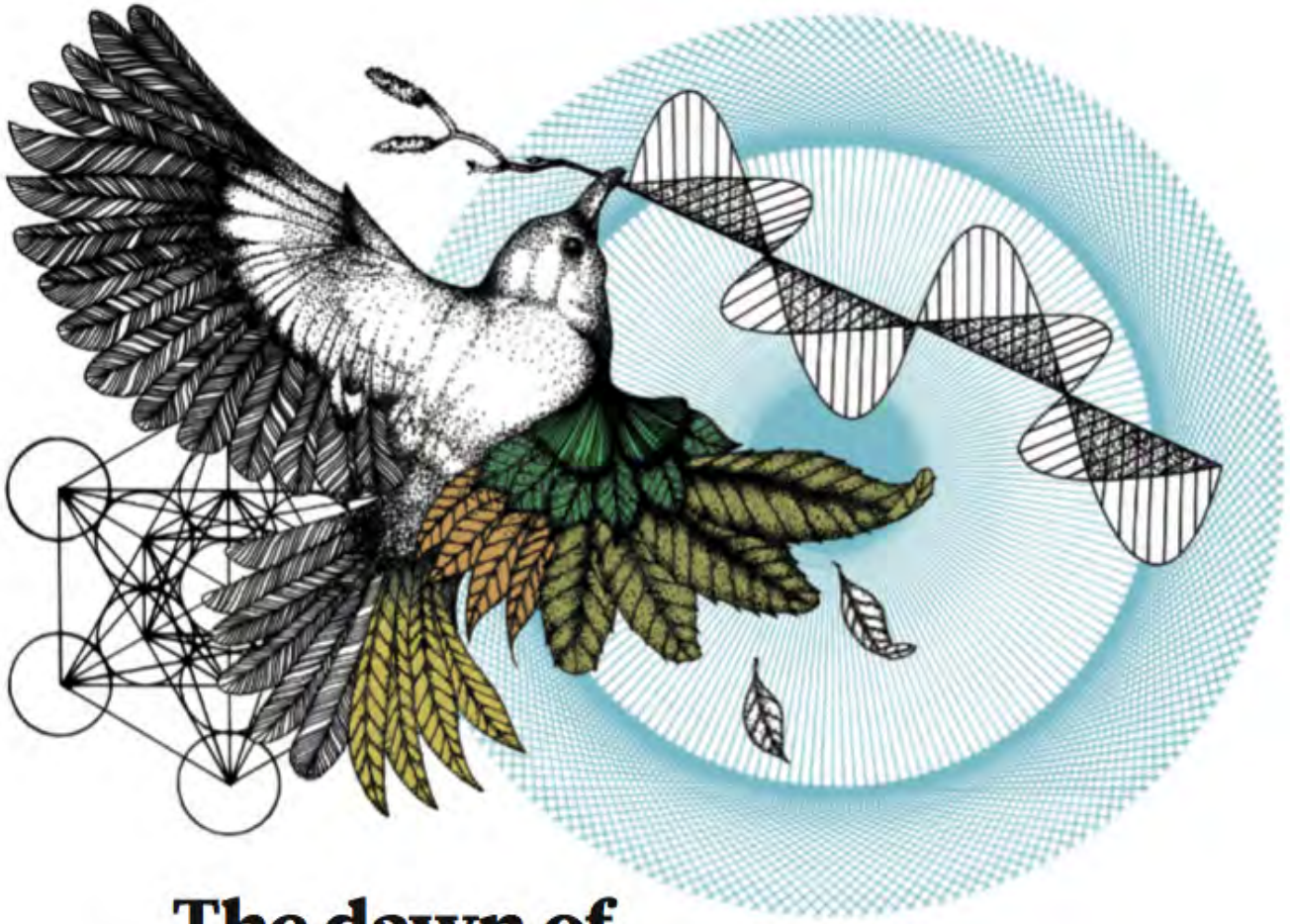


The dawn of quantum biology

The key to practical quantum computing and high-efficiency solar cells may lie in the messy green world outside the physics lab.

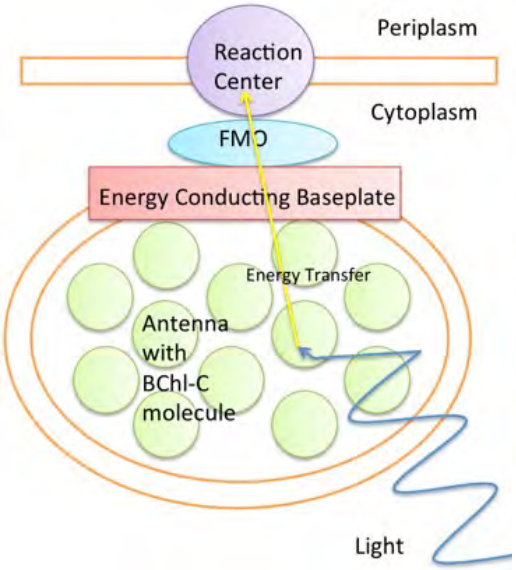
BY PHILIP BALL

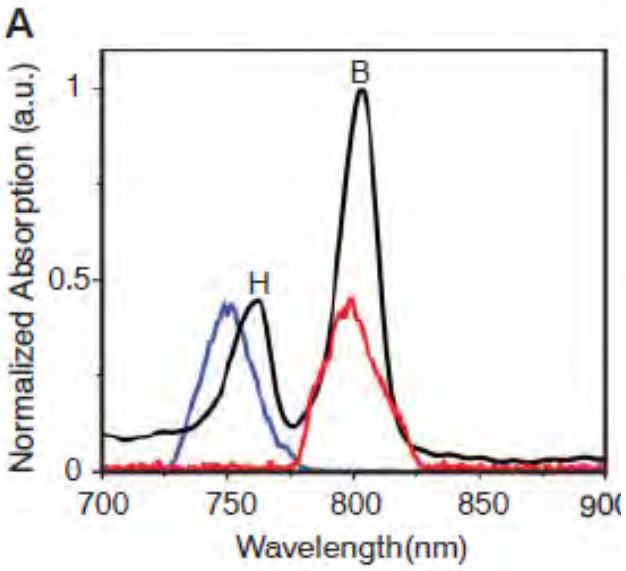
Nature 474:272–274 (2011)

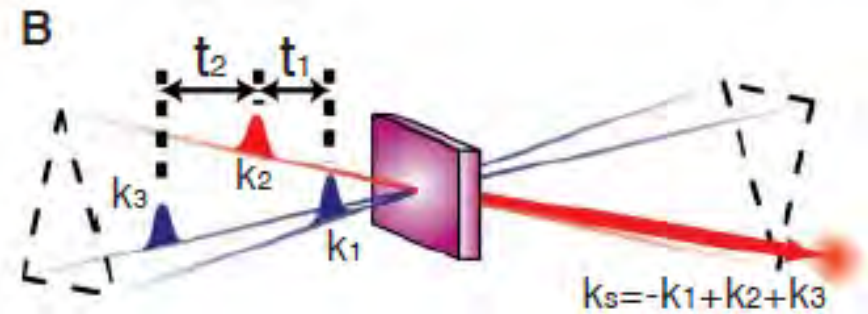
2D electronic spectra of bio-systems

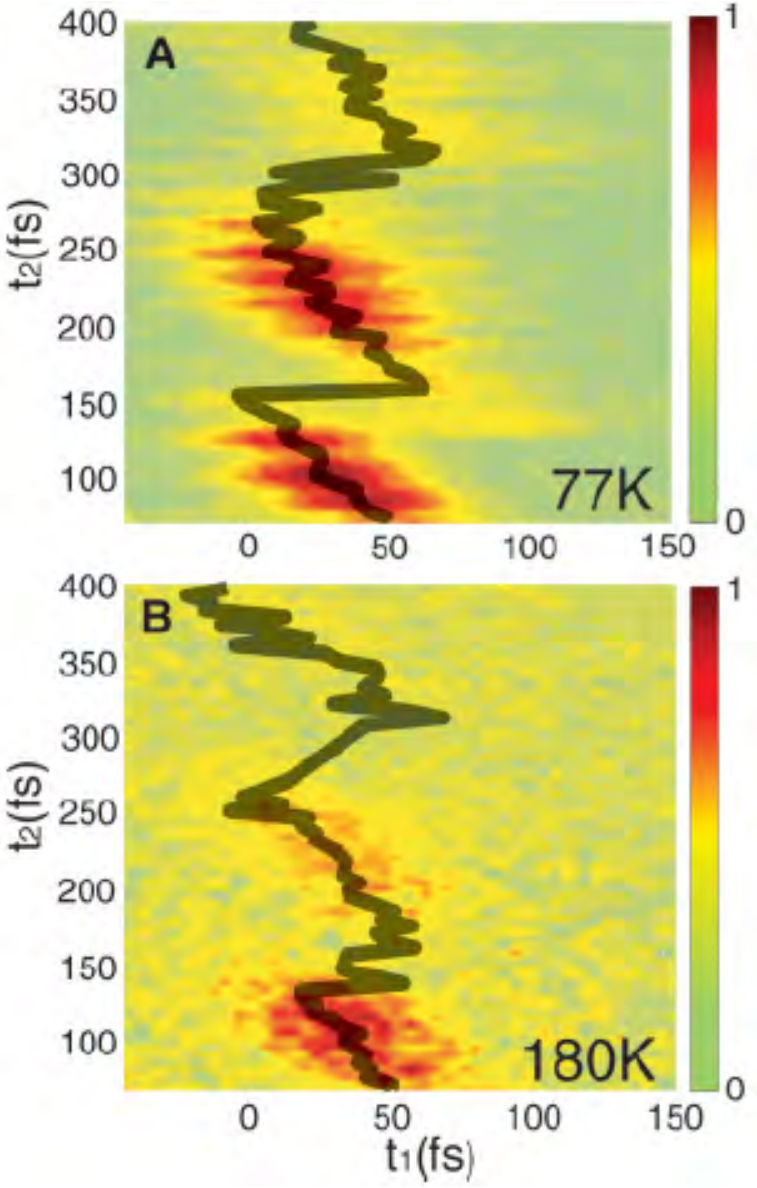
Coherence Dynamics in Photosynthesis: Protein Protection of Excitonic Coherence

Hohjai Lee, Yuan-Chung Cheng, Graham R. Fleming*





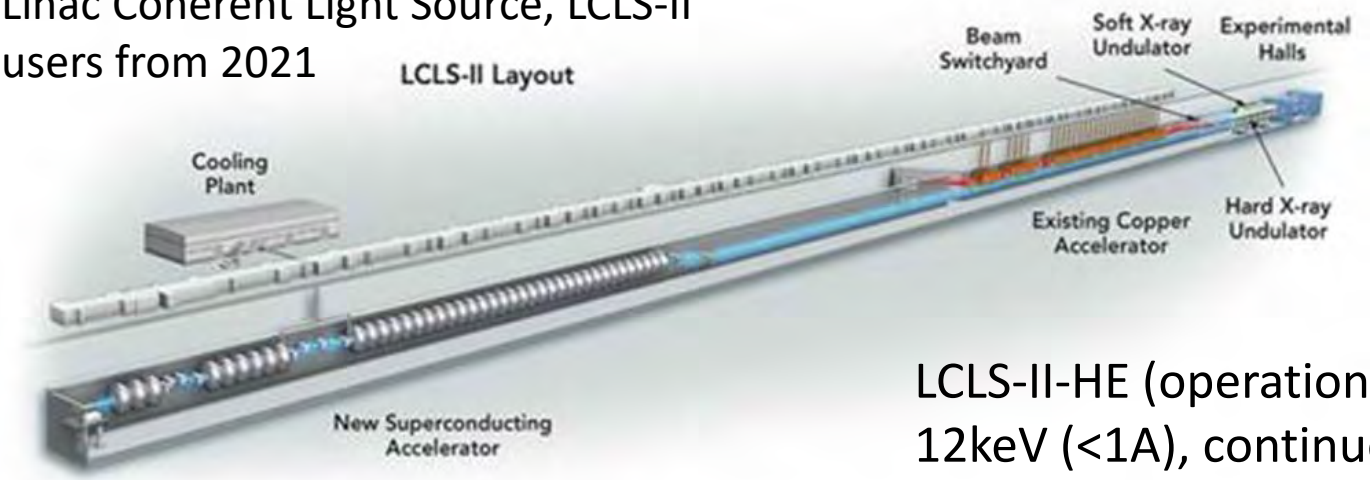




Science, 316, 1462 (2007)

Probing time and space: X-Ray lasers

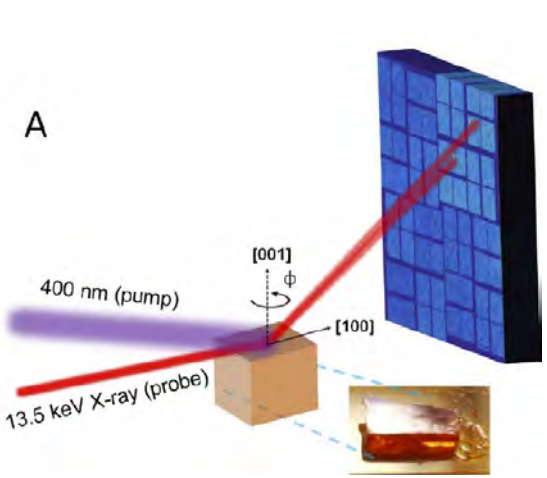
Linac Coherent Light Source, LCLS-II users from 2021

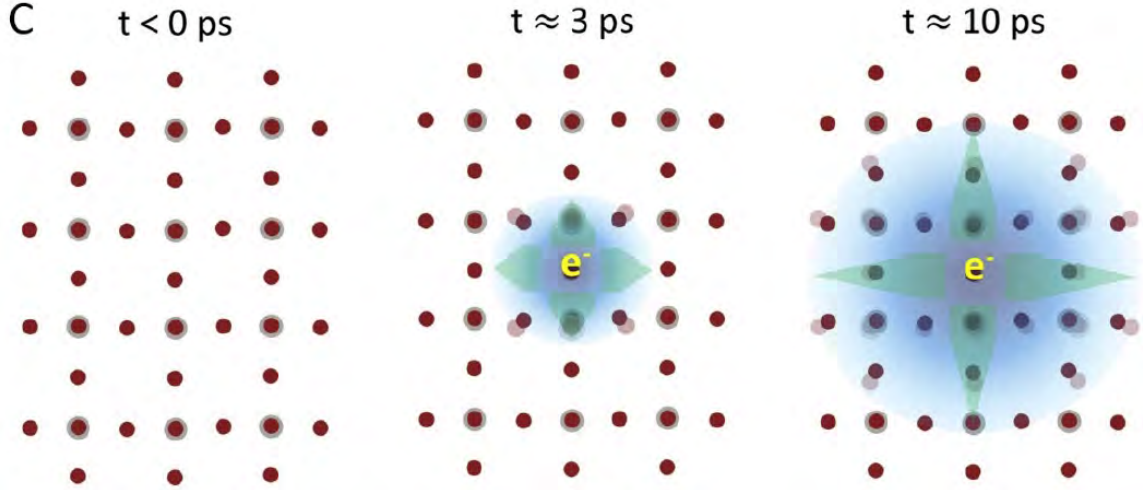


X-ray wavelengths extend down to the atomic scale, while x-ray pulse durations now lie in the femtosecond range.

LCLS-II-HE (operational from 2024): beyond 12keV (<1A), continuous pulse train (1 MHz).

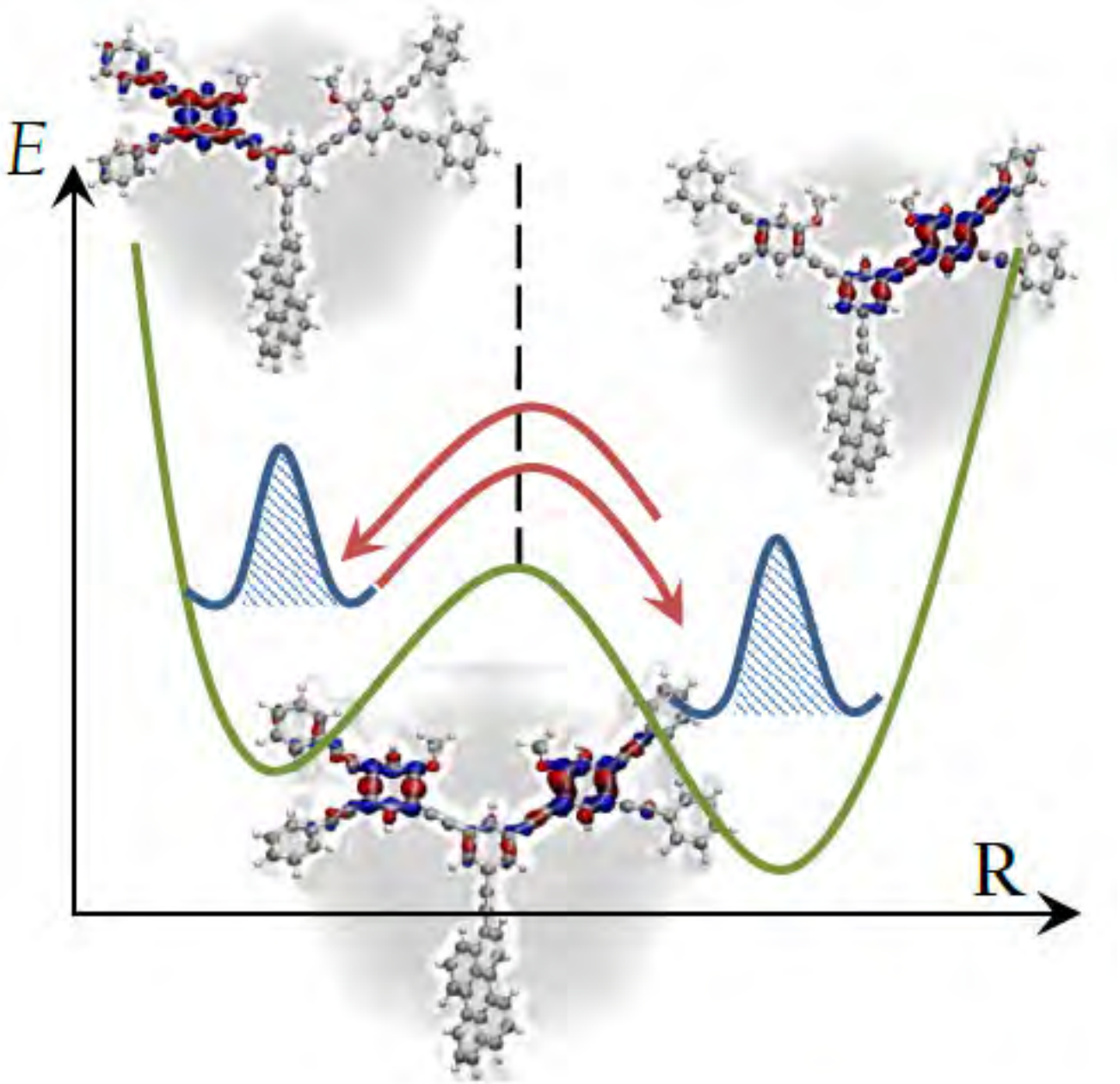
Visualization of polaronic effects in halide perovskites





B. Guzelturk, T. Winkler, T. Van de Goor, M. D. Smith, S. A. Bourelle, S. Feldmann, M. Trigo, S. Teitelbaum, H-G. Steinruck, G. A. de la Pena, R. Alonso-Mori, D. Zhu, T. Sato, H. I. Karunadasa, M. F. Toney, F. Deschler, A. M. Lindenberg, Nature Materials (2020, in press)

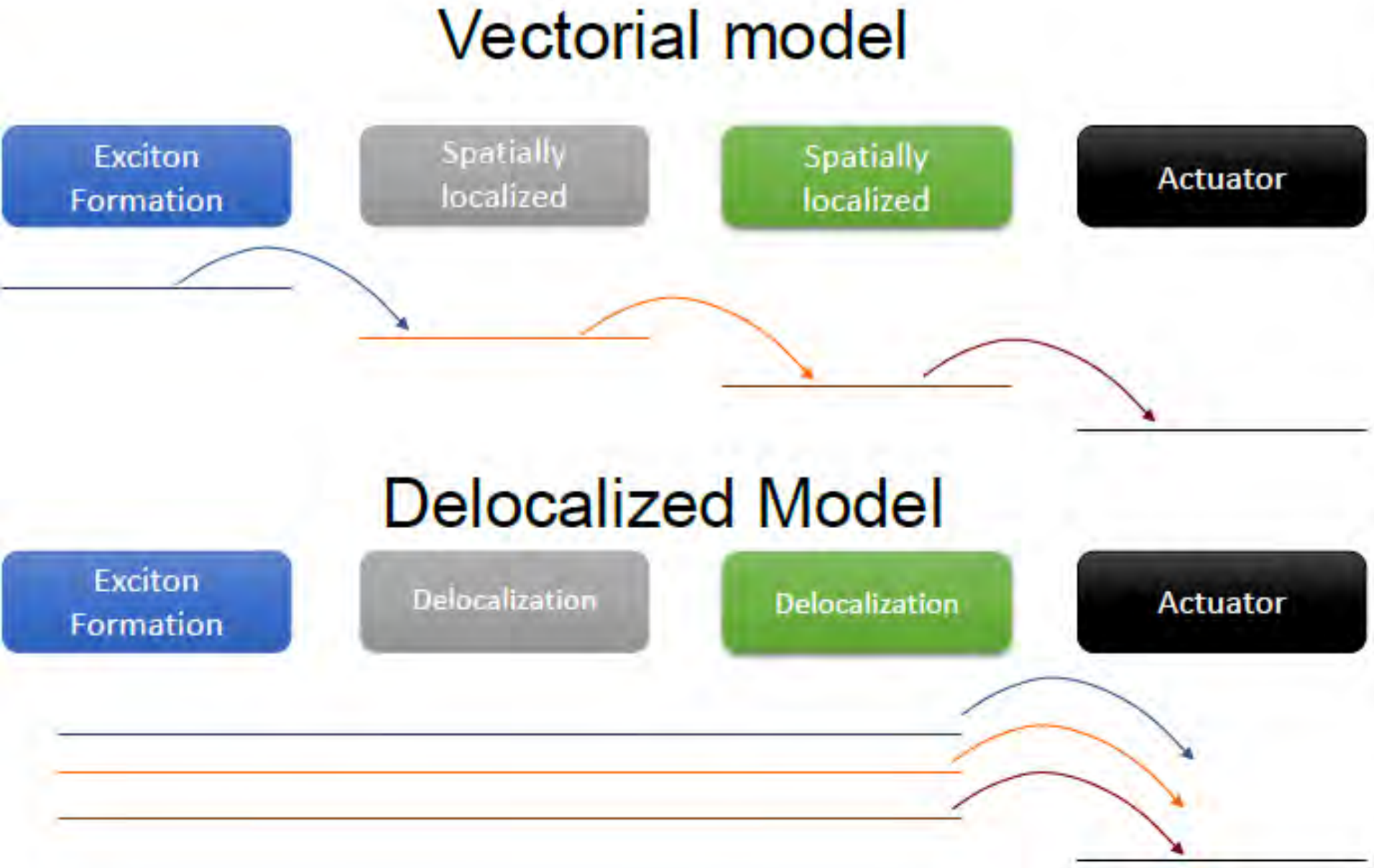
Coherent electron-vibrational dynamics



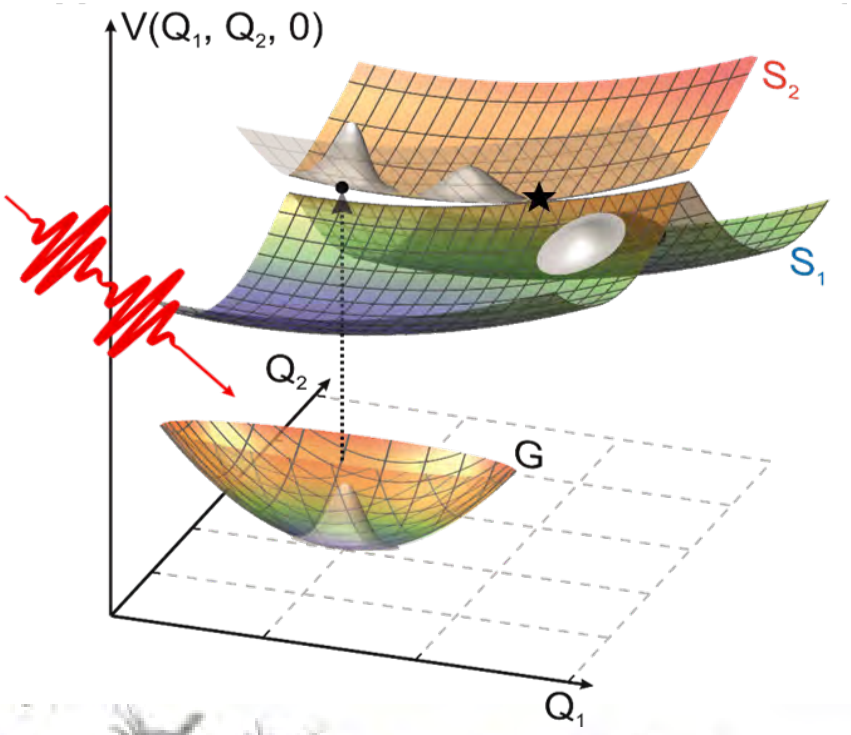
Coherent vibronic dynamics in a dimer

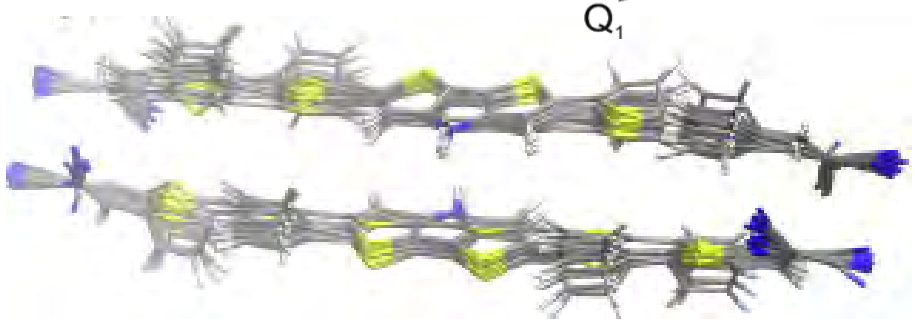
T. Nelson, D. Ondarse-Alvarez, N. Oldani, B. Rodriguez-Hernandez, L. Alfonso-Hernandez, J.F. Galindo, V. D. Kleiman, S. Fernandez-Alberti, A. E. Roitberg, S. Tretiak Nature Comm. 9, 2316 (2018)

Light harvesting -> sensitization pathways

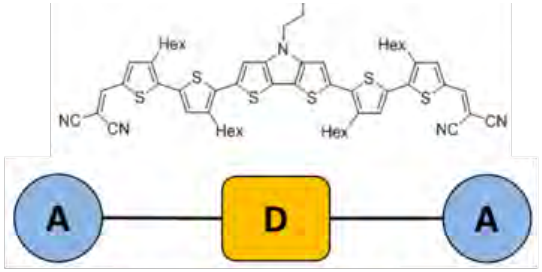


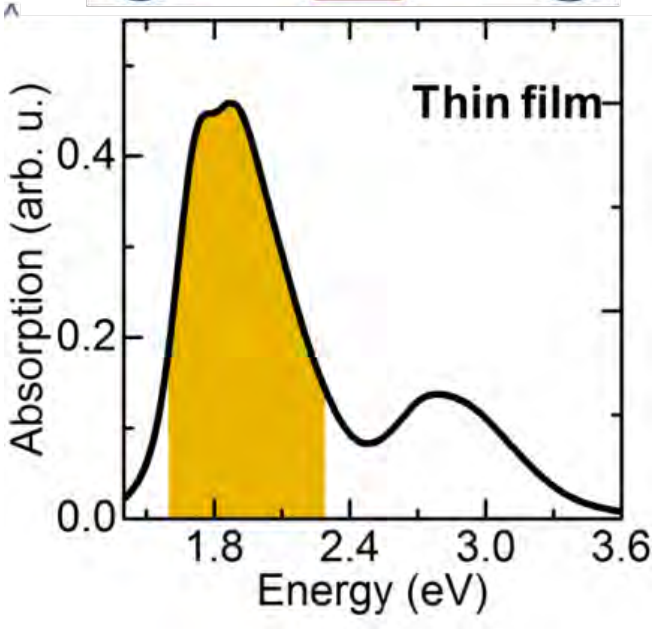
Energy transfer through intermolecular conical intersections in organic photovoltaics





Experimental observation of coherent vibrational dynamics in thin film

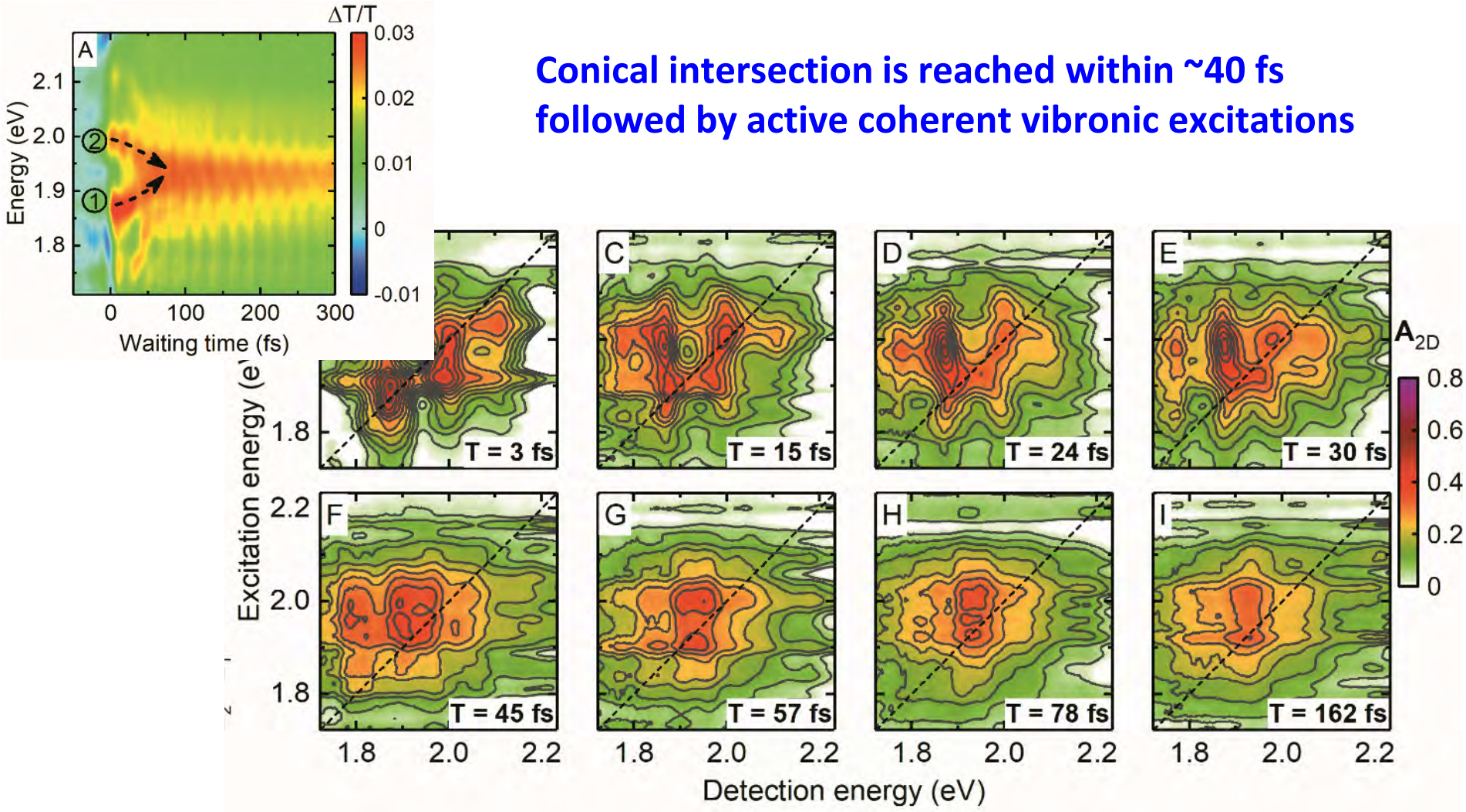




A. De Sio, E. Sommer, X. T. Nguyen, L. Gross, D. Popović, B. Nebgen, S. Fernandez-Alberti, S. Pittalis, C. A. Rozzi, E. Molinari, E. Mena-Osteritz, P. Bäuerle, T. Frauenheim, S. Tretiak, C. Lienau, Nature Nanotech. (2020, https://doi.org/10.1038/s41565-020-00791-2)

Two-dimensional electronic spectra suggest coherent passing of intermolecular CoIns

Conical intersection is reached within ~40 fs followed by active coherent vibronic excitations



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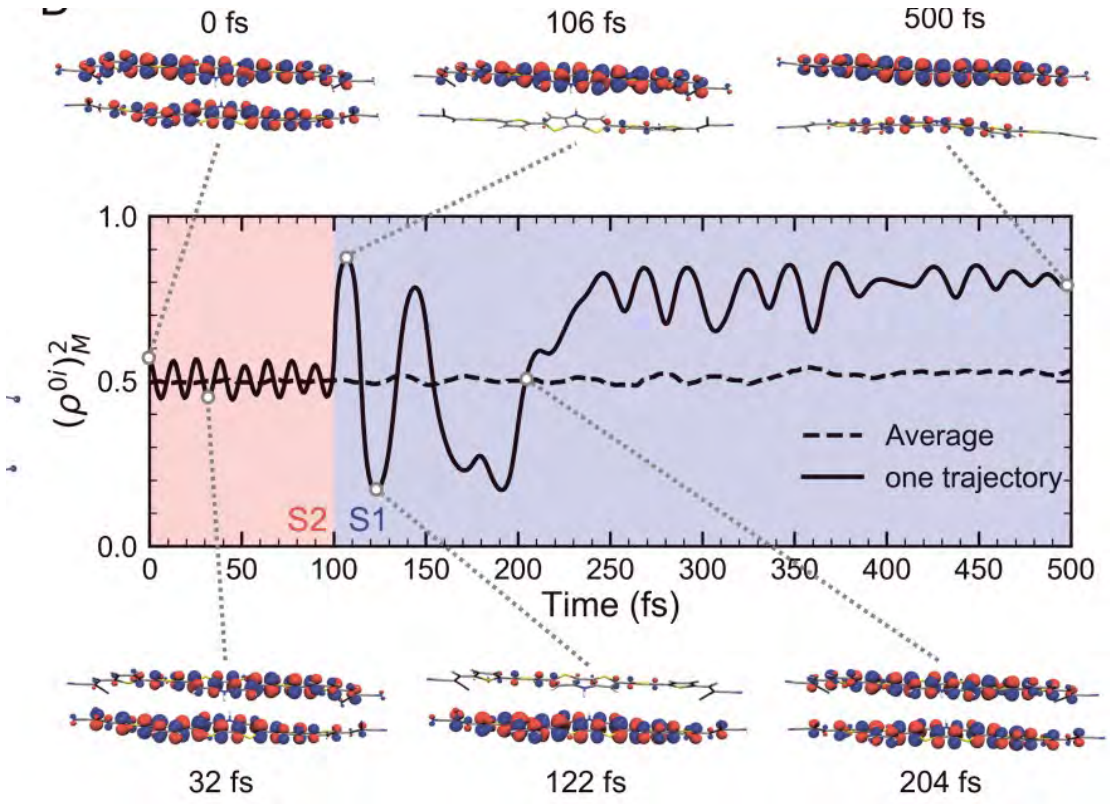
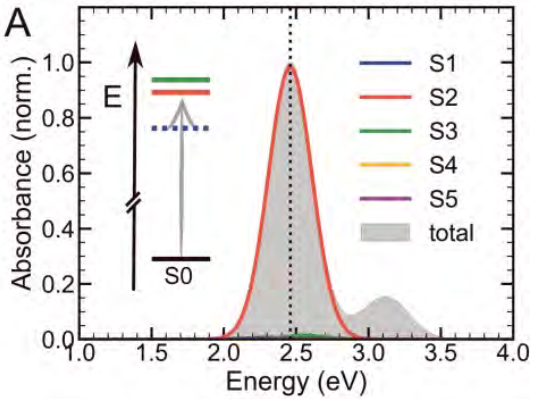
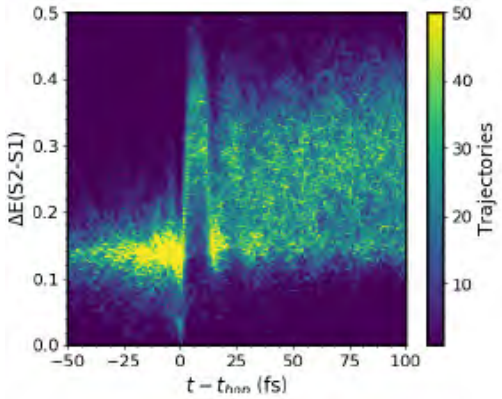
Modeling of coherent non-adiabatic dynamics in a molecular dimer (H-aggregate)

Intermolecular conical intersection is reached within 100 fs. Excess of electronic energy excites vibrational modes coupled on upper and lower surfaces (modulation of dynamics), the wavefunction "collapses" (self-trapping).







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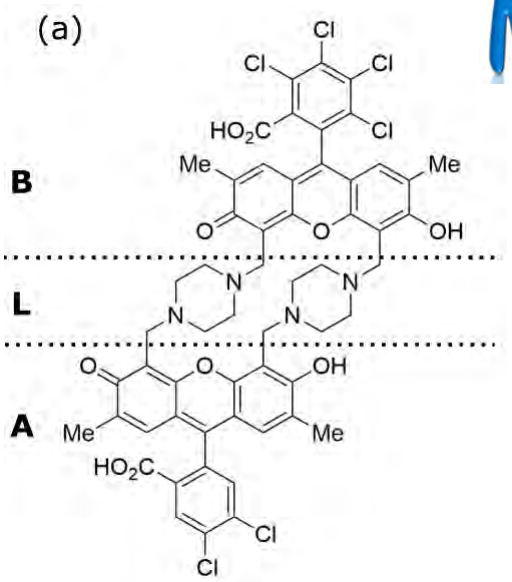
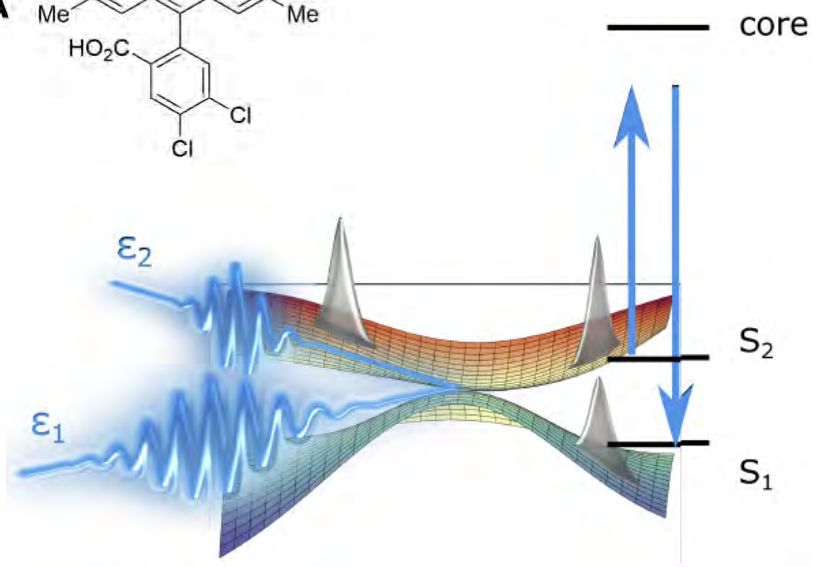
Monitoring Molecular Vibronic Coherences by Ultrafast X-Ray Spectroscopy

- **Large synthetic heterodimer was experimental testbed for studying vibronic coherences (G. Engel group)**
- **Use the TRUECARS signal to monitor the coherences in this heterodimer**
- NEXMD was used for MCE-AIMC modeling of photoexcited dynamics
- Calculated evolution of vibrational wavepackets was used for computing X-ray signals with Spectron code

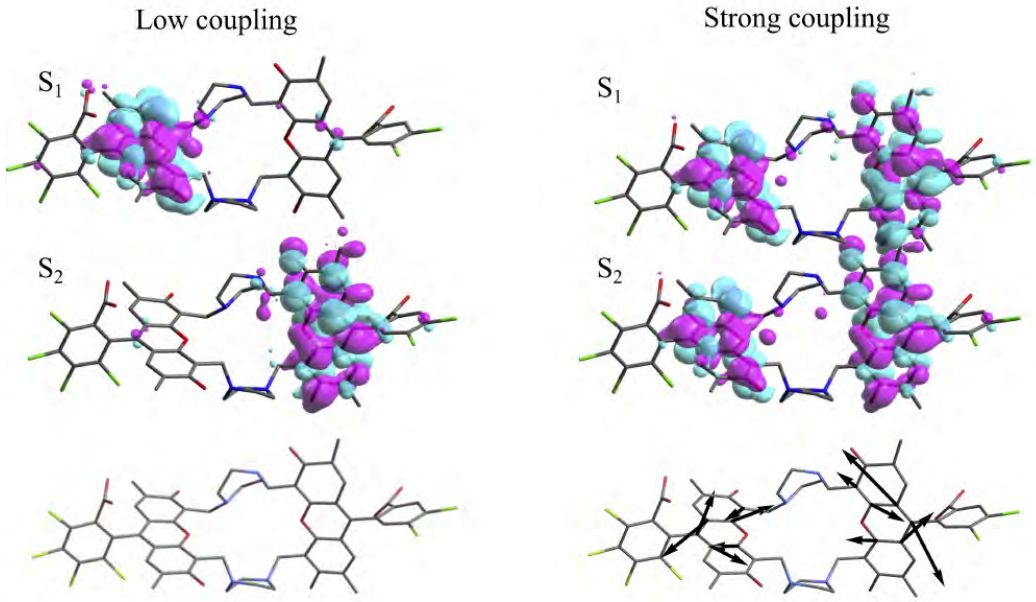


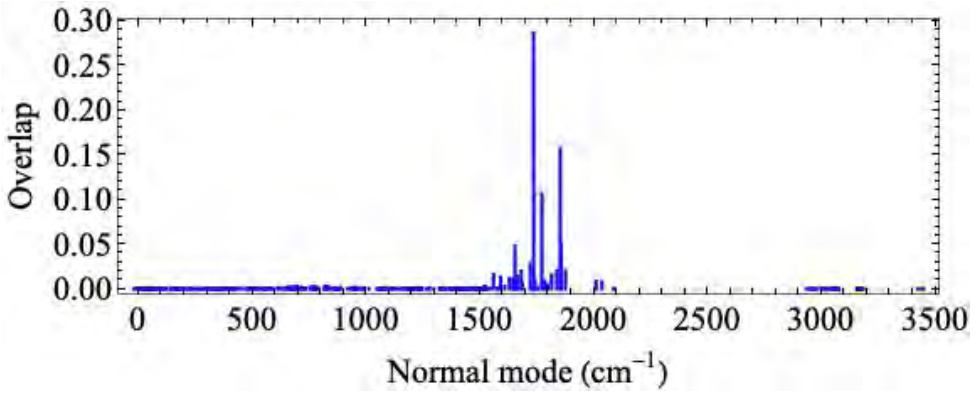


D. Keefer, V. M. Freixas, H. Song, S. Tretiak, S. Fernandez-Alberti, and S. Mukamel, (2020, submitted)

Analysis of excited state dynamics in a heterodimer

- Photoexcited dynamics leads to periodic localized and delocalized dynamics of the electronic wavefunction
- The dynamics spans regions of low- and high- couplings with multiple crossings of conical intersection seam
- Vibrational motions aligned with non-adiabatic coupling vector are enabled





D. Keefer, V. M. Freixas, H. Song, S. Tretiak, S. Fernandez-Alberti, and S. Mukamel, (2020, submitted)

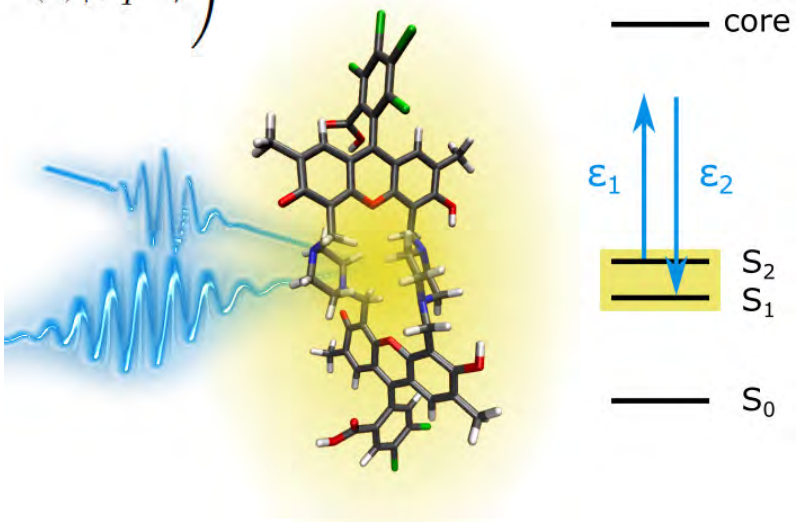
Calculation of X-ray Raman (TRUECARS) signal

- MCE-AIMC provide all the ingredients (electronic and vibrational wvefunctions) with **phases and wavepacket overlaps**:

$$|\Psi(t)\rangle = \sum_n c_n |\psi_n(t)\rangle \qquad |\psi_n(t)\rangle = |\chi_n\rangle \left(\sum_I a_I^{(n)}(t) |\phi_I^{(n)}\rangle \right)$$

- Calculated coherence between states:

$$\rho_{KL} = \frac{1}{2} \sum_{m,n} c_m^* c_n \langle \chi_m | \chi_n \rangle \sum_I \left[(a_K^{(m)})^* a_I^{(n)} \langle \phi_L^{(m)} | \phi_I^{(n)} \rangle + (a_I^{(m)})^* a_L^{(n)} \langle \phi_I^{(m)} | \phi_K^{(n)} \rangle \right]$$



- TRUECARS Raman signal

$$S(\omega_R, T) = 2\mathcal{I} \int_{-\infty}^{\infty} dt e^{i\omega_R (t-T)} \varepsilon_0^*(\omega_R) \varepsilon_1(t-T) \times \langle \Psi(t) | \hat{\alpha} | \Psi(t) \rangle \quad ,$$

Realization of fully atomistic approach:
NEXMD simulations of non-adiabatic dynamics -> experimentally measurable spectra

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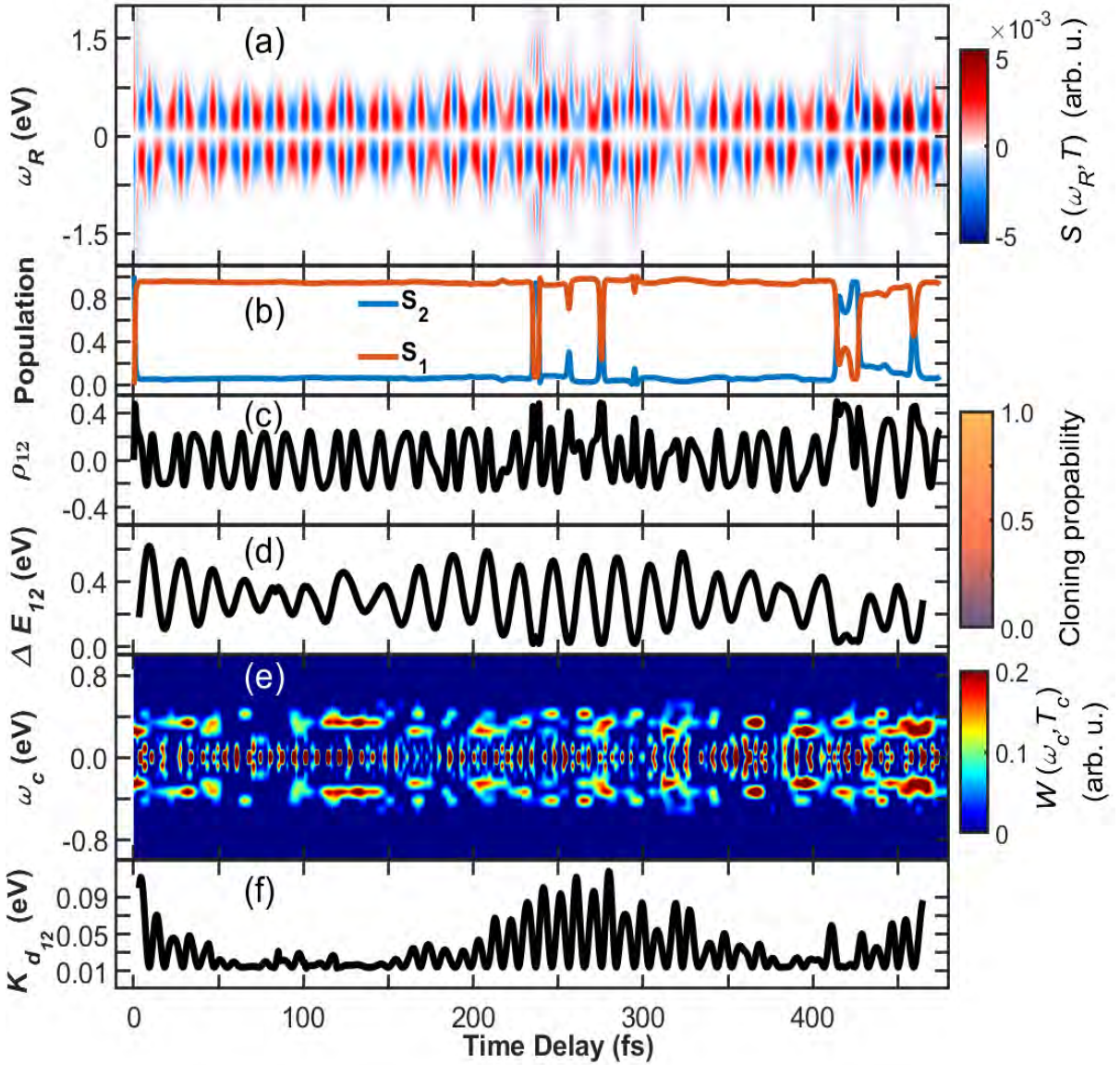
Trajectory example



- (a) TRUECARS signal. Strong coherence throughout the dynamics
- (b) Population. Multiple regions of strong coupling
- (c) Coherence magnitude
- (d) S_2-S_1 Energy splitting
- (e) Wigner spectrogram of the TRUECARS signal. Energy splitting is mapped
- (f) Excess kinetic energy due to non-adiabatic events

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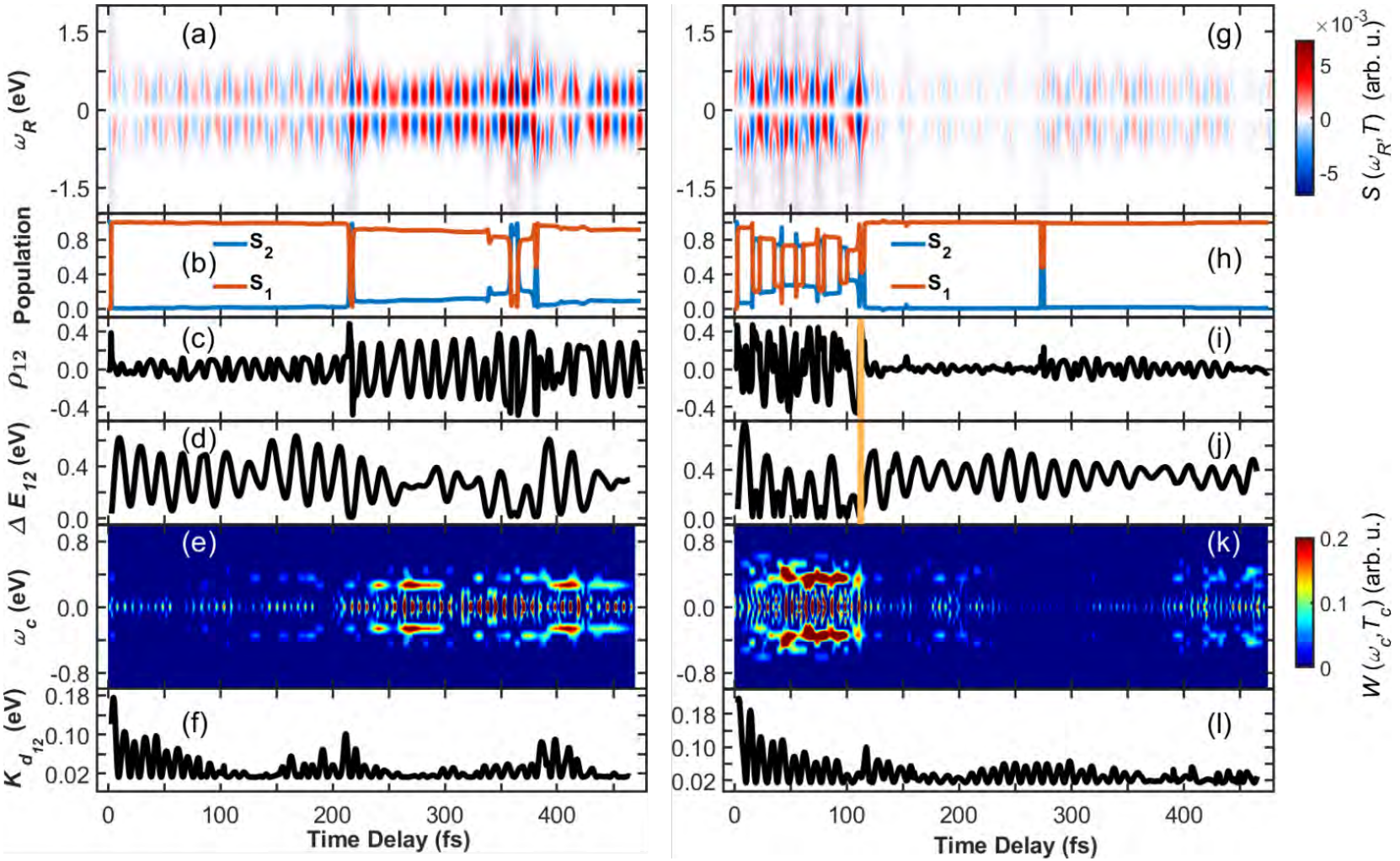
Other trajectory examples



- Left: Coherence emerges later in the dynamics
- Right: Strong initial coherence, fading out after 120 fs
- Cloning event represented by vertical yellow line

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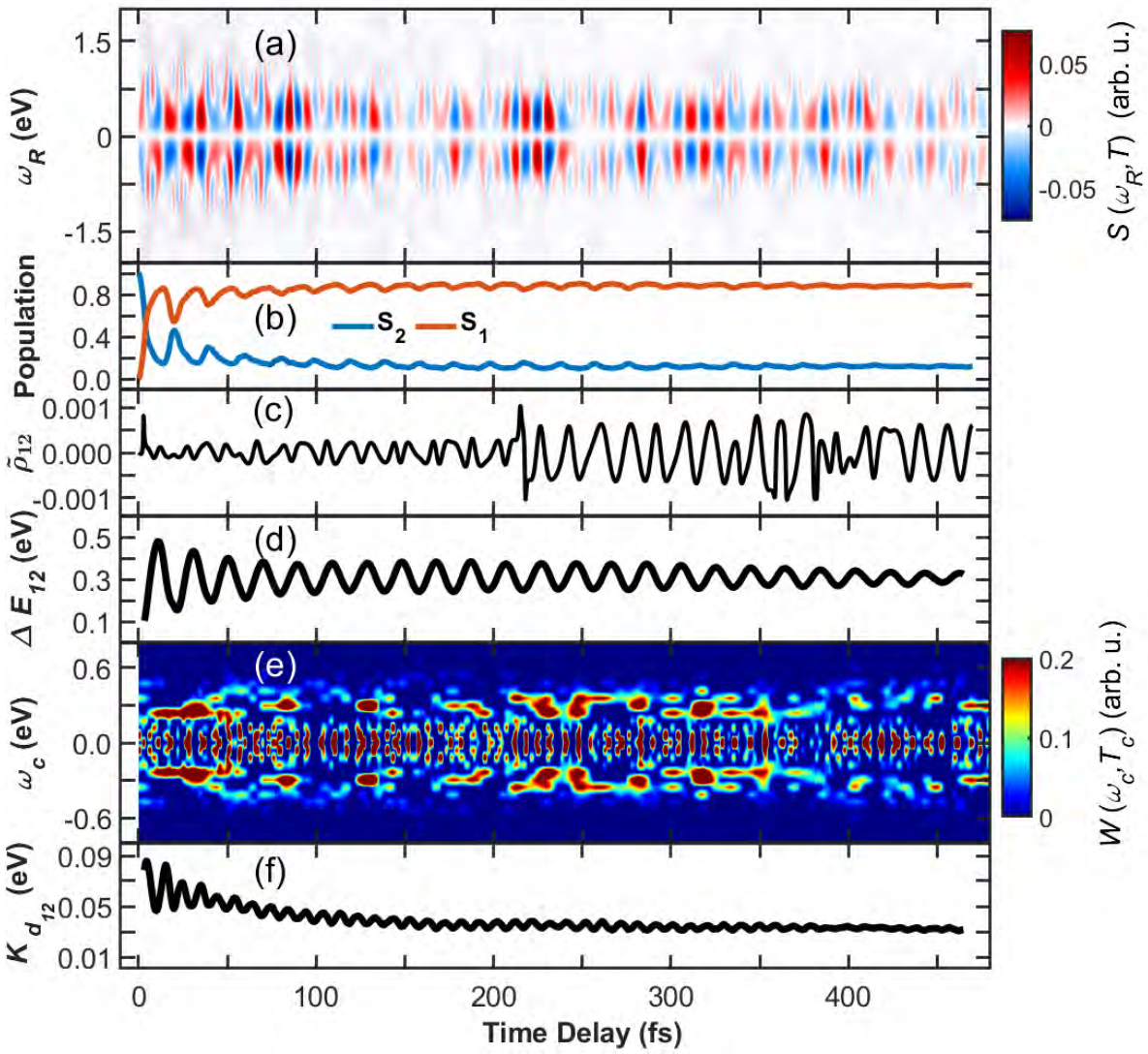
Signal in the Trajectory Ensemble



- Individual trajectories contribute to the ensemble
- **Only** the average signal over all trajectories is observable
- Signal is visible in the ensemble average
- Strong throughout the dynamics due to balanced contributions of initial and late coherence
- Average energy splitting is mapped by the Wigner spectrogram here as well

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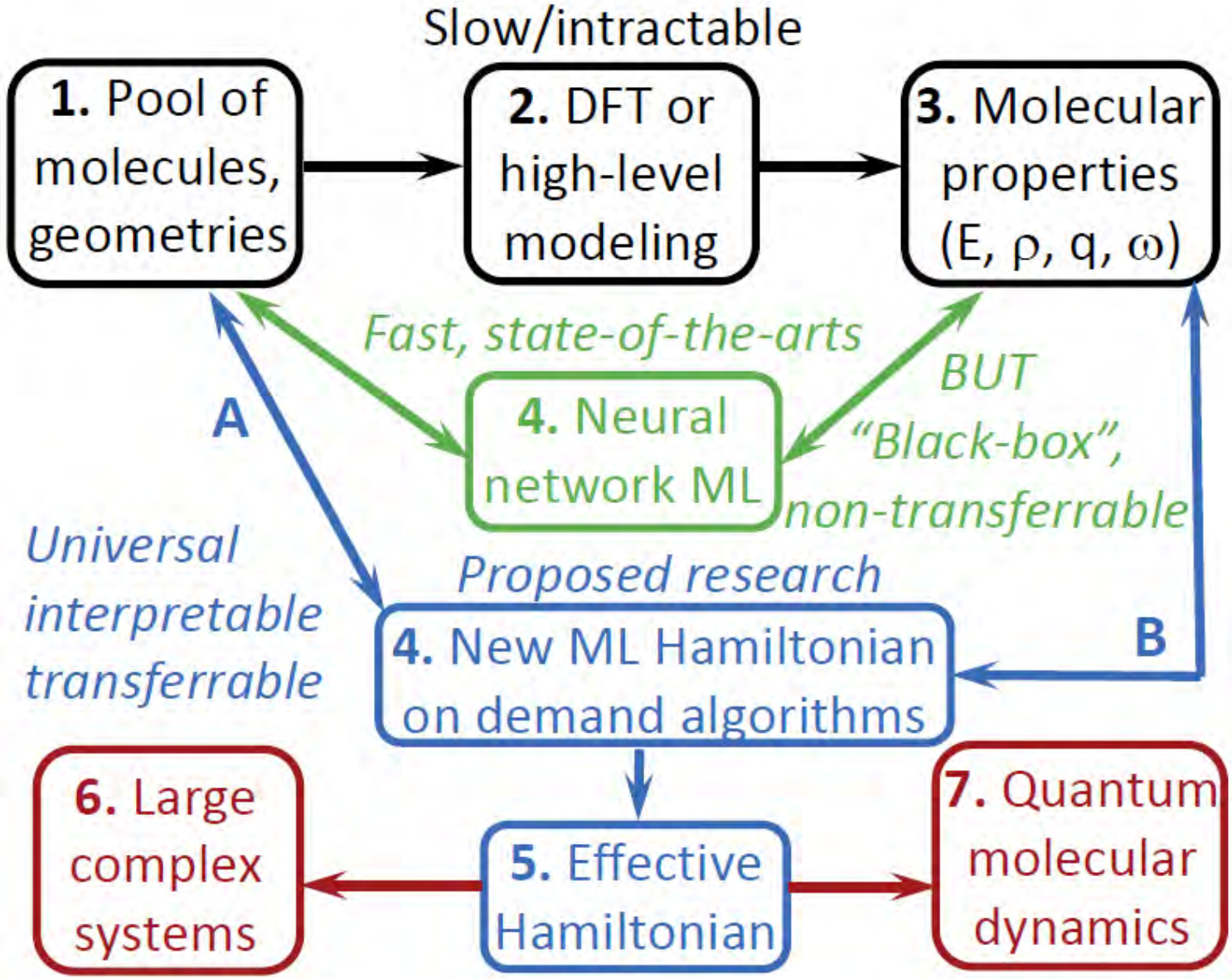
Outline

- *A brief outline of non-adiabatic excited state molecular dynamics modeling*
- *Side to side comparison of Ehrenfest (Ehr), surface hopping (SH) and Multiconfigurational Ehrenfest-Ab Initio Multiple Cloning (MCE-AIMC) results*
- *Coherent passage through intermolecular conical intersections*
- *XFEL spectroscopy (TRUECARS Raman) for monitoring coherent dynamics*
- *Machine learning of Hamiltonians (time allowed)*

Concept of ML derived reduced Hamiltonians



Our goal: learn the entire matrix

Density matrix

q_1	ρ_{12}	ρ_{13}	…	…
ρ_{21}	q_2	ρ_{23}	…	…
ρ_{31}	ρ_{32}	q_3	…	…
…	…	…	…	…
…	…	…	…	…

Hamiltonian

α_{11}	β_{12}	β_{13}	…	…
β_{21}	α_{22}	β_{23}	…	…
β_{31}	β_{32}	α_{33}	…	…
…	…	…	…	…
…	…	…	…	…

A. Sifain, N. Lubbers, B. Nebgen, J.S. Smith, A.Y. Lokhov, O. Isayev, A.E. Roitberg, K. Barros, S. Tretiak, J. Phys. Chem. Lett. 9, 4495 (2018);

B. Nebgen, N. Lubbers, J. S. Smith, A. Sifain, A. Y. Lokhov, O. Isayev, A. E. Roitberg, K. Barros, S. Tretiak, J. Chem. Theory Comput., 14, 4687 (2018);

S. Magedov, C. Koh, N. Lubbers, B. Nebgen, J. S. Smith, K. Barros, S. Tretiak, (2020, submitted)

T. Zubatiuk, B. Nebgen, N. Lubbers, J. S. Smith, R. Zubatiuk, G. Zhou, C. Coh, K. Barros, O. Isayev, S. Tretiak, (2020) https://arxiv.org/abs/1909.12963

Extended Hückel Theory

Extended Hückel theory is one of the simplest methods for simulating the electronic structure of molecules.

Hamiltonian form:

$$H_{ij} = \frac{1.75}{2}\left(H_i + H_j\right)S_{ij}$$

$H_{carbon,\,S} = -21.4\ eV;\ H_{carbon,\,P} = -11.4\ eV;\ H_{hydrogen,\,S} = -13.6\ eV$

Solve the Schrodinger equation:

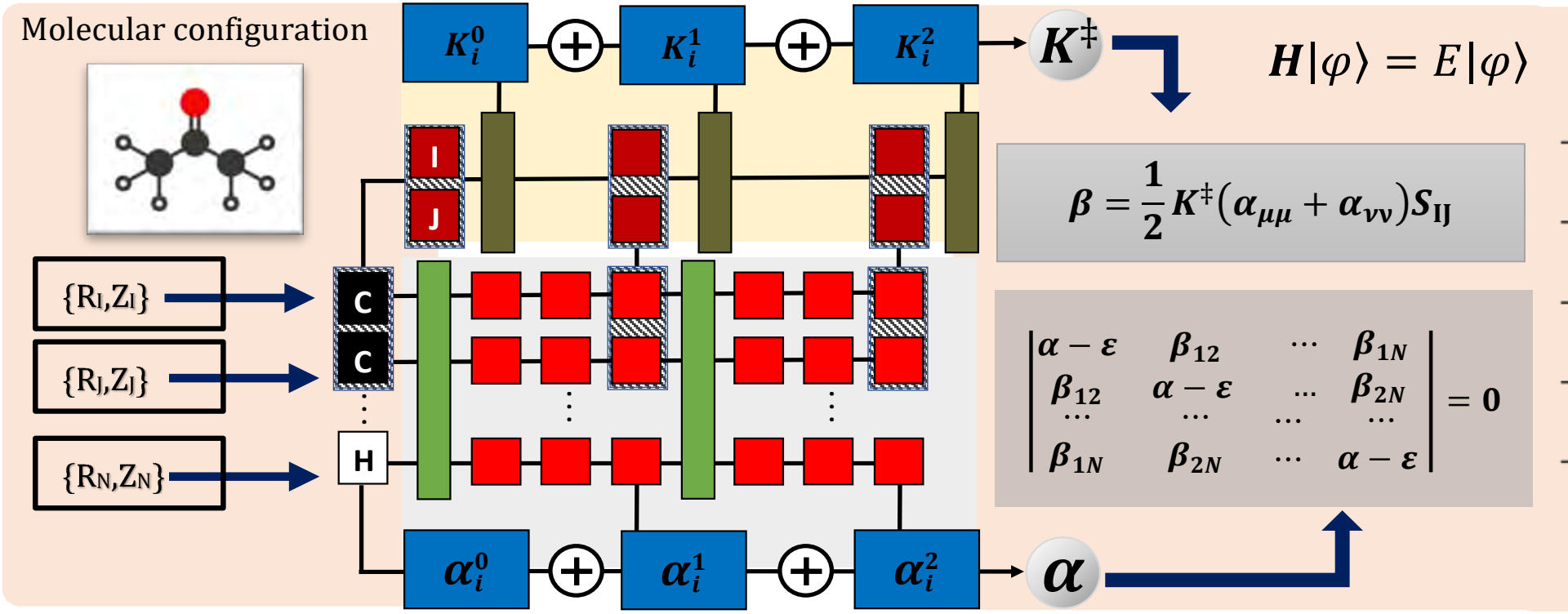
$$H\psi = ES\psi$$

Can we optimize the Hamiltonian parameters to match DFT eigenvalues and energies?

ML-scheme for learning Hückel Hamiltonians

Hierarchically Interacting Particle Neural Network

ML Effective Hamiltonian



Diagonal predictions that occur on each atom are used to parameterize the orbital energies. The layers (top) added to HIP-NN allow predictions off-diagonal Hamiltonian elements ($K^{\ddagger}$).

T. Zubatiuk, B. Nebgen, N. Lubbers, J. S. Smith, R. Zubatiuk, G. Zhou, C. Coh, K. Barros, O. Isayev, S. Tretiak, (2020) https://arxiv.org/abs/1909.12963

ML task and loss function

We would like to learn both molecular orbital energies and shapes.

Compute "Orbital Mulliken Charge" for orbital i and atom m:

$$q_{i,m} = \frac{\sum_{k=1}^{N_m} C_{i,k}^2}{\sum_{k=1}^{N} C_{i,k}^2}$$

Where N_m is the number of orbitals on atom m and N is the total number of orbitals.

The q matrix always has the same dimensionality (# of atoms, # of states)

$$Orbital\ Energy\ Error = \sum_{i}^{N_{orb}} \left(\varepsilon_i^{DFT} - \varepsilon_i^{Hückel}\right)^2$$

$$Density\ Error = \sum_{i}^{N_{orb}} \sum_{j}^{N_{atoms}} \left(\sum_{k}^{N_{AO}^j} qDFT_{ijk}^2 - \sum_{k}^{N_{AO}^j} qML_{ijk}^2 \right)^2$$

$$L = W_1 \times Orbital\ Energy\ Error + W_2 \times Density\ Error$$

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Training Dataset and obtained accuracy

200,000 element database made of molecules

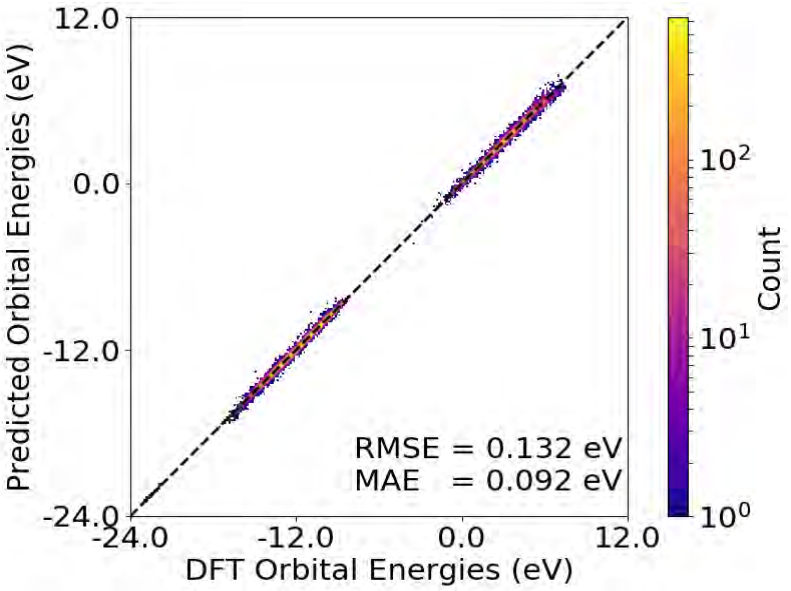
Subsampled from the original ANI-1x dataset

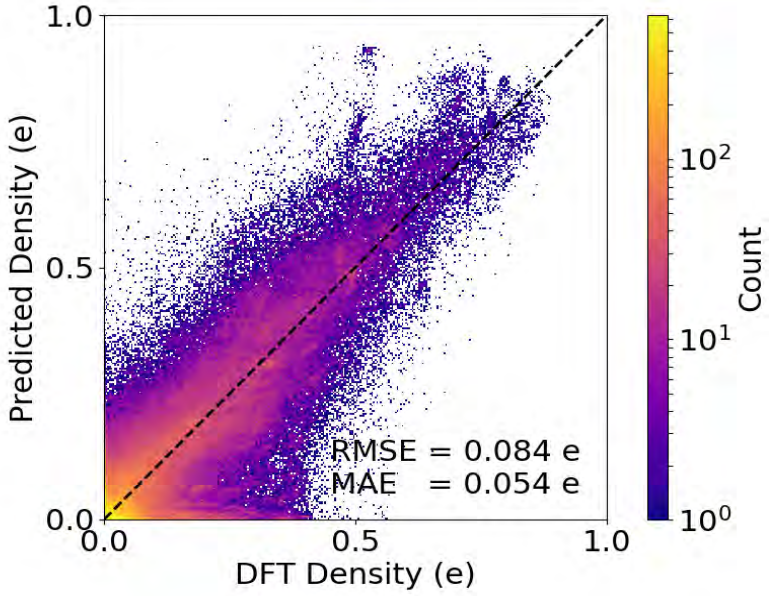
Small Database because diagonalization required at every computation

Energies have an accuracy of roughly 100meV ~ 2 kcal/mol

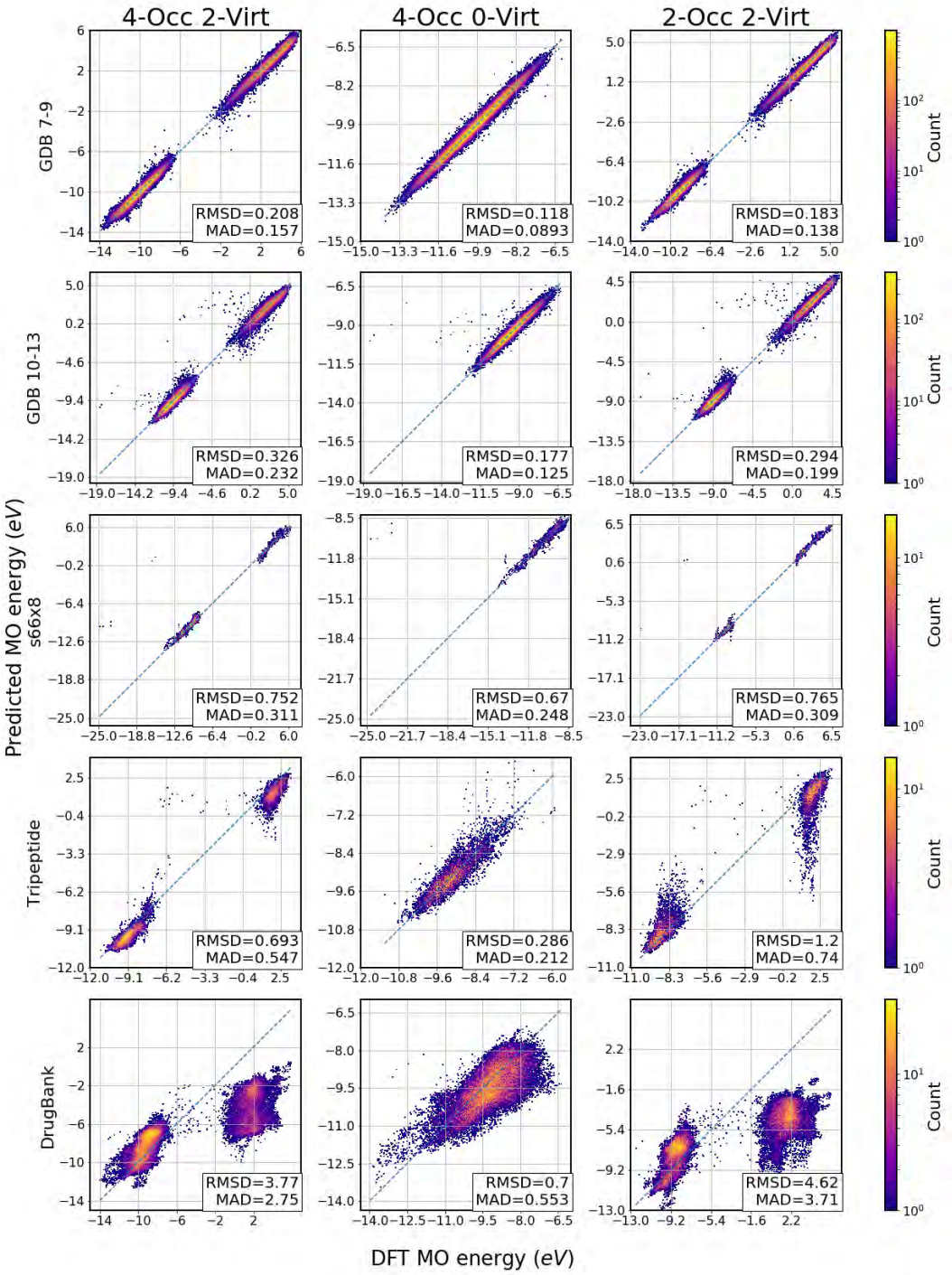
Densities have an accuracy of ~.05 e$^-$

$$W_1 = 1.0;\ W_2 = 10^{-1}$$





T. Zubatiuk, B. Nebgen, N. Lubbers, J. S. Smith, R. Zubatiuk, G. Zhou, C. Coh, K. Barros, O. Isayev, S. Tretiak, (2020) https://arxiv.org/abs/1909.12963



Validation of ML-Hückel prediction on COMP-6 database

For the smaller COMP6 sets, agreement very good.

Predictions on Tripeptides remain reasonable.

Predictions on Drugbank is degraded, likely due to the presence of aromatic systems

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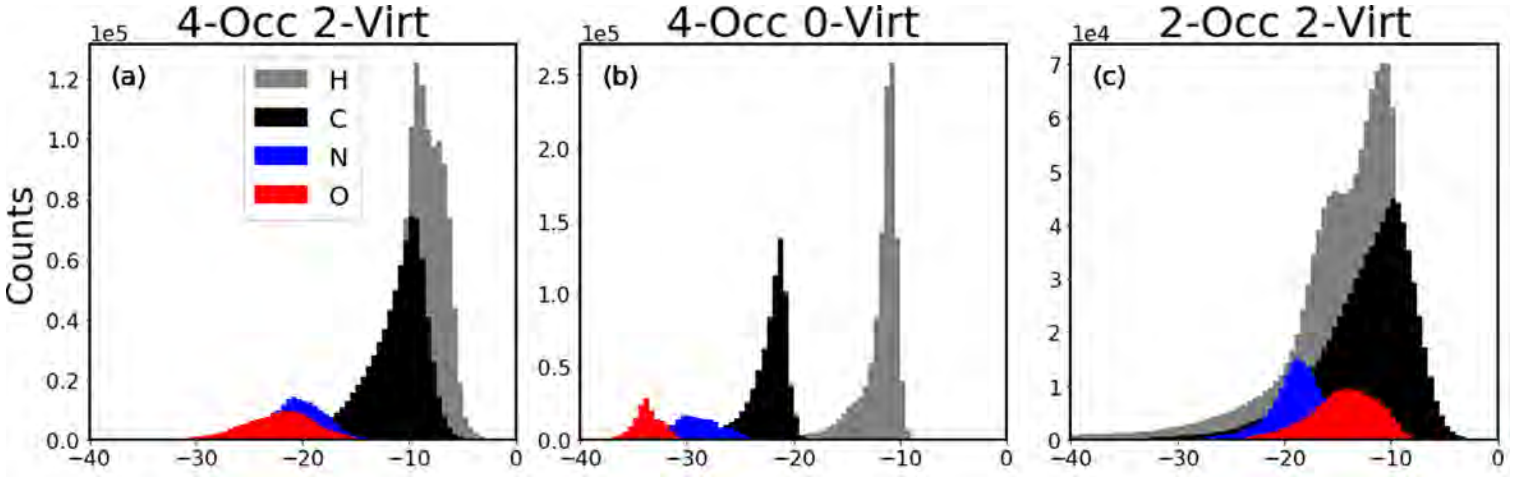
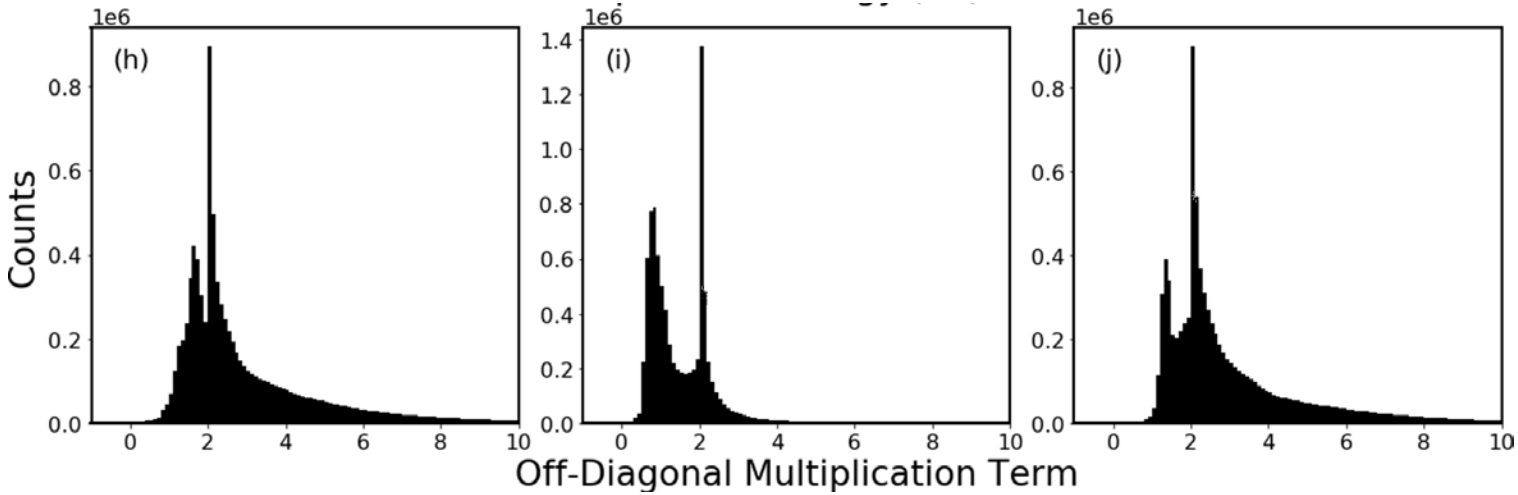
Is learned tight-binding model physical?

α



For 4-Occ 0-Virt" mode $\alpha_{H,s}$ orbital energy is -13.6 eV and O<N<C

$K^{\ddagger}$



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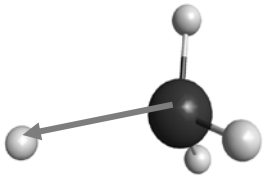
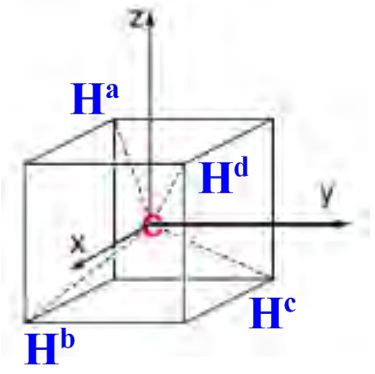
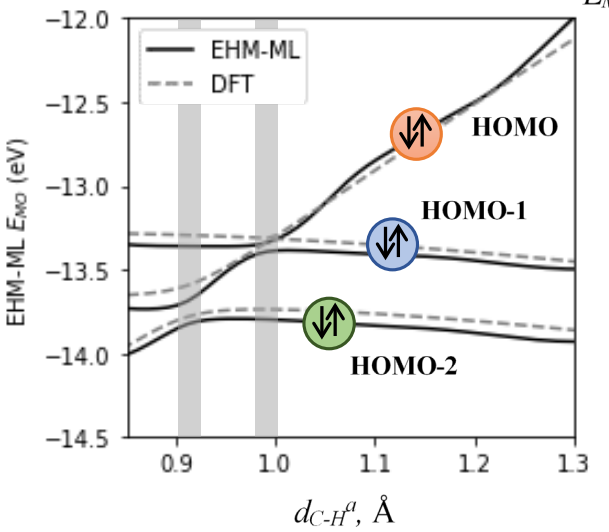
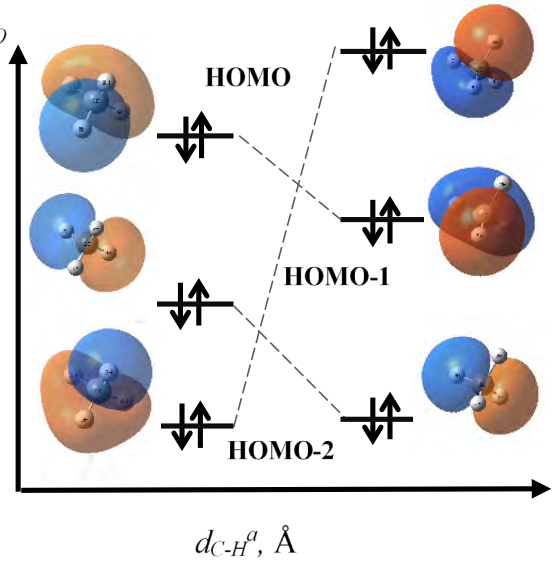
Distribution of $K^{\ddagger}$ has average of 1.5, close to original parameterization 1.75

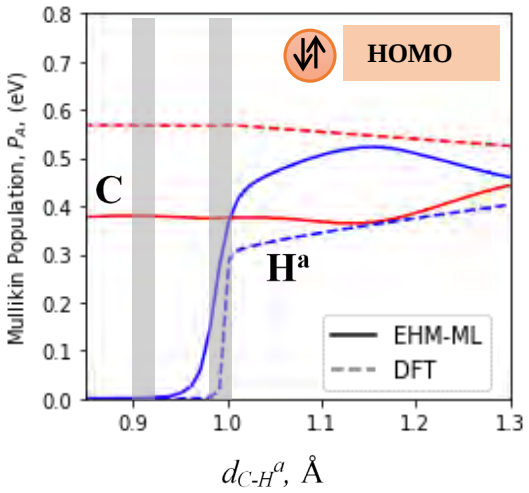
Interesting orbital properties are captured

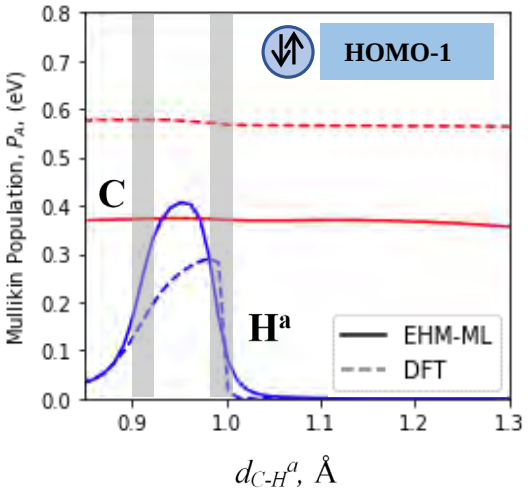


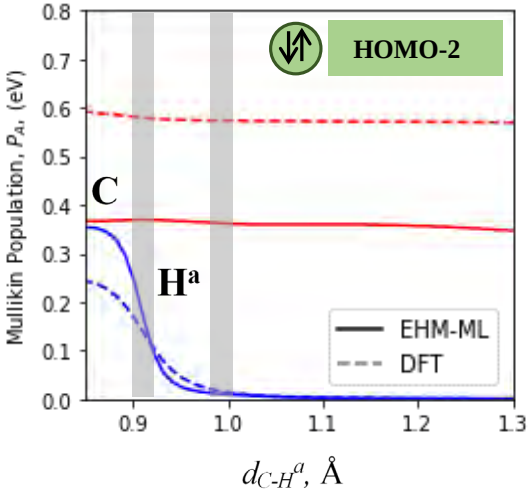








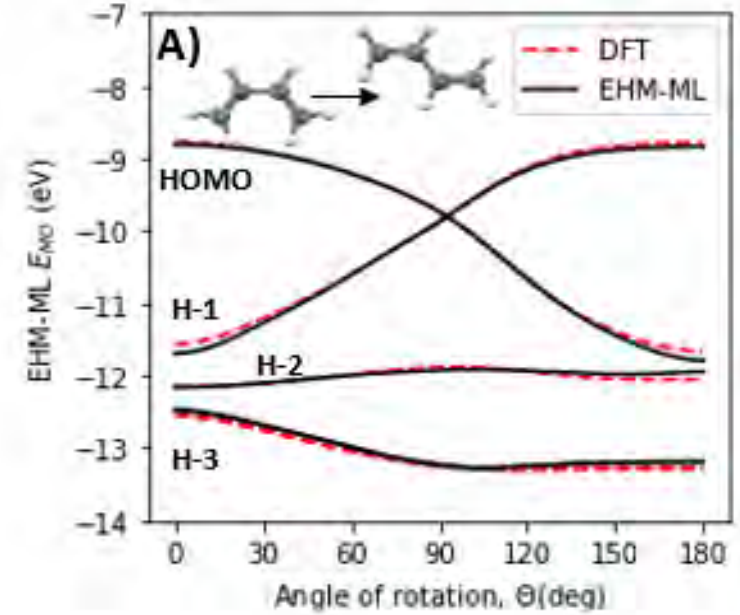


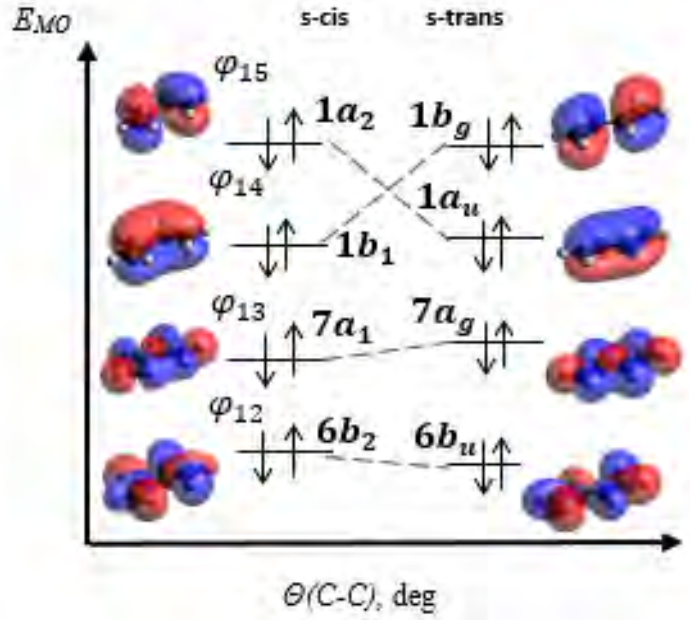


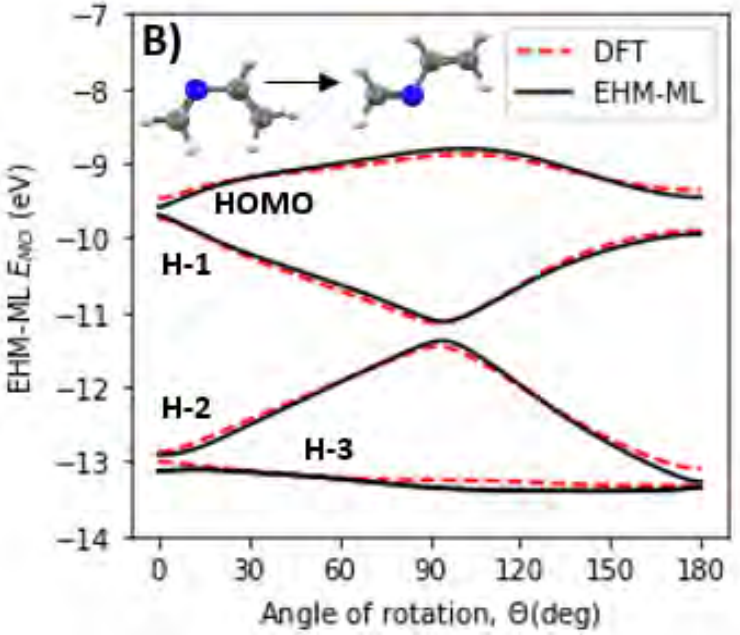
T. Zubatiuk, B. Nebgen, N. Lubbers, J. S. Smith, R. Zubatiuk, G. Zhou, C. Coh, K. Barros, O. Isayev, S. Tretiak, (2020) https://arxiv.org/abs/1909.12963

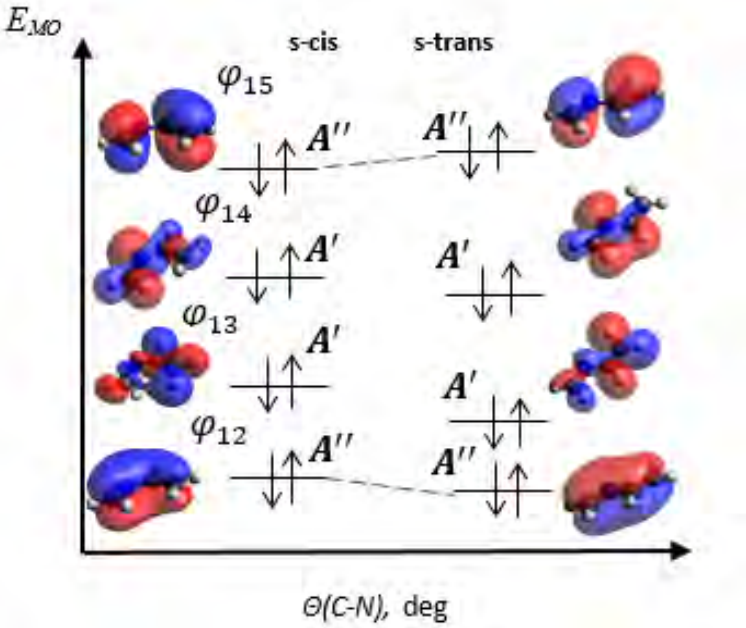
We observe structure in orbital interactions

Description of reactions: butadiene & aza-butadiene









Path forward: pyTorch Semi-Empirical Package (PySeQM) https://github.com/lanl/PYSEQM

❖ **Features:**

- AM1/PM3 with future models (PM6, OM2, OM3,…) to be added
- Ultra fast ground state Molecular Dynamics on GPU
- SP2 for rapid density matrix determination
- Extended Lagrangian method for rapid MD propagation

❖ **Batched Processing For ML Applications**

- cuSolver for Batched Diagonalization
- Batched Matrix Construction
- Batched SCF Convergence

❖ **The code is released in 2020, collaborations are welcome.**

❖ **Future plans**

- ML for ground state Hamiltonian (use of Hellmann-Feynman to avoid back propagation through SCF iterations);
- Excited states (RPA/CIS)
- ML Hamiltonian for excited state PES toward photodynamics

Conclusions

- ***Non-adiabatic dynamics simulations are useful – these complement spectroscopies***
- ***Coherent vibronic dynamics is ubiquitous***
- ***Intermolecular conical intersections propel energy transfer***
- ***XFEL experiments can sensitively probes coherences*** ***(TRUECARS does not have population contributions, only monitor coherences)***

Acknowledgments

Code and applications

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Team: Sebastian Fernandez-Alberti (Argentina)
Victor Freixas
Team: Thomas Frauenheim (Bremen, Germany)
Lynn Gross
Team: Shaul Mukamel (UCI)
Daniel Keefer

Group homepage: http://cnls.lanl.gov/~serg
tretiak@lanl.gov
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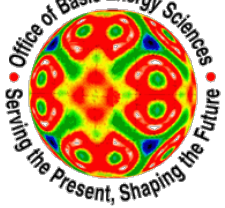
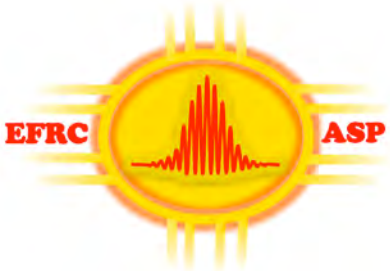
Nick Lubbers (LANL)
Guoqing Zhou (USC)

Experiment: many!

Team Christoph Lienau (Oldenburg)
Antonietta De Sio





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Thank you!