Non-adiabatic excited state molecular dynamics:

Identification, monitoring and freezing normal modes

Sebastian Fernandez-Alberti

Universidad Nacional de Quilmes

Los Alamos NATIONAL LABORATORY EST. 1943

Photoinduced dynamics in multichromophoric conjugated molecules

Non-adiabatic EXcited-state molecular dynamics (NEXMD)

- *Vibrational energy redistribution during electronic relaxation*
- *State-specific vibrations*
- *Vibronic couplings*
- *Identification of active normal modes during intramolecular energy transfer*
- *Vibrational relaxation pathways*

"Non-adiabatic Excited State Molecular Dynamics: theory and applications for modeling photophysics in extended molecular materials" T. Nelson, et al., Chem. Rev., 120, 4, 2215-2287 (2020).

NEXMD
(Non-adiabatic EXcited-State Molecular Dynamics)

- Energies, gradients, and vibronic couplings between multiple electronic excited states calculated "on the fly" .
- Configuration interaction singles (CIS) using the Collective Electronic Oscillator (CEO) at AM1 level.
- Ground state conformational sampling at constant temperature

→ Fotoexcitation and ultrafast dynamics in the excited states

Surface Hopping,

Ehrenfest (Mean Field)

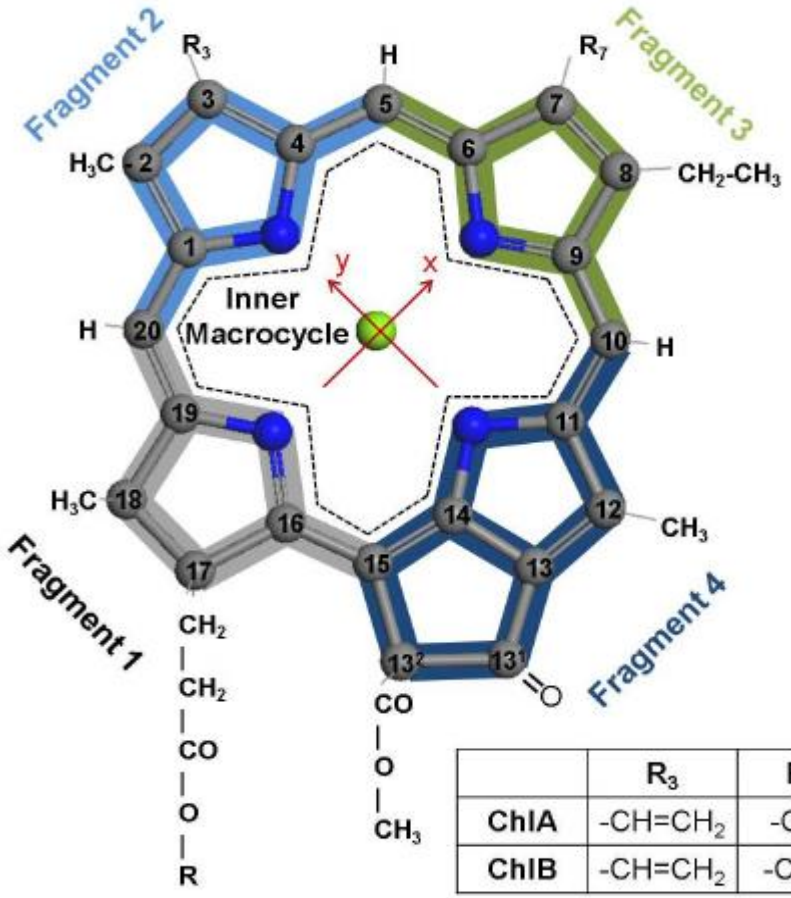
Multiconfigurational Ehrenfest

Cloning

"NEXMD Software Package for Non-adiabatic Excited State Molecular Dynamics Simulations" W. Malone et.al., J. Chem. Theory Comput. 16, 9, 5771–5783 (**2020**)

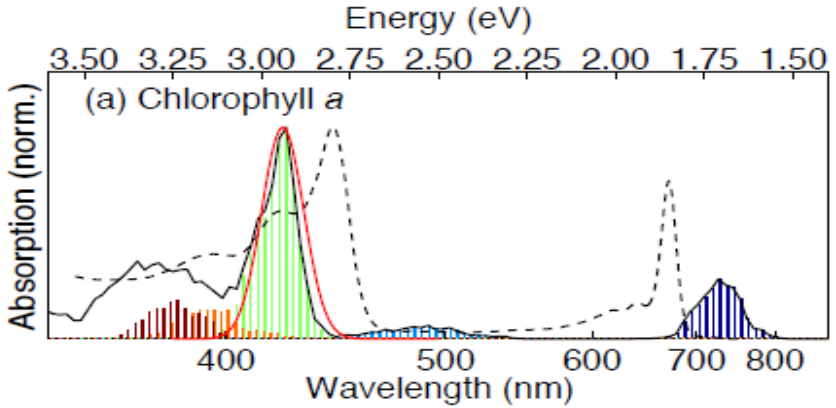
LANL Github: https://github.com/lanl/NEXMD

Electronic and vibrational energy relaxation and redistribution in Chlorophylls



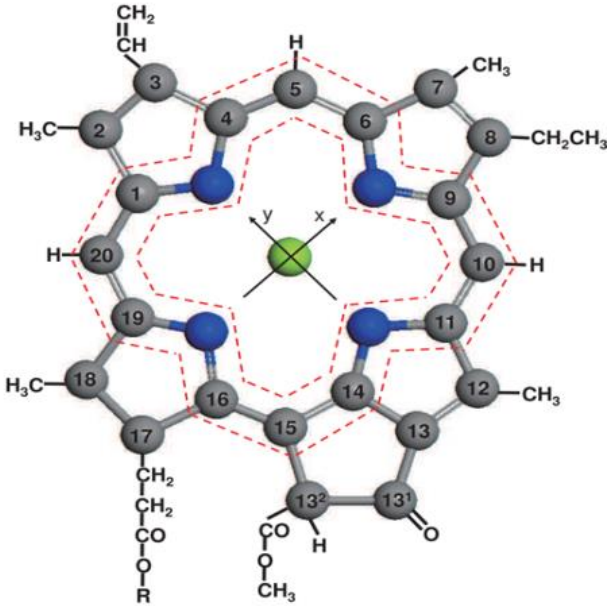
	R_3	R_7
ChlA	-CH=CH$_2$	-CH$_3$
ChlB	-CH=CH$_2$	-CHO

- Light-harvesting (beginning of photosynthesis)
- Internal conversion processes following photoexcitation
- Under ambient light conditions, a relatively rapid decay to the S_1 is essential to initiate the inter-molecular excitation energy transfer



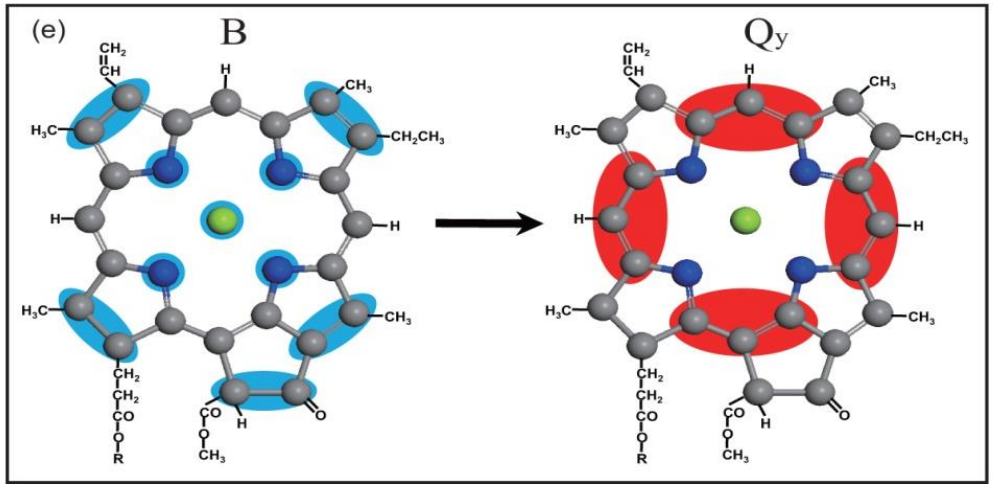
$$B \longrightarrow Q_x \longrightarrow Q_y$$

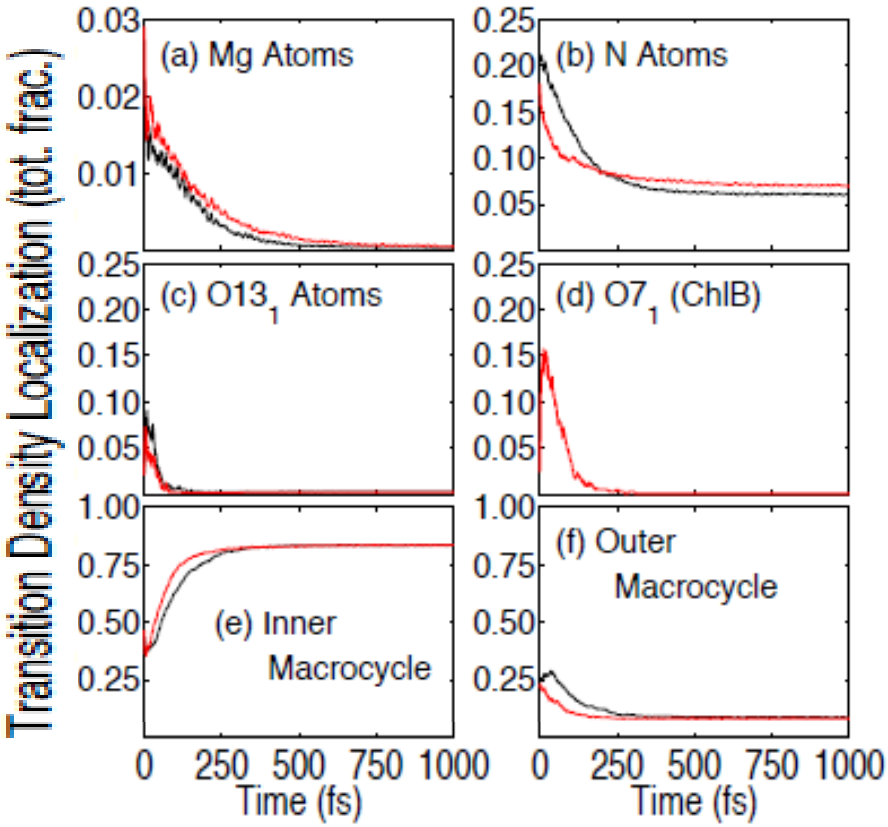
Chl *a* and Chl *b* :
Intramolecular Electronic Transition Density Redistribution



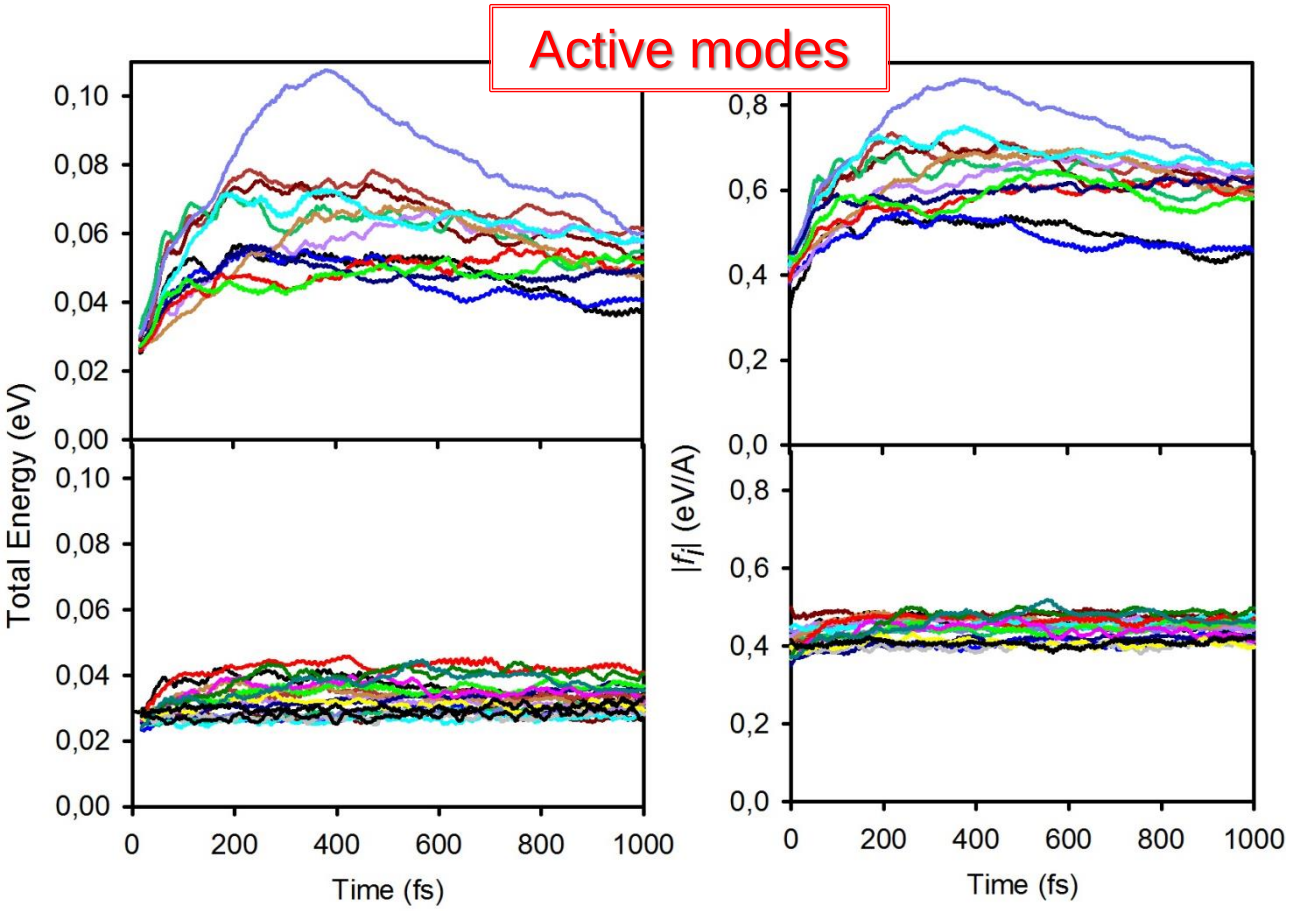
ChlA

ChlB





Intramolecular Vibrational Energy Redistribution
monitored by evaluating individual normal mode energies



- The intramolecular vibrational energy redistribution is not statistical
- Active modes: they experience a transient accumulation of excess of energy and related to the direction of the *non-adiabatic coupling vector* (overlap) and different *intramolecular energy relaxation pathways.*
- The rest of the modes act as a bath

≈ 10-12 middle-high frequency modes are active (less than 5% of vibrations)

"Internal Conversion and Vibrational Energy Redistribution in Chlorophyll A", P. M. Shenai, S. Fernandez-Alberti, W. P. Bricker, S. Tretiak, and Y. Zhao, J. Phys. Chem. B 120(1), 49-58 (2016).*

Intramolecular Vibrational Energy Redistribution

Representative vectors of the paths

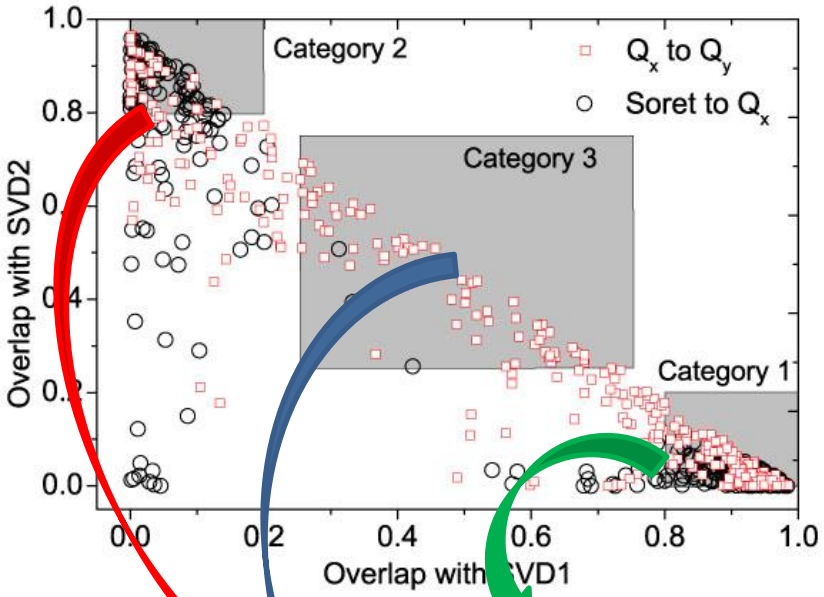
Singular Value Decomposition of A_{IJ} ($3N$xK) built with columns representing the d_{ij} vectors of the K NEXMD simulations

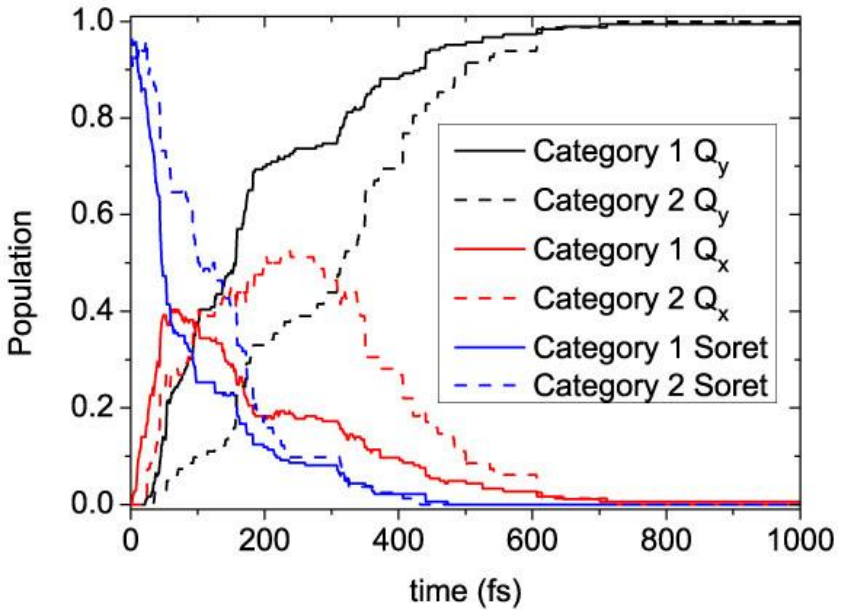
$$[A_{IJ}] = [\ U_{IJ}\ ] . [\ W_{IJ}\ ] . [\ V_{IJ}^{\mathrm{T}}\ ]$$

The SVD vectors $u^{i}{}_{IJ}$ with the highest $w^{i}{}_{IJ}$ are considered representatives of the original d_{ij} vectors.

Intramolecular Vibrational Energy Redistribution

Two different pathways





d_{IJ} overlap more than 80% with SVD1

d_{IJ} overlap more than 80% with SVD2

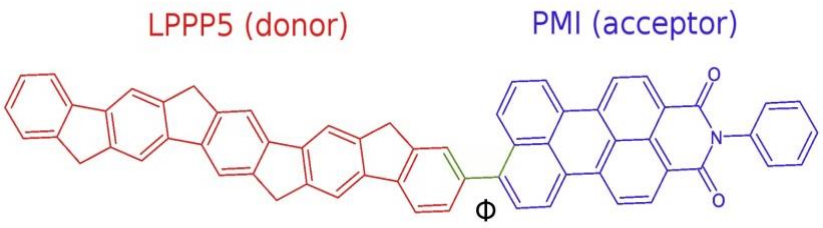
d_{IJ} as a mixture of SVD1 and SVD2

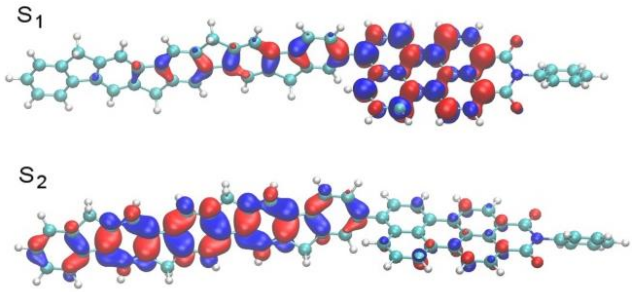
The distribution of active modes that participate in each path is different

Despite the large number of degrees of freedom in the molecule, only a few of them are active and they correspond to those involved in the direction of d_{IJ} and they are different for the different relaxation pathways

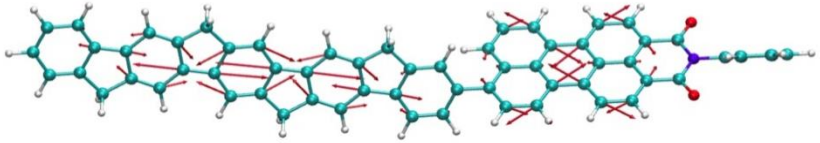
Vibrational energy redistribution during donor-acceptor electronic energy transfer:

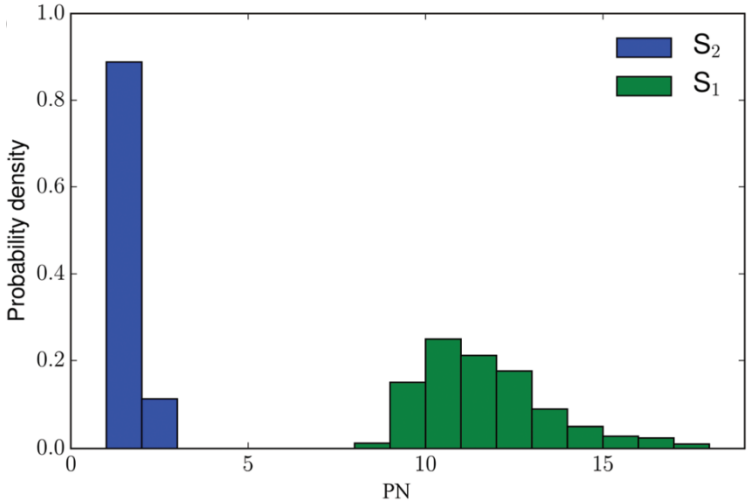
only a few normal modes participate actively during the electronic relaxation





Non-adiabatic coupling vector (NACR)





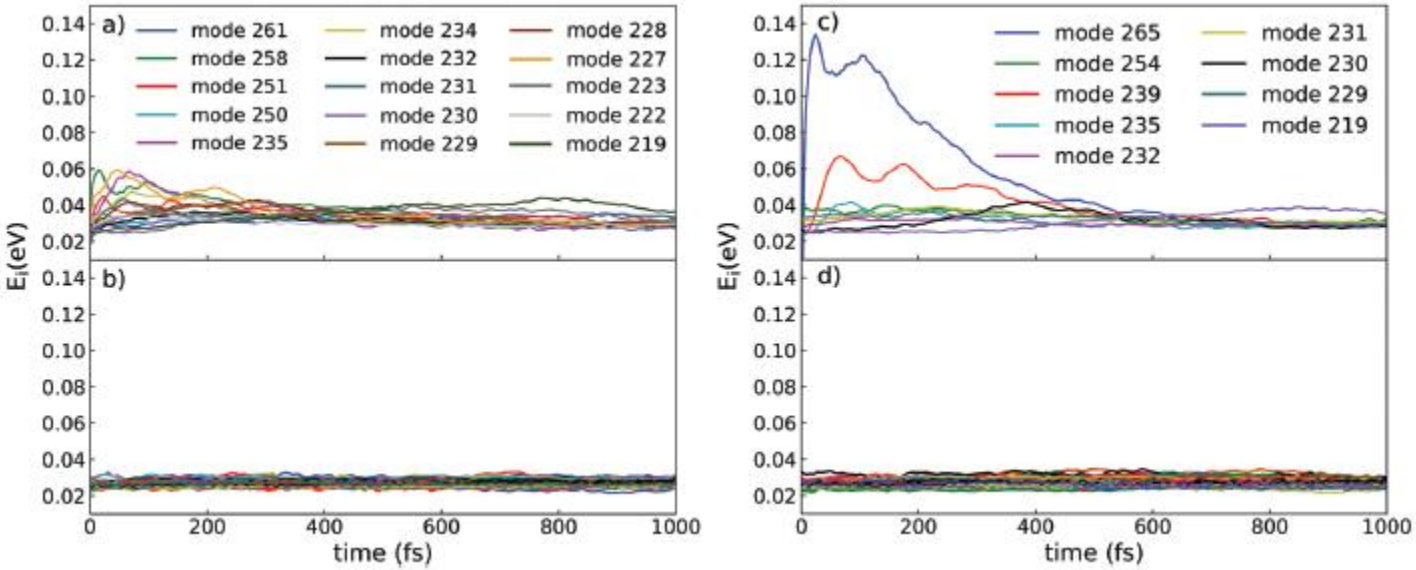
Projection of NACR on the basis of Excited-State Normal Modes (ES-ENM) calculated on S_1 and S_2 Potential Energy Surfaces

Vibrational energy redistribution during donor-acceptor electronic energy transfer:

Excited-State-Equilibrium Normal Modes (ES-ENM)

ES-ENM(S_1)

ES-ENM(S_2)

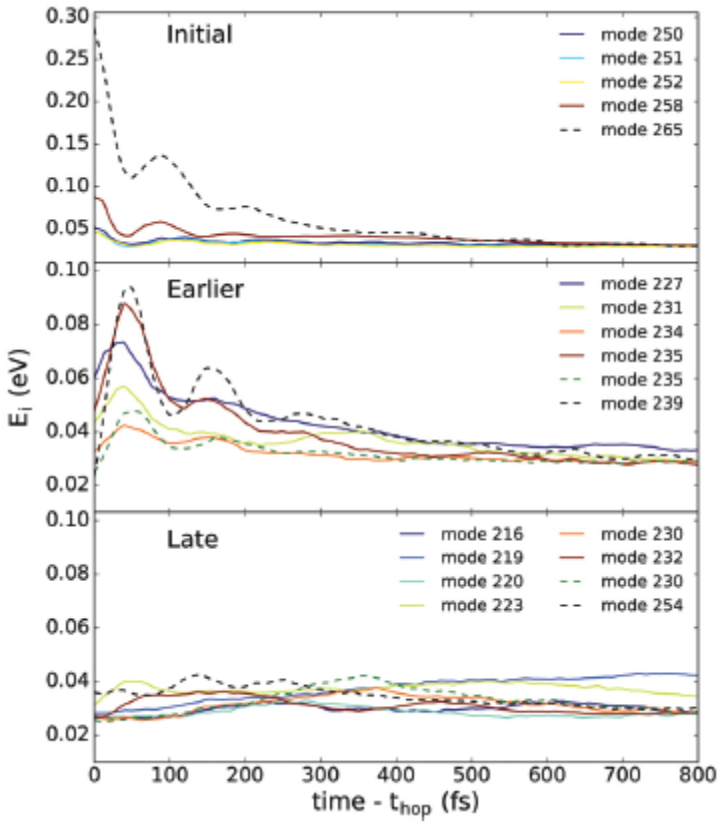


Vibrational energy associated to each ES-ENM

The $S_2 \rightarrow S_1$ energy transfer takes place mainly through a unique ES-ENM(S_2) but once the system reaches the S_1 state the vibrational flux experiences a dispersion within a bunch of different directions.

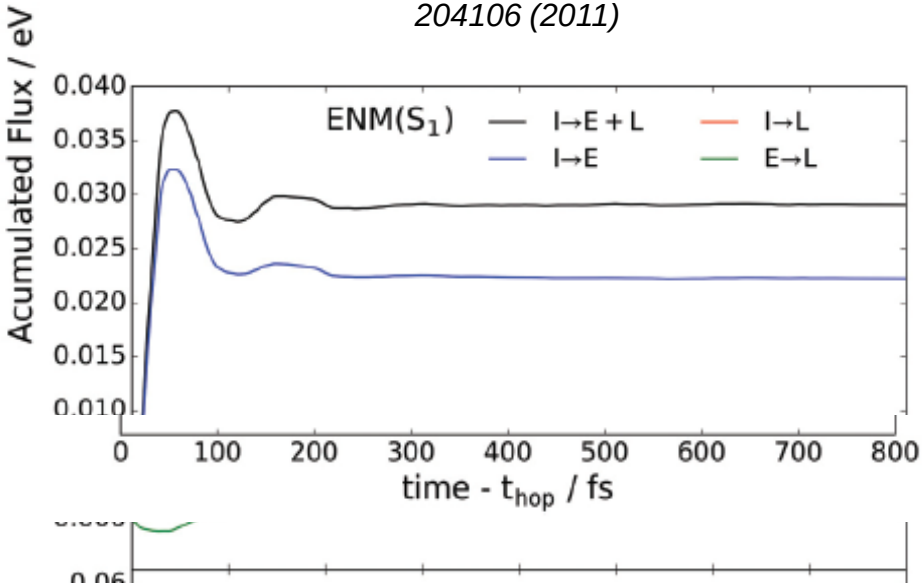
Vibrational energy redistribution during donor-acceptor electronic energy transfer:

Classification of normal modes-vibrational relaxation pathways



Statistical Minimum Flow method

"A method for analyzing the vibrational energy flow in biomolecules in solution", M. A. Soler et al. J. Chem. Phys. 135, 204106 (2011)



The intramolecular vibrational energy relaxation and redistribution pathways allow us to classify the role of the different active normal modes.

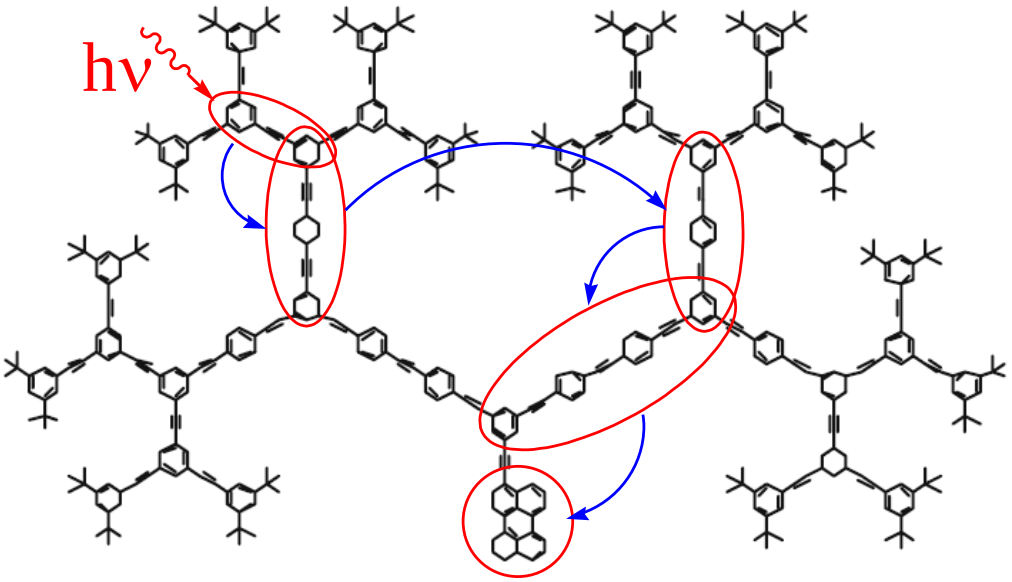
"Vibrational energy redistribution during donor-acceptor electronic energy transfer: criteria to identify subsets of active normal modes" L. Alfonso-Hernandez et. al, Phys. Chem. Chem. Phys. ,22, 18454-18466 (2020)

Dendrimers

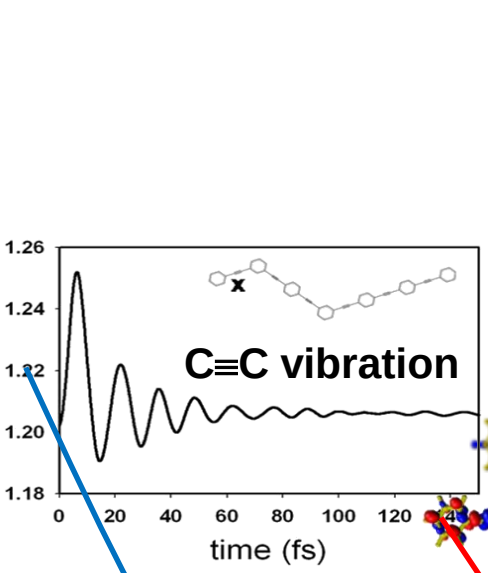
- Highly branched conjugated macromolecules:
  - peripheral groups
  - Branched repeat units (layers)
  - a core
- Unidirectional energy transfer:

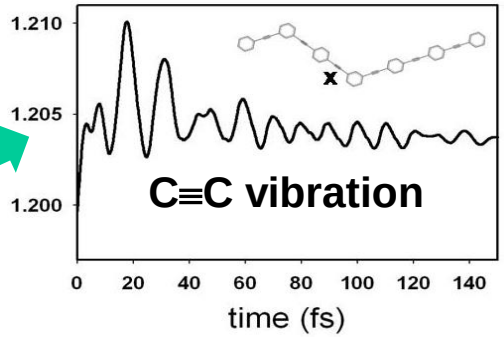
  periphery → core

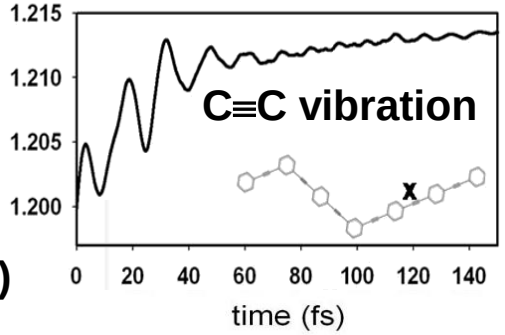
Nanostar



Unidirectional electronic and vibrational energy transfer







NACR(3,2)

NACR(2,1)

S_3

S_2

S_1

S_0

"Nonadiabatic Excited-State Molecular Dynamics: Modeling Photophysics in Organic Conjugated Materials", T. Nelson et al. Acc. Chem. Res., 47(4), 1155-1164 (2014)

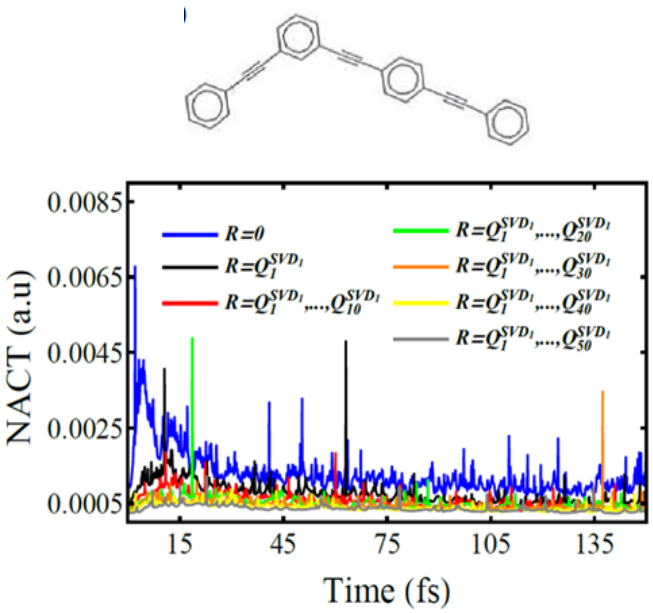
The vibrational energy relaxation is concomitant to the electronic energy relaxation.

Photoinduced dynamics with constrained vibrational motion

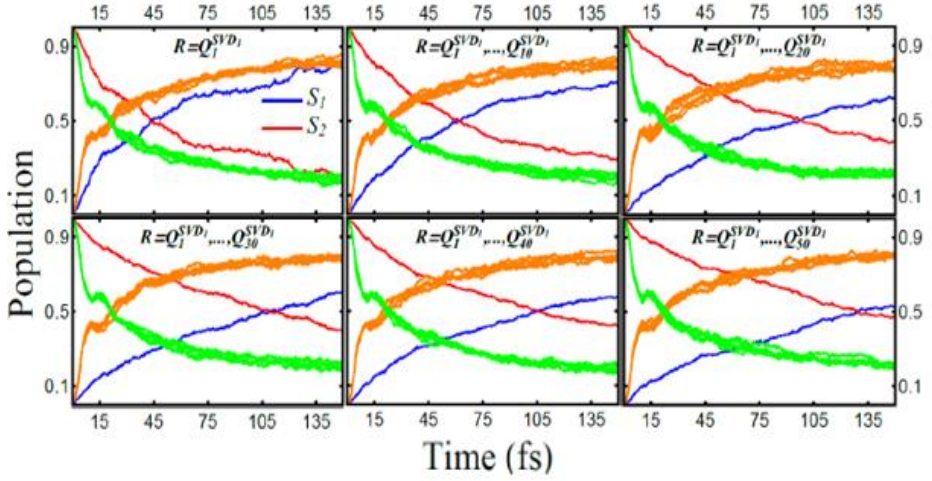
FrozeNM algorithm

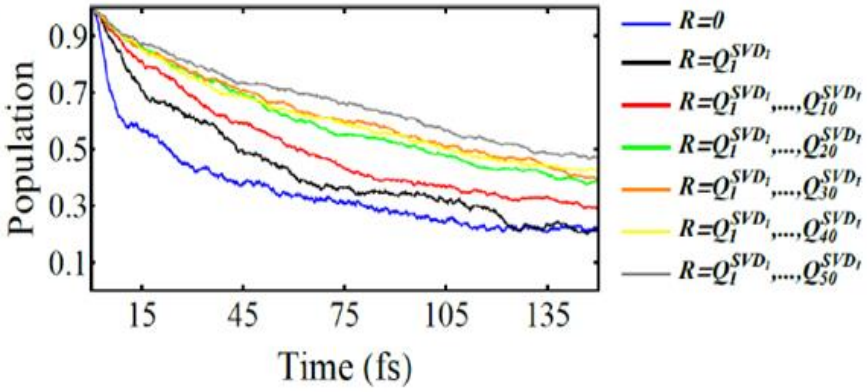
We apply normal mode constraints in NEXMD code:

ENM are constrained in decreasing order of overlap with NACR.



The relaxation rates can be significantly reduced by freezing a well-defined small subset of active normal modes.

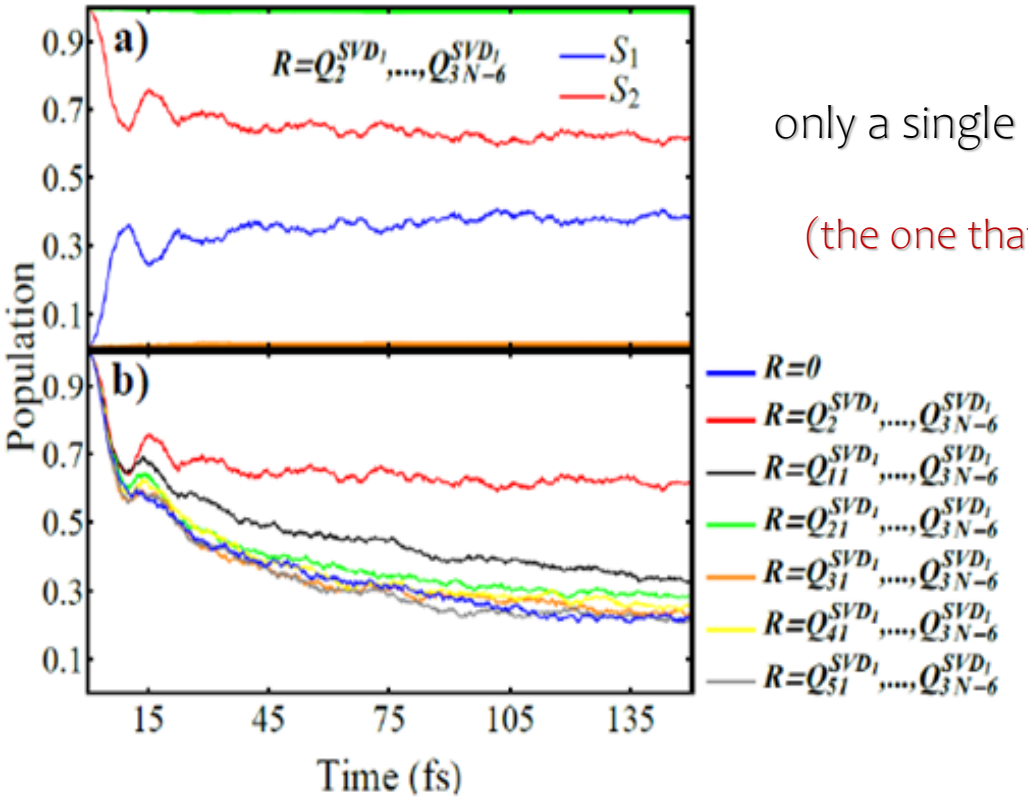




"Photoinduced dynamics with constrained vibrational motion: FrozeNM algorithm"
,H. Negrin-Yuvero et al, JCTC (submitted)

Photoinduced dynamics with constrained vibrational motion

FrozeNM algorithm



only a single nuclear degree of freedom is unfrozen
(the one that overlap the most with NACR)

systematically increasing the number of participating ENMs (selected in decreasing order of overlap with NACR)

Freezing normal modes is useful for guiding development of reduced dimensionality Hamiltonians that can be further used for more accurate treatment of non-adiabatic dynamics

Collaborators

- Sergei Tretiak & Tammie Nelson
- Adolfo Bastida
- Stavros Athanasopoulos
- Adrian Roitberg & Valeria Kleiman

Molecular physics and Biophysics group

Universidad Nacional de Quilmes

http://ufq.unq.edu.ar/mpbg/

Collaborators

Main conclusions

- Concomitant electronic and vibrational energy relaxation and redistribution
- The intramolecular vibrational energy redistribution is not statistical
- Active modes:
  - related to the direction of the non-adiabatic coupling vector associated to different intramolecular energy relaxation pathways.
  - The rest of the modes act as a bath
- FrozeNM: useful for guiding development of reduced dimensionality Hamiltonians