Photoinduced dynamics in organic chromophores:

vibronic couplings, efficiency and transient absorption

Sebastian Fernandez-Alberti

Photoinduced dynamics in multichromophoric conjugated molecules

Non-adiabatic EXcited-state molecular dynamics (NEXMD)

- *Electronic relaxation pathways*
- *Vibronic coherences*
- *Transient absorption*

"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).

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

→ Photoexcitation and ultrafast dynamics in the excited states

Surface Hopping,

Ehrenfest (Mean Field)

Multiconfigurational Ehrenfest

Cloning

"NEXMD v2.0 Software Package for Nonadiabatic Excited State Molecular Dynamics Simulations" V. M. Freixas, et al, J. Chem. Theory Comput. 19, 5356−5368 (2023).

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

Nonadiabatic Molecular Dynamics

Mixed quantum/classical methods

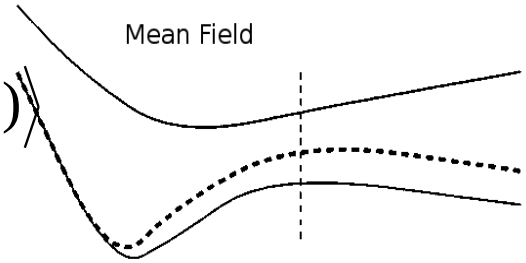
$$H(\mathbf{r},\mathbf{R}) = H_{cl}(\mathbf{R}) + H_q(\mathbf{r}) + H_{int}(\mathbf{R},\mathbf{r})$$

$$|\psi(t)\rangle = \sum_i c_i(t)|\phi_i\rangle$$

$$i\hbar\dot{c}_i(t) = c_i(t)E_i - i\hbar\sum_j c_j(t)\dot{\boldsymbol{R}}\cdot\boldsymbol{d}_{ij}$$

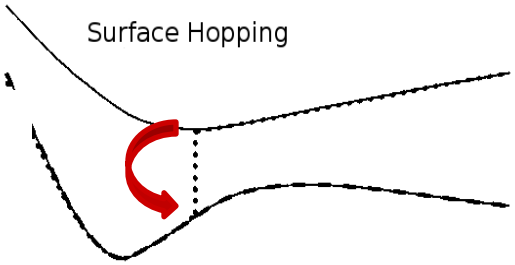
Nonadiabatic couplings:

$$\dot{\boldsymbol{R}}\cdot\boldsymbol{d}_{ij} = \left\langle \psi_i \left| \frac{\partial \psi_j}{\partial t} \right. \right\rangle \qquad \boldsymbol{d}_{ij} = \left\langle \psi_i(\boldsymbol{x};\boldsymbol{R}) \left| \nabla_{\boldsymbol{R}} \psi_j(\boldsymbol{x};\boldsymbol{R}) \right. \right\rangle$$



Mean field :

$$\dot{\mathbf{R}} = \langle\psi(t)|\frac{\partial H}{\partial \mathbf{P_R}}|\psi(t)\rangle \,;\, \dot{\mathbf{P}}_{\mathbf{R}} = -\langle\psi(t)|\frac{\partial H}{\partial \mathbf{R}}|\psi(t)\rangle$$



surface hopping:

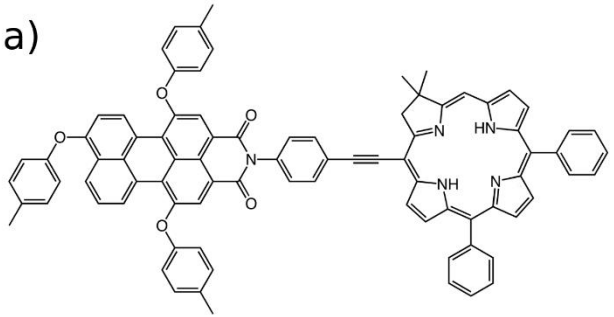
$$\begin{cases} \dot{\mathbf{R}} = \langle\phi_i|\frac{\partial H}{\partial \mathbf{P_R}}|\phi_i\rangle / \langle\phi_i|\phi_i\rangle \\ \dot{\mathbf{P}}_{\mathbf{R}} = -\langle\phi_i|\frac{\partial H}{\partial \mathbf{R}}|\phi_i\rangle / \langle\phi_i|\phi_i\rangle \end{cases}$$

Probability to hop

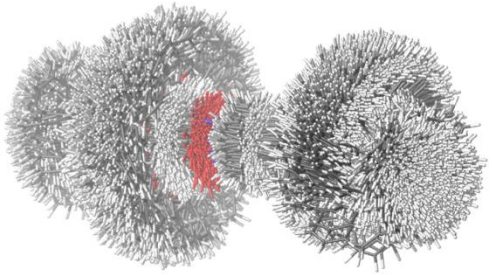
$$|\phi_i\rangle \rightarrow |\phi_j\rangle$$

Back-and-forth energy transfer during electronic relaxation in a chlorin-perylene dyad

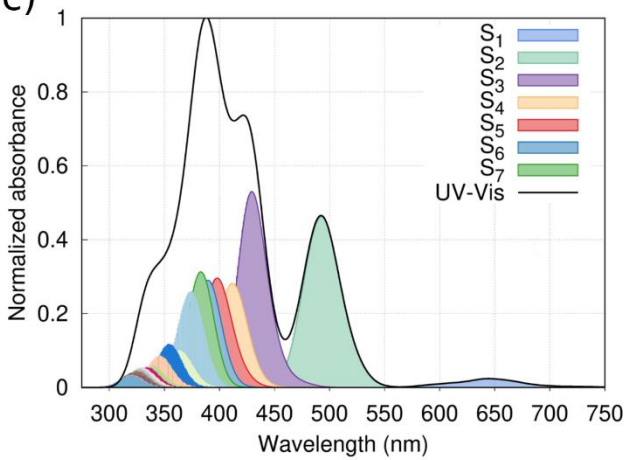
a)



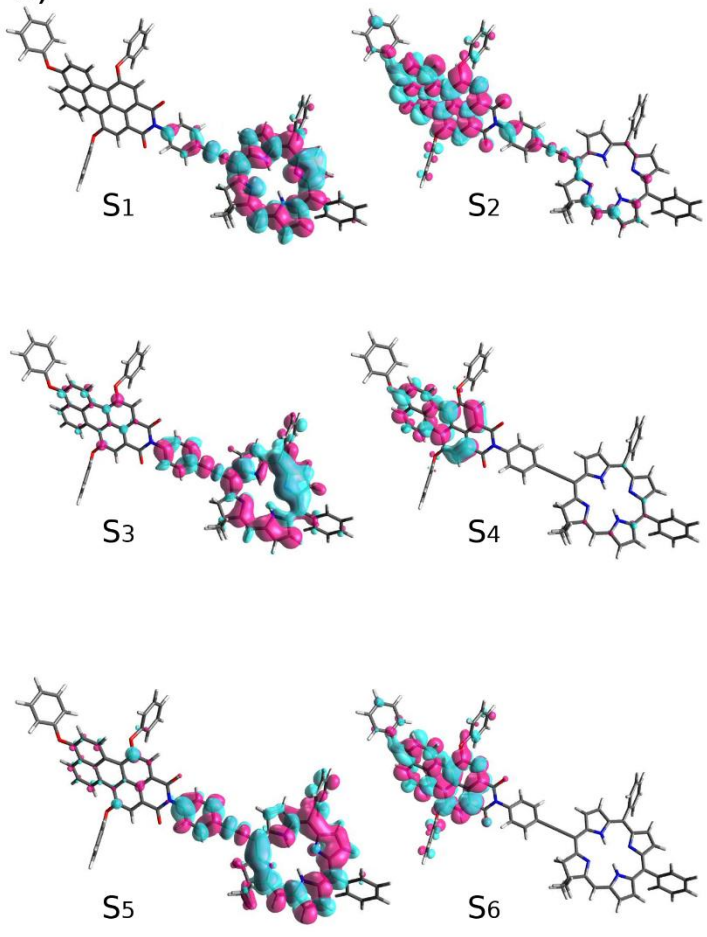
b)



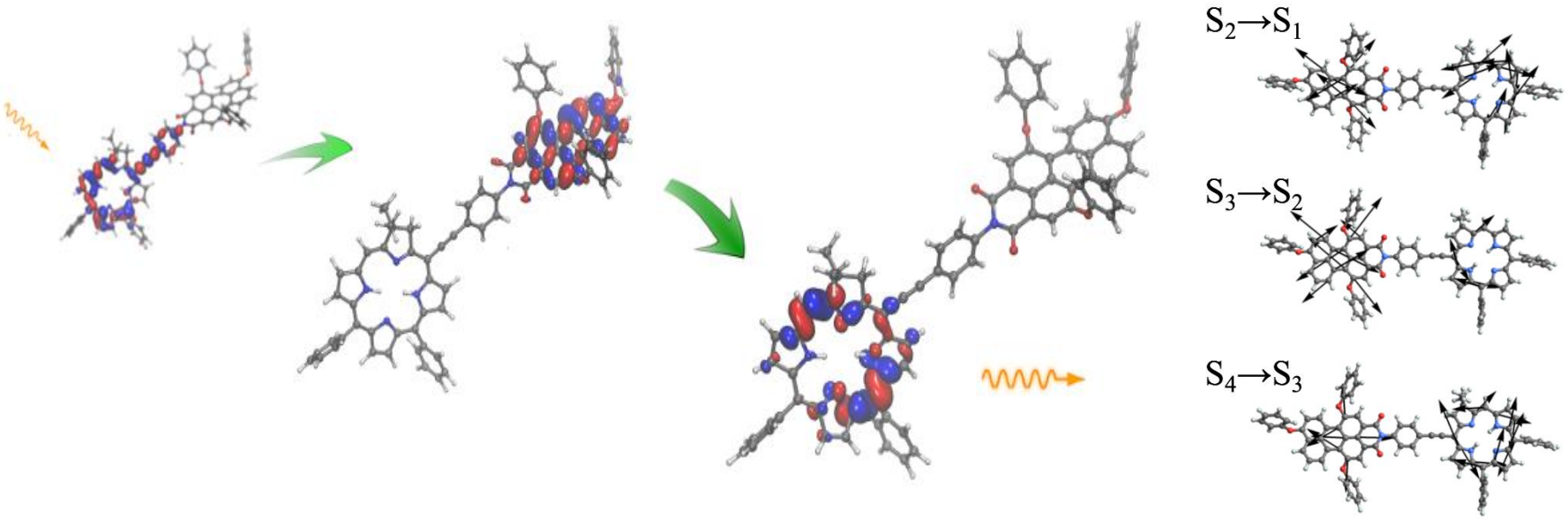
c)

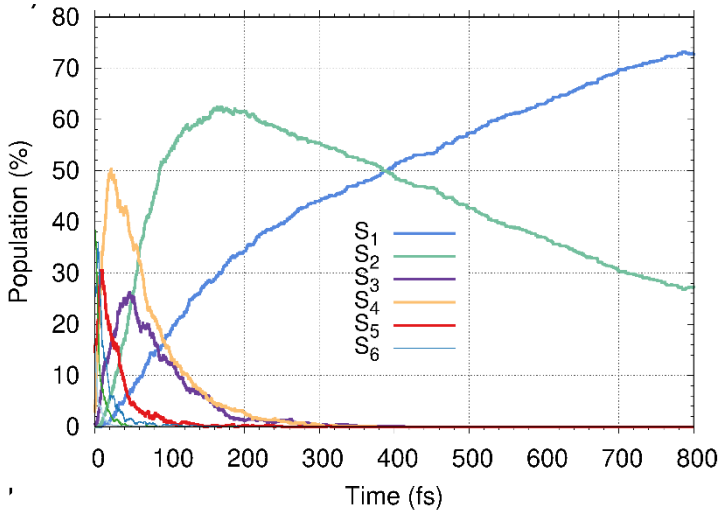


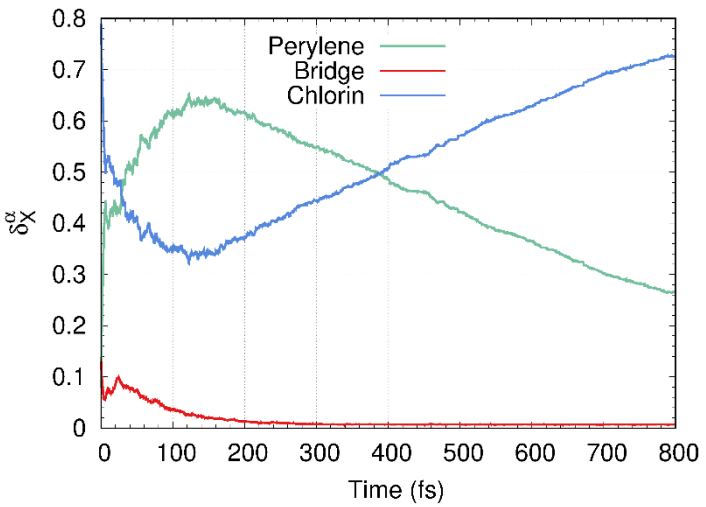
d)



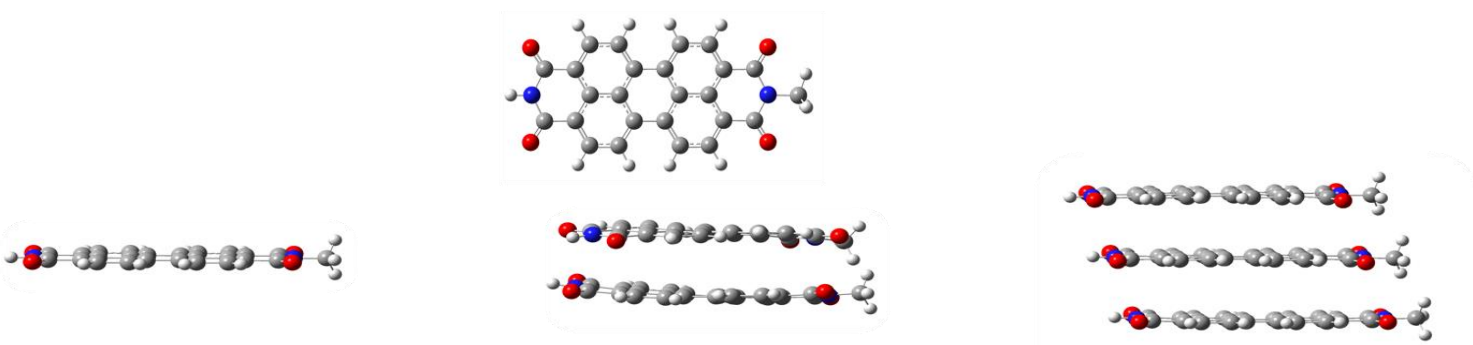
Back-and-forth energy transfer during electronic relaxation in a chlorin-perylene dyad

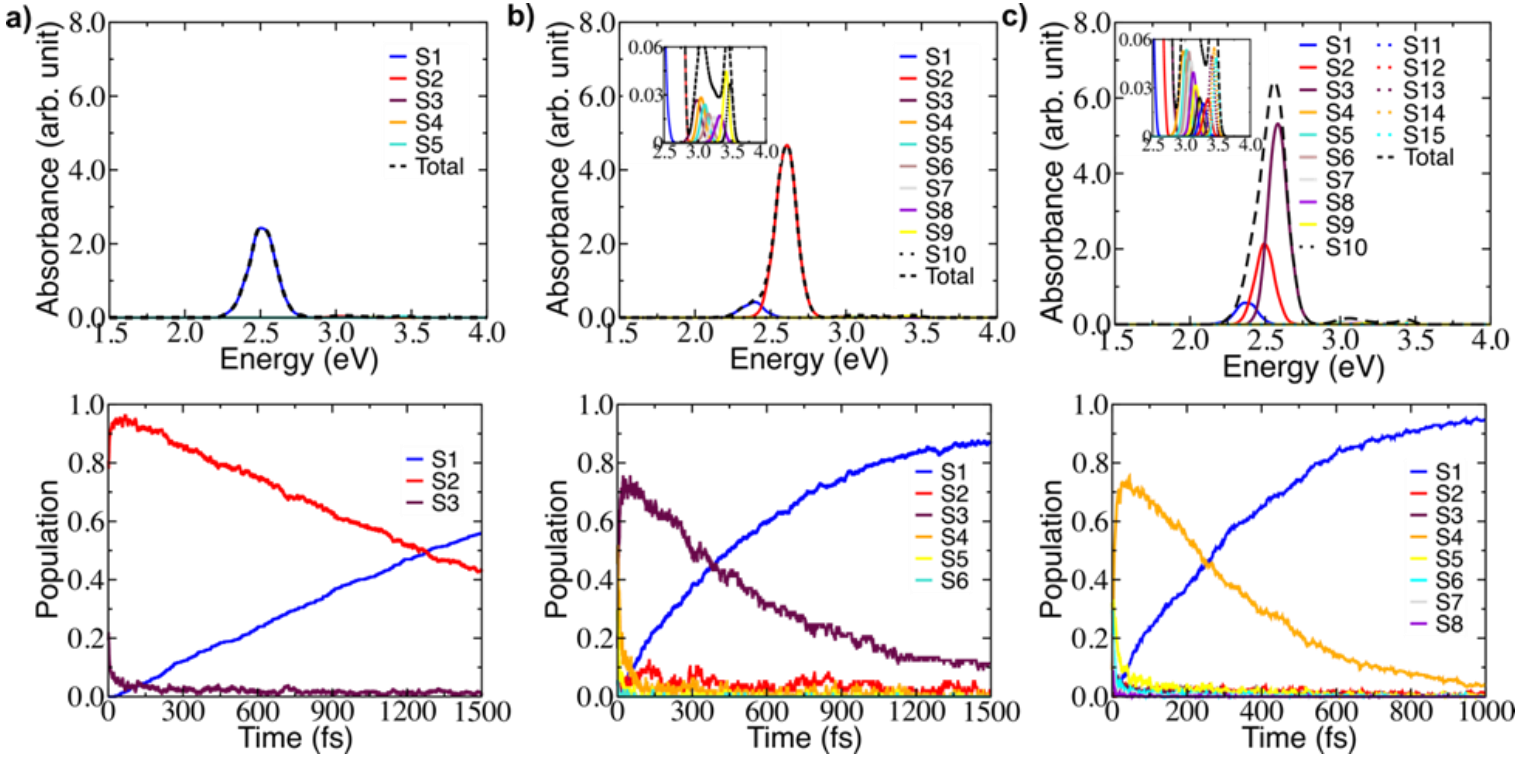






Electronic and vibrational relaxations within molecular assemblies of Perylene diimide



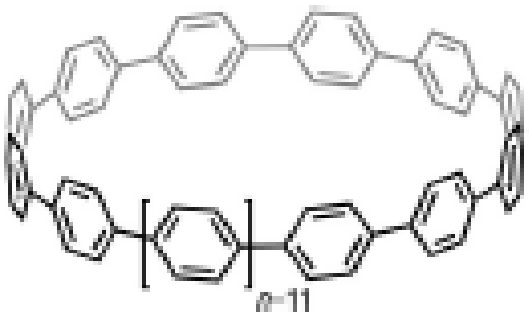


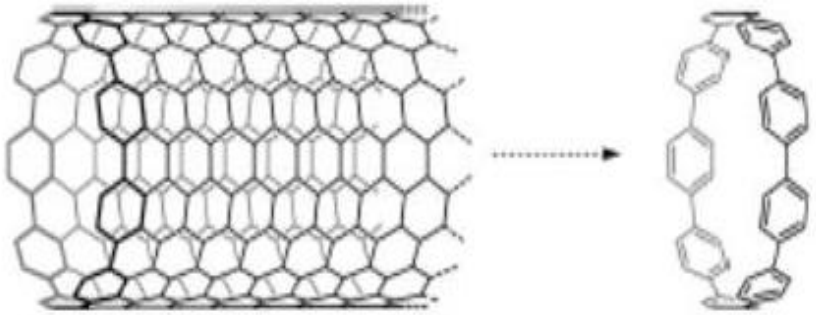
Electronic and vibrational relaxations within molecular assemblies of Perylene diimide

Dimer				Trimer					
$S_2 \rightarrow S_1$		$S_3 \rightarrow S_2$		$S_2 \rightarrow S_1$		$S_3 \rightarrow S_2$		$S_4 \rightarrow S_3$	
Mode # (Freq.)	Overlap	Mode # (Freq.)	Overlap	Mode # (Freq.)	Overlap	Mode # (Freq.)	Overlap	Mode # (Freq.)	Overlap
226 (1865)	0.88	226 (1865)	0.78	256 (1402)	0.53	256 (1402)	0.51	259 (1410)	0.45
223 (1795)	0.16	209 (1693)	0.27	265 (1431)	0.39	265 (1431)	0.40	325 (1763)	0.38
222 (1792)	0.16	207 (1679)	0.25	316 (1719)	0.38	316 (1719)	0.37	257 (1408)	0.37
207 (1679)	0.14	222 (1792)	0.14	258 (1408)	0.31	259 (1410)	0.33	265 (1431)	0.32
225 (1797)	0.12	199 (1596)	0.13	259 (1410)	0.31	258 (1408)	0.31	262 (1419)	0.25
122 (908)	0.10	223 (1795)	0.13	310 (1647)	0.18	310 (1647)	0.18	264 (1428)	0.16
121 (904)	0.10	122 (908)	0.11	274 (1480)	0.17	274 (1480)	0.18	261 (1418)	0.16
209 (1693)	0.10	175 (1416)	0.10	271 (1476)	0.11	261 (1418)	0.12	294 (1580)	0.15
224 (1795)	0.09	121 (904)	0.10	261 (1418)	0.10	271 (1476)	0.11	286 (1524)	0.14
234 (2025)	0.08	234 (2025)	0.09	264 (1428)	0.10	287 (1525)	0.09	244 (1335)	0.13

- Only a few normal modes significantly overlap with the nonadiabatic coupling vectors. The set of these active modes are equivalent for $S_4 \rightarrow S_3$, $S_3 \rightarrow S_2$ and $S_2 \rightarrow S_1$ transitions.
- The overall sequential $S_4 \rightarrow S_1$ relaxation pathway involves a common bundle of states that leads to no transient accumulation of electronic populations in the intermediate S_3 and S_2 states.
- This process activates a positive feedback mechanism involving a common set of vibrational normal modes that accelerate the process by increasing the efficiency of its vibronic dynamics.

Carbon nanorings (Cycloparaphenylenes (CPPn)





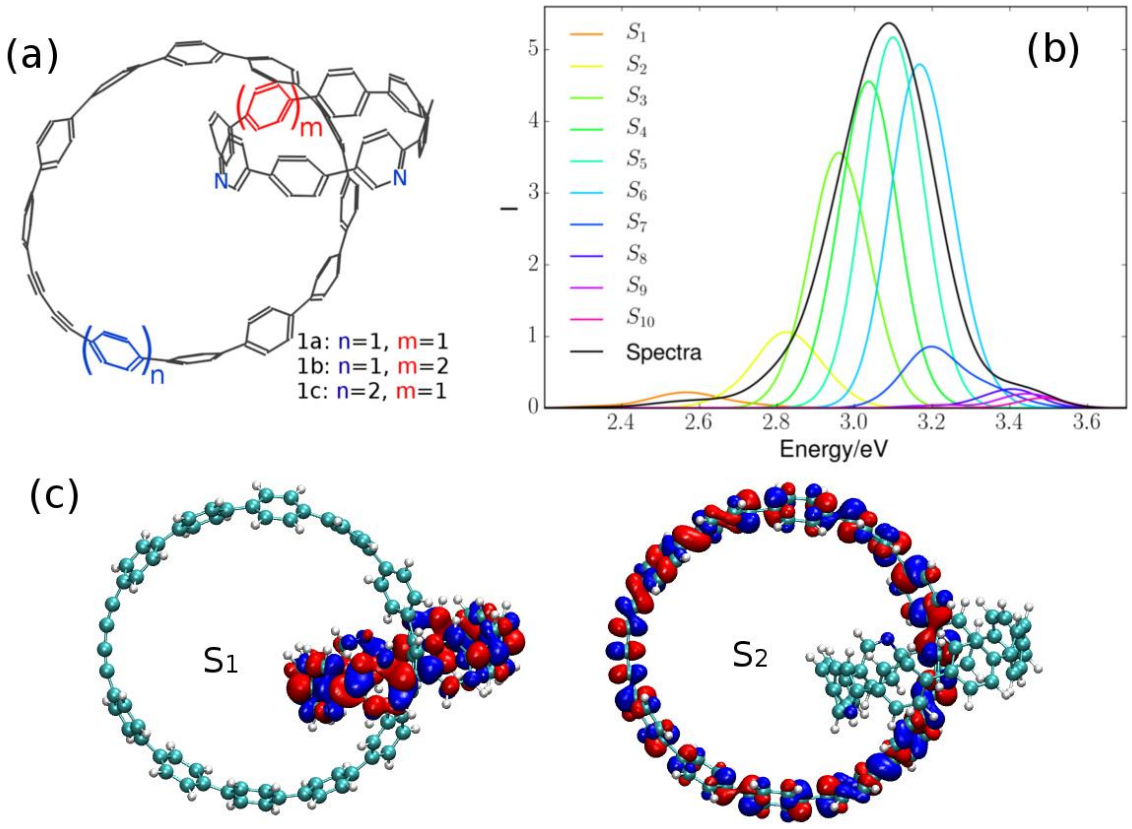
the smallest possible fragments of armchair carbon nanotubes

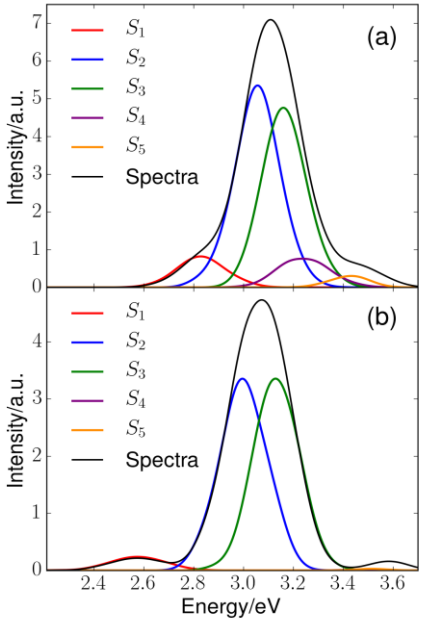
radially cyclic conjugated systems

unique photophysical properties

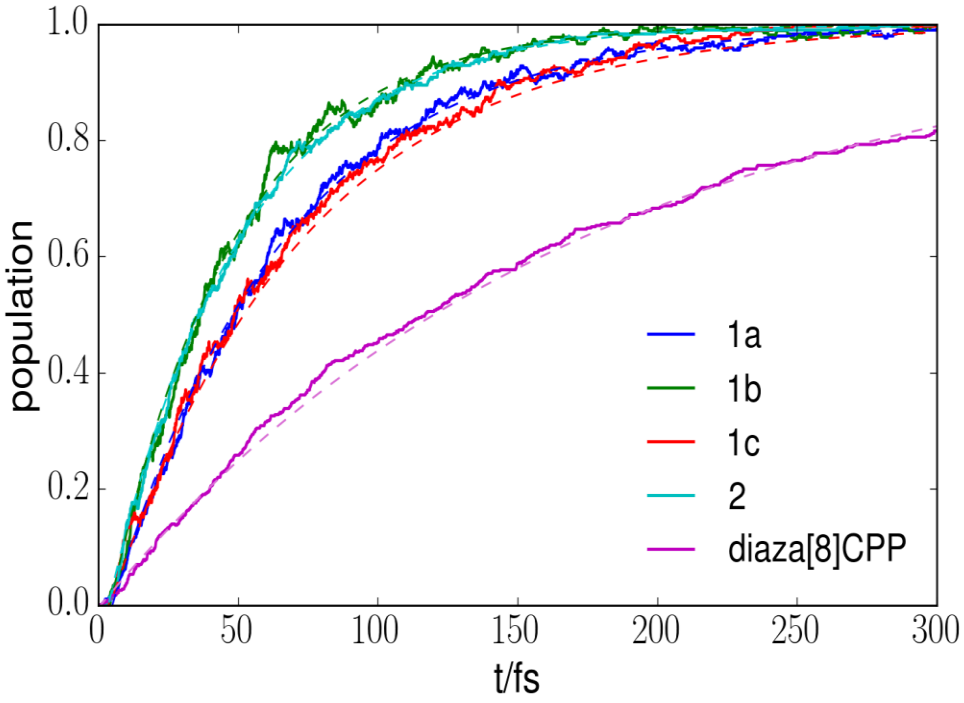
promising materials for implementation as organic semiconductors and sensors.

Tuning electronic relaxation of nanorings through their interlocking.

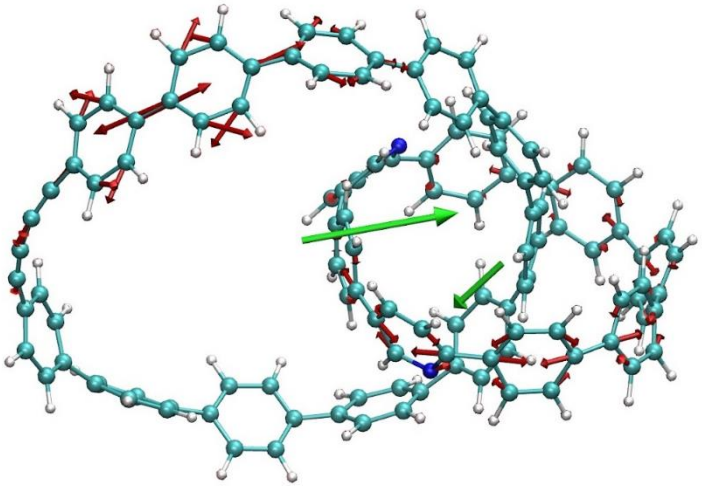


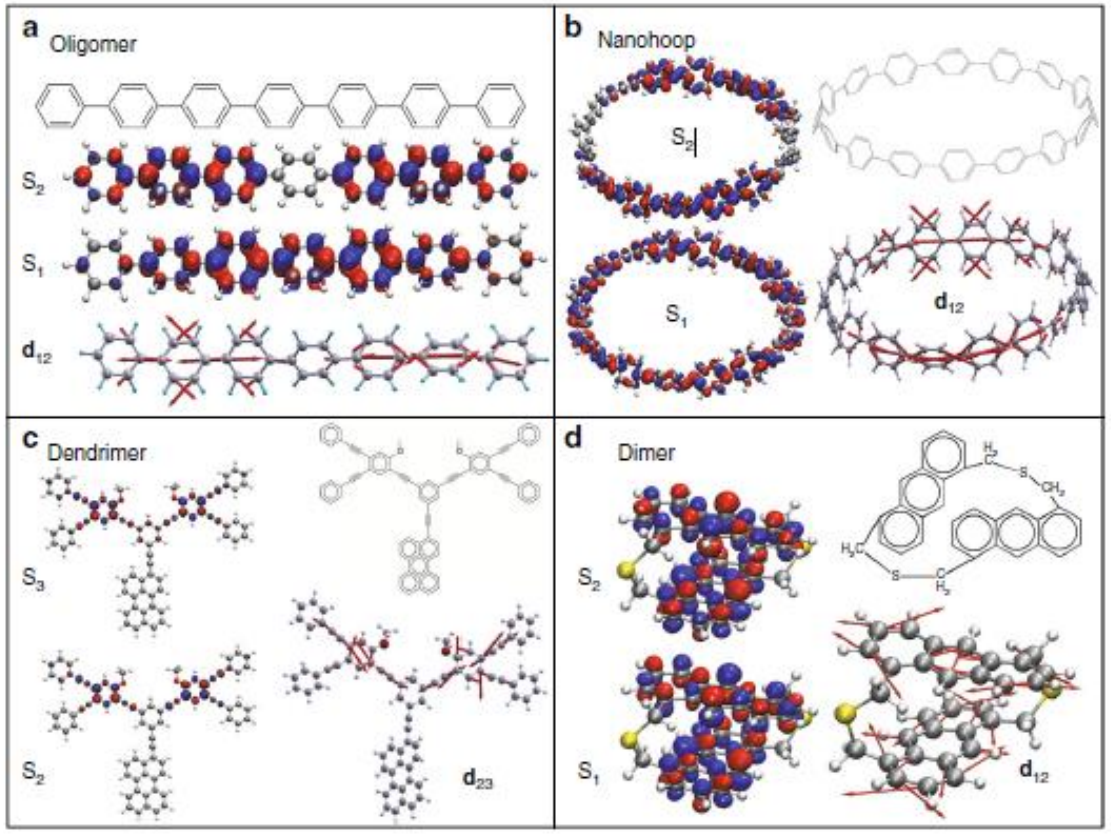


Tuning electronic relaxation of nanorings through their interlocking.



Antisymetric-to-symetric S_2->S_1 transition



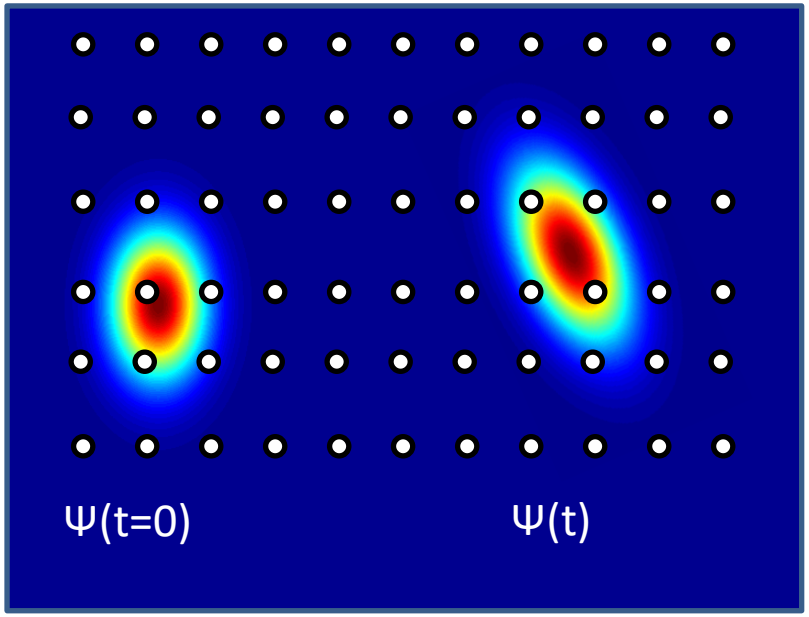


T R. Nelson et al., Nature Comm. Vol. 9, Article number: 2316 (**2018**).

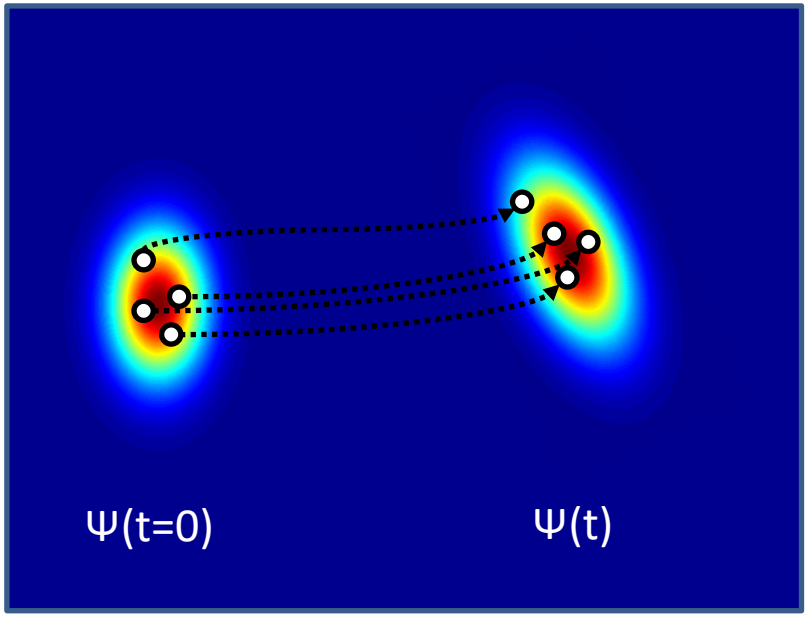
Ultrafast vibronic coherences

Multiconfigurational Ehrenfest approach (MCE)

Trajectory guided basis



Regular static grid



Trajectory guided grid

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

"Ab initio quantum direct dynamics simulations of ultrafast photochemistry with Multiconfigurational Ehrenfest approach", D. Makhov, C. Symonds, S. Fernandez-Alberti, and D. Shalashilin, Chem. Phys. 493, 200–218 (2017).

MCE

we represent the wavefunction on a trajectory-guided basis $|\psi_n(t)\rangle$

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

with

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

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).

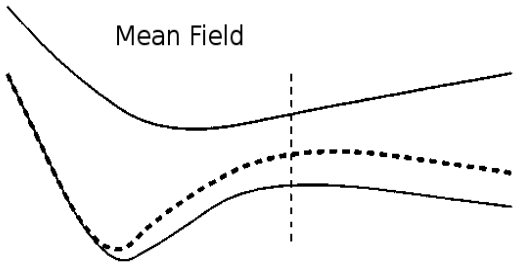
MCE: Evolution of nuclear basis function

the motion of the centers of Gaussians is determined by the usual set of Hamilton's equations

$$\dot{\bar{\mathbf{R}}}_n = \mathbf{M}^{-1}\bar{\mathbf{P}}_n$$

$$\dot{\bar{\mathbf{P}}}_n = \bar{\mathbf{F}}_n$$

$$\frac{\mathrm{d}\gamma_n}{\mathrm{d}t} = \frac{\bar{\mathbf{P}}_n \dot{\bar{\mathbf{R}}}_n}{2}$$



with Ehrenfest forces

$$\bar{\mathbf{F}}_n = \sum_I \left(a_I^{(n)}\right)^* a_I^{(n)} \nabla_{\mathbf{R}} V_I(\bar{\mathbf{R}}_n)$$

$$+ \sum_{I,J} \left(a_I^{(n)}\right)^* a_J^{(n)} \mathbf{d}_{IL}(\bar{\mathbf{R}}_n)(V_I(\bar{\mathbf{R}}_n) - V_J(\bar{\mathbf{R}}_n)),$$

$$\langle \phi_I | \nabla_R | \phi_J \rangle$$

MCE: Evolution of electronic basis function

the evolution of the Ehrenfest amplitudes is determined by

$$\dot{a}_I^{(n)} = -\frac{i}{\hbar} V_I(\bar{\mathbf{R}}_n) a_I^{(n)} - \sum_J \dot{\bar{\mathbf{R}}}_n \cdot \mathbf{d}_{IJ}(\bar{\mathbf{R}}_n) a_J^{(n)}.$$

$$\langle \phi_I | \nabla_R | \phi_J \rangle$$

In the original MCE method $|\phi_I^{(n)}\rangle$ *are* ***adiabatic states***

Ehrenfest trajectories

- Nonadiabatic molecular dynamics (Ehrenfest)
- Electronic energies, gradients, and nonadiabatic coupling vectors calculated "on the fly" .
- Configuration interaction singles (CIS) using the Collective Electronic Oscillator (CEO) at AM1 level.
- Equilibration on the ground state at 300K

→ Fotoexcitation and ultrafast dynamics in the excited states

- *An Ab Initio Multiple Cloning approach for the simulation of photoinduced dynamics in conjugated molecules"* V. M. Freixas et al, Phys. Chem. Chem. Phys. 20, 17762 - 17772 (**2018**).
- *"NEXMD Software Package for Non-adiabatic Excited State Molecular Dynamics Simulations"* W. Malone et al., J. Chem. Theory Comput.,16, 9, 5771–5783 (**2020**).

MCE: Evolution of the whole wave-function

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

$$\sum_n \langle\psi_m(t)\,|\,\psi_n(t)\rangle\dot{c}_n(t) = -\frac{i}{\hbar}\sum_n\left(H_{mn} - i\hbar\langle\psi_m(t)|\frac{\mathrm{d}}{\mathrm{d}t}|\psi_n(t)\rangle\right)c_n(t),$$

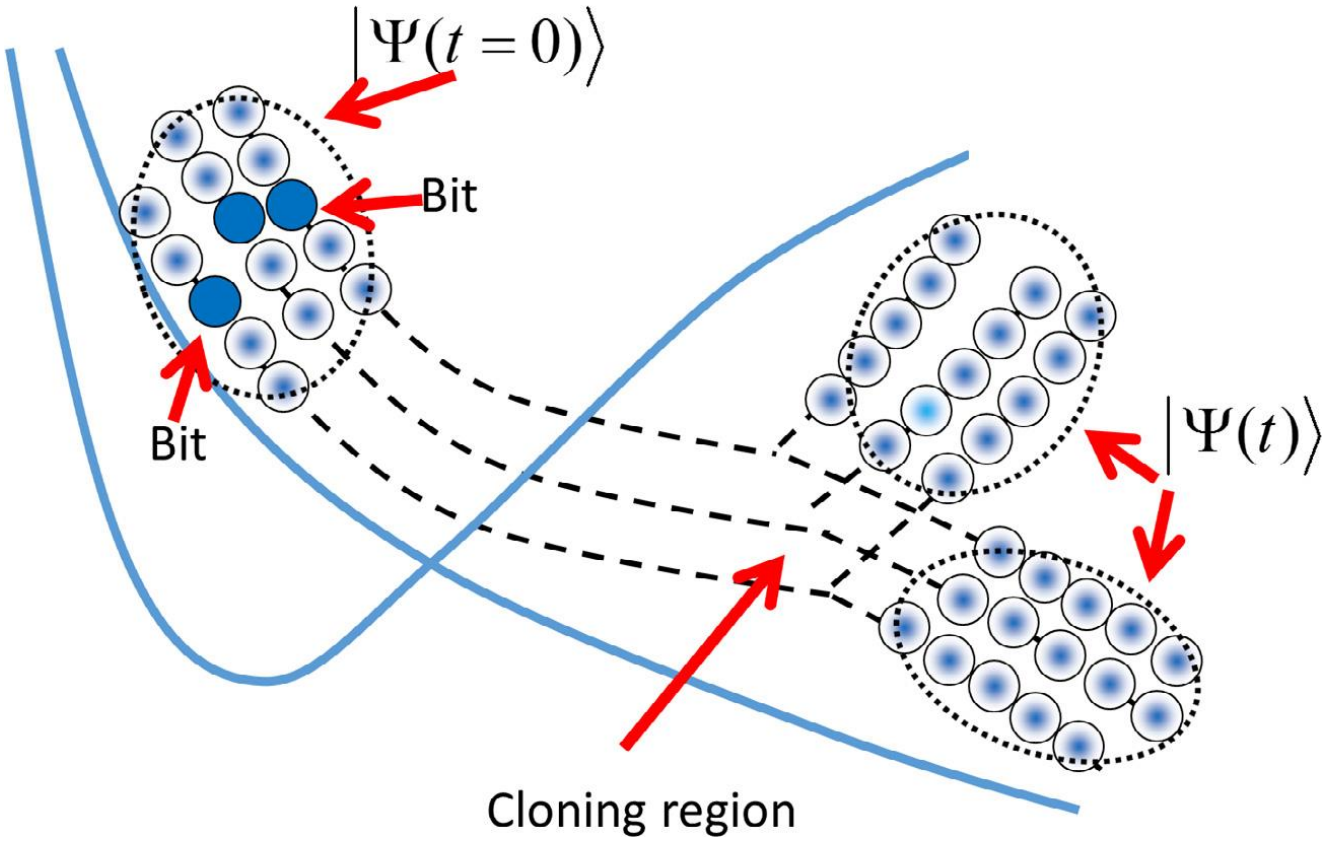
where

$$H_{mn} = \sum_{J,I}\left(a_J^{(m)}\right)^* a_I^{(n)}\left\langle\chi_m\phi_J^{(n)}\left|(\hat{T}+\hat{V})\right|\chi_n\phi_I^{(n)}\right\rangle.$$

Note that overlaps include both nuclear part and electronic parts

$$\langle\psi_m(t)\,|\,\psi_n(t)\rangle = \langle\chi_m\,|\,\chi_n\rangle\sum_{I,J}\left(a_I^{(m)}\right)^* a_J^{(n)}\left\langle\phi_I^{(m)}\,\middle|\,\phi_J^{(n)}\right\rangle.$$

AIMC-TDDB: 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

AIMC-TDDB: cloning criteria

Criterion #1

Cloning events should take place only when at least two adiabatic electronic states are sufficiently populated

$$W_n = \frac{1}{\sum_I^N \left| a_I^{(n)} \right|^4}. \quad W_n > \delta_{\text{clone},1} = 2$$

Criterion #3

We limit the cloning to regions of phase space where the electronic states are not strongly coupled

$$\sum_I \left| \frac{2\rho_I}{\rho_M} cos(\theta_I - \theta_M) \dot{R} \cdot \boldsymbol{d}_{IM} \right| \leq \delta_{clone,3}$$

Criterion #2

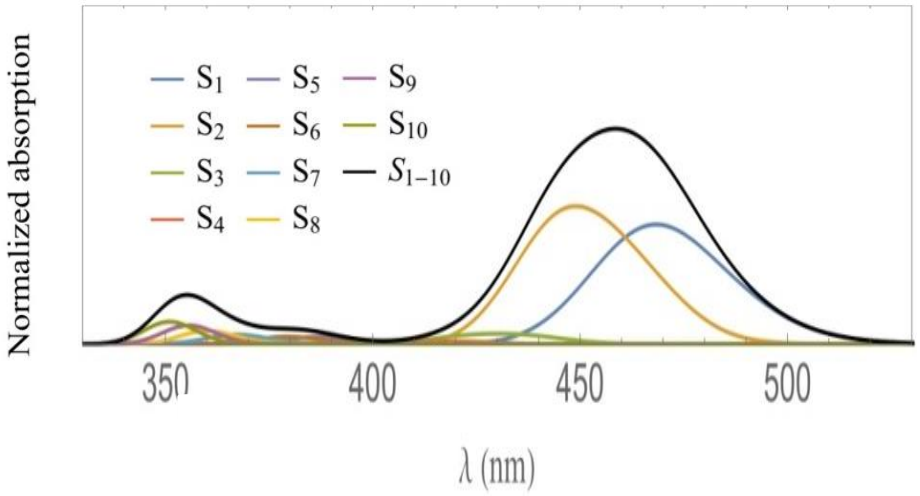
Cloning events should prevent situations in which the nuclear motion guided by the average Ehrenfest force lacks physical significance

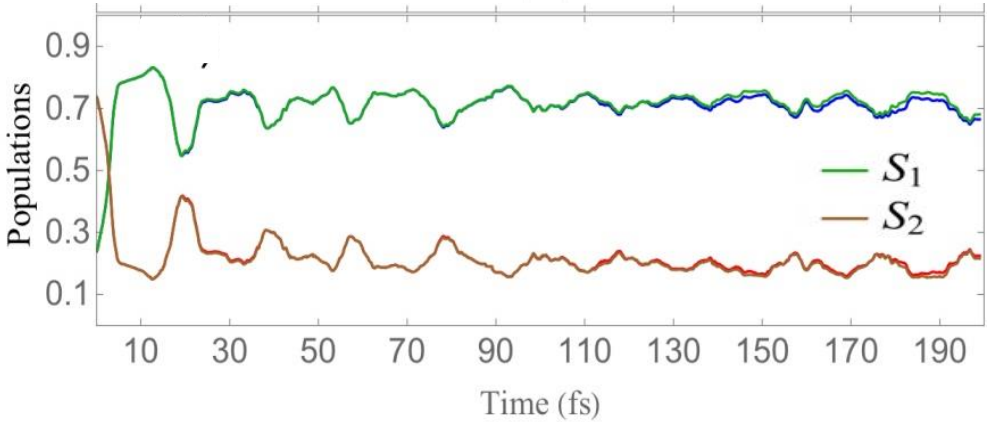
$$\mathbf{F}_M^{(n)} = -\sum_I \left| a_I^{(n)} \right|^2 \nabla_{\mathbf{R}_n} V_I^{(n)}$$

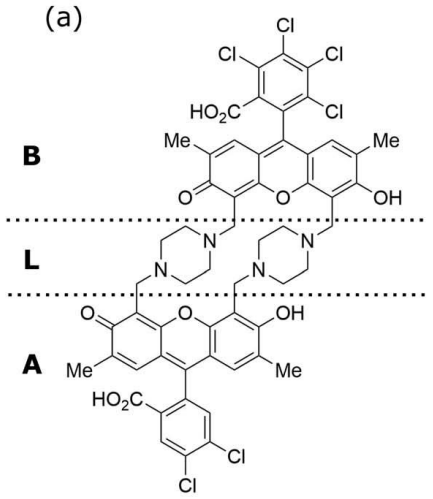
$$\theta^{(n)} = \arccos\left(\frac{2\mathbf{F}_{\mathrm{M}}^{(n)} \cdot \mathbf{F}_{\max}^{(n)}}{\left|\mathbf{F}_{\mathrm{M}}^{(n)}\right|^2 + \left|\mathbf{F}_{\max}^{(n)}\right|^2} \right)$$

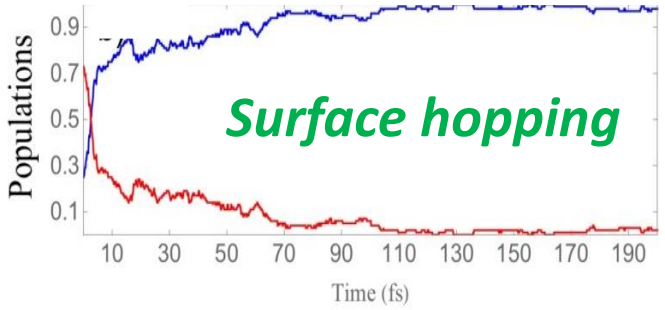
$$\theta^{(n)} > \delta_{\text{clone},2} = \frac{\pi}{12}$$

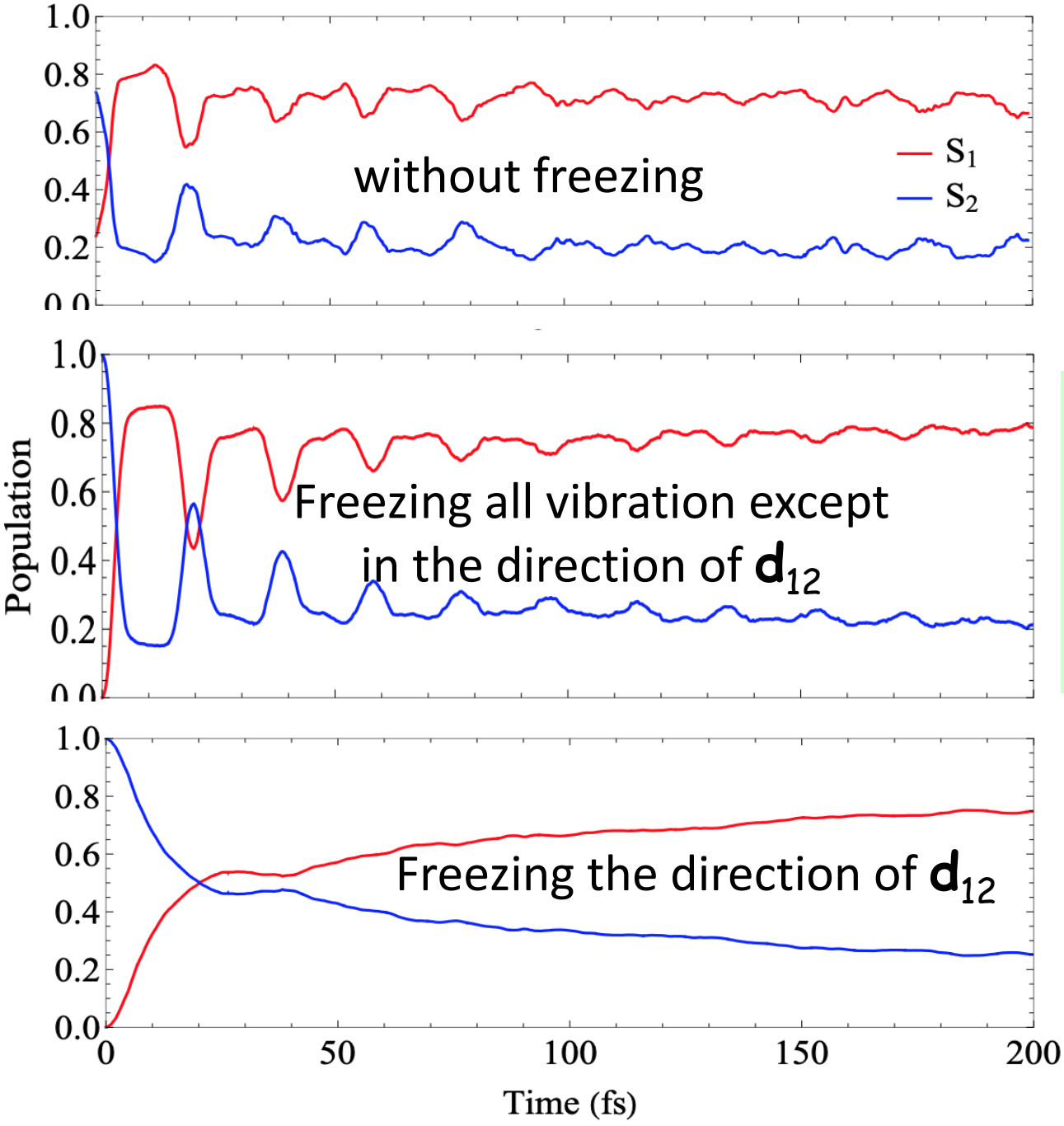
Vibronic quantum beating between electronic excited states in a heterodimer





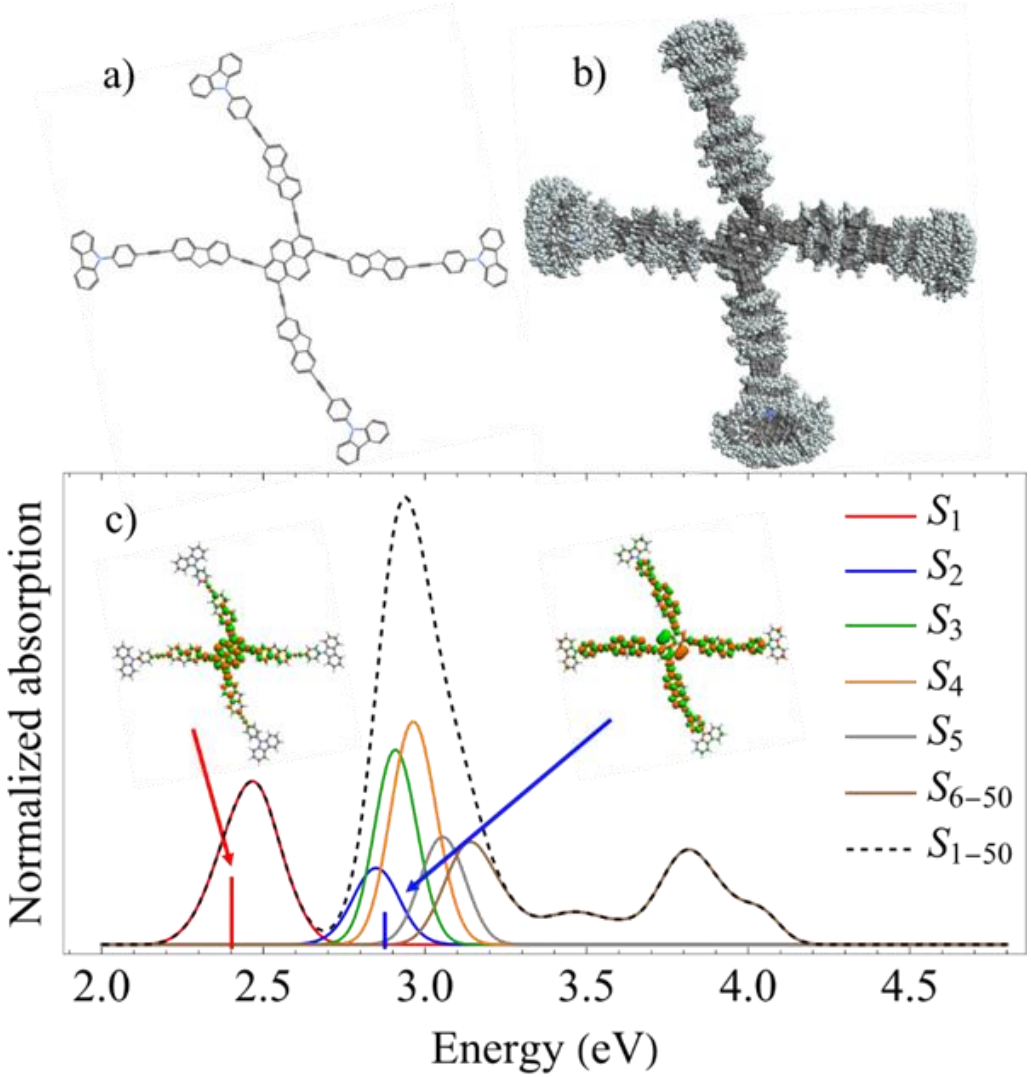




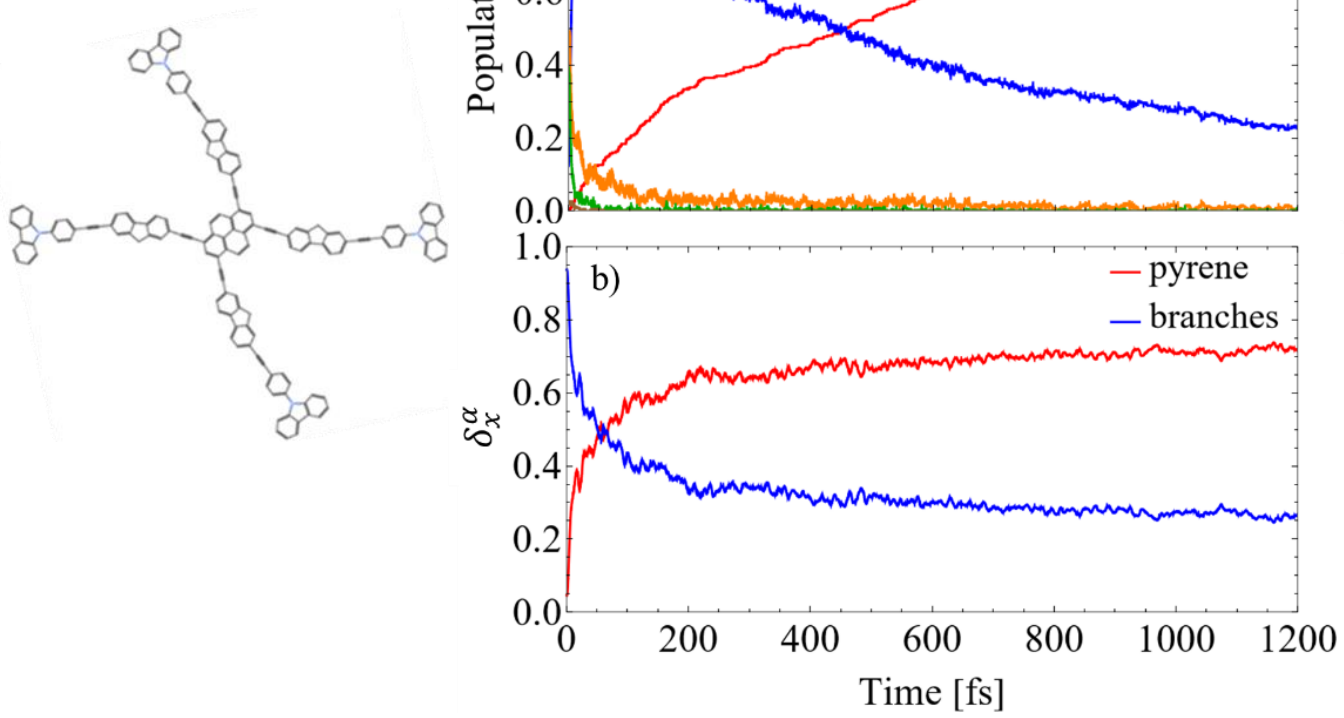


Freezing nuclear motions

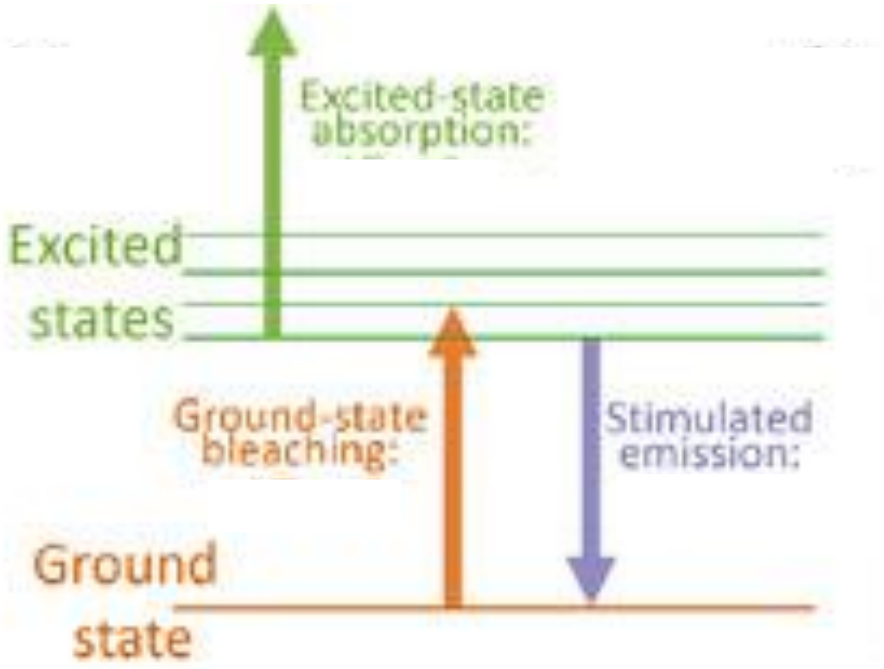
Transient Absorption pump-probe signals in dendrimers



Transient Absorption pump-probe signals in dendrimers



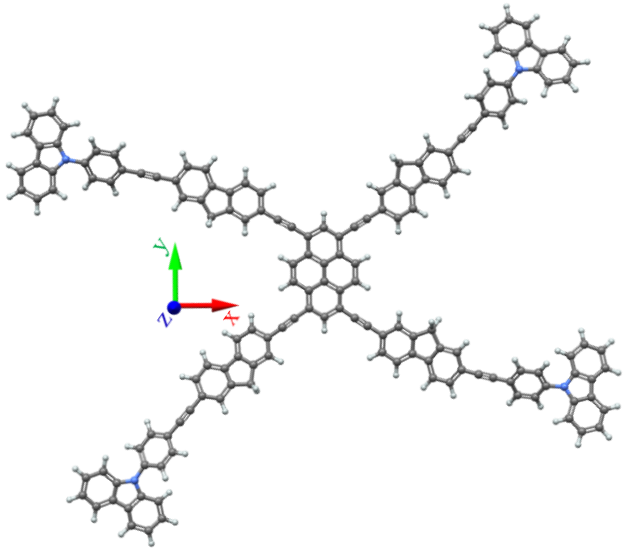
Transient Absorption pump-probe signals in dendrimers



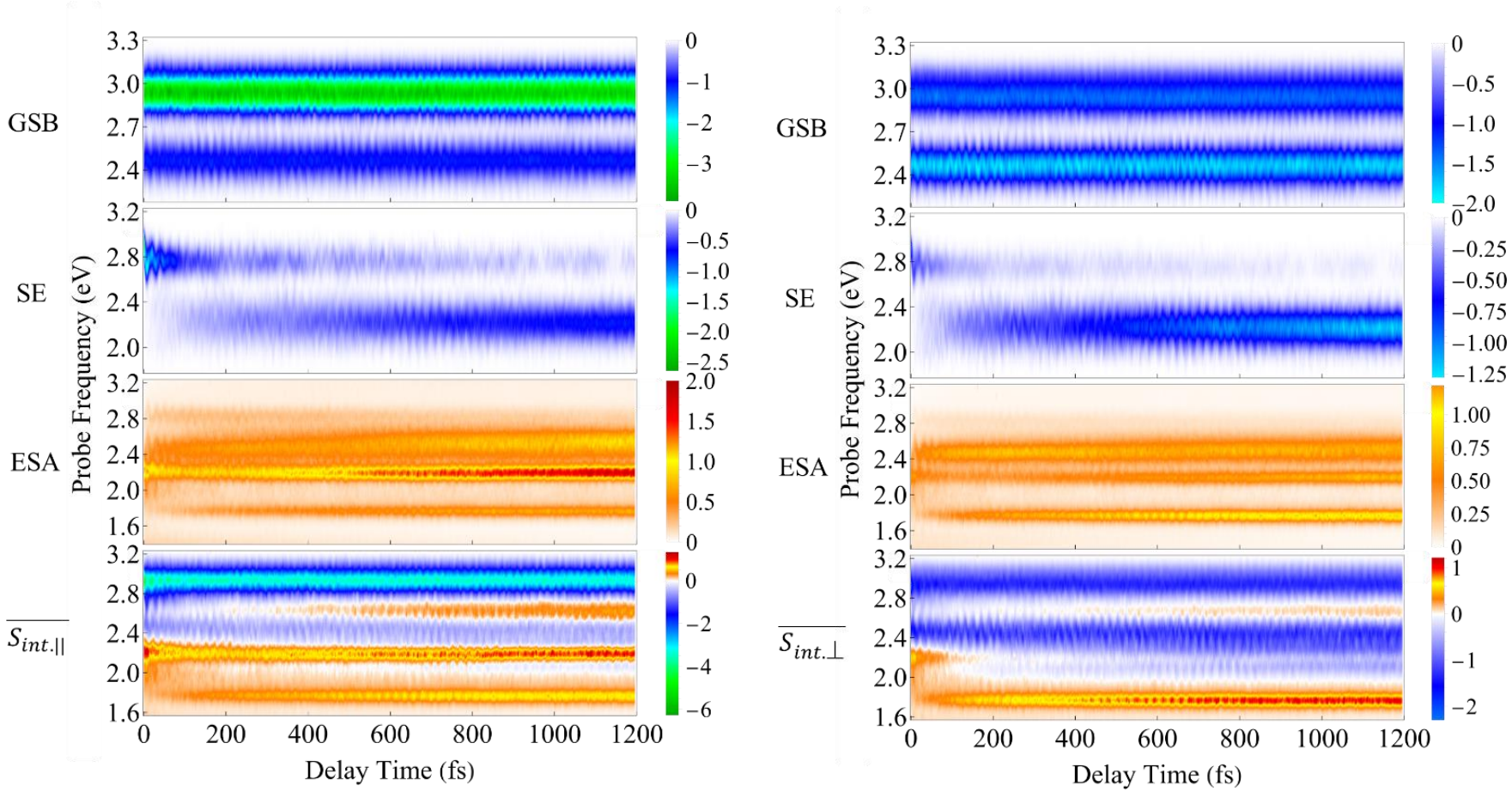
Transient Absorption pump-probe signals in dendrimers

Table I. Vertical Excitation Energies (VEE) and transition dipole moments (μ) of the five low-energy electronic states at the ground state energy minimum.

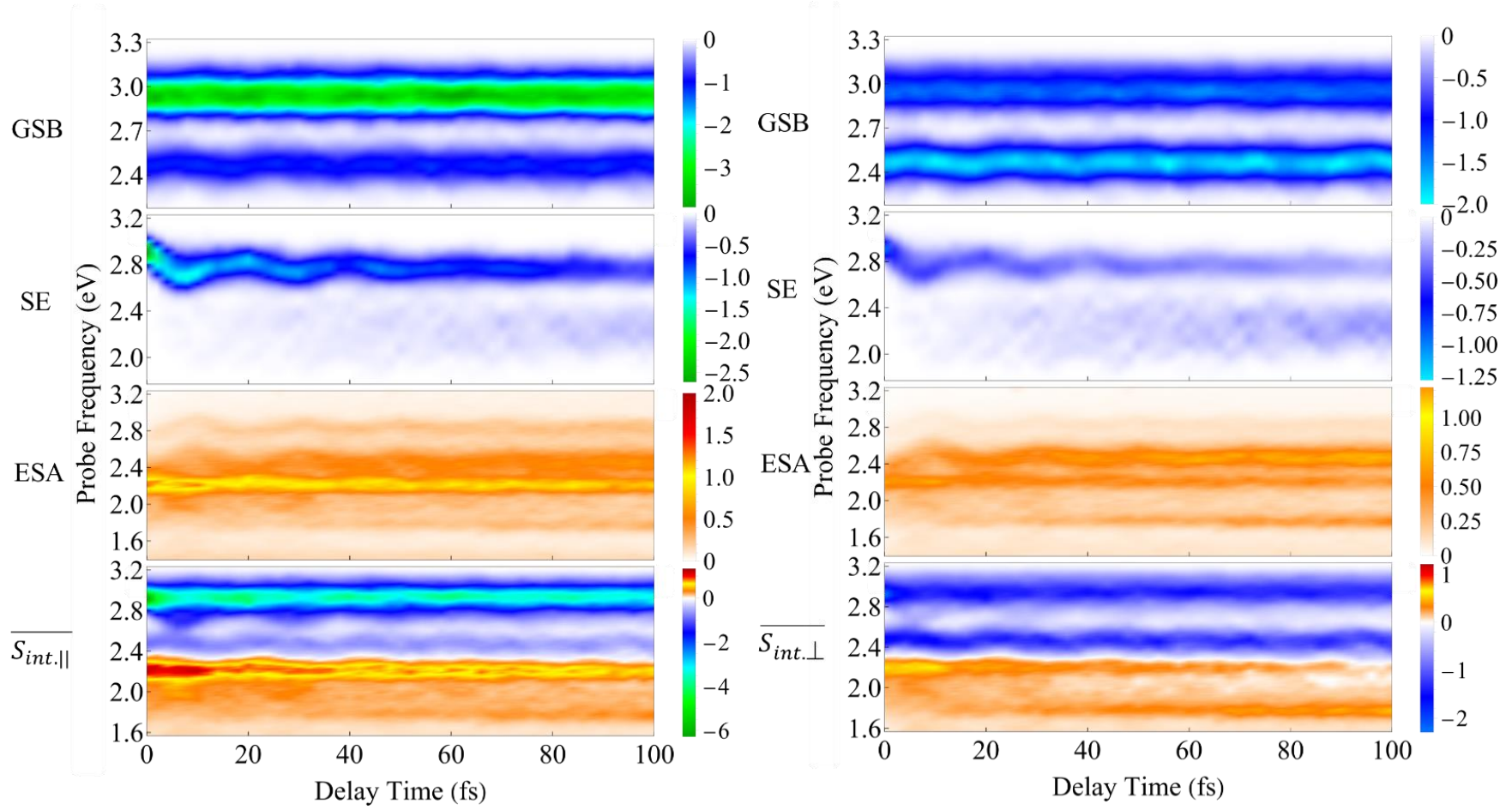
		μ(a.u.)			
	VEE(eV)	x	y	z	tot
S_1	2.40	-0.45	5.13	-0.14	26.51
S_2	2.88	-0.03	0.01	0.01	0.00
S_3	2.90	5.67	1.42	1.17	34.19
S_4	2.90	-5.88	-1.28	0.00	36.24
S_5	3.01	-0.28	0.36	-0.55	0.51



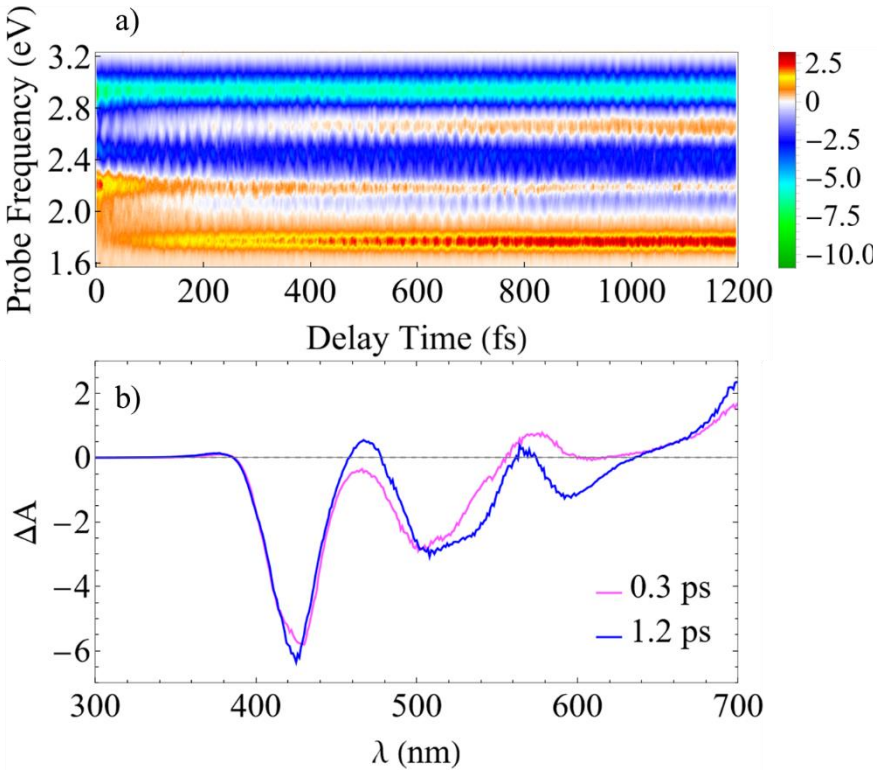
Transient Absorption pump-probe signals in dendrimers

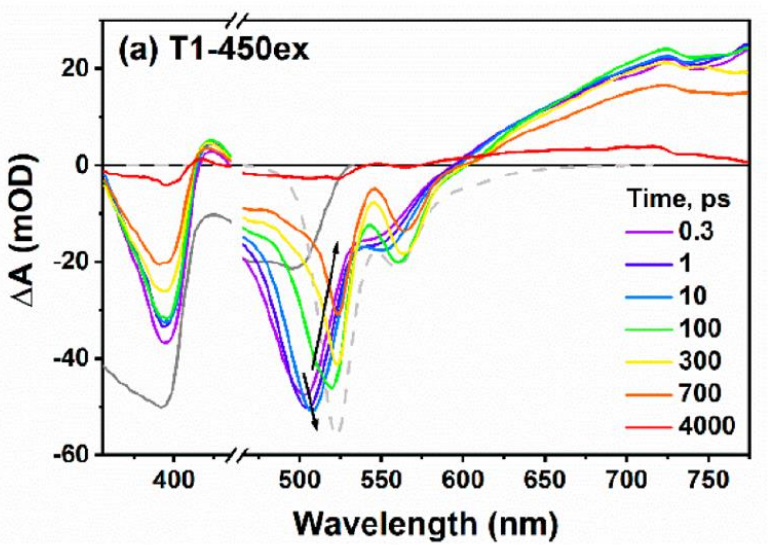


Transient Absorption pump-probe signals in dendrimers



Transient Absorption pump-probe signals in dendrimers





Main conclusions

- The efficiency of electronic energy relaxation can be speeded up by adding a chromophore, oligomerization, interlinking
- AIMC naturally account for decoherence of vibronic wavepackets.
- Atomistic simulations of pump-probe experiments in dendrimers can be achieved.

Molecular physics and Biophysics group

Universidad Nacional de Quilmes

Dianelys Ondarse Alvarez

Galo Balatti

Nicolas Oldani

Royle Perez Castillo

Tadeo E. Saldaño

Hassiel Negrin Yuvero

Matias Chiappinelli

Laura Alfonso Hernandez

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

Collaborators

- Sergei Tretiak & Tammie Nelson
- Dmitrii Shalashilin & Dmitry Makhov
- Maxim F. Gelin
- Sahar Sharifzadeh