Environment Effects on the Optical Properties of a Rhodamine Heterodimer-DNA Supramolecular Complex: A computational and Experimental Study

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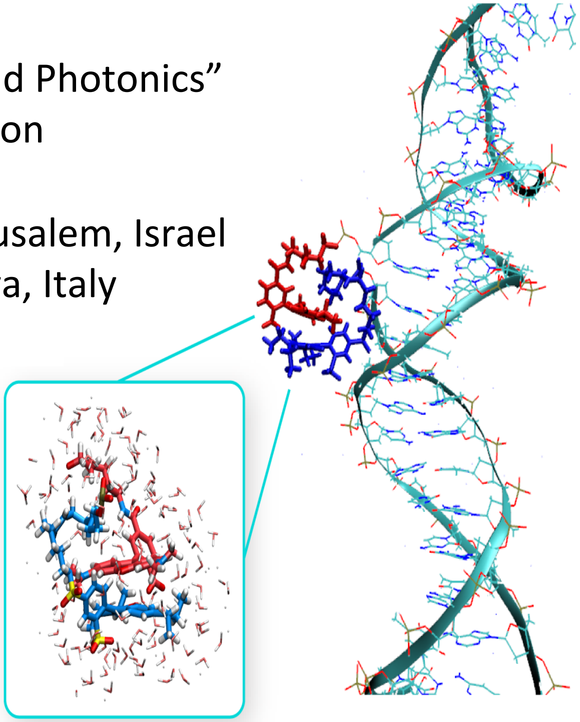
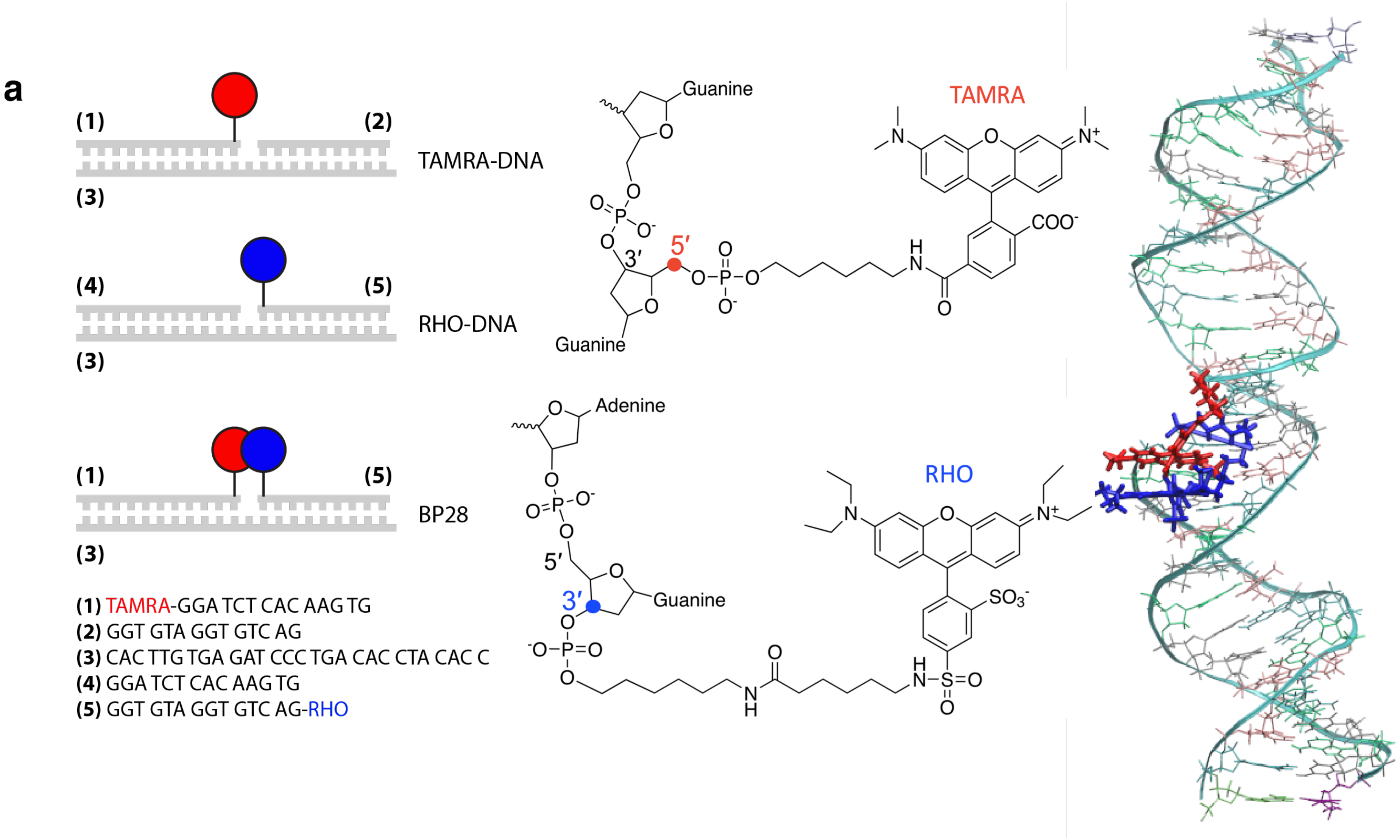


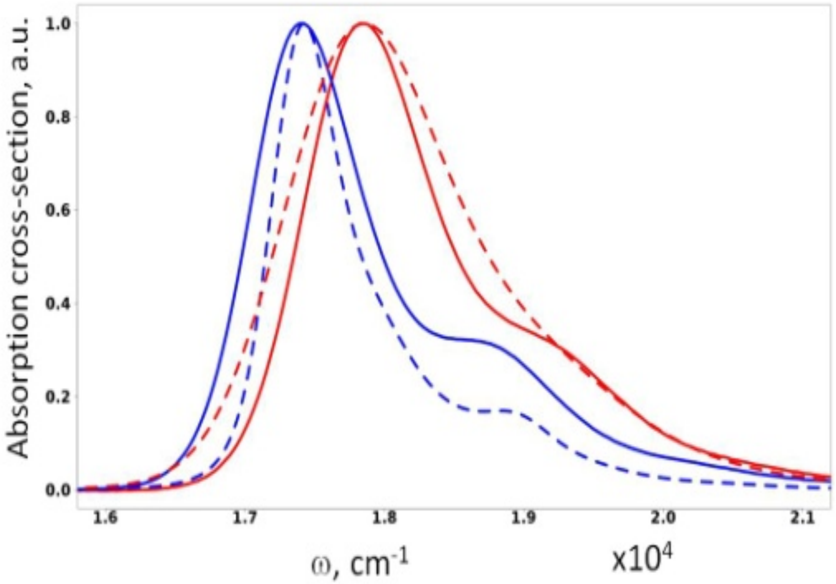
RHO–TAMRA STRUCTURE



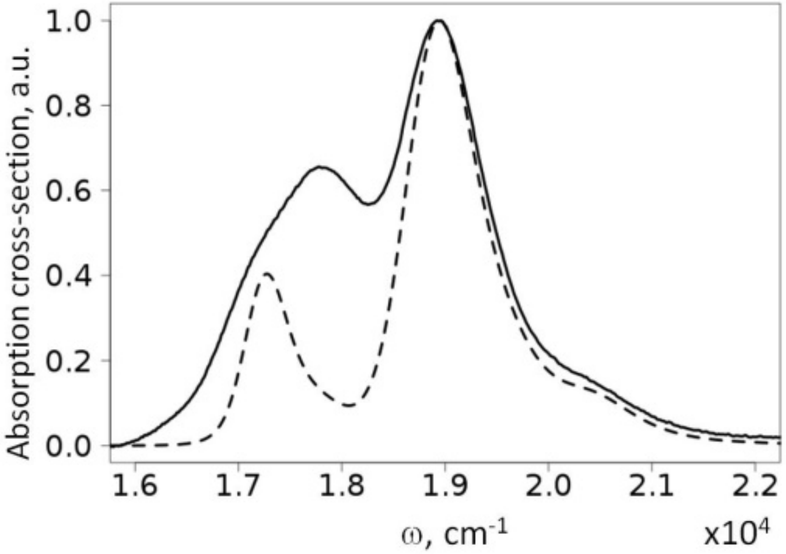
(1) TAMRA-GGA TCT CAC AAG TG
(2) GGT GTA GGT GTC AG
(3) CAC TTG TGA GAT CCC TGA CAC CTA CAC C
(4) GGA TCT CAC AAG TG
(5) GGT GTA GGT GTC AG-RHO

Absorption lineshape of the RHO using state-specific PCM

Monomers RHO (red) TAMRA (blue)



Heterodimer RHO–TAMRA

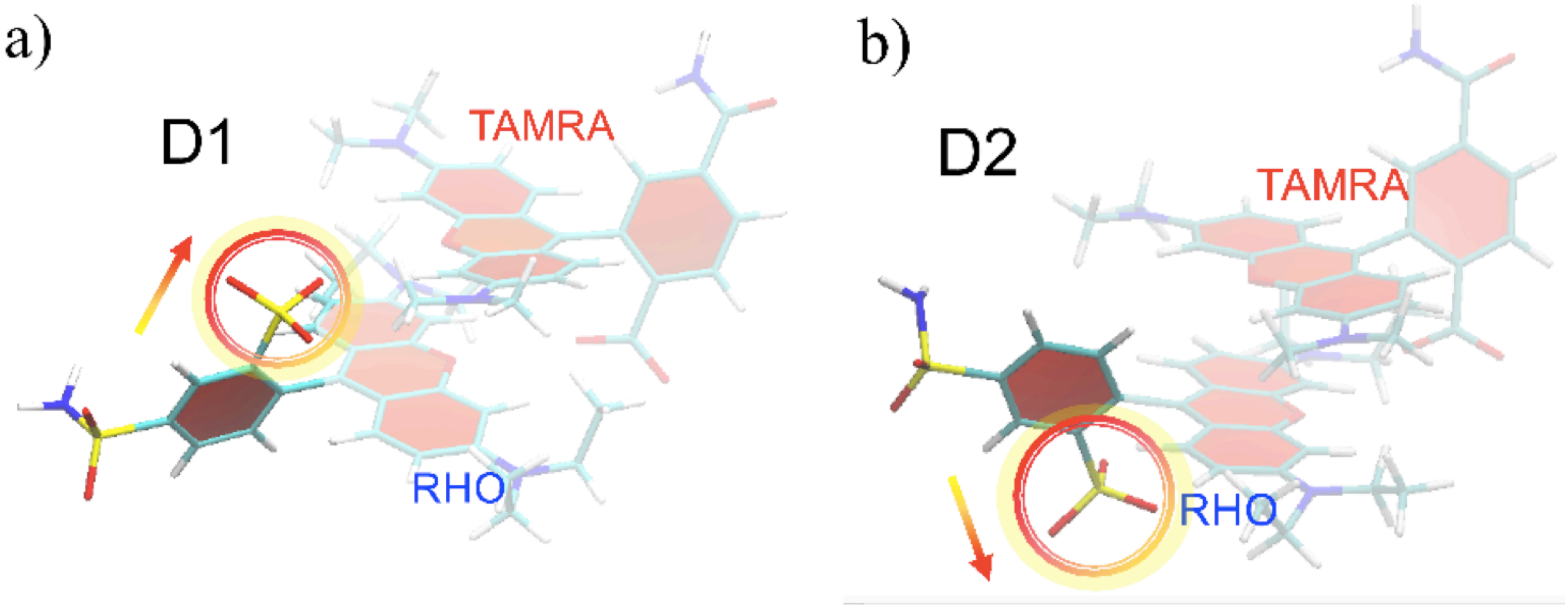


TDDFT/ CAMD-B3LYP/6-311(d,p)/PCM, harmonic oscillator model (M. Lax 1952)

Aims of the work

- Reproduce correctly the spectrum lineshape including the complex media
- Develop the approach for multi-mode harmonic oscillator model including complex media
- Describe correctly active normal modes
- Define the sampling of MD trajectory for the nuclear-ensemble approximation

Two types of conformers



The main difference in the orientation of the anionic sulfo-group of the RHO unit inside (a) and outside (b) the dimer subspace.

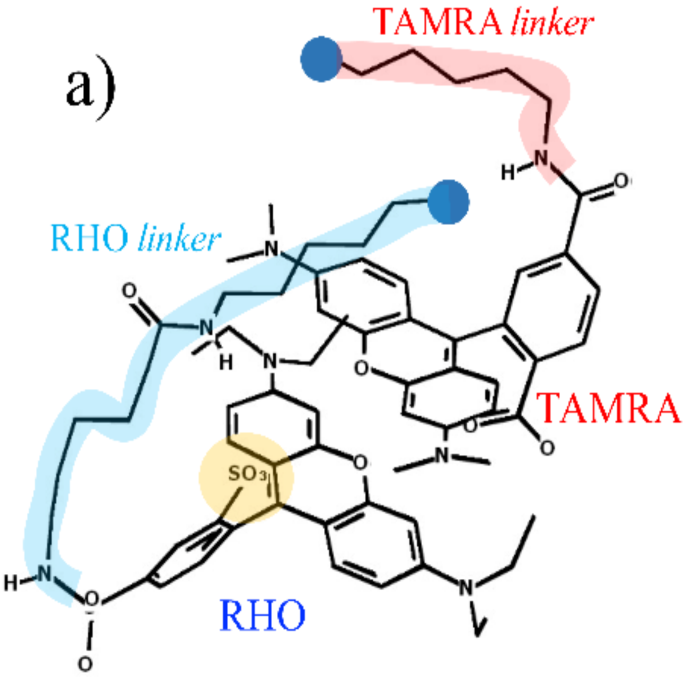
We denote these structures as isomers because they do not interconvert within 60ns MD trajectory at room temperature.

MD Calculation Details

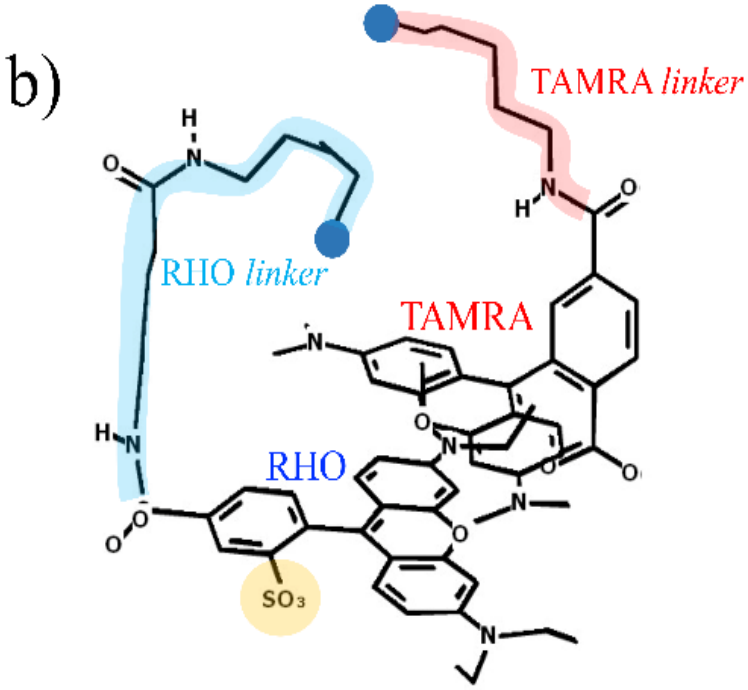
- PARM99/BSC0 force field for DNA,
- GAFF force field for the chromophores and the aliphatic linkers
- Cubic periodic box with waters (TIP3P) with a minimum buffer 10 Å between the atoms of DNA or chromophore and the edge of the box. Sodium counterions were added (27 atoms) to ensure the neutrality of the system

- The duration of the production trajectory: 8 ns (time step 2 fs)
- This step was performed in the canonical NVT ensemble
- Short-range interactions were truncated at a cutoff distance of 9 Å.

Structures along the MD trajectory of D1 and D2

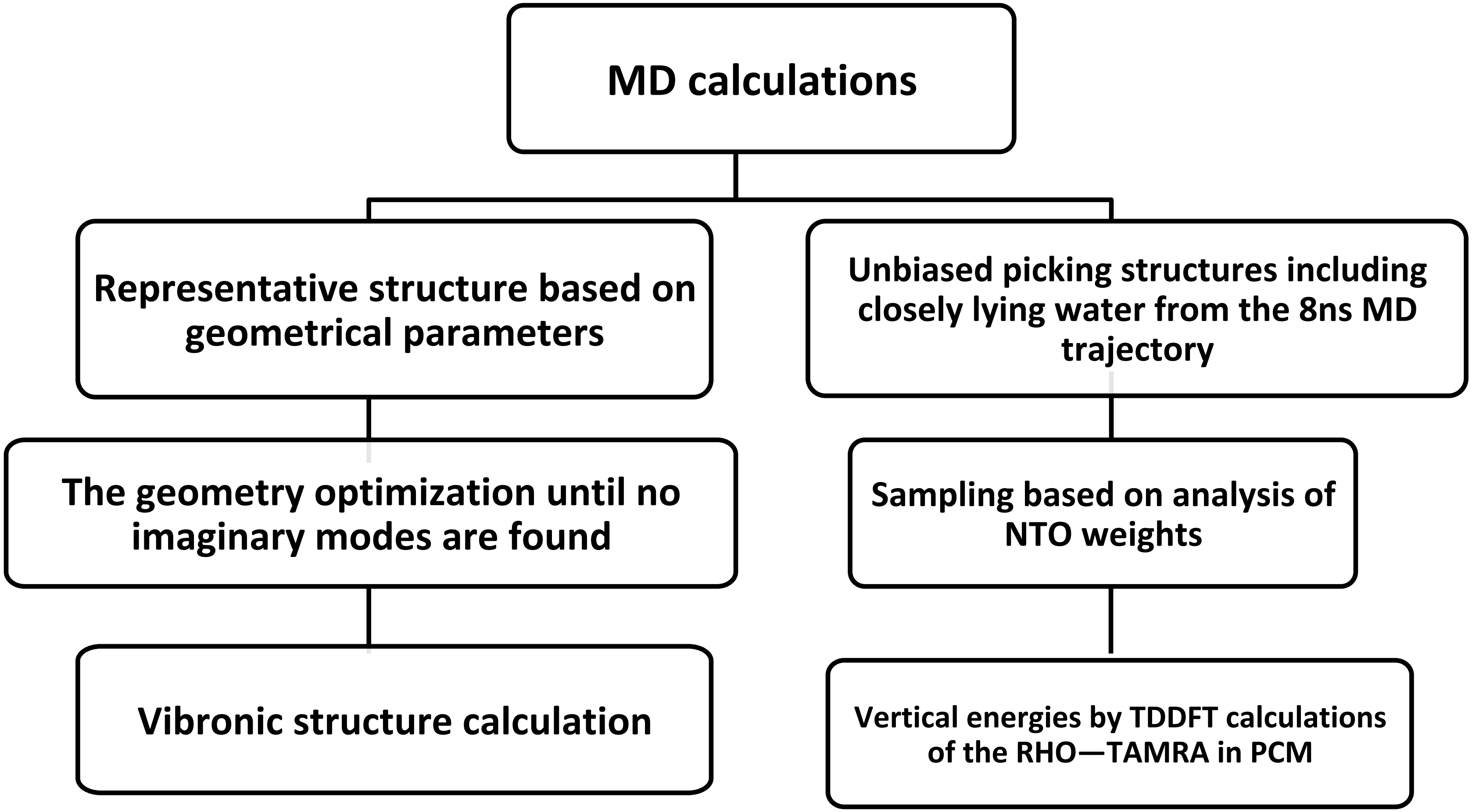


D1



D2

COMPUTATIONAL DETAILS



MD calculations

Representative structure based on geometrical parameters

The geometry optimization until no imaginary modes are found

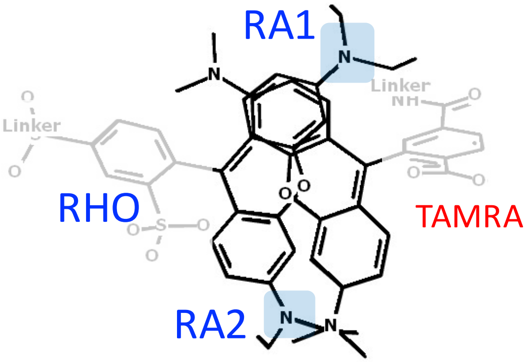
Vibronic structure calculation

Unbiased picking structures including closely lying water from the 8ns MD trajectory

Sampling based on analysis of NTO weights

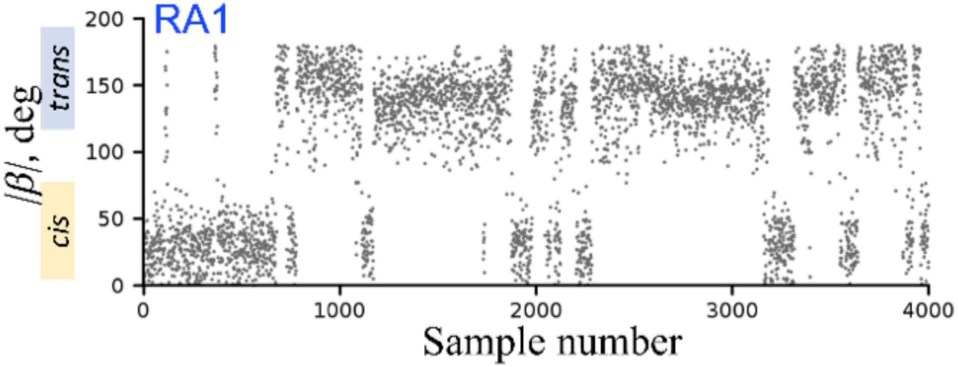
Vertical energies by TDDFT calculations of the RHO—TAMRA in PCM

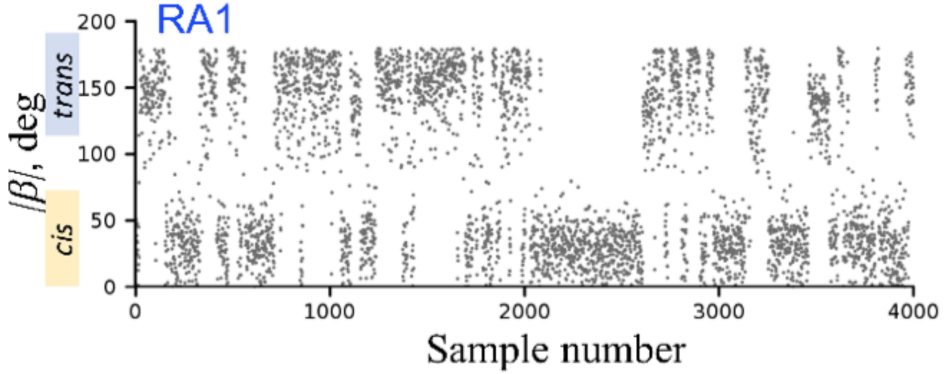
Rhodamine amino-groups conformations along the MD trajectory

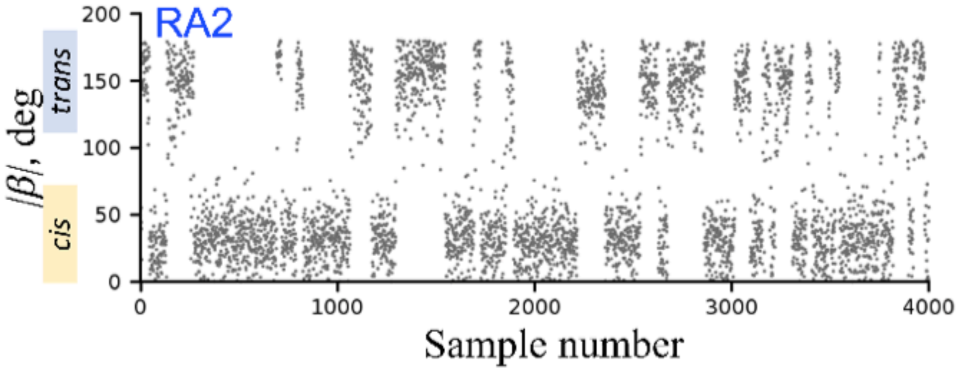


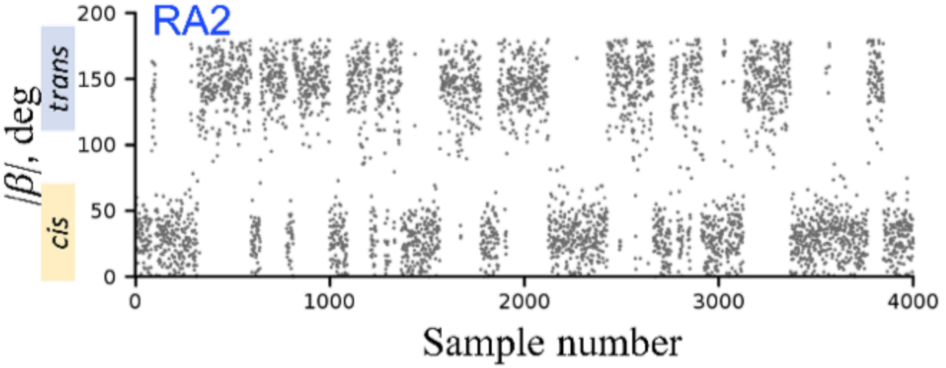
The conformations are determined via the dihedral angle β between the neighbouring ethyl-groups:

angles lower than 90º correspond to the *cis*-conformation, larger than 90º to the *trans*-conformation

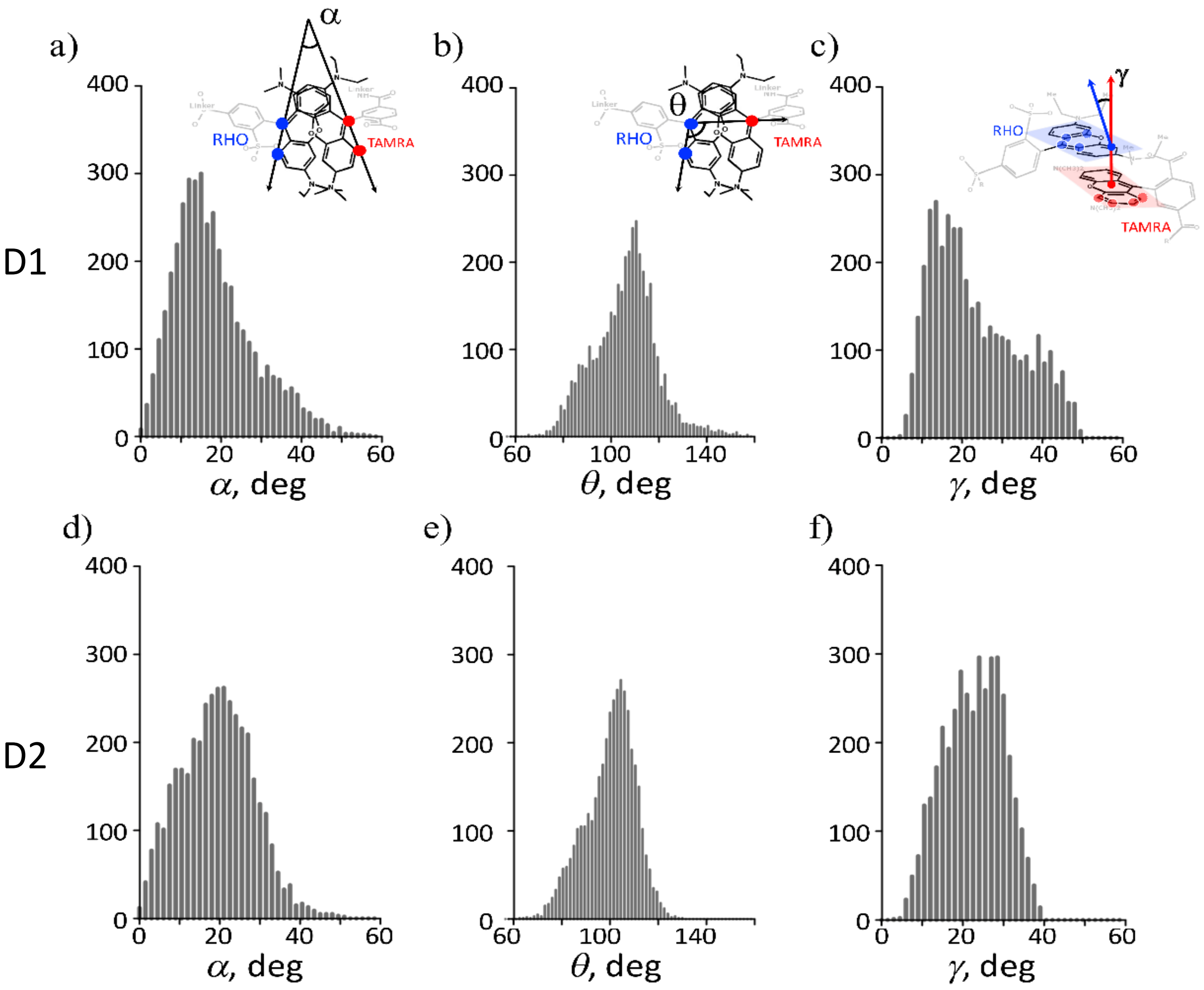








Analysis of intermolecular angles along the MD trajectory

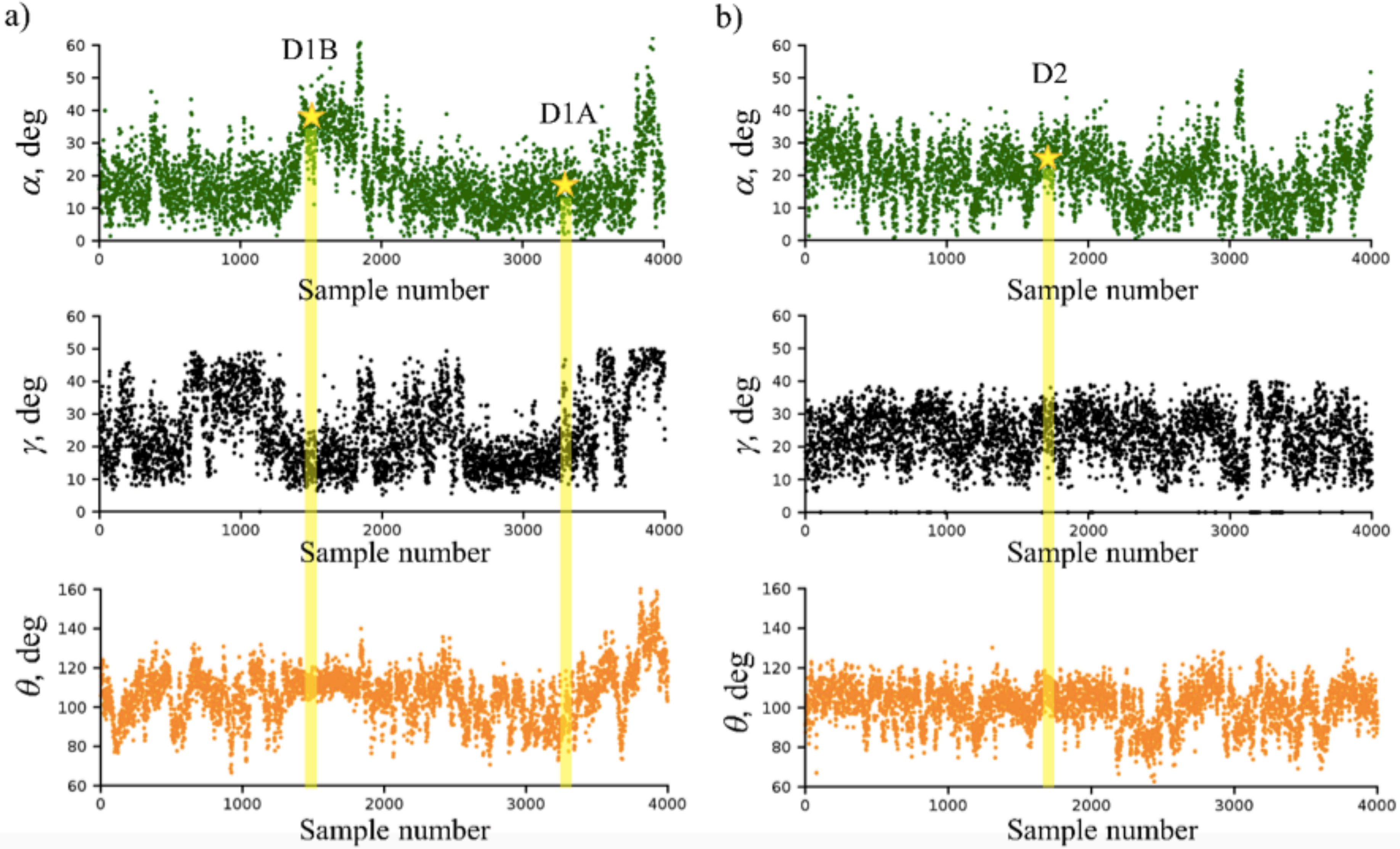


α- angle between the polarization axes of the two units

θ- angle made by the polarization axes of the unit molecule with the line of molecular centre

Y- mean angle between the planes of the xanthene moieties

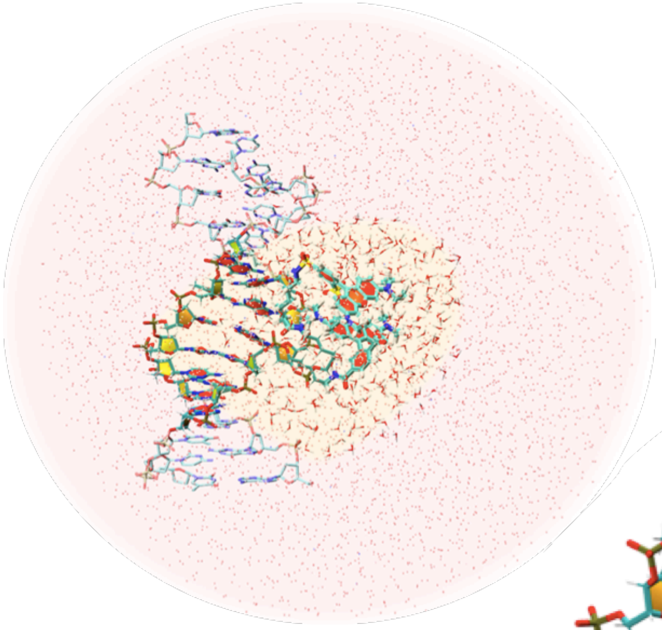
Analysis of intermolecular angles along the MD trajectory



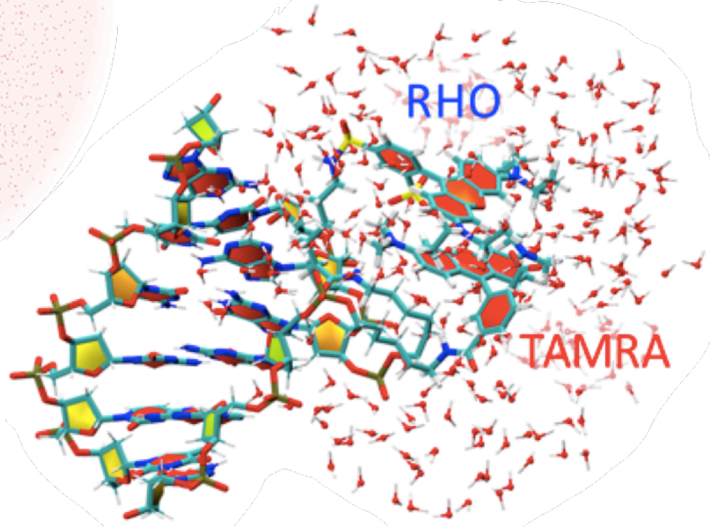
Scheme of QM/MM (ONIOM 2-layers model)

QM: *ground state equilibrium geometry and normal modes*: DFT-D/CAM-B3LYP/6-311G (d,p) with electrostatic embedding

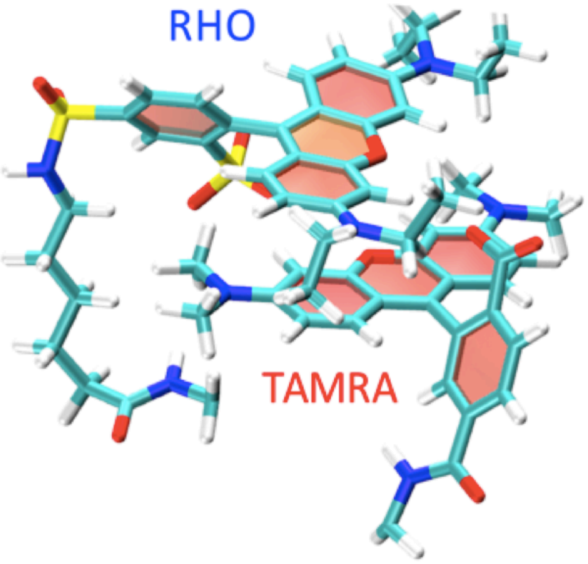
excitation energies, dipoles, oscillator strengths and gradients in QM/MM: TDDFT/CAM-B3LYP/6-311G (d,p)



QM + MM
Frozen water
sphere ~27 Å



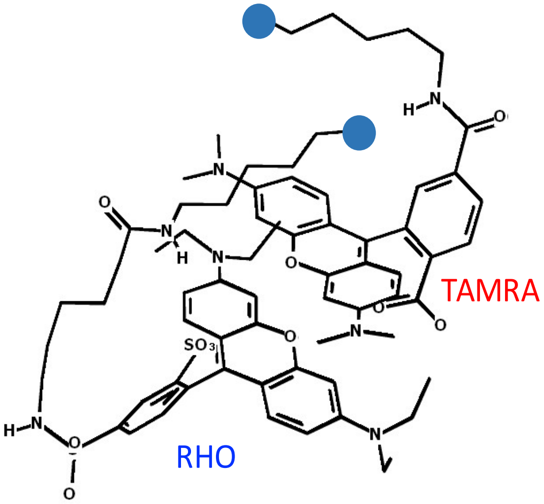
Unfrozen part of
QM + MM
Water sphere ~7 Å



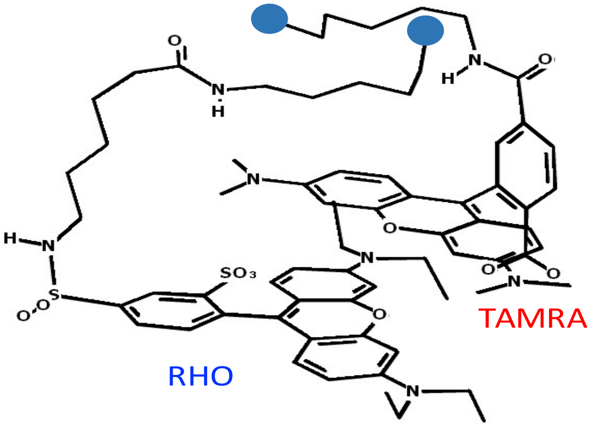
QM part

MM: PARM99/BSC0 force field for DNA, TIP3P - for waters, GAFF - for the chromophores and linkers

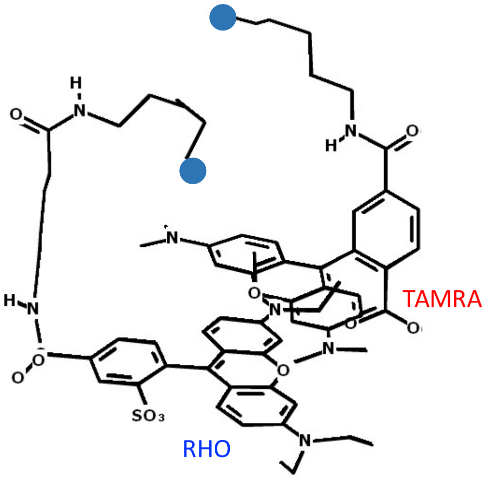
Conformers along the MD trajectory



D1A ($\alpha = 21°$)

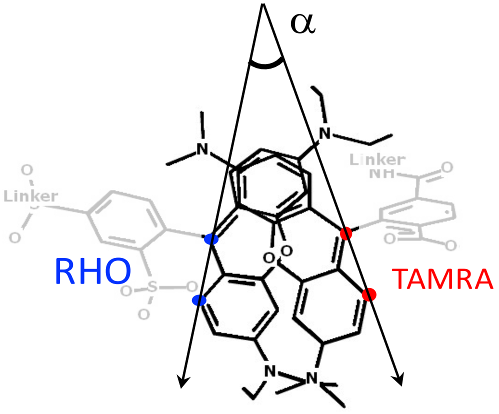


D1B ($\alpha = 35°$)



D2 ($\alpha = 25°$)

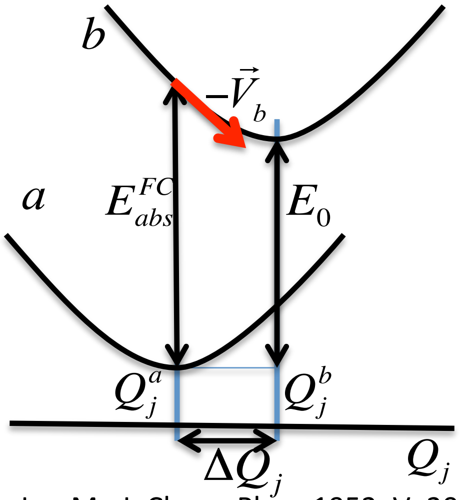
	α,	$\delta E(GS)$,	$\Delta E(S_1\text{-}S_2)$,	$S_0\text{-}S_1$		$S_0\text{-}S_2$	
	degrees	kcal/mol	cm^{-1}	E_{exc}, eV	f	E_{exc}, eV	f
D1A/QM/MM	21	0	1290	2.55	0.76	2.71	1.80
D1B/QM/MM	35	8	2016	2.47	0.95	2.72	1.50
D2/QM/MM	27	13	1210	2.57	0.70	2.72	1.84
D1/PCM	3	0^*	1613	2.58	0.57	2.78	1.94
D2/PCM	5	5^*	1613	2.58	0.47	2.78	2.04



[*] Ground state energies of the bare dimers within PCM solvation are computed relative to the most stable bare dimer, D1/PCM.

Lineshape of the absorption spectra: harmonic approximation

Harmonic approximation for normal modes $\left|\langle \chi_{a0} | \chi_{bn} \rangle\right|^2$ - Franck-Condon factors



Lax M. J. Chem. Phys. 1952. V. 20. Pp. 1752.

Large number of vibrational states – need to use some approximations:

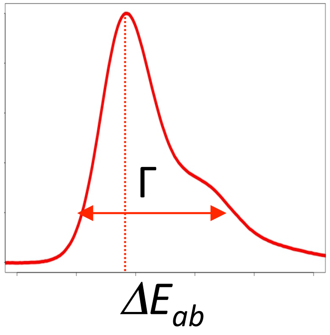
- Condon approximation
- Parallel harmonic approximation
- No Duschinsky rotation effect
- Temperature effect: Boltzmann distribution in the ground state

Input

Normal modes of the ground state
Electronic excitation energies
Electronic transition dipoles
Gradients on the excited state potential

Optically active vibrational modes can be defined

Dispersion of the absorption band



$$(\delta\nu)^2 = \sum_j (\delta\nu_j)^2 = \sum_j S_j \Omega_j^2 \operatorname{cth}\left(\frac{\hbar\Omega_j}{2kT}\right)$$

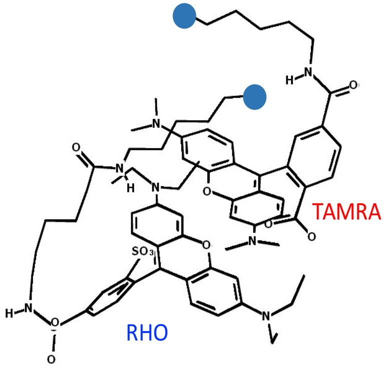
$$\Gamma = 2\sqrt{2\ln 2 \cdot (\delta\nu)^2}$$

Contribution of each normal mode to the broadening: $(\delta\nu_j)^2/(\delta\nu)^2$

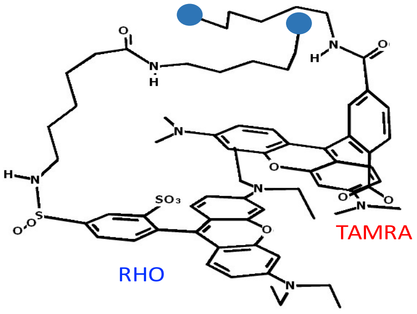
$$S_j = \frac{M\Omega_j(\Delta Q)^2}{2\hbar}$$ - Huang-Rhys factors

Kretov MK, et al. (2012) J Lumin, 132(8):2143.

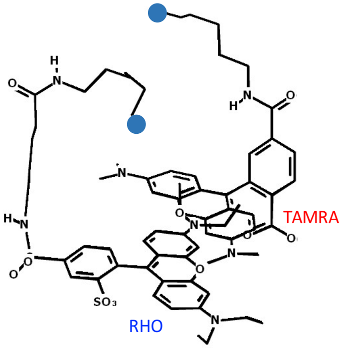
Absorption lineshape of D1 and D2 conformers



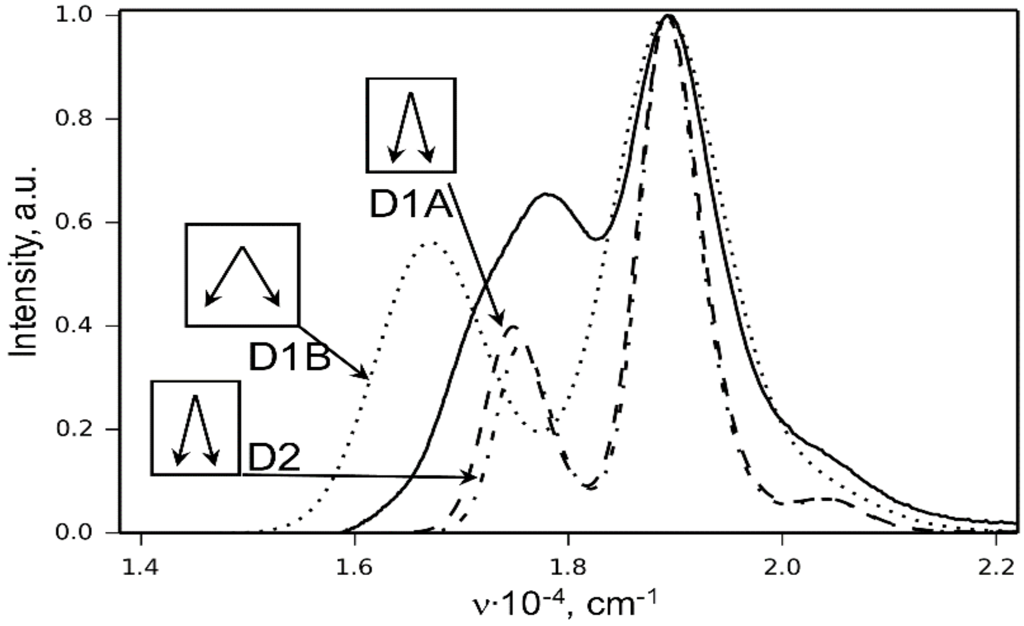
D1A (α = 21°)



D1B (α = 35°)

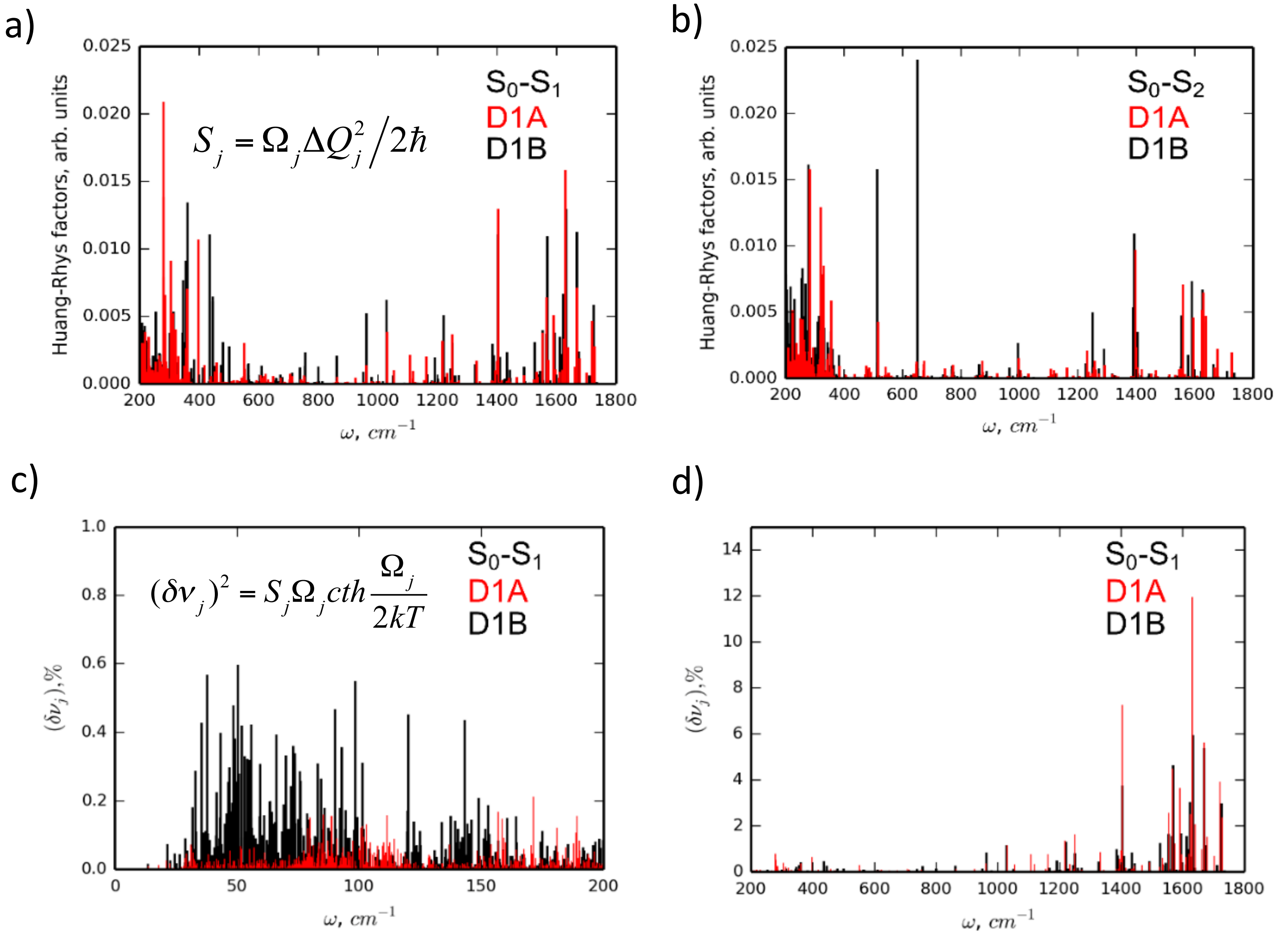


D2 (α = 25°)

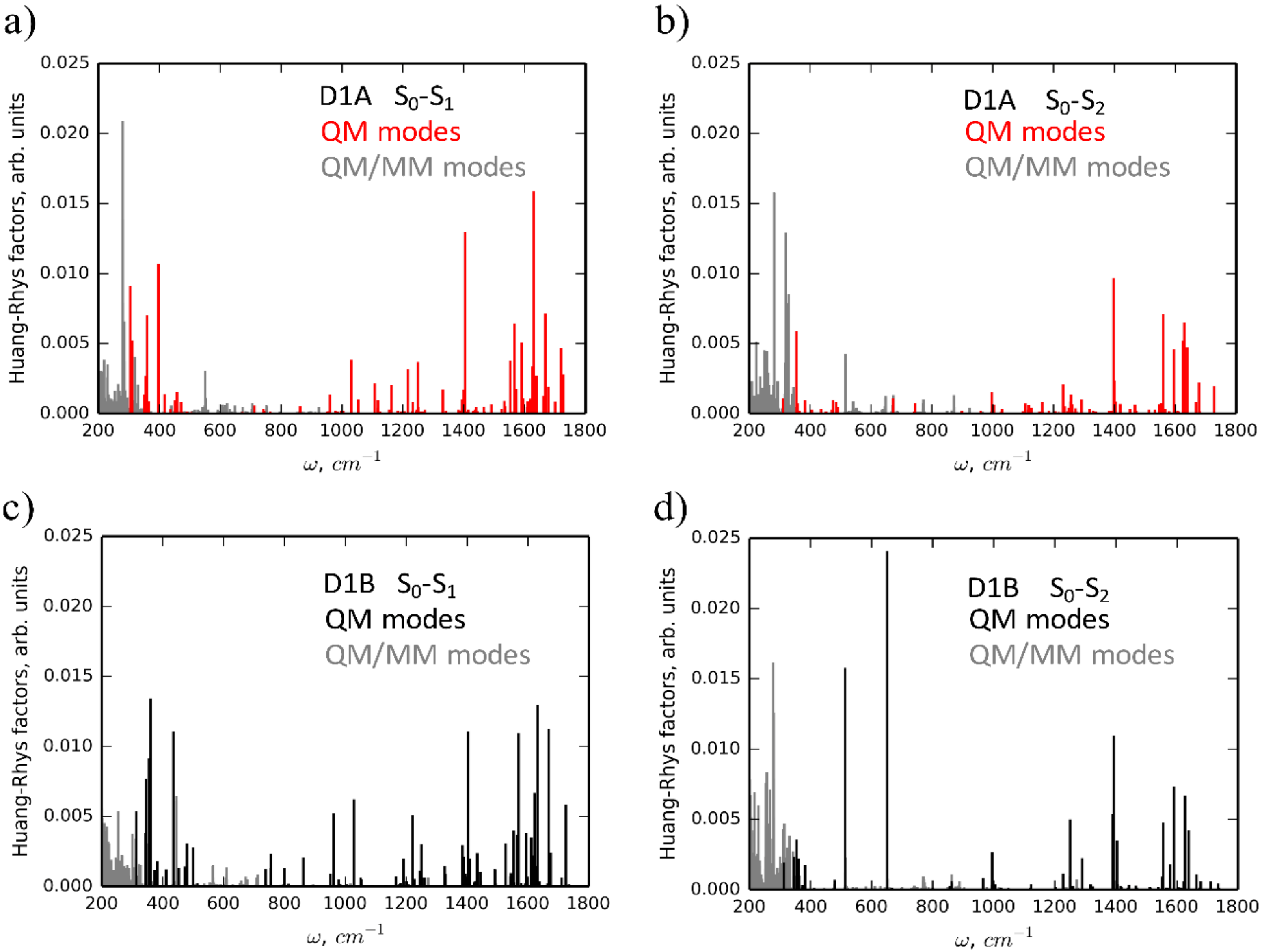


Δ (D1A) = -3086 cm^{-1}, Δ (D1B) = -3070 cm^{-1} and Δ (D2) = -2765 cm^{-1}

Analysis of the optically active normal modes



Analysis of the optically active normal modes



Conclusions of harmonic approximation method

- Harmonic approximation is valid in the description of **high-frequency optically active** modes (S_2 absorption)

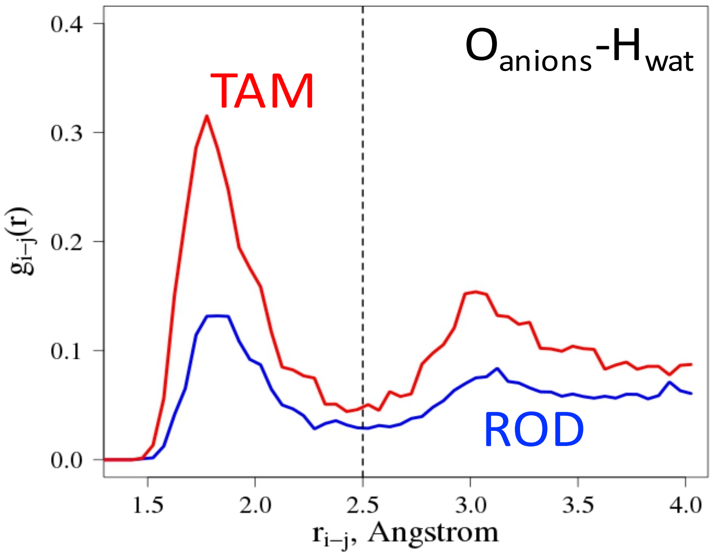
- There is a breakdown of the harmonic approximation for the S_1 absorption

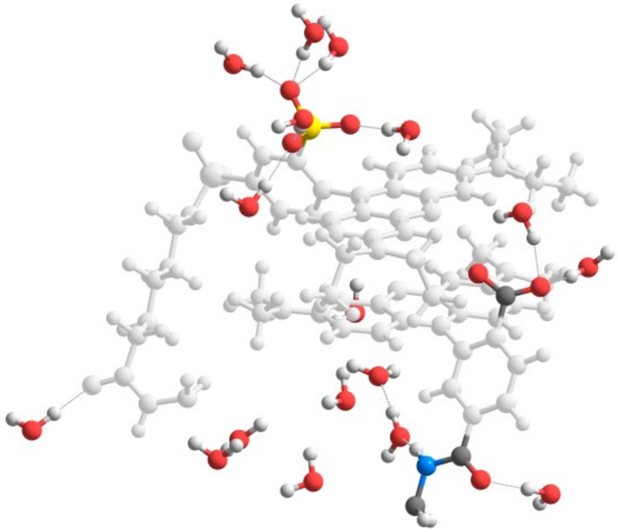
- The Lineshape for the D1A dimer is narrower compare to the experimental absorption spectrum. Significant increase of the broadening of the S_0-S_1/S_0-S_2 bands in D1B dimer is mainly due to its more flexible structure: great number of soft modes with n<100cm^{-1} contributes to its absorption profile .

- For these soft modes harmonic approximation can produce large errors

Thermal sampling from molecular dynamics trajectories

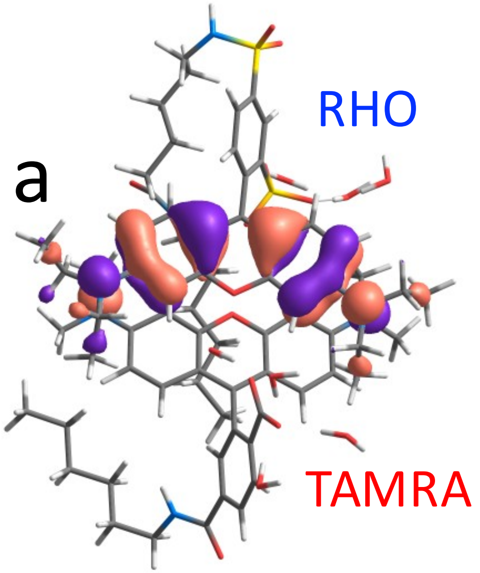
- Unbiased picking structures from the 8ns MD trajectory with the time step of 20ps (each 10th structure)
- For each sample only chromophore with linkers and nearest water molecules (within distance from the dye <2.5A) was taken





- TDDFT/ CAMD-B3LYP/6-311(d,p)/PCM for calculation of excitation energies and oscillator strengths

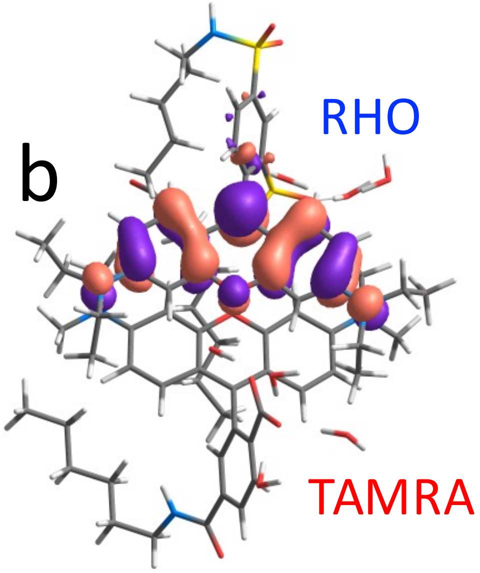
The dominant natural transition orbital pairs



S_0-S_1

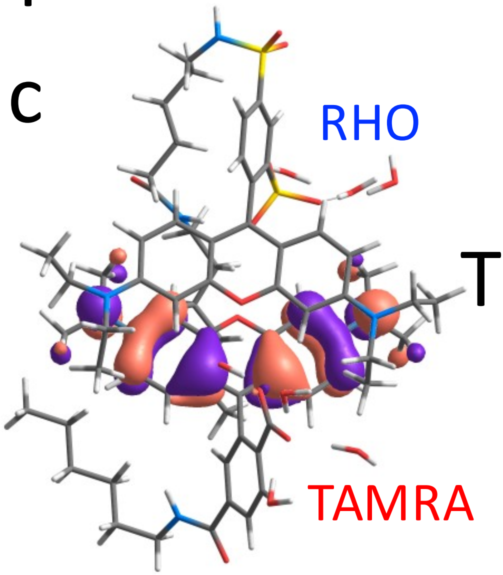
RHO–>RHO

λ =0.93



“particle” NTO

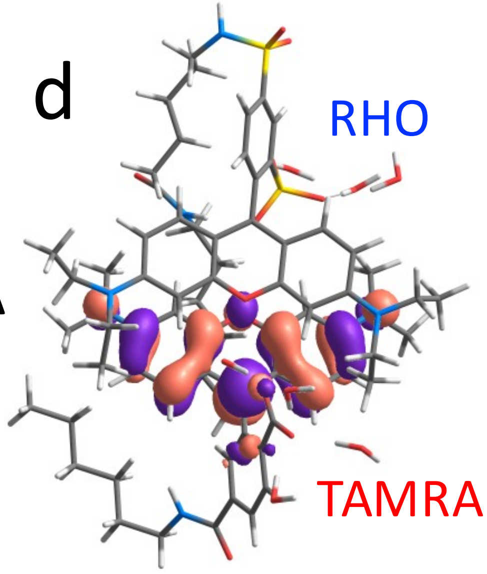
“hole” NTO



S_0-S_2

TAMRA–>TAMRA

λ =0.93



Sampling based on analysis of NTO weights (as a measure of the delocalization). 400 structures. D1

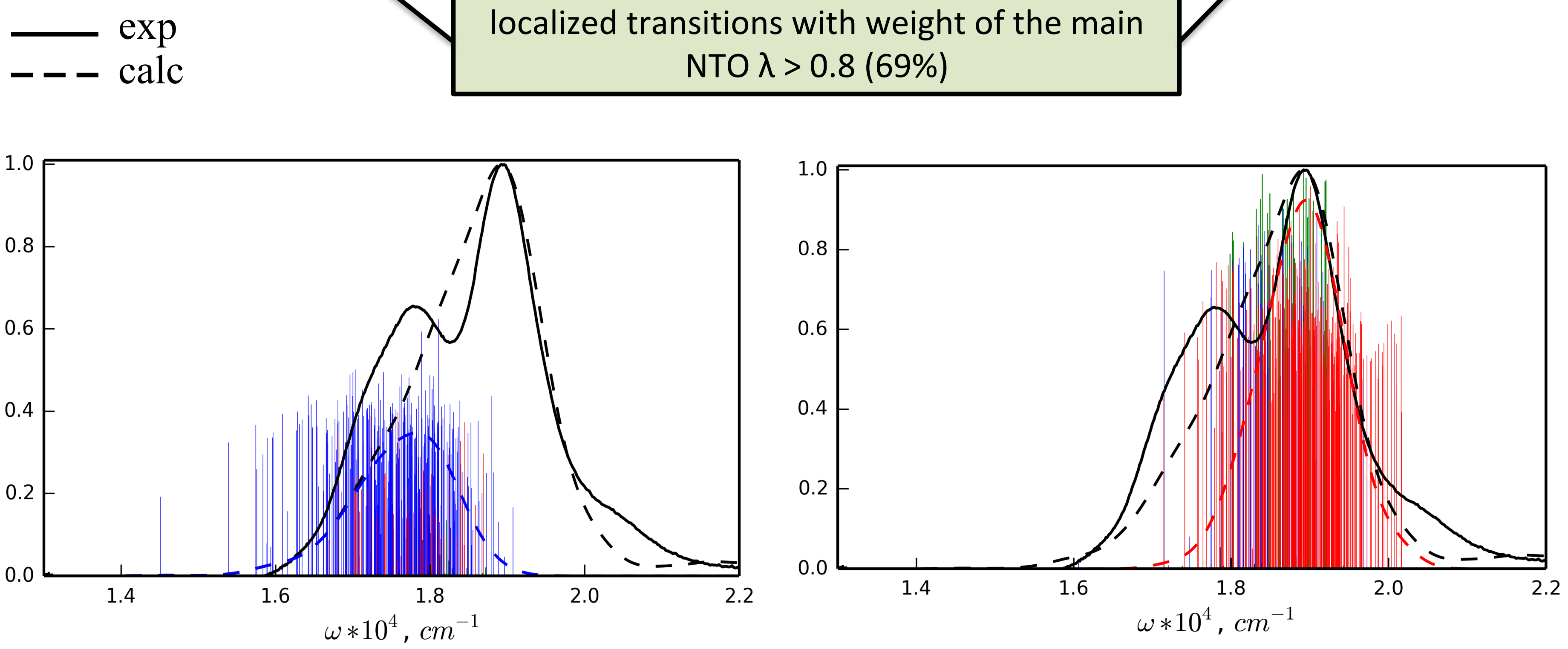
Calculation of NTO weights

Excluding pure charge-transfer states among the two lowest (1%)

delocalized transitions with weight of the main NTO λ < 0.8 (6.25%)

Excluding structures with the second transition is localized on RHO (23.5%)

localized transitions with weight of the main NTO λ > 0.8 (69%)



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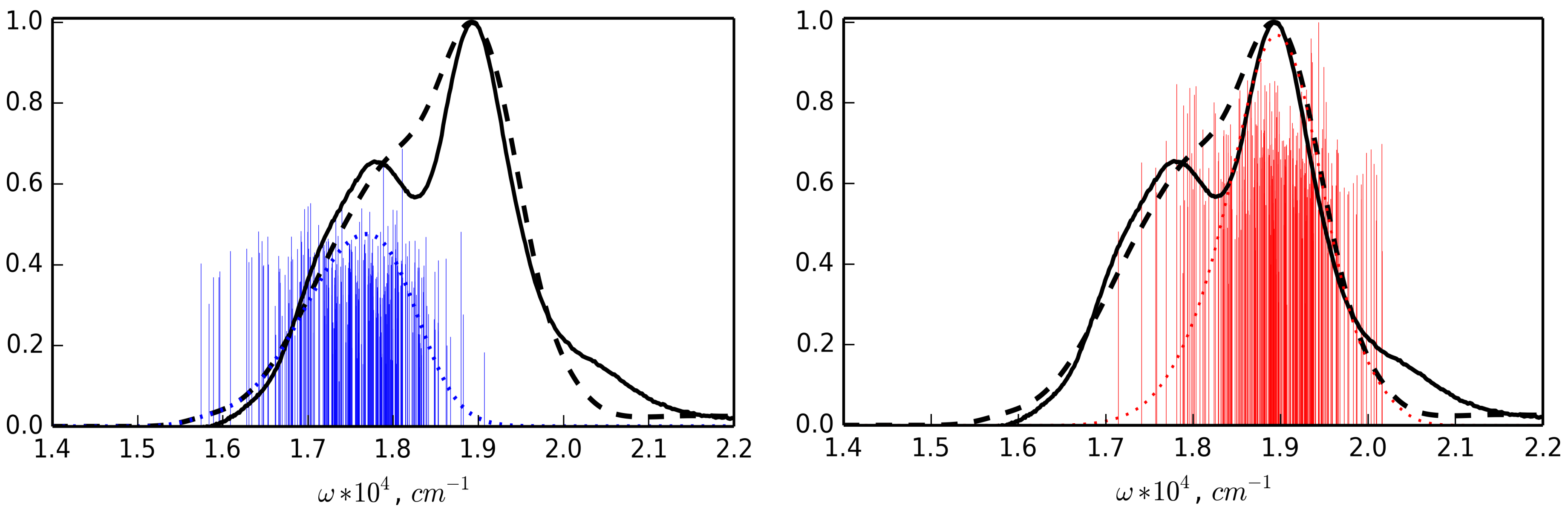
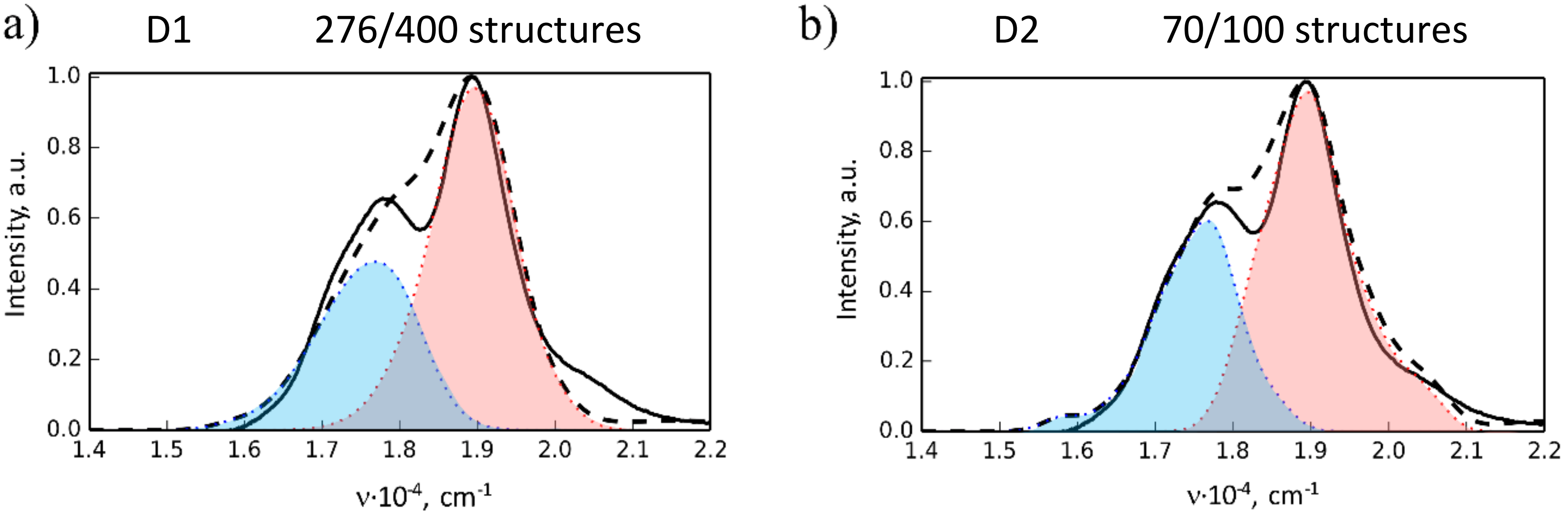


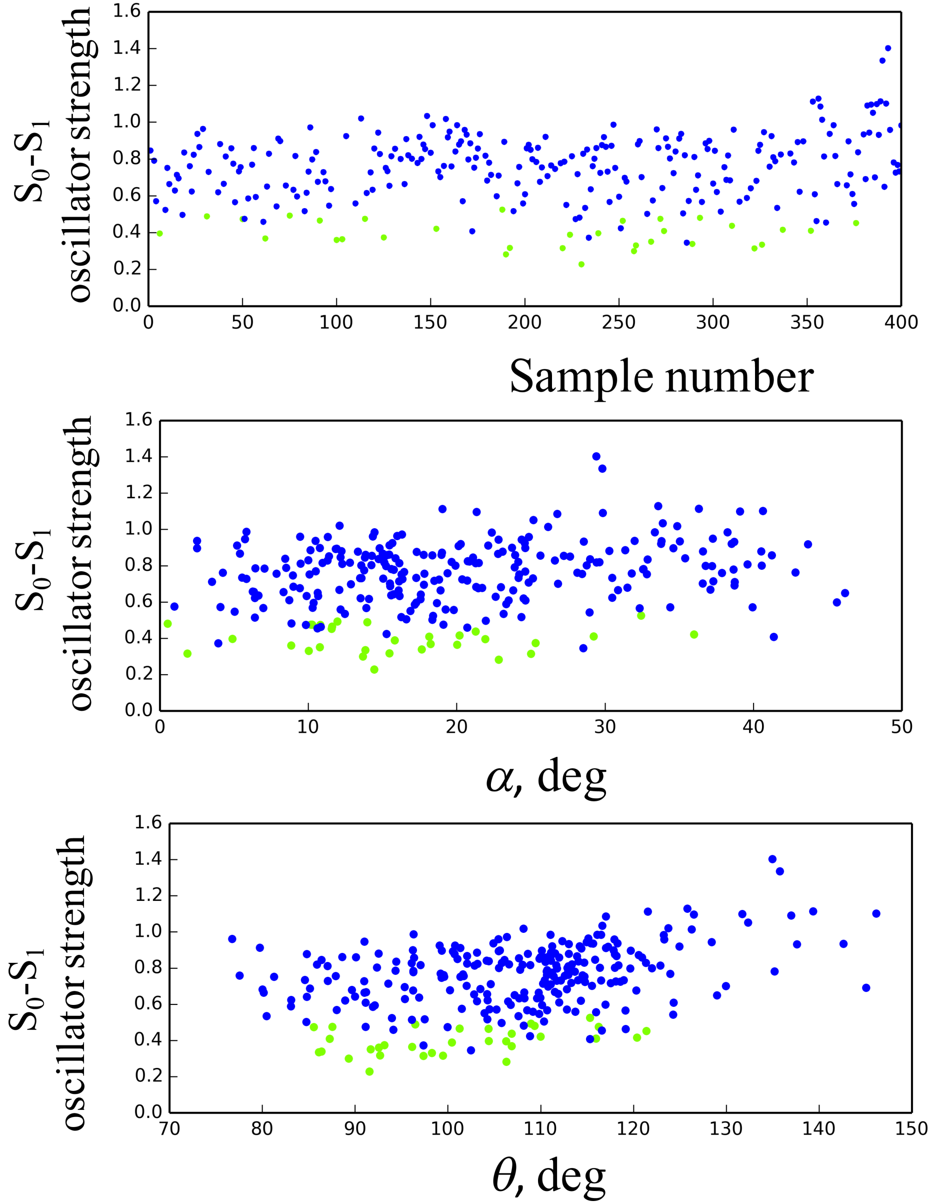
Total spectrum after NTO based sampling



The color corresponds to the localization subunit: RHO (blue), TAMRA (red)

The calculated profiles are shifted to the positions of the experimental maxima (D = -613 cm^{-1} and D = -456 cm^{-1} for the D1 and D2 isomers respectively).

Correlation between the intermolecular angles and oscillator strength of the S0-S1 transition of D1 along MD trajectory.



(Top row) The oscillator strengths *f* of the S_0-S_1 transition for the conformations sampled from the D1 MD trajectory as calculated for the group with localized transitions only (276 samples). The sample number assigned sequentially for the 8ns MD trajectory with 20 ps step (400 samples in total).

(Middle row) Correlation between the angle α between the polarization axes of the monomers and oscillator strength of the S_0-S_1 transition.

(Bottom row) Correlation of the angle θ between the polarization axis of RHO and line connecting the molecular centres in the RHO→TAMRA direction and oscillator strength of the S_0-S_1 transition

The color of the dots denote the weight w of the NTO on RHO, green: w = 80-90%, blue dots: 90-100%.

Conclusions

Conclusions

- Harmonic approximation is valid in the description of **high-frequency hard optically active** modes (S_2 absorption)
- For the **low-frequency** soft modes harmonic approximation can produce large errors

- The Lineshape for the D1A dimer is narrower compare to the experimental absorption spectrum. Significant increase of the broadening of the S_0-S_1/S_0-S_2 bands in D1B dimer is mainly due to its more flexible structure: great number of soft modes with n<100cm^{-1} contributes to its absorption profile .

- Nuclear-ensemble sampling technique is developed. It is better in reproducing S_1 absorption band

- The origin of the high intensity of the first band is coming from the large electronic transition dipole for the dimers with realistic relative orientation between the monomers, when sterical effects of the complex media on the ground state geometry of the dimer are explicitly taken into account.

THANK YOU FOR YOUR ATTENTION

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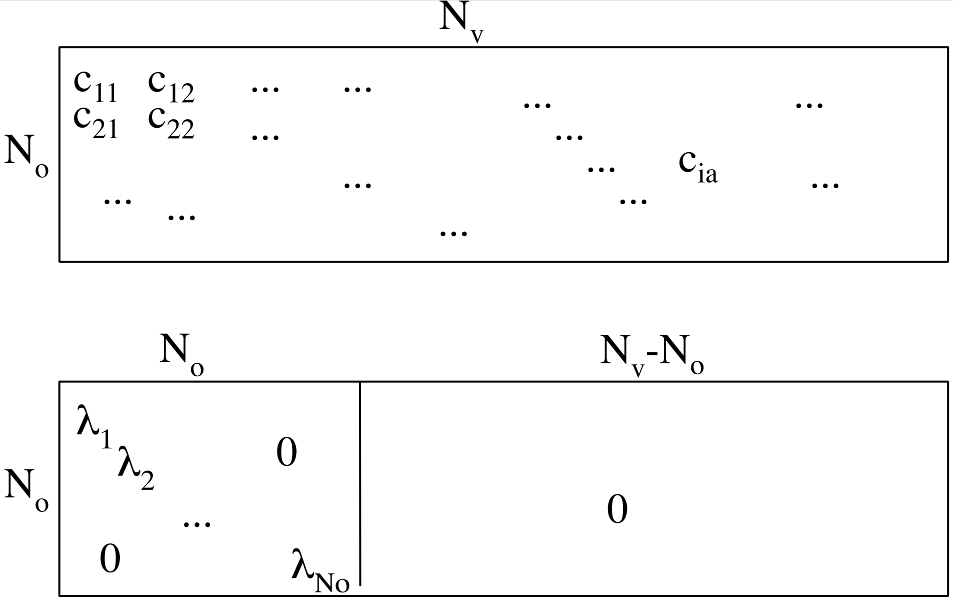
Natural Transition Orbitals (NTO)

- Form transition density matrix **T**:
  the physically relevant quantity.
  $T_{ia} = \langle \Psi_{ex} | c_i^{+} c_a | \Psi_0 \rangle$



- Diagonalize $T T^{\dagger}$ and $T^{\dagger}T$ to obtain occupied and virtual NTOs

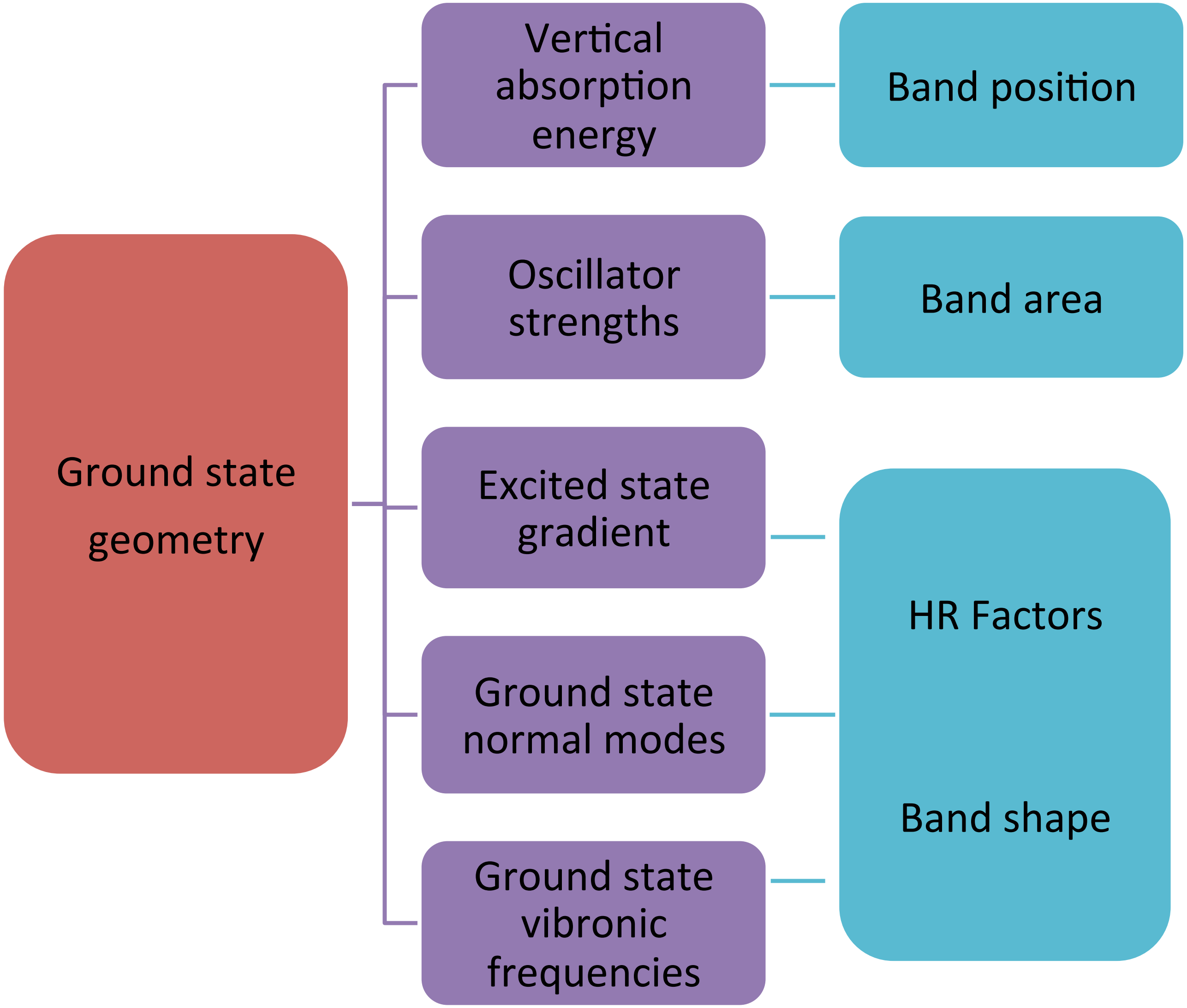
$$T T^{\dagger} U_i = \lambda_i U_i \quad i = 1, n_{occ}$$
$$T^{\dagger}T \; V_i = \lambda_i V_i \quad i = 1, n_{virt}$$

- Each occupied orbital is paired with single virtual orbital; the transition density is unchanged; the magnitude of λ shows how important it is to the transition.

“particle” NTO → “hole” NTO $\lambda = \ldots$

R.L. Martin, JCP **118**, 4775 (2003). Batista and Martin, Encyclopedia of Computational Chemistry, 2004.

The flow chart of the lineshape calculations



Ground state geometry

Vertical absorption energy

Oscillator strengths

Excited state gradient

Ground state normal modes

Ground state vibronic frequencies

Band position

Band area

HR Factors

Band shape

Simulation of the absorption band based on Lax's model

$$I_{total}\left(\Omega\right) = \sum_i w_i \sum_b f^i_{ab} I^i_{ab}\left(\Omega\right)$$

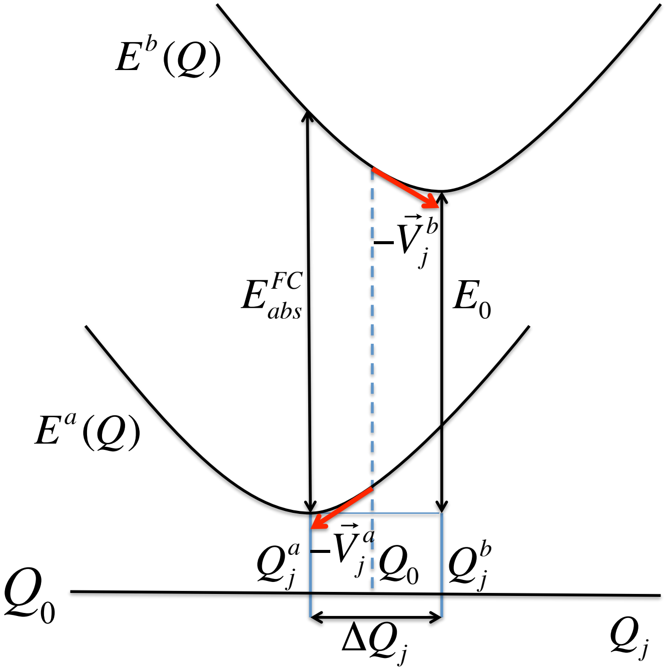
$w_i = \exp\left(-\Delta E_i / k_B T\right) \Big/ \sum_j \exp\left(-\Delta E_j / k_B T\right)$ the fraction of conformer (i)

$I^i\left(\Omega\right) = \sum_b f^i_{ab} I^i_{ab}\left(\Omega\right)$ f^i_{ab} oscillator strength

$I^i_{ab}\left(\Omega\right)$ Intensity of transition $a \to b$

$I_{ab}(\Omega) = \dfrac{1}{2\pi} \int_{-\infty}^{+\infty} \exp(-i\Omega t) G_{ab}(t)\, dt$ Intensity of individual transitions

$$G_{ab}(t) = \exp\left(i\Omega_0 t - \sum_j S_j \left[(2\bar{n}_j + 1)(1 - \cos\Omega_j t) - i \sin\Omega_j t \right] \right)$$



Ω_0 0-0 transition frequency $E_0 = \hbar\Omega_0$

Q_j harmonic normal modes laying close to the initial conf. Q_0

Ω_j vibrational frequencies

$S_j = \Omega_j \Delta Q_j^2 / 2\hbar$ dimensionless Huang–Rhys (HR) parameters

$V^{a,b}_j = \partial E^{a,b} / \partial Q_j$ gradients of potential surfaces along normal modes at initial configuration

$\Delta Q_j = -(V^b_j - V^a_j)/\Omega^2_j$ origin shift in the normal coordinates

$\bar{n}_j = \left[\exp\left(\hbar\Omega_j / k_B T\right) - 1\right]^{-1}$ the Planck's distribution

Simulation of the absorption band based on Lax's model

$$I_{total}(\Omega) = \sum_i w_i \sum_b f^i_{ab} I^i_{ab}(\Omega)$$

$w_i = \exp\left(-\Delta E_i / k_B T\right) \Big/ \sum_j \exp\left(-\Delta E_j / k_B T\right)$ the fraction of conformer (i)

$I^i(\Omega) = \sum_b f^i_{ab} I^i_{ab}(\Omega)$ f^i_{ab} oscillator strength

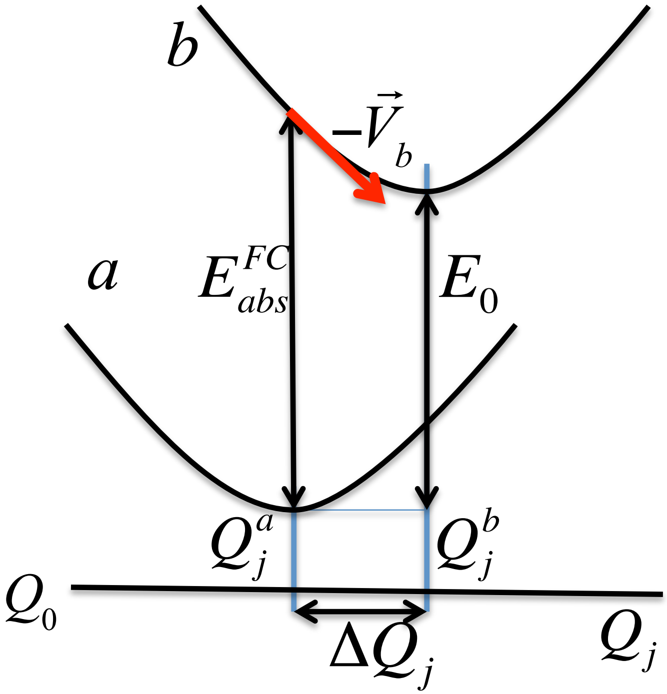
$I^i_{ab}(\Omega)$ Intensity of transition $a \to b$

$$I_{ab}(\Omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \exp(-i\Omega t) G_{ab}(t)\, dt$$

$$G_{ab}(t) = \exp\left(i\Omega_0 t - \sum_j S_j \left[(2\bar{n}_j + 1)(1 - \cos\Omega_j t) - i \sin\Omega_j t \right] \right)$$

Ω_0 0-0 transition frequency $E_0 = \hbar\Omega_0$

Q_j harmonic normal modes laying close to the initial conf.



Ω_j vibrational frequencies

$S_j = \Omega_j \Delta Q_j^2 / 2\hbar$ dimensionless Huang–Rhys (HR) parameters

$V^{a,b}_j = \partial E^{a,b} / \partial Q_j$ gradients of potential surfaces along normal modes at initial configuration

$\Delta Q_j = -(V^b_j - V^a_j) / \Omega^2_j$ origin shift in the normal coordinates

$\bar{n}_j = \left[\exp\left(\hbar\Omega_j / k_B T\right) - 1 \right]^{-1}$ the Planck's distribution