# Solvent-Enhanced Symmetry-breaking and Singlet-Fission in the Covalently-Bound Tetracene Dimer

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## Singlet fission (SF)

- Fascinating process to enhance the efficiency of single junction solar cells beyond the Shockley-Queisser limit because of the capability of generating **two low energy triplet excitons from each absorbed photon**
- SF is usually based on organic materials with attractive low-weight properties and good processability

The SF process is defined as the conversion of a singlet excited state into two triplet excitons located on two separate monomers **in an overall spin-allowed process**

$$S^* \rightarrow T_1 + T_1$$

This creates two pairs of charge carriers from a single photon. The triplet excitons have a significantly longer lifetime than singlet excitons due to spin selection rules. The long triplet exciton diffusion lengths facilitate the migration and dissociation of the triplet pair.

The process of singlet fission is frequently described as the sequence of two consecutive steps by starting from the lowest excited singlet state $S_1$ of a chromophore

$$S_1 \rightleftharpoons {}^1TT \rightleftharpoons T_1 + T_1$$

The initial photo absorption is followed by the formation of an **intermediate state**, denoted as the **singlet fission precursor**. Its electronic structure is prepared for the separation into two triplet states in the subsequent reaction step. **This is a spin-allowed process.**

Two energetic conditions are usually formulated to assess the feasibility of a compound for singlet fission:

For spontaneous SF to proceed, the energy of $S_1$ must be equal or higher than twice the lowest triplet energy, i.e.:

$$E\left(S_1\right) \geq 2E\left(T_1\right)$$

It has been found that a too exoergic deactivation process slows down the process of SF. Moreover, it would also result in energy loss due to heating of the system. Optimal energetic situations are achieved when the $S_1$ state is located only slightly above twice the energy of the $T_1$ state.

To make the SF process efficient, alternative deactivation channels, such as the recombination of the SF triplets to a higher triplet or quintet state must be suppressed.

$$\mathrm{T}_1 + \mathrm{T}_1 \rightarrow \mathrm{T}_2$$

$$\mathrm{T}_1 + \mathrm{T}_1 \rightarrow \mathrm{Qt}_1$$

Suppression of the triplet-triplet combination is achieved by the second criterion

$$E(\mathrm{T}_2) > 2E(\mathrm{T}_1)$$

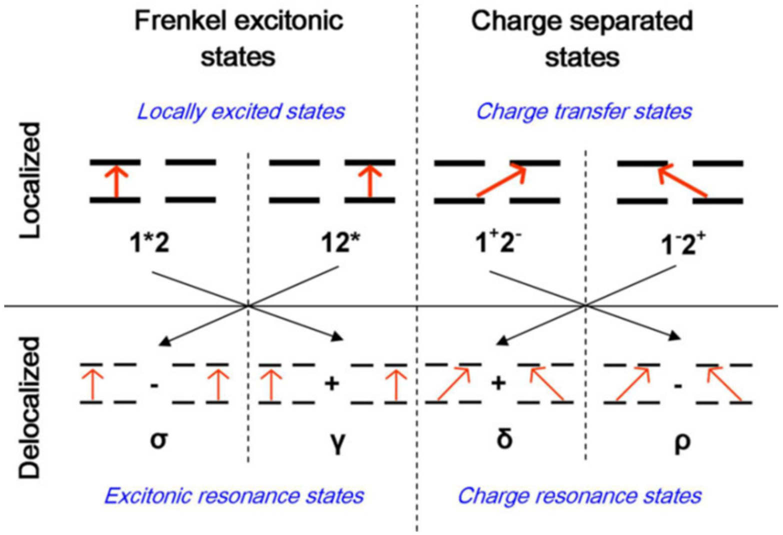
since the $T_2$ state lies higher than the two lowest triplets. The quintet state lies usually quite high in energy and the condition $E(\mathrm{Qt}_1) > 2E(\mathrm{T}_1)$ is easily fulfilled.

Various organic materials are available, mostly based on polycyclic aromatic hydrocarbons (PAHs), such as **6,13-bis(triisopropylsilylethynyl) pentacene (TIPS-Pn)** molecules in the solid state

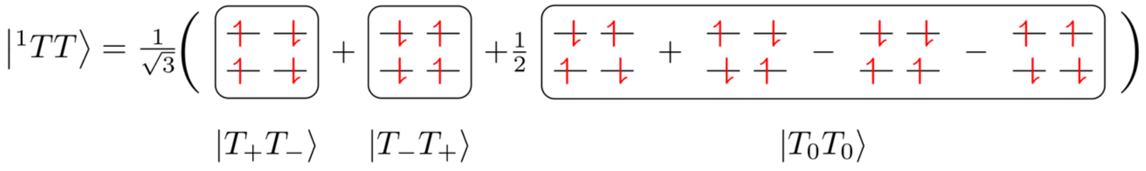
In recent years, an alternative approach has been found that is based **covalently bound dimers of pentacene or tetracene in solution**
Advantage: **better tunability through solvent polarity**
**Note: Molecular processes can be more complicated**!

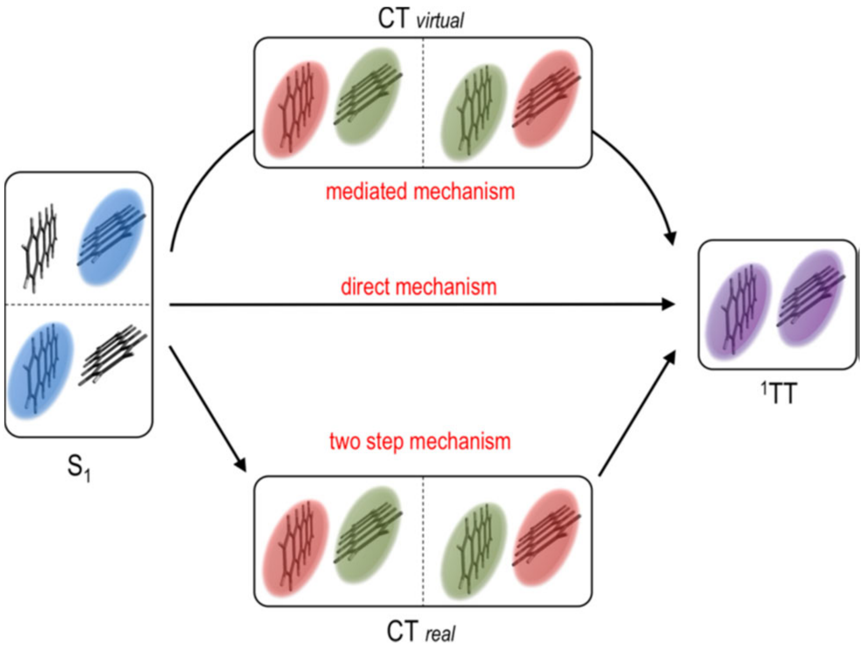
## Electronic states involved in the molecular processes of the covalent dimers:

1. Excitonic states
2. Charge transfer states



3. $^1$TT (singlet coupled triplet states)

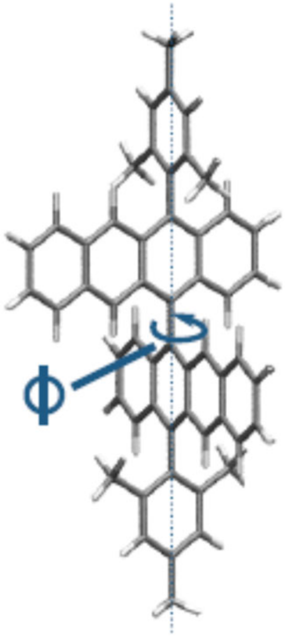




D. Casanova, Chem. Rev. 118, 7164 (2018)

State types 1 and 2 can be treated with popular standard methods such as TDDFT or ADC(2), which are based on single excitations

The $^1$TT state is more complicated and requires some kind of multireference approach



- Photodynamics of SF in the **mesityl-tetracene dimer (DT)** by Musser et al. (J. Am. Chem. Soc. 2019, **141**, 17558−17570) using transient absorption spectroscopy and empirical models based on a parametrized **diabatic Hamiltonian**
- Our goals: non-parametrized ab initio calculations, including solvent effects, survey of potential energy surfaces (curves) for selected vibrational modes ⇒ overview of the photodynamical processes

(R. S. Mattos, I. Burghardt, A. J. A. Aquino, Th. M. Cardozo, H. Lischka, J. Am. Chem. Soc. 2022, 144, 23492−23504)

# Computational Methods

For the LE and CT states:

- Second-order Algebraic Diagrammatic Construction (ADC(2))
- Resolution of the identity (RI)
- Solvent effects using the conductor-like screening model (COSMO)

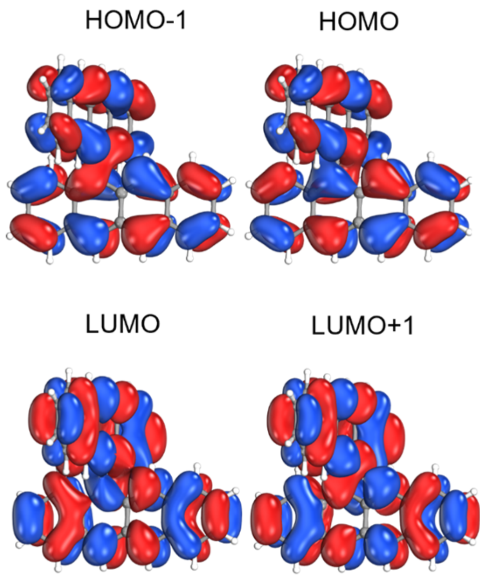
For the $^1$TT state: DFT/MRCI with CAS(6,6) reference space restricted to double excitations

Basis set SV(P)

Programs: Turbomole 7.5 and the DFT/MRCI program by Marian, Heil and Kleinschmidt based on the work by Grimme and Waletzke

Analysis of transition densities is performed with TheoDORE (analysis of transition density matrices)

# Orbital Excitations



| | Orbitals | ADC(2) | DFT/MRCI |
|---|---|---|---|
| LE$_1$ | H → (L+1) | 51.5% | 43.3% |
| | (H-1) → L | 46.0% | 39.1% |
| LE$_2$ | H → L | 53.8% | 47.4% |
| | (H-1) → (L+1) | 43.4% | 33.7% |
| CT$_1$ | (H-1) → (L+1) | 53.3% | 47.5% |
| | H → L | 42.5% | 33.9% |
| CT$_2$ | (H-1) → L | 50.8% | 42.4% |
| | H → (L+1) | 45.1% | 38.2% |
| $^1$(TT) | (H-1) + H → L + (L+1) | | 42.0% |
| | 2* H → 2*L | | 10.5% |
| | 2*(H-1) → 2*(L+1) | | 10.0% |

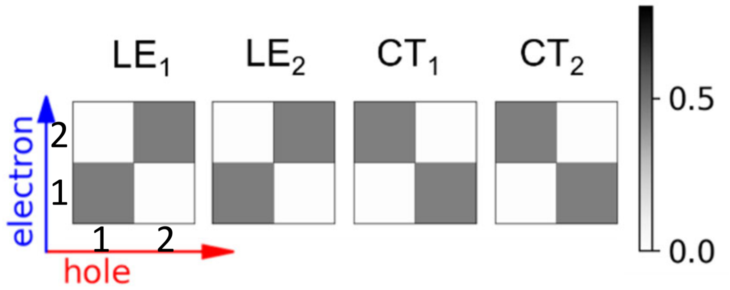
# Analysis of Electronic States

$$\Omega^{\alpha}_{AB} = \frac{1}{2}\sum_{\substack{a\in A\\ b\in B}}\left(D^{0\alpha.[AO]}S^{[AO]}\right)_{ab}\left(S^{[AO]}D^{0\alpha.[AO]}\right)_{ab}$$

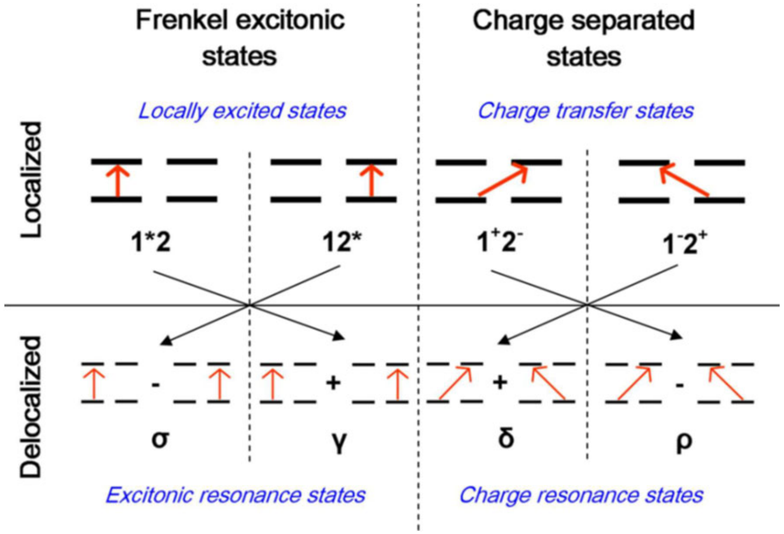
$$q(\mathrm{CT}) = \frac{1}{\Omega^{\alpha}}\sum_{A}\sum_{A\neq B}\Omega^{\alpha}_{AB}$$

$$\Omega^{\alpha} = \sum_{A,B}\Omega^{\alpha}_{AB}$$

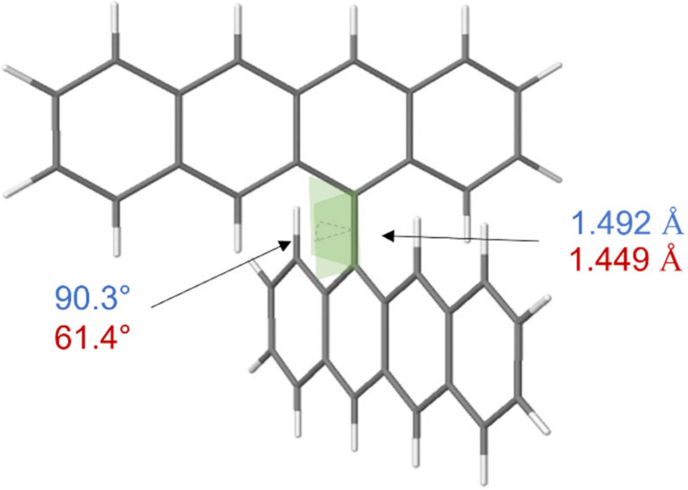
Two segments: each tetracene is one segment



Excitonic resonance and CT resonance states



# Characterization of Vertical Excitations



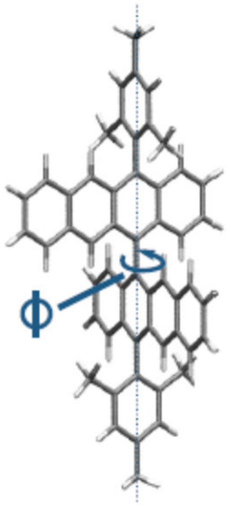
Ground-state geometry: blue
$S_1$ geometry: red
$C_2$ symmetry

Gas phase

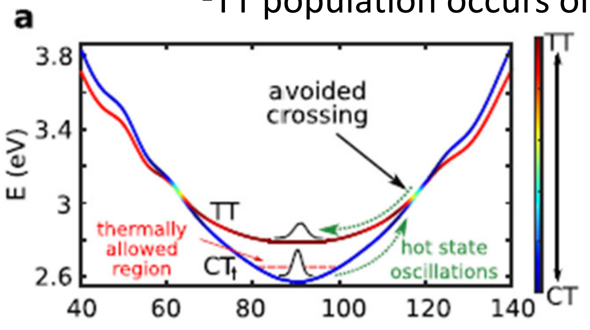
| | ADC(2) (f) | qCT (ADC(2)) | DFT/MRCI (f) | qCT (DFT/MRCI) | Exp. |
|---|---|---|---|---|---|
| **LE$_1$ (B)** | 2.93 (0.30) | 0.03 | 2.52 (0.33) | 0.03 | 2.48$^a$ |
| **LE$_2$ (A)** | 2.99 (0.00) | 0.03 | 2.62 (0.00) | 0.03 | -- |
| **CT$_1$ (B)** | 3.19 (0.00) | 0.95 | 2.74 (0.00) | 0.95 | 2.75$^b$ |
| **CT$_2$ (A)** | 3.19 (0.00) | 0.95 | 2.75 (0.00) | 0.96 | -- |
| **$^1$(TT) (A)** | -- | -- | 2.92 (0.00) | -- | 3.0$^c$ |

Exp.: Musser et al. J. Am. Chem. Soc. 2019, 141 (44), 17558

$^a$ Nonpolar solvent, $^b$ Extrapolated to the vacuum, $^c$ Twice the energy of the first triplet excitation.

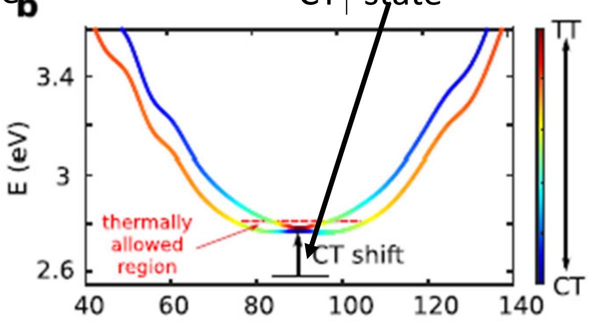


$^1$TT population occurs only here



Nonpolar solvent

Solvent destabilization of the CT↑ state



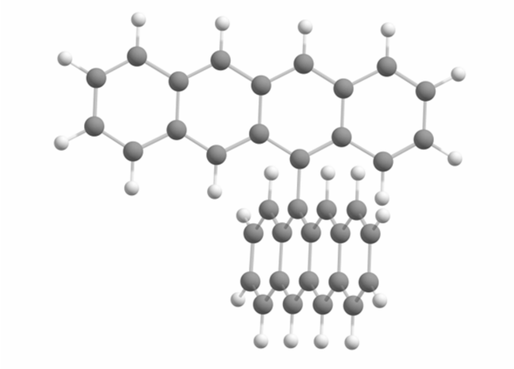
Polar solvent

- Singlet fission appears only above a threshold of 2.8 eV
- The $^1$TT state is never formed directly from the bright LE$_1$(B) state, but involves always a preceding CT state
- For polar solvents, singlet fission is mediated by destabilized upper gateway state (**CT$_\uparrow$**), the $^1$TT and **CT$_\uparrow$** states are close in energy (coherent singlet fission)
- The splitting of the two CT states, CT$_\downarrow$ and CT$_\uparrow$, comes from **antisymmetric fluctuations of solvent**.

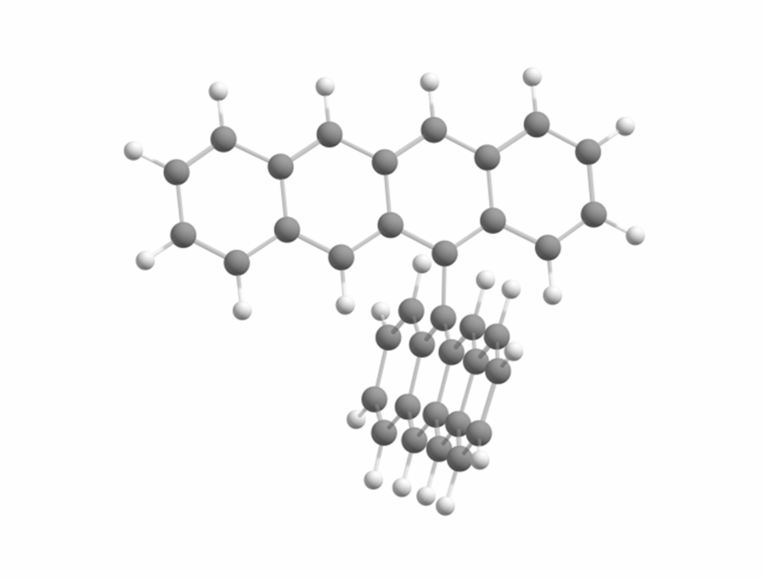
A. M. Alvertis, St. Lukman, T. J. H. Hele, E. G. Fuemmeler, J. Feng, J. Wu, N. C. Greenham, A. W. Chin, A. J. Musser, J. Am. Chem. Soc. 2019, **141**, 17558−17570

Are really only the solvent fluctuations responsible for the antisymmetric environment? How does the molecular structure respond? Will it actually stay symmetric?

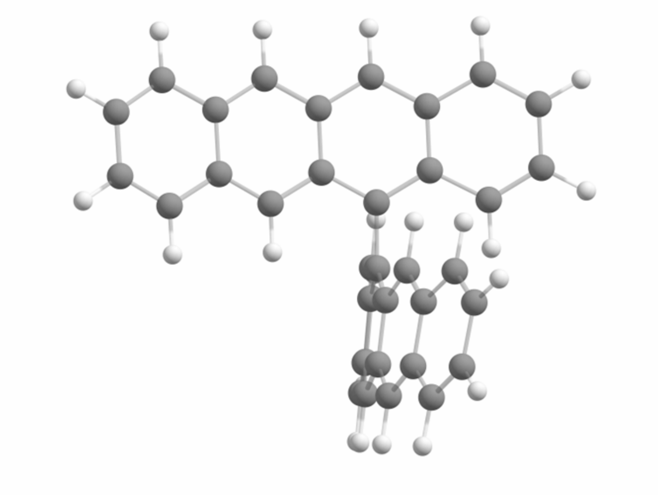
# Normal Modes



**Mode 1 (A): 7.9 cm$^{-1}$**

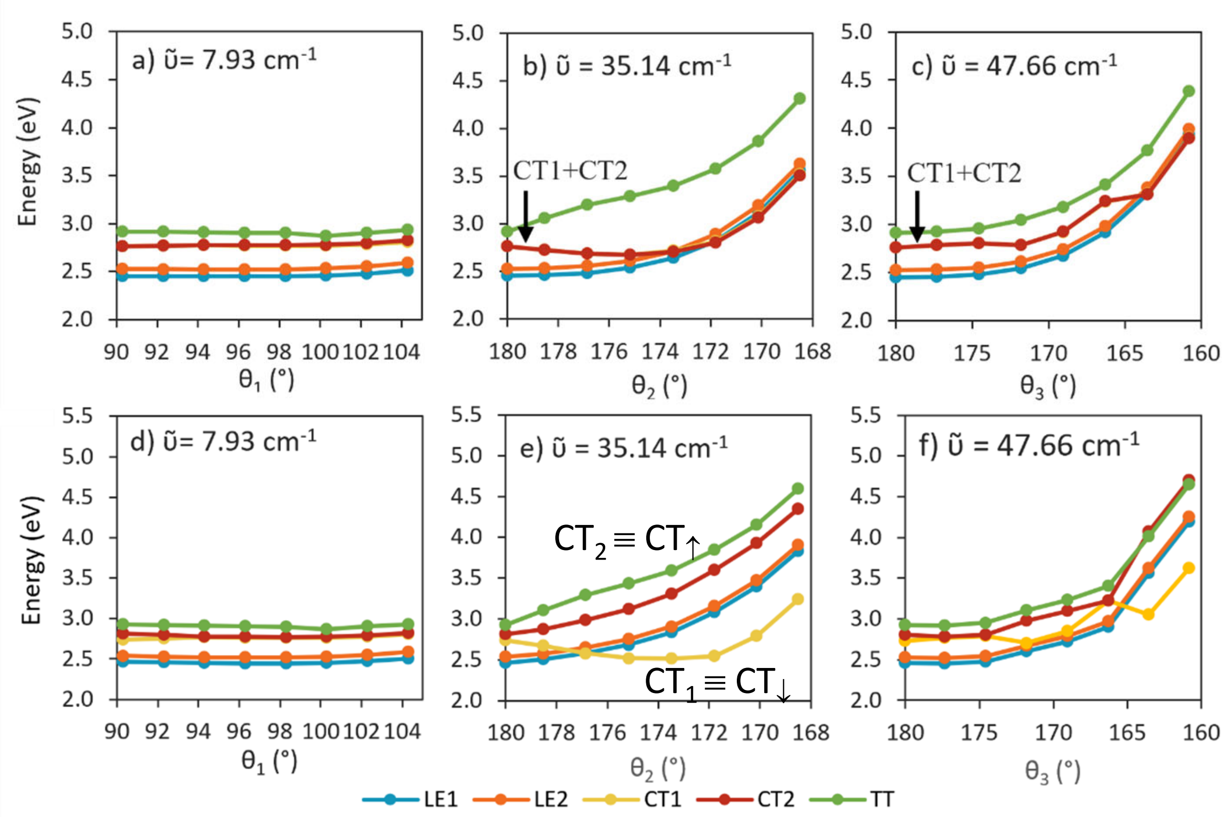


**Mode 3 (B): 35.1 cm$^{-1}$**



**Mode 4 (B): 47.7 cm$^{-1}$**

# The Coupling of the State Electronic Structure and the Solvent Structure



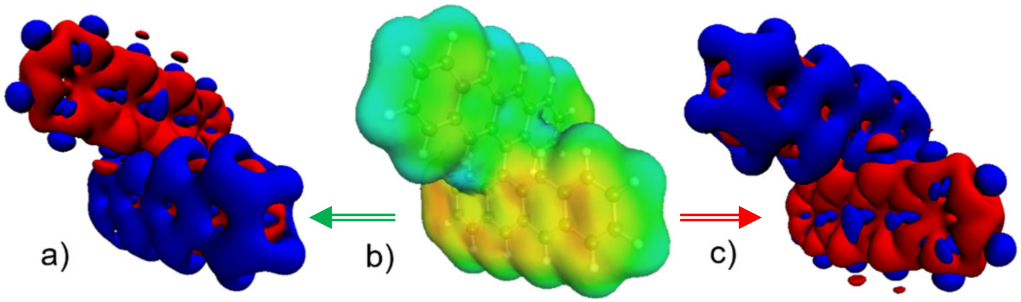
Solvent o-dichlorobenzene (o-DCB)

**Solvent equilibration for the ground state**, similar for $S_1$ state

**Solvent equilibration for the $CT_1$ state**, splitting of the two states, one is stabilized by the solvent, the other one is destabilized

The symmetric ($C_2$) $CT_1$ structure is **instable** and will stabilize by an antisymmetric distortion (mode 3)

# Solvent Stabilization/Destabilization by Antisymmetric Mode



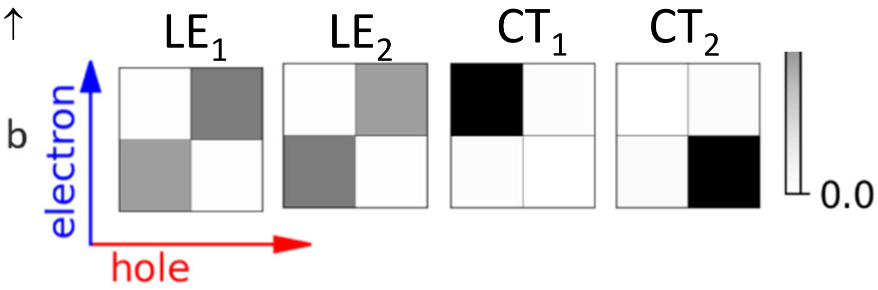
Density difference for CT$_1$ (CT$_\downarrow$) state

Density difference for CT$_2$ (CT$_\uparrow$) state

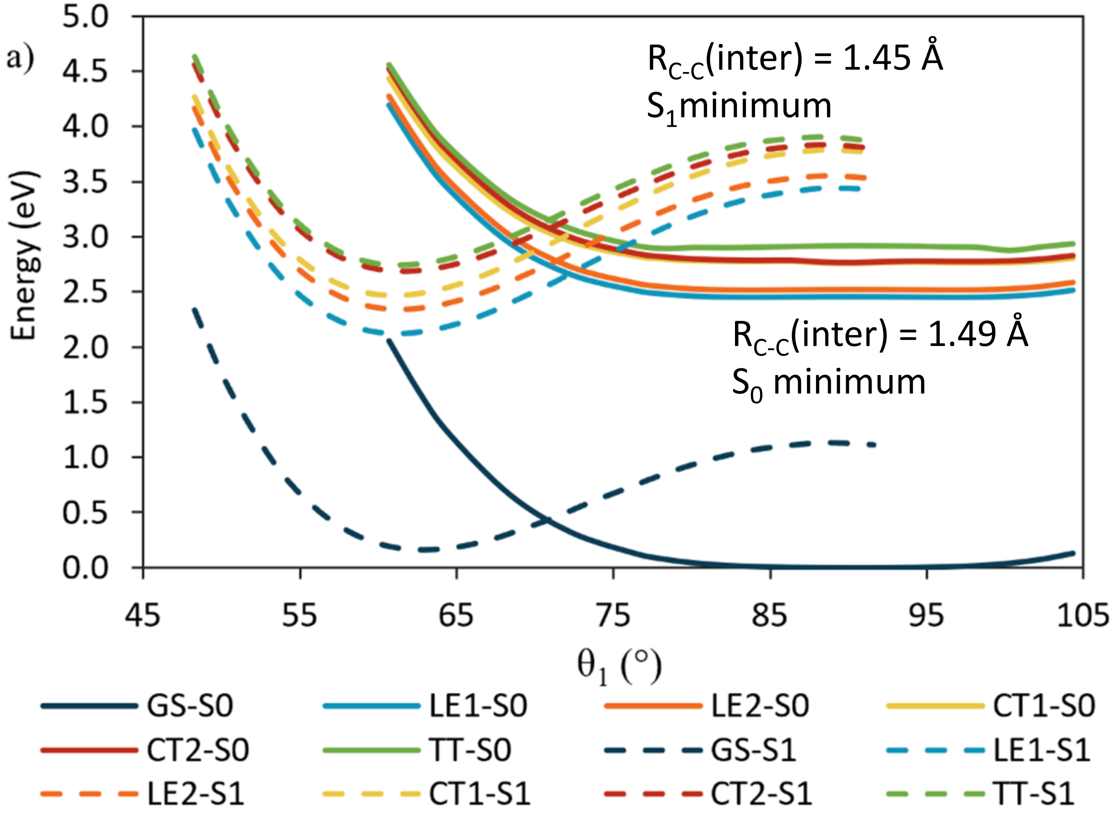
solvation charge distribution **optimized for the CT1 state**

For a) and c): isovalues -0.0005 e/bohr$^3$ (blue) and 0.0005 e/bohr3 (red)
For b): 1.08 e/nm$^2$ (yellow to reddish) to -1.00 e/nm$^2$ (aqua to green)

CT$_1$ is occupied, leads to **stabilization** through the solvent $\Rightarrow$ CT$_\downarrow$, at the same time CT$_2$ is **destabilized** $\Rightarrow$ CT$_\uparrow$



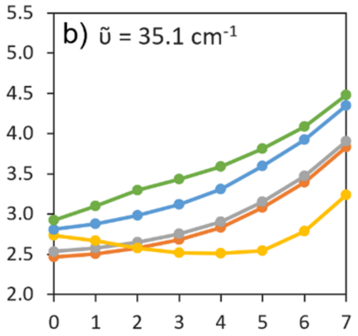
# $S_1$ Relaxation

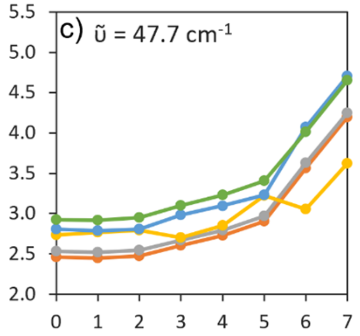


- Our analysis shows that **antisymmetric modes** play an important role for the creation of localized CT states; they are also important for the interaction between CT and the $^1$(TT) state (leading to singlet fission)
- Solvent stabilization based on solvent equilibration for the CT state, in combination with antisymmetric distortions, leads to the formation of a $CT_{\downarrow}$/ $CT_{\uparrow}$ pair; the $CT_{\downarrow}$ state is **instable at the symmetric $C_2$ geometry**, and will, consequently, stabilize into a pronounced $S_1$ minimum, which can act as a trap for the photodynamics
- If the $CT_{\downarrow}$ state is alternatively formed by solvent fluctuations, it will also transform to the antisymmetric $S_1$ minimum because of the just-mentioned structural instability
- **Such charge localization processes are probably important in other cases such as donor-acceptor-donor compounds**

# Photodynamical Pathways for the Explanation of SF

1. Symmetric rotation of the two tetracenes around their connecting covalent bond (between $S_0$ and $S_1$ geometries) $\Rightarrow$ flattened and perpendicular structures, mixing of state characters in the former case, no separation of CT state energies
2. Antisymmetric distortion along mode 3, formation of an energy minimum for $CT_{\downarrow}$ leads to CT state production for all excess energies, formation of $^1$(TT) state not likely
3. Access of $^1$(TT) state and $CT_{\uparrow}$ via antisymmetric mode 4
4. Solvent fluctuations at the symmetric structure: can be important, but will lead to the same CT minimum since the di-tetracene structure is unstable to antisymmetric displacements





# Summary

- The relevant structural manifold is more complex than the symmetric intersegment torsion; several traps in the form of energy minima exist
- In particular, symmetry-distorted structures have to be considered
- For the energetic splitting, the polar solvent plays a crucial role stabilizing one localized CT state ($CT_{\downarrow}$), and destabilizing the other ($CT_{\uparrow}$)
- Under these conditions, the $CT_{\downarrow}$ structure in $C_2$ symmetry is instable on the energy surface and will be stabilized by an antisymmetric distortion
- These distortions will be supported by antisymmetric solvent fluctuations invoked in the experimental work
- The interaction between the $CT_{\uparrow}$ state and the $^1TT$ state appear also in our work as essential for the singlet fission process.

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