Singlet fission mechanism in carotenoids

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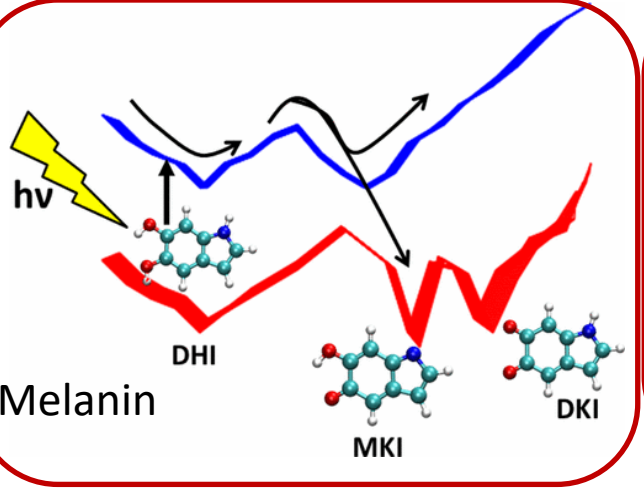
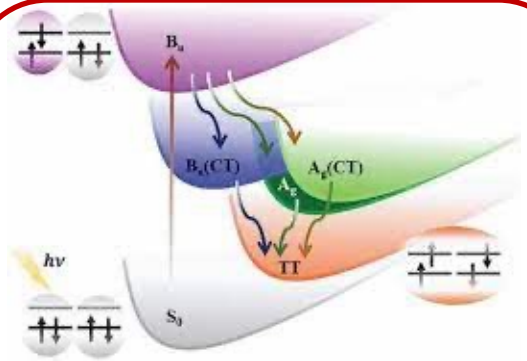
Indian Association for the Cultivation of Science



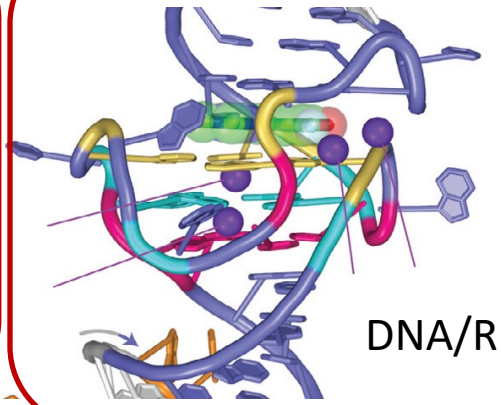
Melanin

J. Phys. Chem. B, 2017
Phys. Chem. Chem. Phys., 2018
WIREs Comput Mol Sci, 2020
Chem Comm, 2020
Chem Comm, 2024



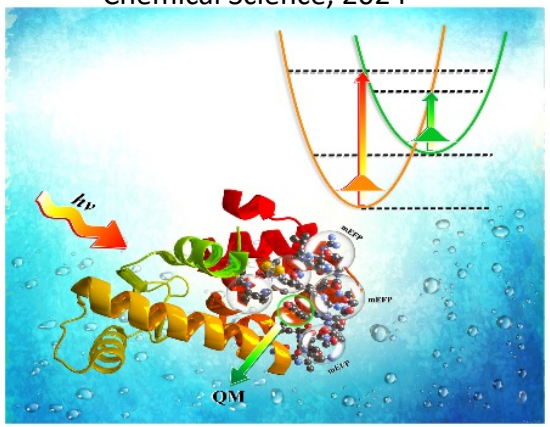
Singlet fission

J. Phys. Chem. Lett., 2022
J. Phys Chem. Lett, 2023
Chemical Science, 2024

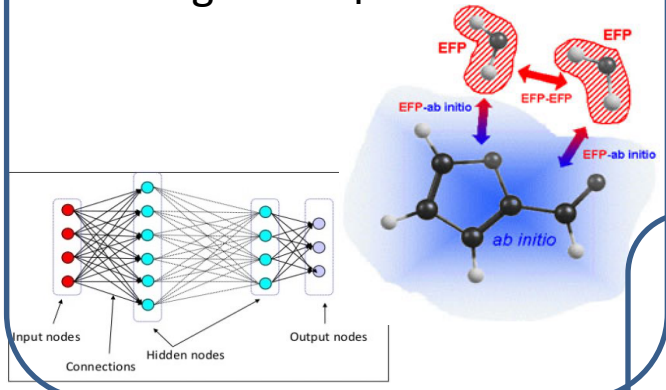


DNA/RNA

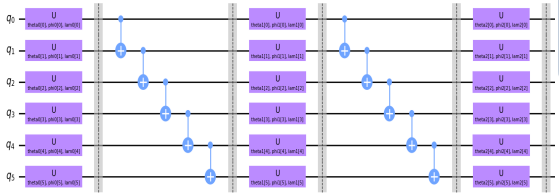
J. Phys. Chem. B, 2017
J. Phys Chem. B, 2018



Fragment and Machine learning based polarizable FF

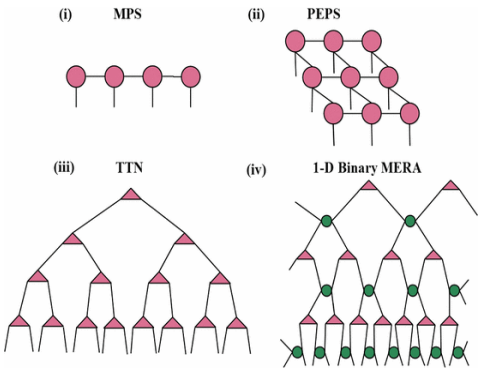


J. Comput. Chem., 2013
J. Chem. Phys., 2014
J. Phys. Chem. A, 2017
J. Phys. Chem. B, 2018



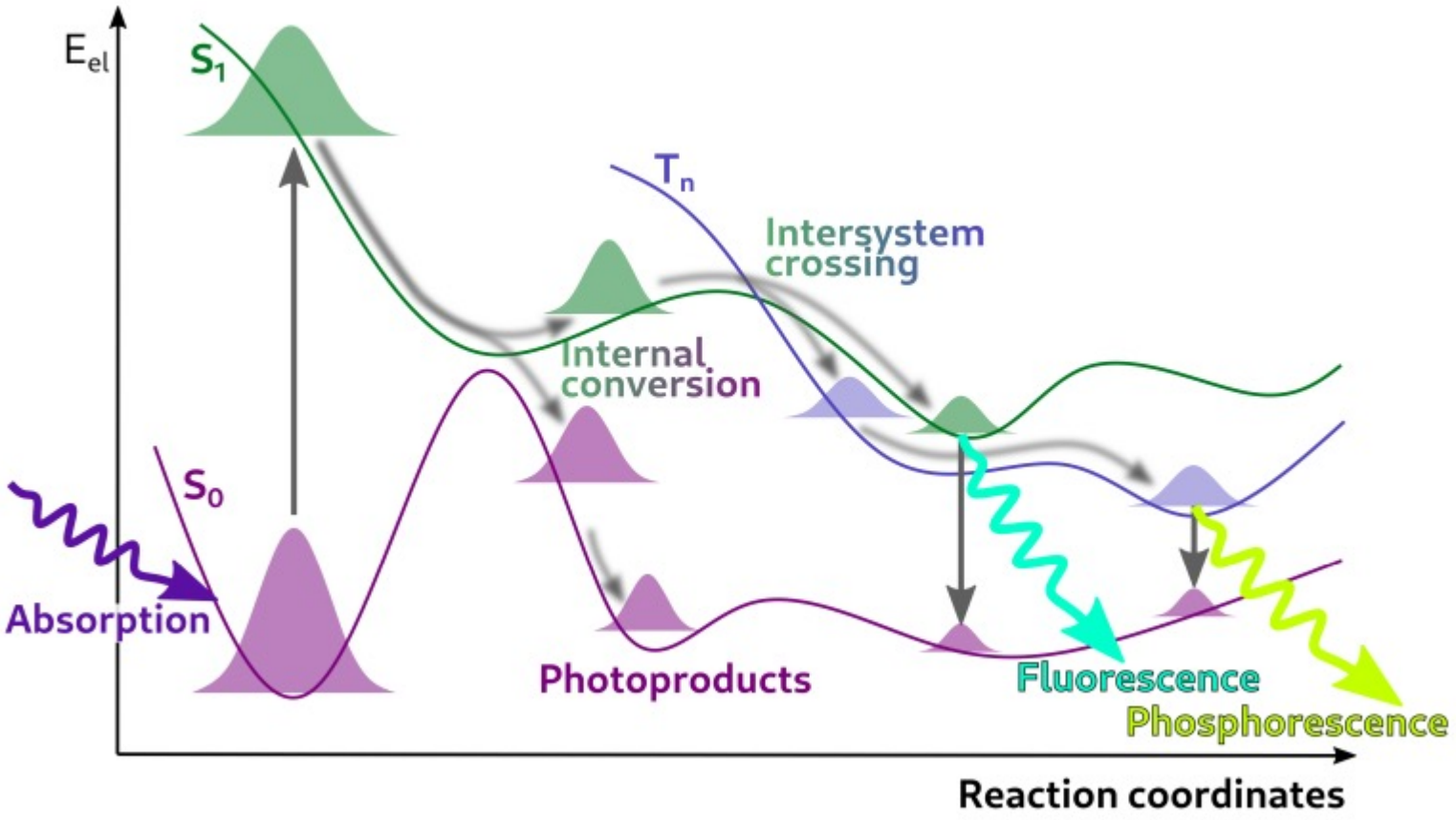
Quantum computers

Tensor product states



Chemical Science, 2019
Chemical Science, 2020
J. Chem. Phys,, 2021
J. Chem. Theory Comput, 2023

Excited state chemistry



Choudhury, Santra, **DG**, *J Chem Theory Comput.*, 2024, **20**, 4951.

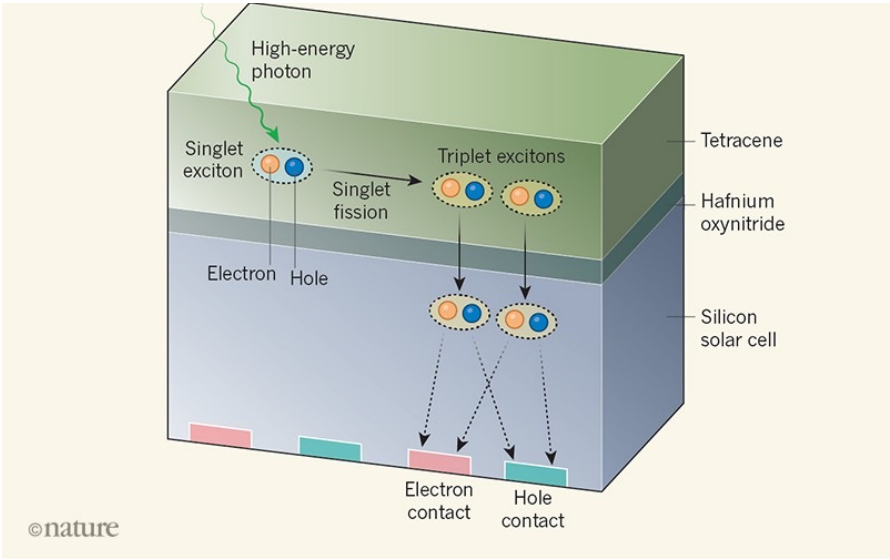
Singlet fission

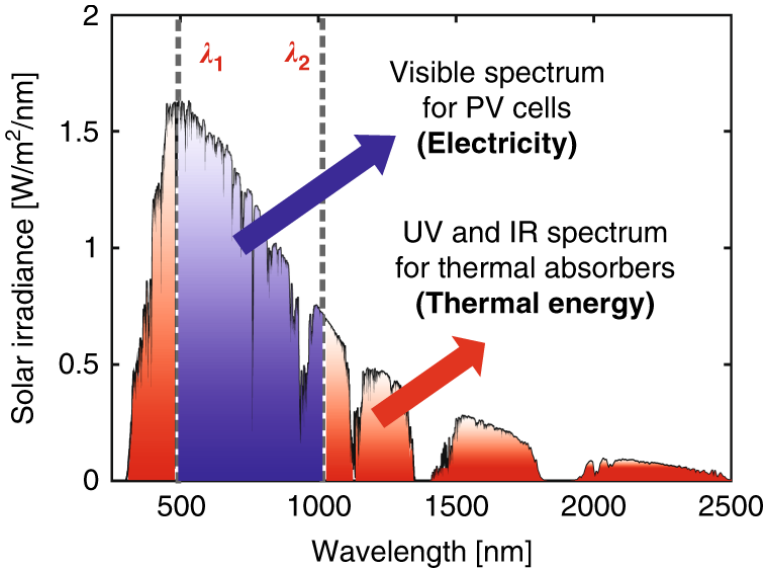
NEWS & VIEWS

ENGINEERING

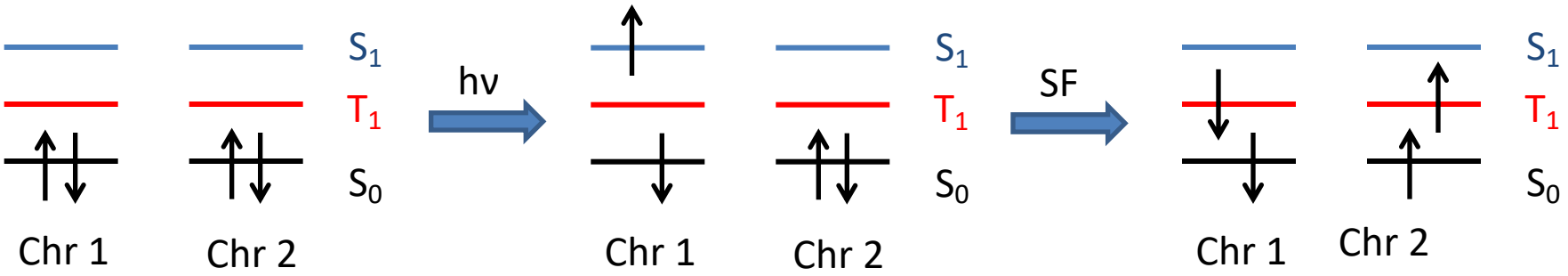
An exciting boost for solar cells

A process called singlet fission has the potential to enhance the efficiency of solar cells. The mechanism has been difficult to implement in such devices, but experiments demonstrate a way forward. SEE LETTER P.90





Singlet fission



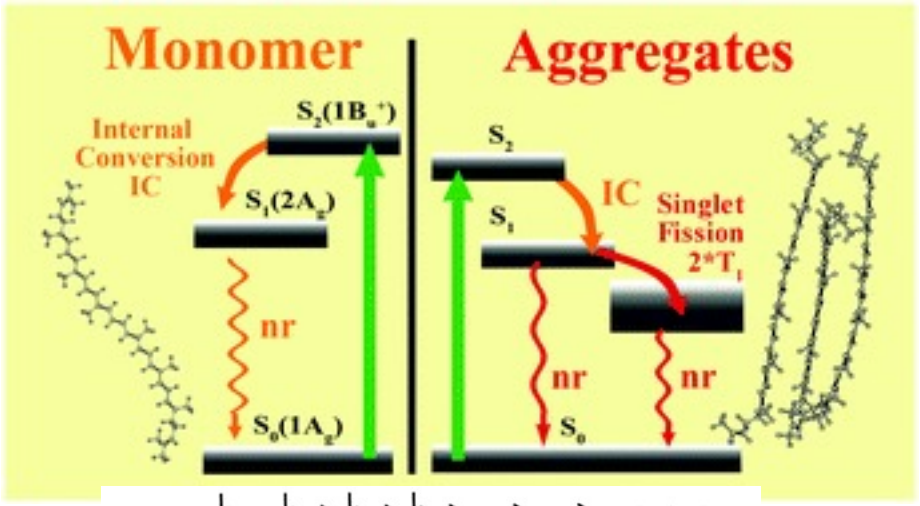
- Transforms a molecular singlet excited state into two excited triplet states.
- Each of the triplet states have half the energy of the singlet excited state.
- Spin allowed process.
- Mechanism of the process?
- Suitable SF materials?

Energy conservation

$$E(S_1 - S_0) \geq 2 \times E(T_1 - S_0)$$

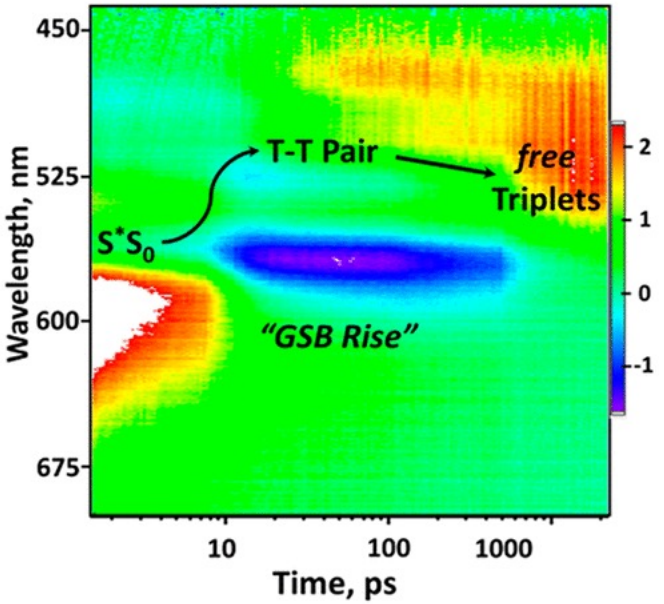
Singlet fission in carotenoids

- Singlet fission observed in H-aggregate structures of carotenoids.
- Not observed in non-polar J-aggregates
- Observed in polar J-aggregates



- Transient excited state absorption following excitation at 3.5 eV

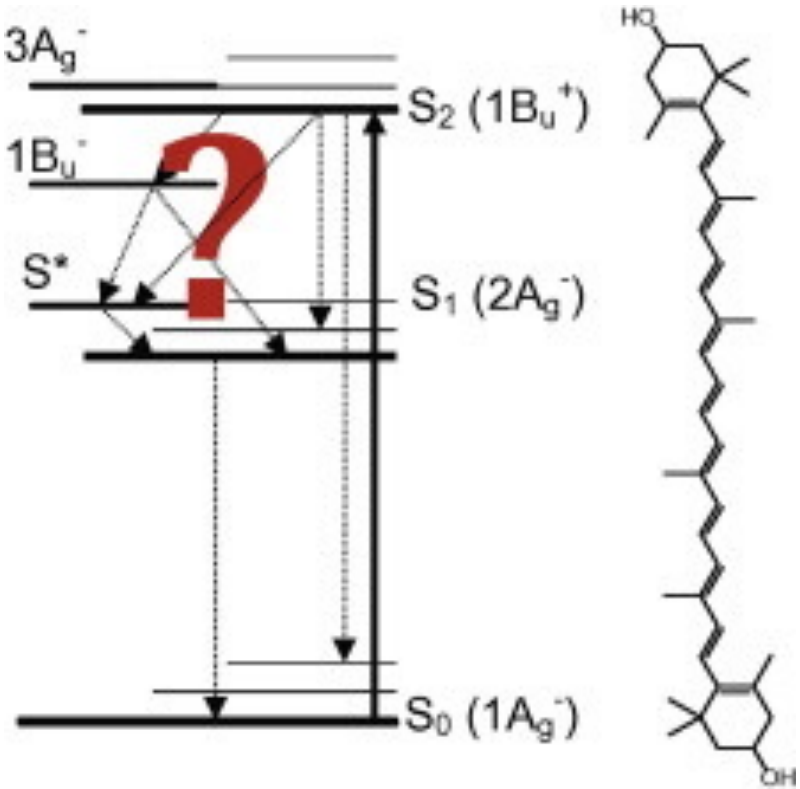
- Possible signature of dark A_g state on the way to singlet fission.

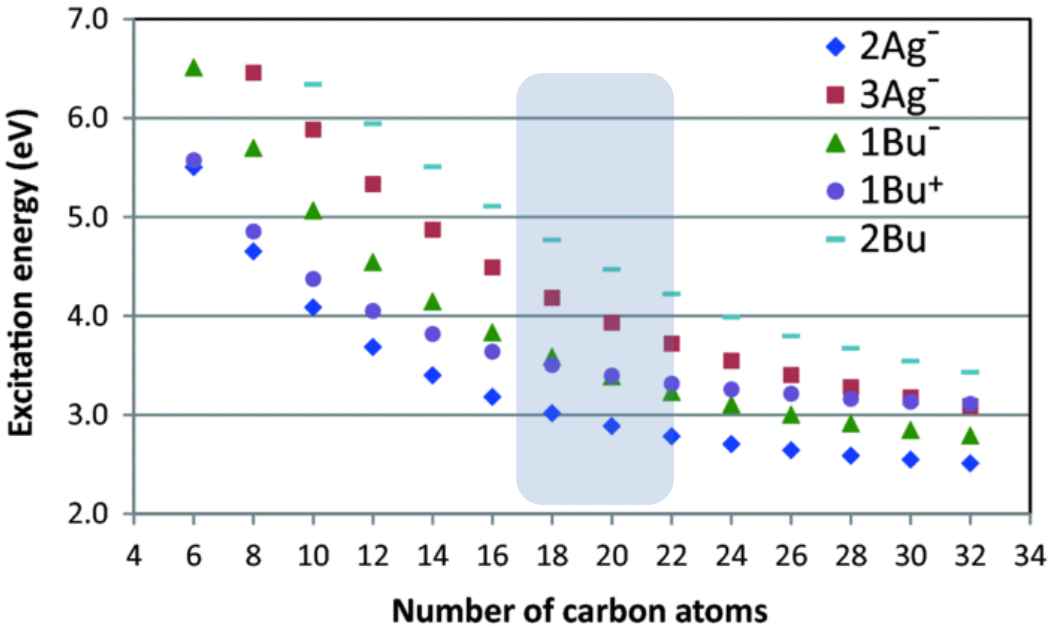


JACS, 137, 5130 (2015)
Dasgupta, JPCL, 12, 1468 (2021)

Carotenoids

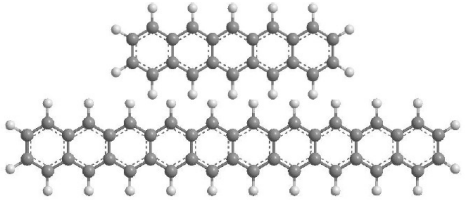
- No of states between the Bu and Ag?
- Tavan and Schulten proposed another S* state near the dark state.
- Finally, this confusion was put to rest by Yanai (2014).





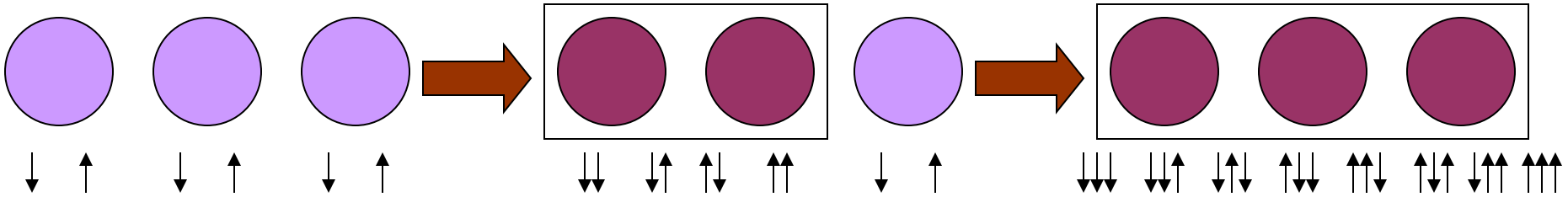
Chem Phys Lett, **477**, 1 (2009)
J Chem Phys, **141**, 174111 (2014)

Challenges in ST gap computation



- CSFs in the active (valence) space is an exponentially scaling problem.
- CSF space is large ~10^{33} for 30 π orbitals with 30 electrons
- For a matrix diagonalization of this size, one requires to perform 10^{99} operations.
- Comparison – No of atoms in universe is 10^{82}

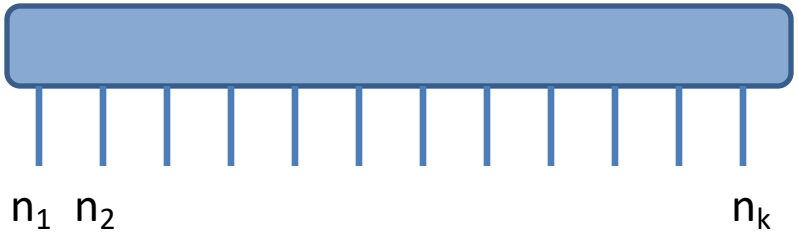
Exponential Hilbert space



2^N or d^N

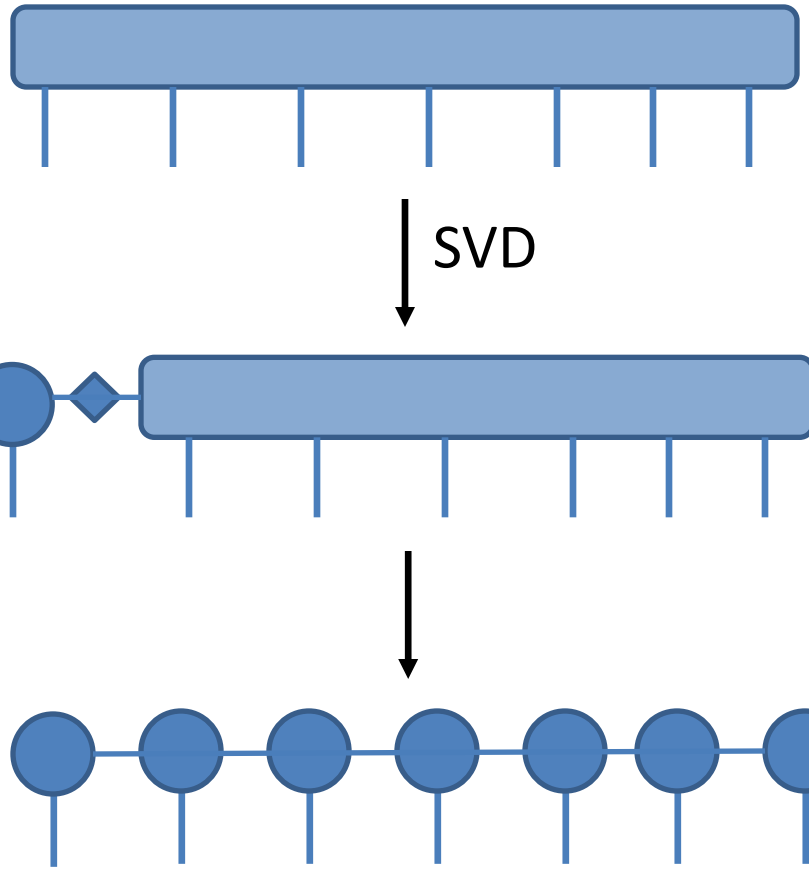
Thus, the exact wavefunction can be written as a many dimensional tensor

$$|\Psi_{FCI}\rangle = \sum_{n_1 n_2 n_3 \ldots} \Psi^{n_1 n_2 n_3 \ldots n_k} \, | n_1 n_2 n_3 \ldots . n_k \rangle$$



Matrix Product State ansatz

$$\sum_{n_1 n_2 n_3 \ldots} \Psi^{n_1 n_2 n_3 \ldots n_k} \, | n_1 n_2 n_3 \ldots n_k \rangle$$



d^N

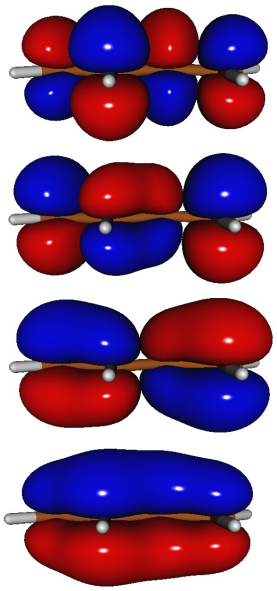
Exponential saving!

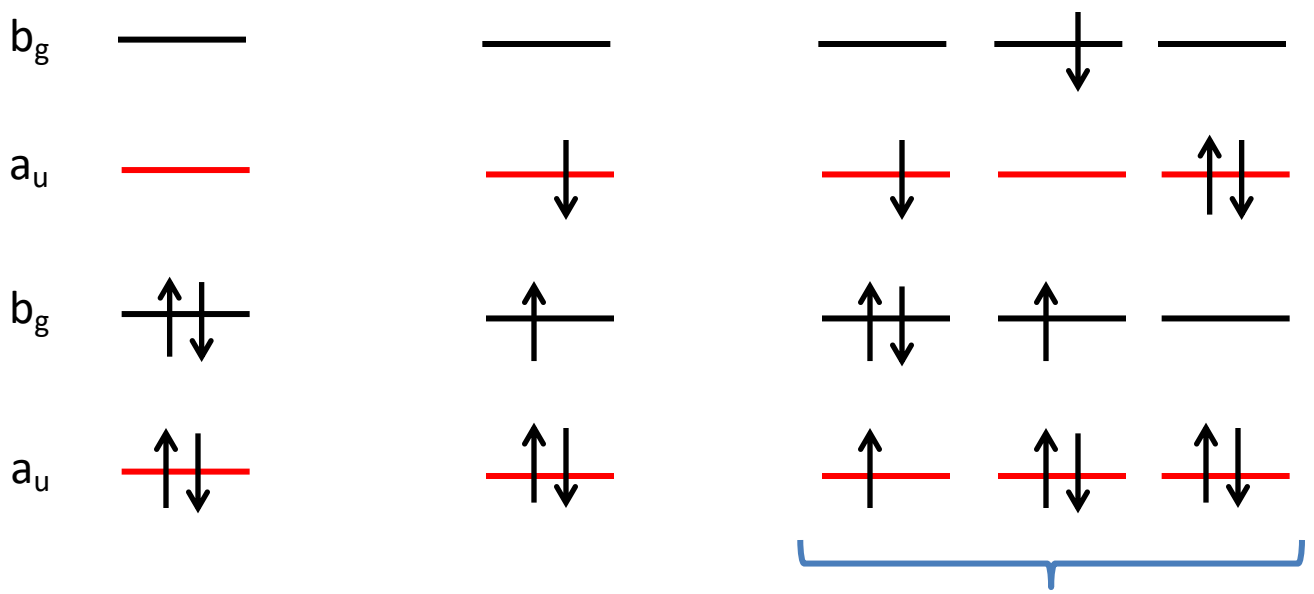
NdM^2

$$\Psi^{n_1 n_2 n_3 \ldots n_k} \approx \sum_{i_1 i_2 i_3 \ldots i_{k-1}} A^{n_1}_{i_1 \; i_1} A^{n_2}_{i_2 \; i_2} A^{n_3}_{i_3} \ldots_{i_{k-1}} A^{n_k}_{i_k}$$

Verstraete, Garcia-Ripoll, Cirac, PRL, (2004)
Kliesch, Gross, Eisert, PRL (2014)

Polyenes – monomer spectra

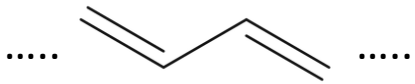




1^1A_g (GS)

1^1B_u
(optically active)

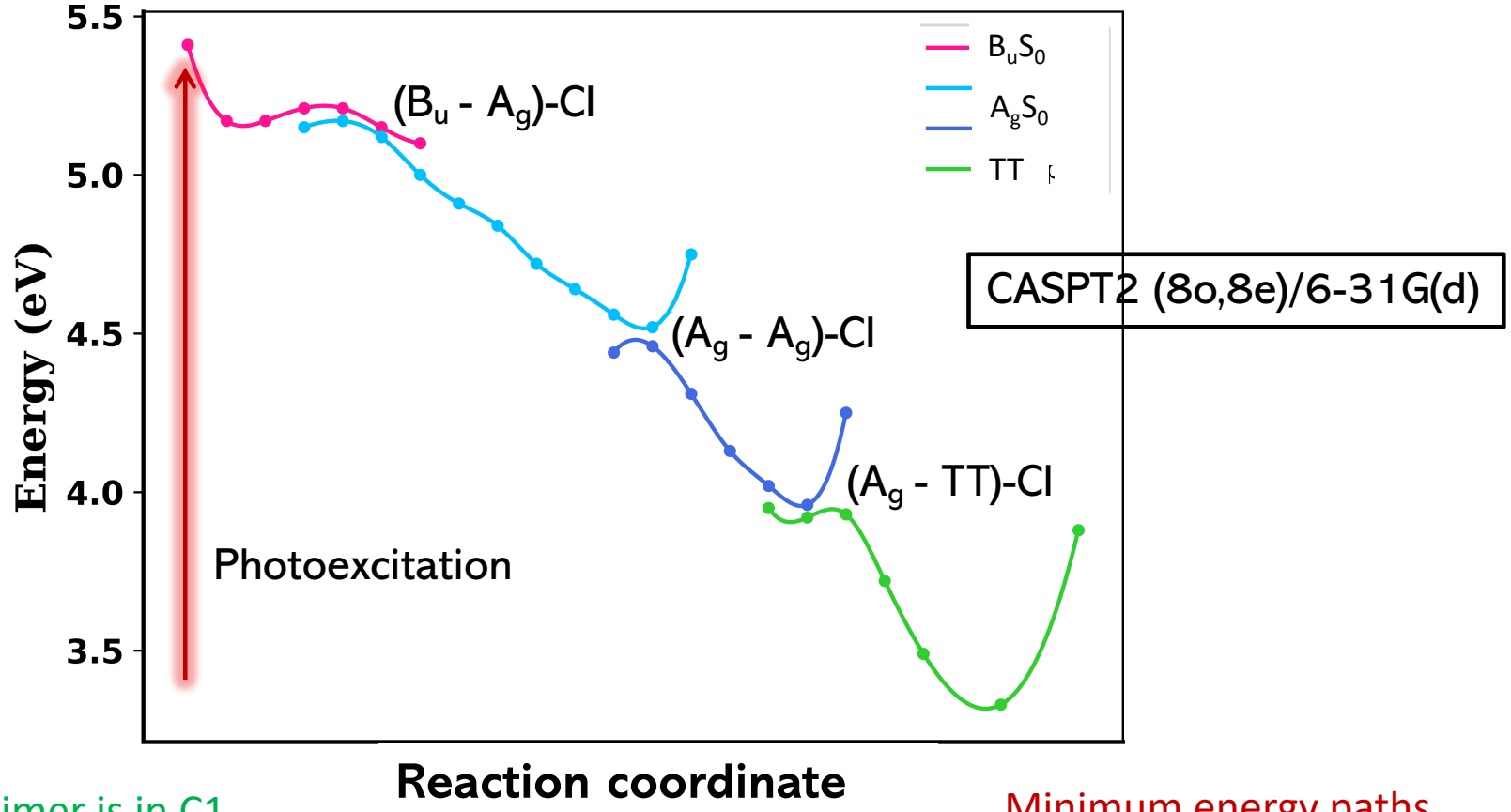
2^1A_g
(optically dark)



C_{2h} sym

Santra, Ray, **DG**, *J Phys Chem Lett*, 2022, **13**, 6800
Santra, **DG**, *J Phys Chem A*, 2025, **129**, 2738

Energy order for dimers



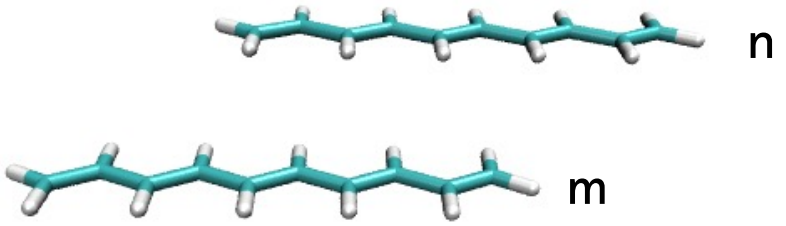
CASPT2 (8o,8e)/6-31G(d)

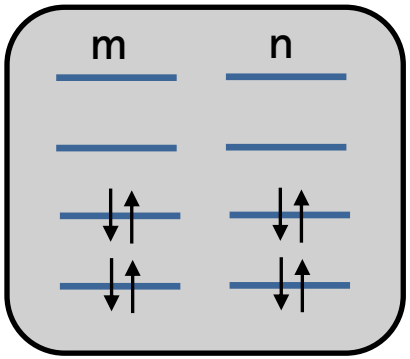
Aggregate/dimer is in C1 symmetry

Minimum energy paths between stationary points.

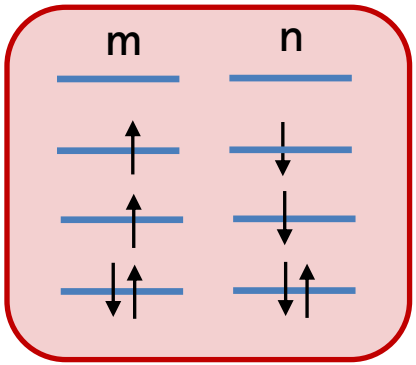
Barrier less pathway to access the TT pair state from the initially excited B_u state.

Low-lying states

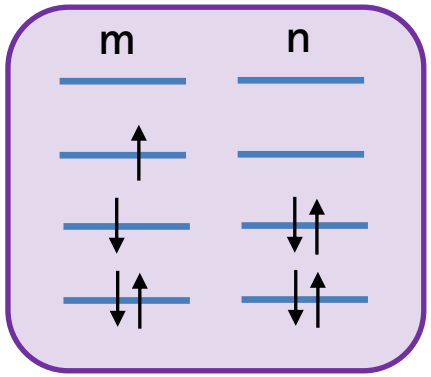




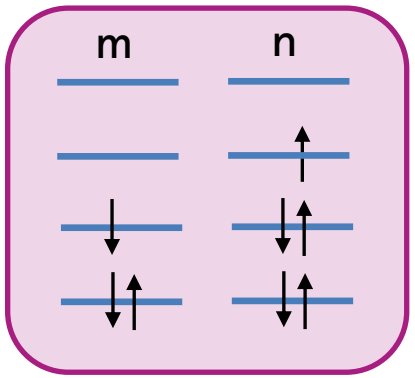
(i) GS



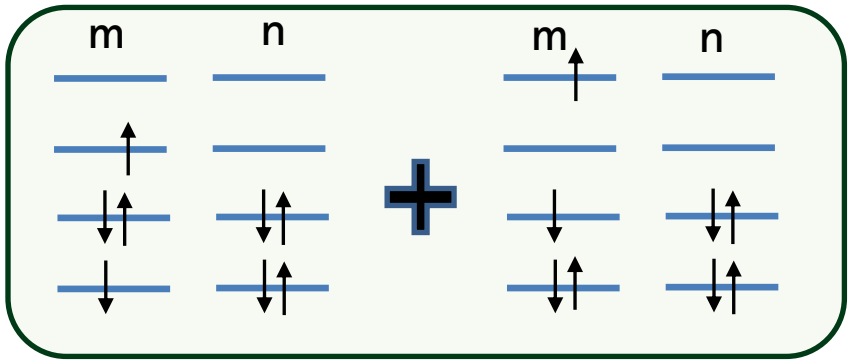
(ii) ^{1}(TT)



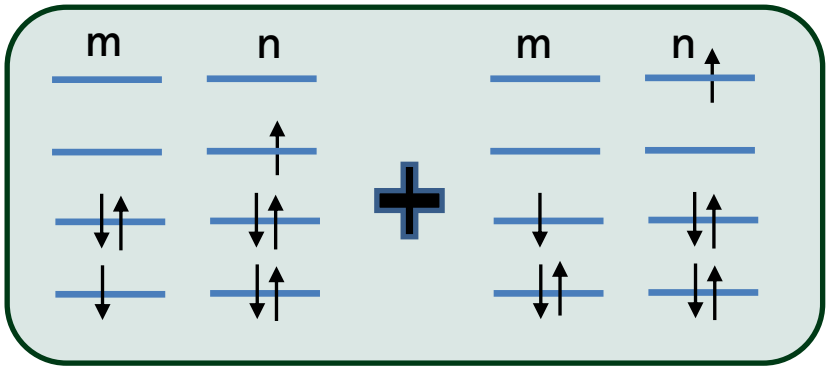
(iii) $B_u(m)$



(iv) $B_u(CT)(m)$



(v) $A_g(m)$



(vi) $A_g(CT)(m)$

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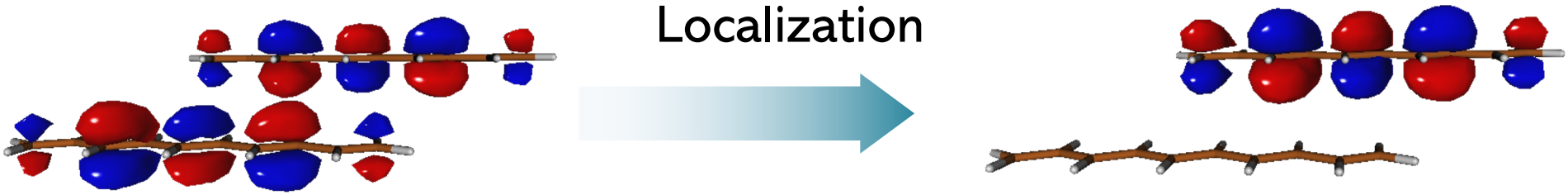
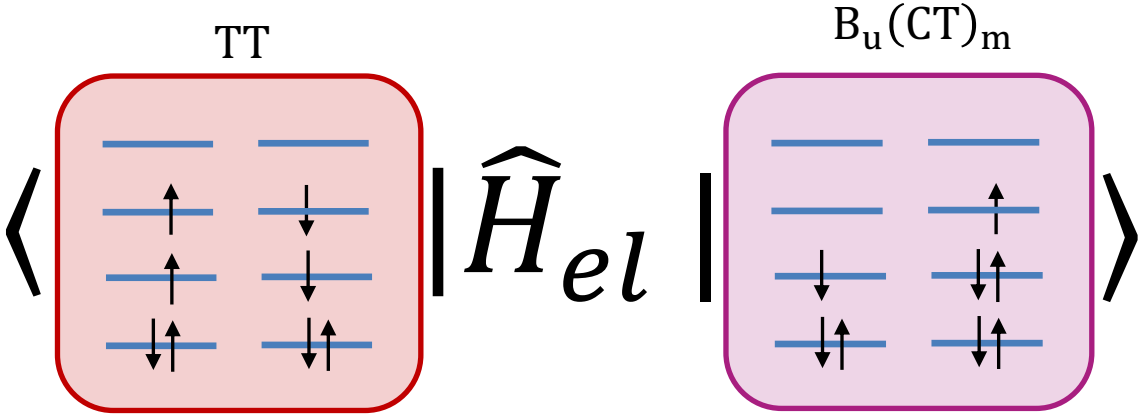
Santra, **DG**, *J Phys Chem A*, 2025, **129**, 2738

Coupling between states





$$\langle TT|\hat{H}_{el}|B_u(CT)_m\rangle = \sqrt{\frac{3}{2}}\,[(L_m|F|H_n) + (L_mH_n|L_nL_n) - (L_mH_n|H_mH_m)]$$

SF mechanism?

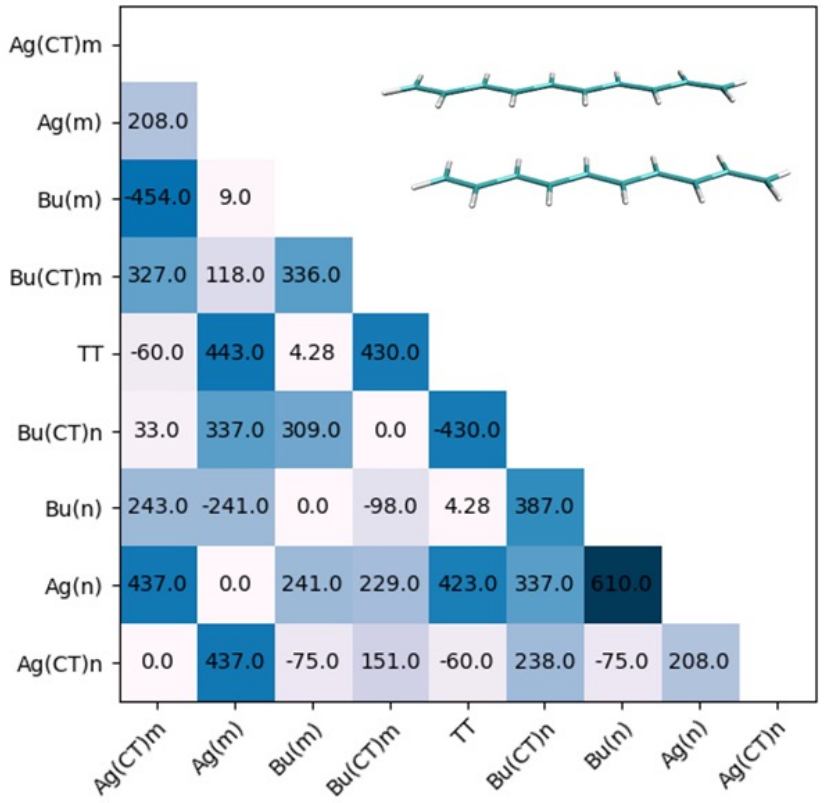
1^1B_u
(optically active)
Locally excited

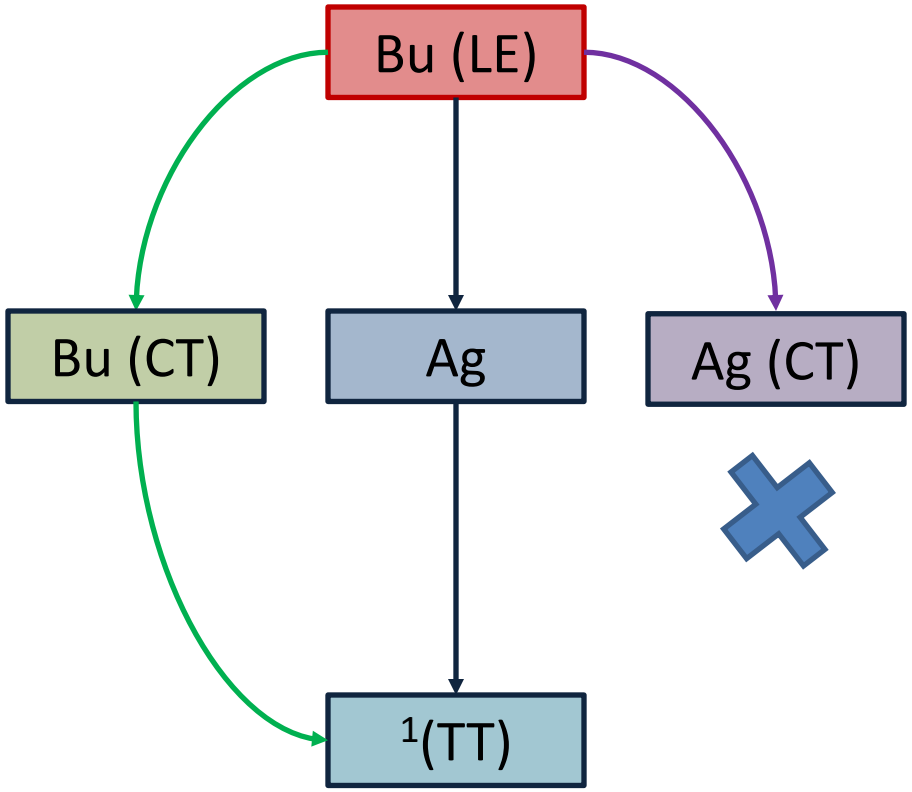
TT pair state

$$\left(\Psi_{B_u(LE)} \mid \hat{H} \mid \Psi_{TT}\right) = \sqrt{\frac{3}{2}}\left[\left(L_m H_n \mid L_n L_m\right) - \left(H_m L_n \mid H_n H_m\right)\right] \approx 0$$

No coupling!

Coupling and pathways (H-dimer)

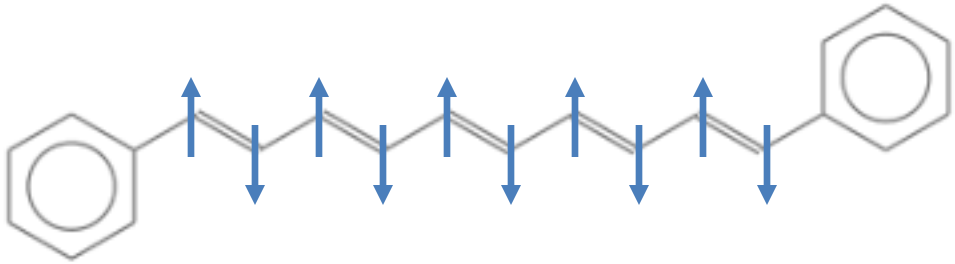




Multiple pathways from optically active Bu state to TT state
Via CT and Ag states!

Santra, Ray, **DG**, J Phys Chem Lett (2022)

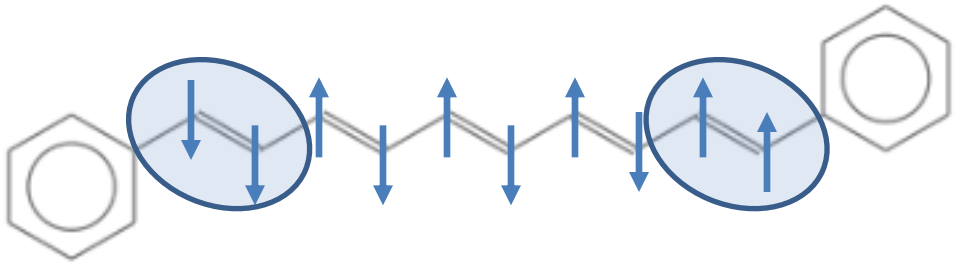
TT state formation via Ag state



Ground state

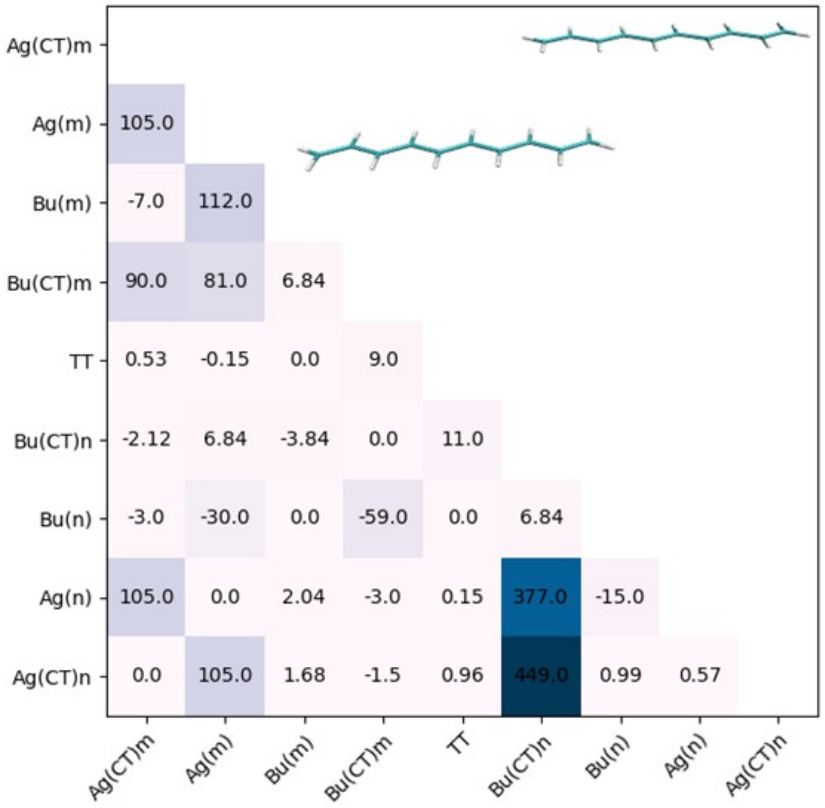
Extended Hubbard model

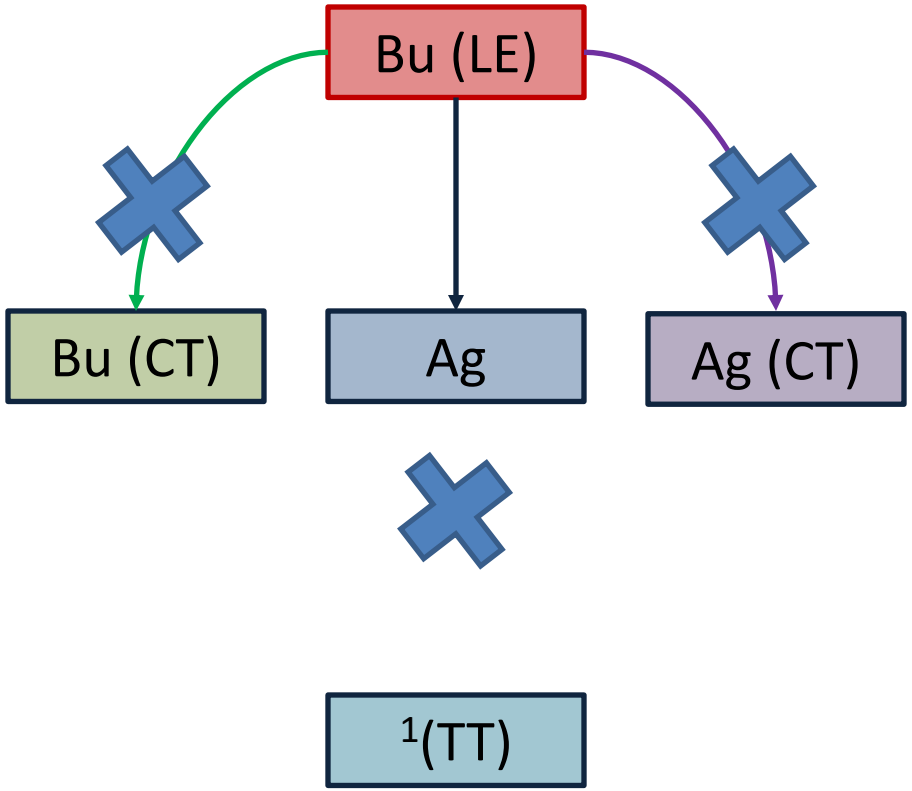
We can think of a Bu (optically bright) state as a holon-doublon pair state



(2Ag state) Bimagnon state

Coupling and pathways (J-dimer)

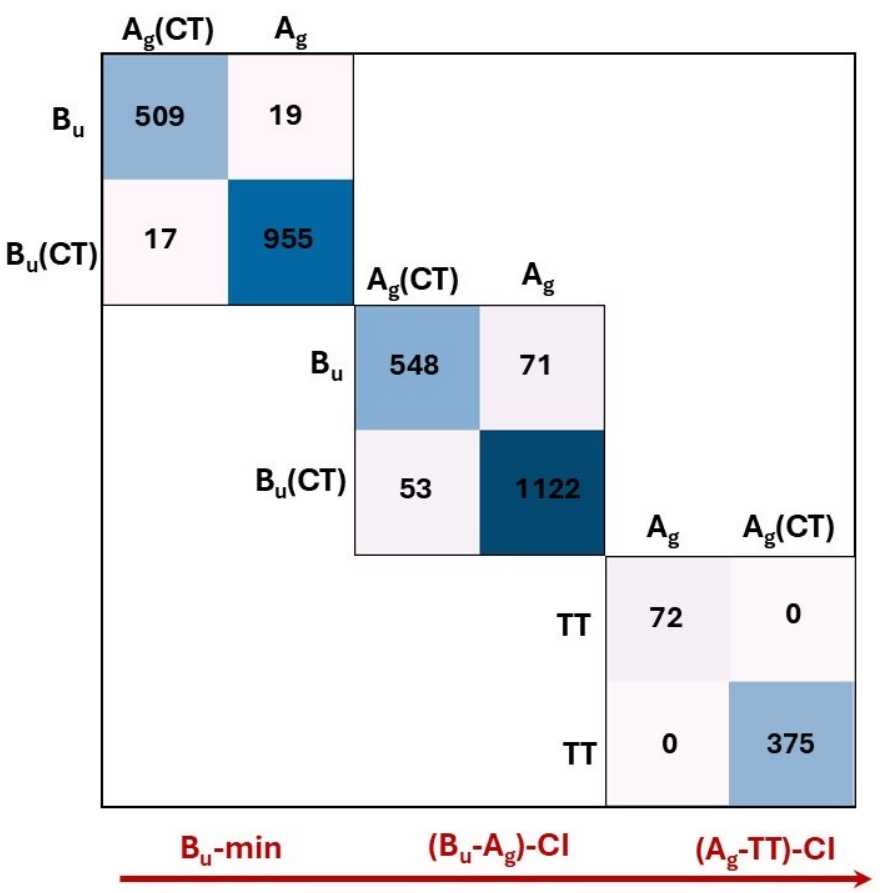


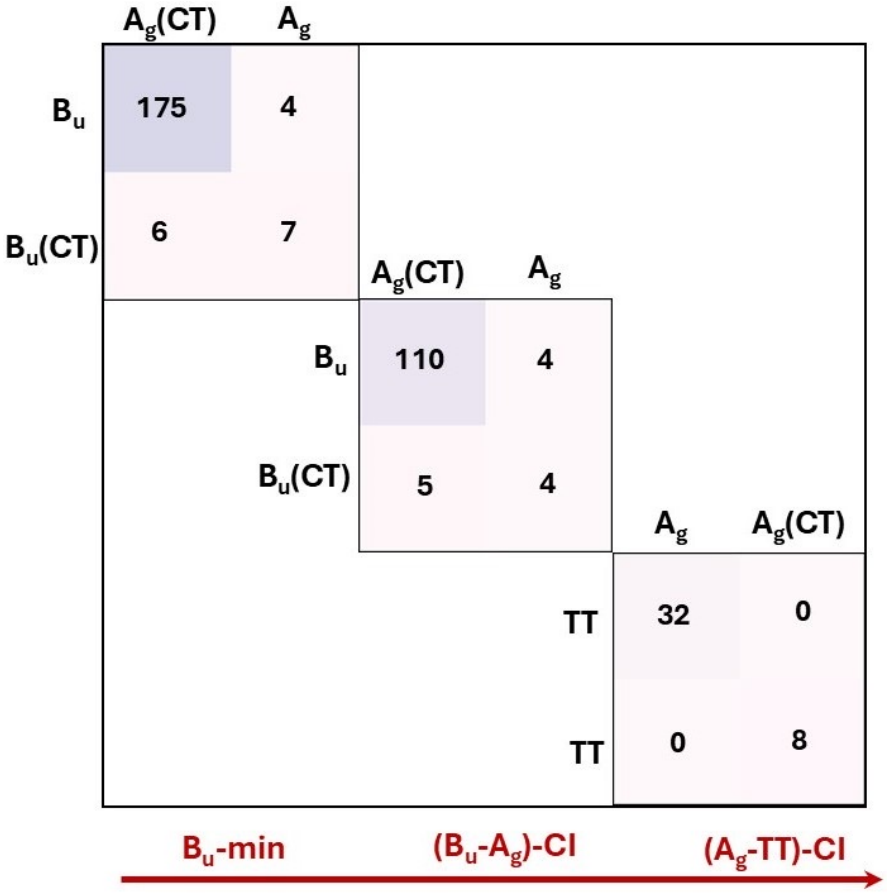


No pathway to TT state. No SF in J-dimer of non-polar molecule!

Santra, Ray, **DG**, J Phys Chem Lett (2022)

Structural effects on electronic coupling



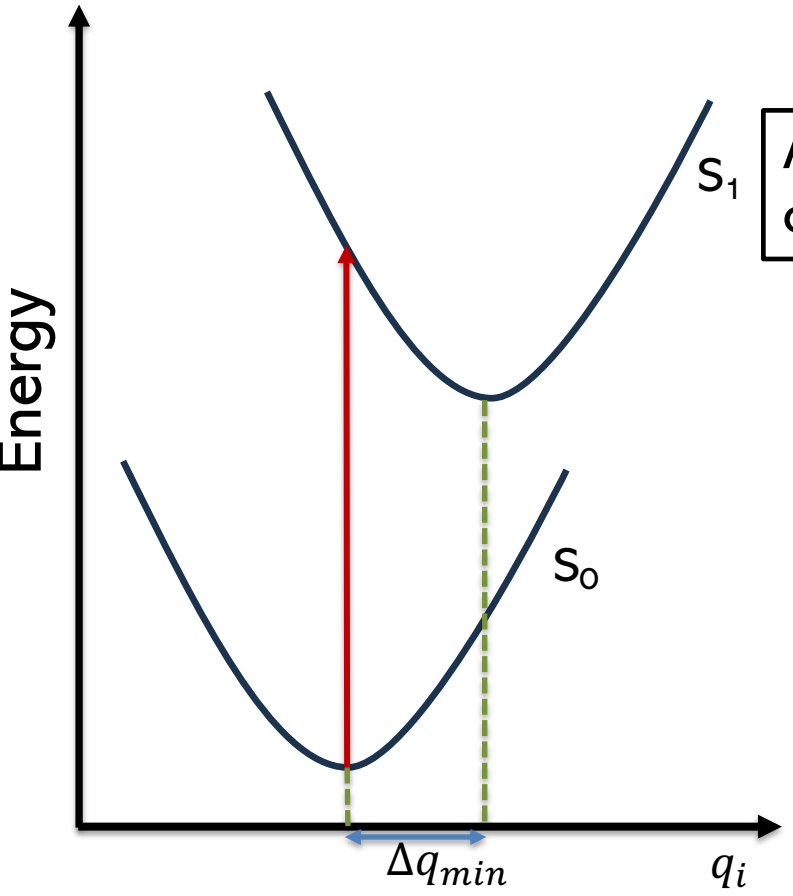


- Electronic coupling is very sensitive to the relative orientation of the monomers.
- A_g states with CT component play major role.

Santra, Ray, **DG**, *J Phys Chem Lett*, 2022, **13**, 6800

Santra, **DG**, *J Phys Chem A*, 2025, **129**, 2738

Vibronic effect – Huang Rhys factor



A measure associated with nuclear displacements of the equilibrium position on photoexcitation

$$S_i = \frac{b_i^2}{2}$$

$$b_i = \left(\frac{\omega_i}{\hbar}\right)(\Delta q_{min})[M]^{\frac{1}{2}} L_i^{S_0}$$

where,

ω_i - Frequency of the i-th mode

Δq_{min} - Difference between minimum geometries

$[M]$ - (3N X 3N) matrix of the atomic masses

$L_i^{S_0}$ - Normal mode coordinates

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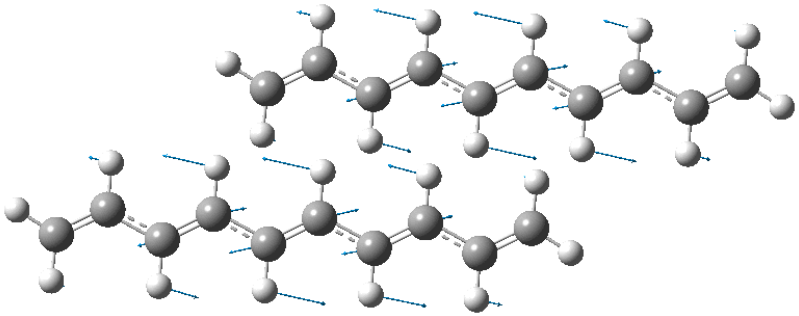
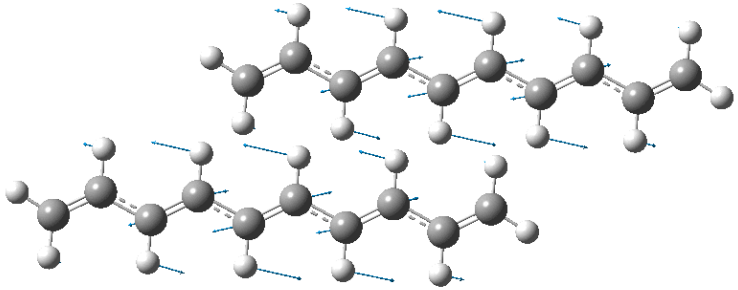
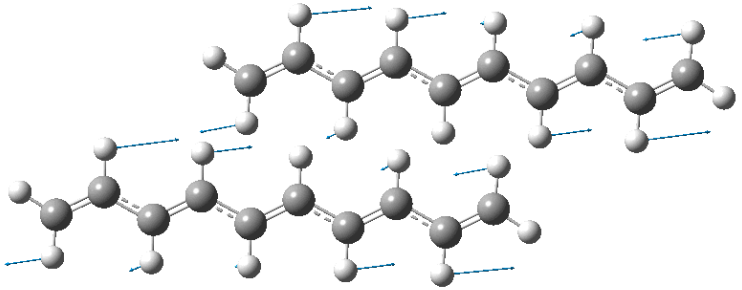
Vibronic coupling modes



Between Bu and TT state

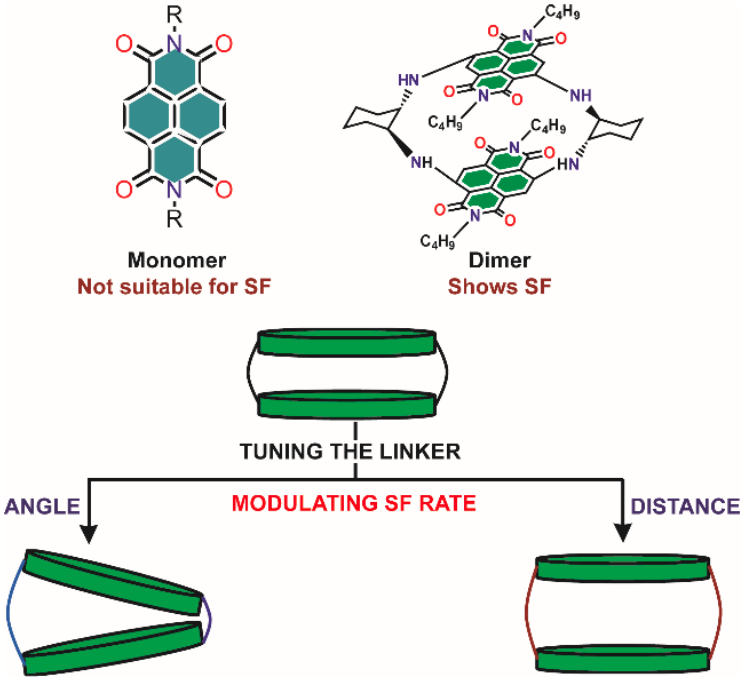


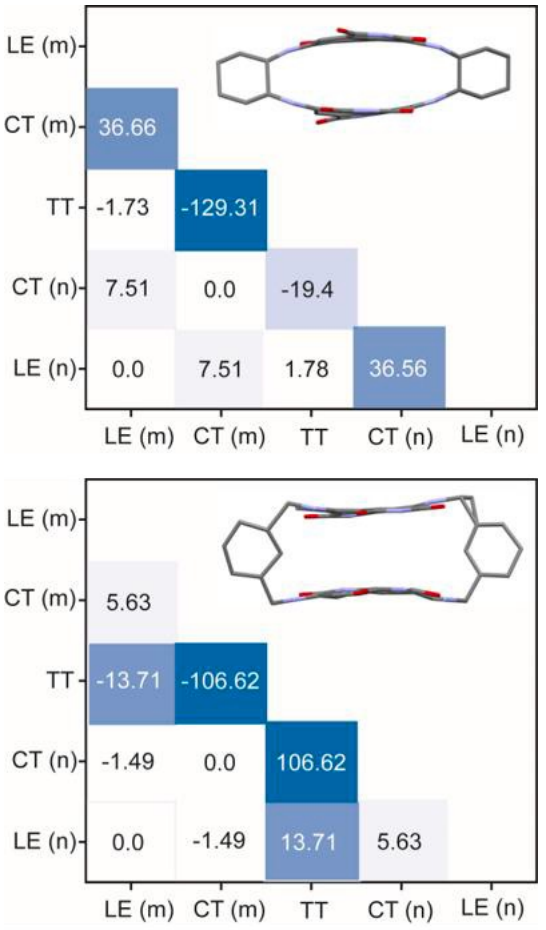
Between Bu and Ag
Monomer BLA



Between Ag and TT
Dimer modes (slow)

Strong electronic coupling

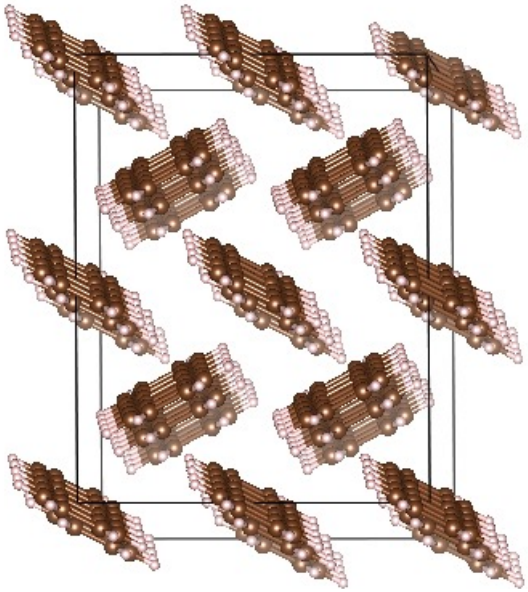




- Difficult to describe the states in terms of the diabatic components.
- Analysis of such molecular systems are complicated by both strong electronic coupling and vibronic effects.

DG, Dasgupta, and co-workers Chemical Science, 2025

Towards bulk



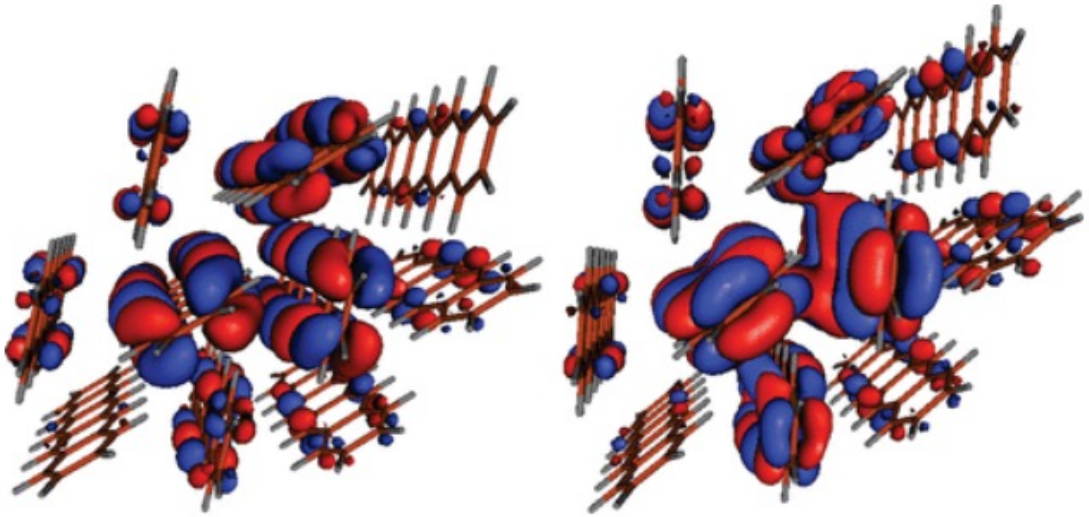
	Dilute solution	Aggregate
Radiative lifetime	29 ns	2.8 ns

Radiative rate, $\Gamma \propto N$

Radiative lifetime, $T \propto \frac{1}{N}$

The excitation is delocalized over ~ 10 molecules

Spano, Bardeen, *PRL*, 2004



Dimer is an inadequate model

Zimmerman, Casanova, Head-Gordon, *JACS*, 2011

Effective Hamiltonian

M1 M2 .....

.....

Basis - $|G\rangle, |S\rangle, |T\rangle, |C\rangle, |A\rangle$

$$\hat{H} = \hat{H}_{site} + \hat{H}_{corr} + \hat{H}_{hop} + \hat{H}_{S\to C} + \hat{H}_{S\to A} + \hat{H}_{CA\to TT} + \cdots$$

$$\hat{H}_{\text{site}} = \sum_j \left(\epsilon^{(G)} |G_j\rangle\langle G_j| + \epsilon_j^{(S)} |S_j\rangle\langle S_j| + \epsilon_j^{(T)} \sum_s |T_{sj}\rangle\langle T_{sj}| + \epsilon_j^{(C)} \sum_s |C_{sj}\rangle\langle C_{sj}| + \epsilon_j^{(A)} \sum_s |A_{sj}\rangle\langle A_{sj}| \right)$$

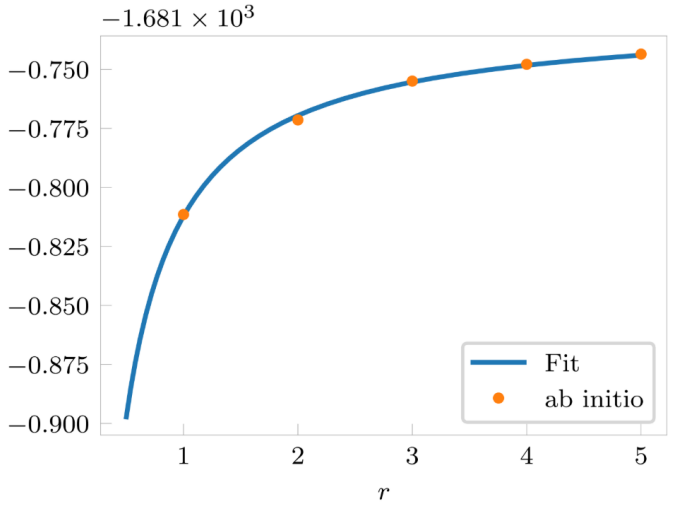
These parameters are obtained from the monomer calculations

Santra, Bose, **DG** (submitted)

$$\hat{H} = \hat{H}_{site} + \hat{H}_{corr} + \hat{H}_{hop} + \hat{H}_{S\to C} + \hat{H}_{S\to A} + \hat{H}_{CA\to TT} + \cdots$$

$$\begin{aligned}\hat{H}_{\rm corr} = &\sum_{j<k}\sum_{s,s'}\left(\epsilon^{(CA)}(|j-k|)\,|C_{sj}A_{s'k}\rangle\langle C_{sj}A_{s'k}| + \epsilon^{(AC)}(|j-k|)\,|A_{s'j}C_{sk}\rangle\langle A_{s'j}C_{sk}|\right)\\ &+\sum_{j<k}\epsilon^{(TT)}(|j-k|)\sum_{s,s'}|T_{sj}T_{s'k}\rangle\langle T_{sj}T_{s'k}|\\ &+\sum_{j<k}\epsilon^{(GG)}(|j-k|)\,|G_jG_k\rangle\langle G_jG_k|\\ &+\sum_{j<k}\epsilon^{(SG)}(|j-k|)\,|S_jG_k\rangle\langle S_jG_k| + \sum_{j<k}\epsilon^{(GS)}(|j-k|)\,|G_jS_k\rangle\langle G_jS_k|\end{aligned}$$

These parameters are obtained from the dimer calculations of suitable diabatic states by varying the distances.



Santra, Bose, **DG** (submitted)

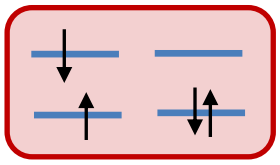
$$\hat{H} = \hat{H}_{site} + \hat{H}_{corr} + \hat{H}_{hop} + \hat{H}_{S\to C} + \hat{H}_{S\to A} + \hat{H}_{CA\to TT} + \cdots$$

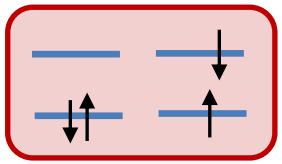
These parameters are obtained from coupling calculation on a dimer.

$$\hat{H}_{\text{hopping}} = \sum_j h^{(S)} \left(|S_j G_{j+1}\rangle\langle G_j S_{j+1}| + \text{h.c.}\right) + \sum_j h^{(T)} \sum_s \left(|T_{sj} G_{j+1}\rangle\langle G_j T_{s,j+1}| + \text{h.c.}\right)$$

$$\hat{H}_{S\to C} = \sum h^{(SG\to CA)} |S_j G_{j+1}\rangle\langle CA_{j,j+1}| + h.c.$$

$$\langle \quad | \hat{H}_{el} | \quad \rangle$$



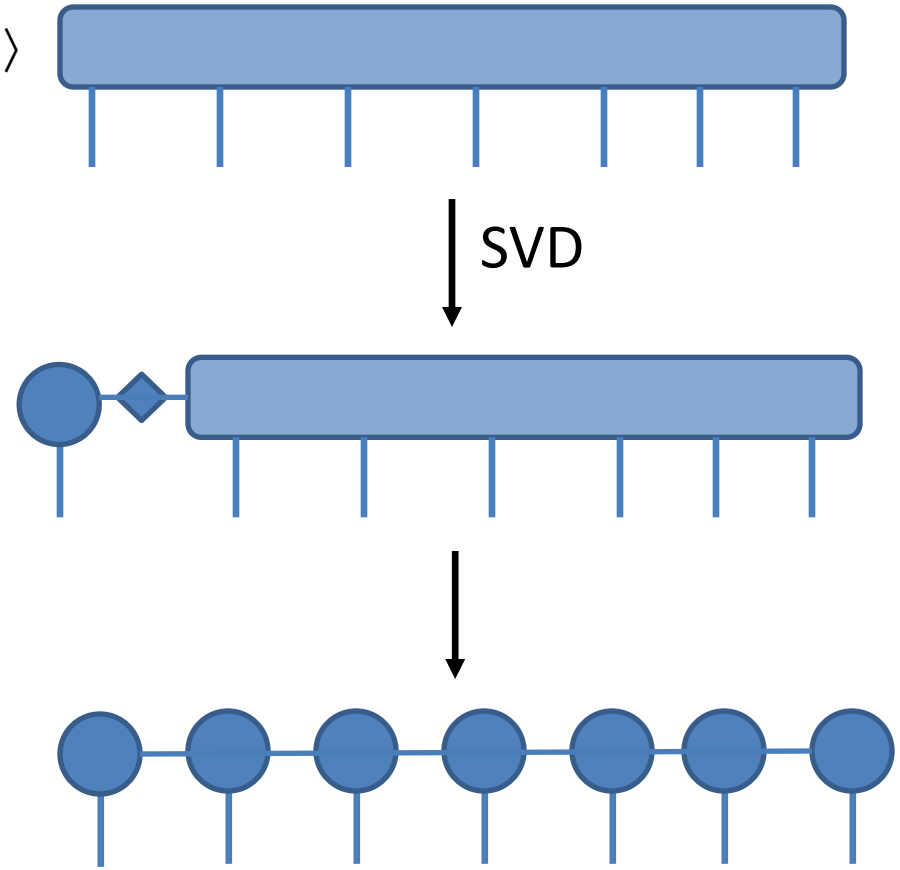


From only monomer and dimer calculation the Hamiltonian can be parameterized.

Santra, Bose, **DG** (submitted)

Dimer to aggregate: MPS ansatz

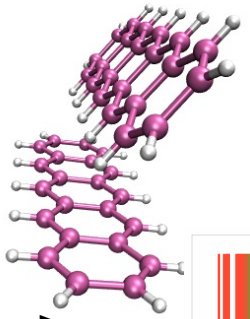
$$\sum_{n_1 n_2 n_3 \ldots} \Psi^{n_1 n_2 n_3 \ldots n_k} \, | n_1 n_2 n_3 \ldots n_k \rangle$$



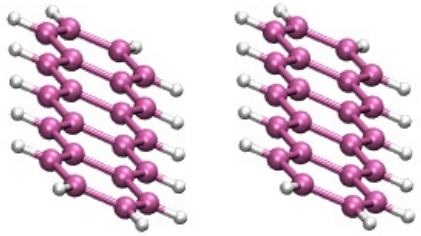
$$\Psi^{n_1 n_2 n_3 \ldots n_k} \approx \sum_{i_1 i_2 i_3 \ldots i_{k-1}} A^{n_1}_{i_1 \; i_1} A^{n_2}_{i_2 \; i_2} A^{n_3}_{i_3} \ldots . A^{n_k}_{i_k}$$

Spectra of aggregate

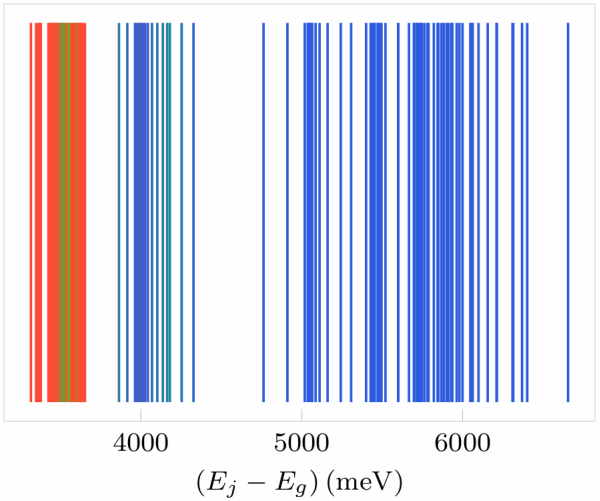
Herringbone

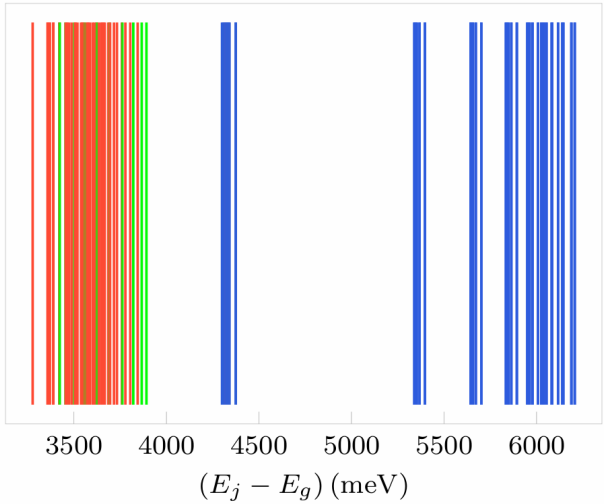


Parallel

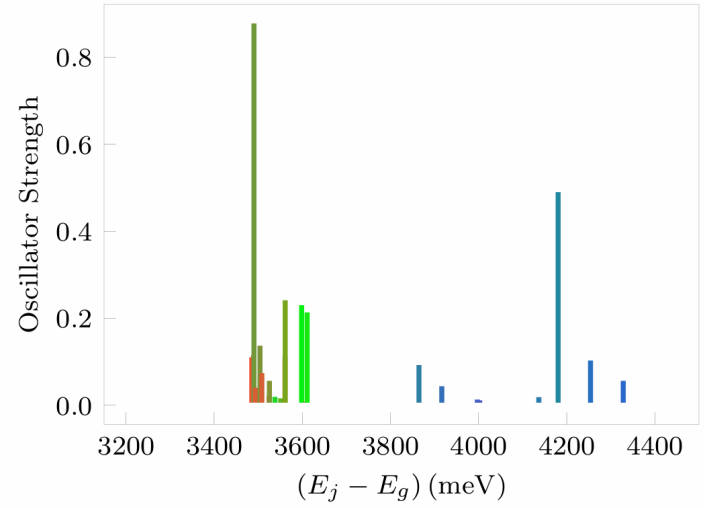


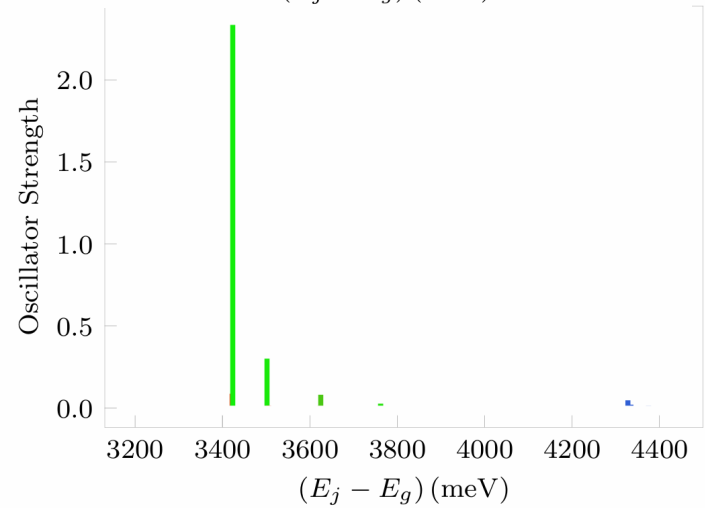
State density





Spectra





Conclusion

- The energetic rules are satisfied by polyenes and carotenoids.
- Carotenoids and polyenes larger than octatetraene have 2^1A_g state below the optically active ^1B_u state.
- For SF to occur, the coupling between the states need to be high
- This will provide a conduit from ^1B_u to ^{1}(TT) state
- In carotenoids, there are several efficient conduits via Ag, Ag(CT) and Bu(CT) states (unlike in acenes)
- Vibronic effects can improve efficiency of SF.
- Effect of aggregates from model Hamiltonian

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