Excitonic Effects in the Calculated Spectra of Molecular Aggregates by Time-Dependent Density-Functional Theory

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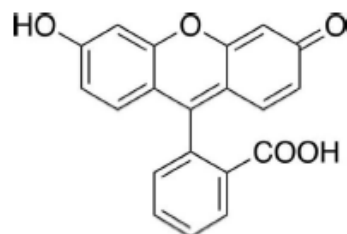*abdichem2006@gmail.com*

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INTRODUCTION

➤Quantum mechanics in general and DFT/TDDFT in particular help to describe the properties of the matter.

➤The color is obviously one of the most attractive properties of the matter.

➤The fluorescein molecule is a fascinating molecule appearing in many colors
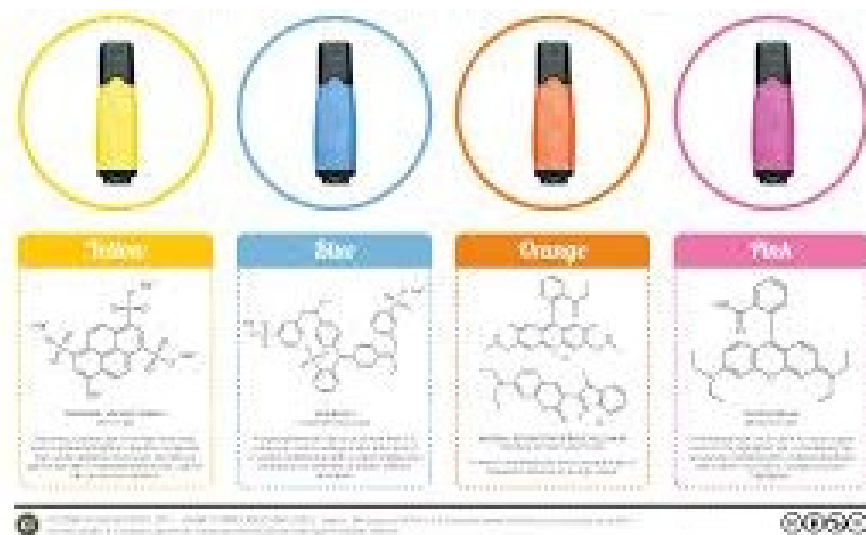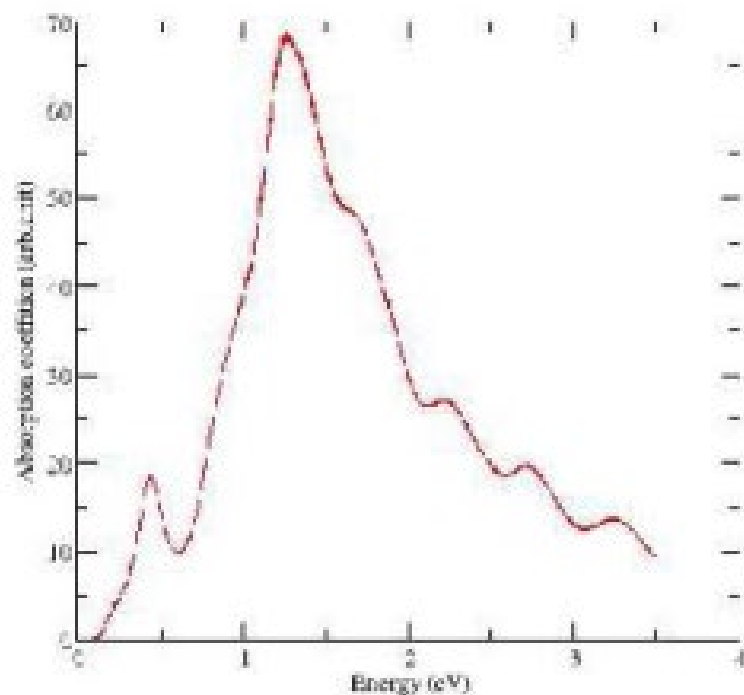
FLUORECEIN

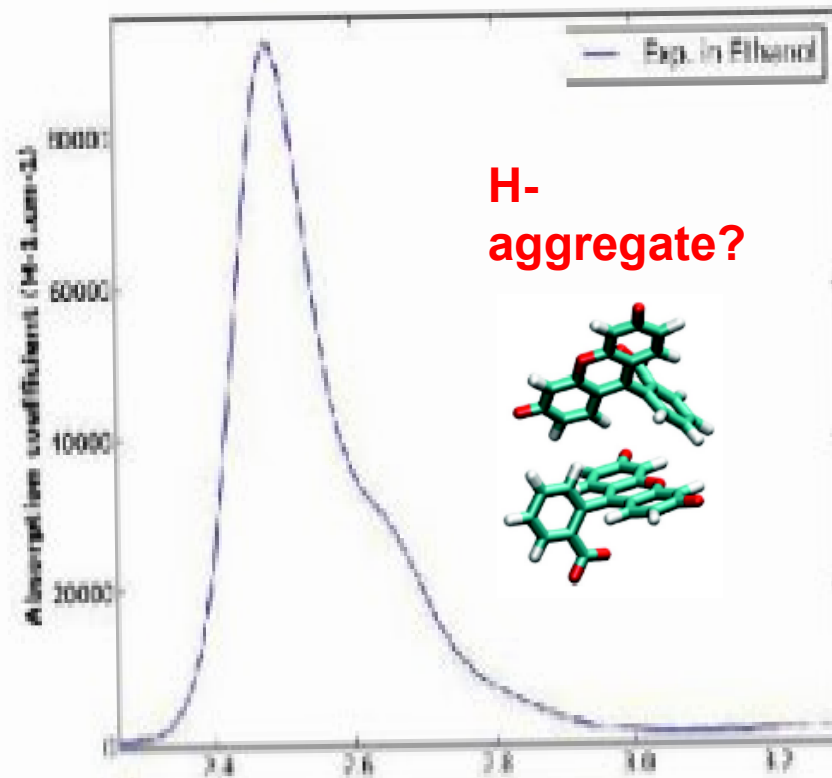FIG. 1: Results obtained with QUANTUM ESPRESSO at ASESMA in Accra.

FIG.2: Absorption spectrum of fluorecein in ethanol.

Spectral effects seen in dye aggregates:
J-aggregates (Jelly/Scheibe) spectrum shifts to lower energies and new narrow peaks appear.
H-aggregates (hypsochromic) spectrum shifts to higher energies.
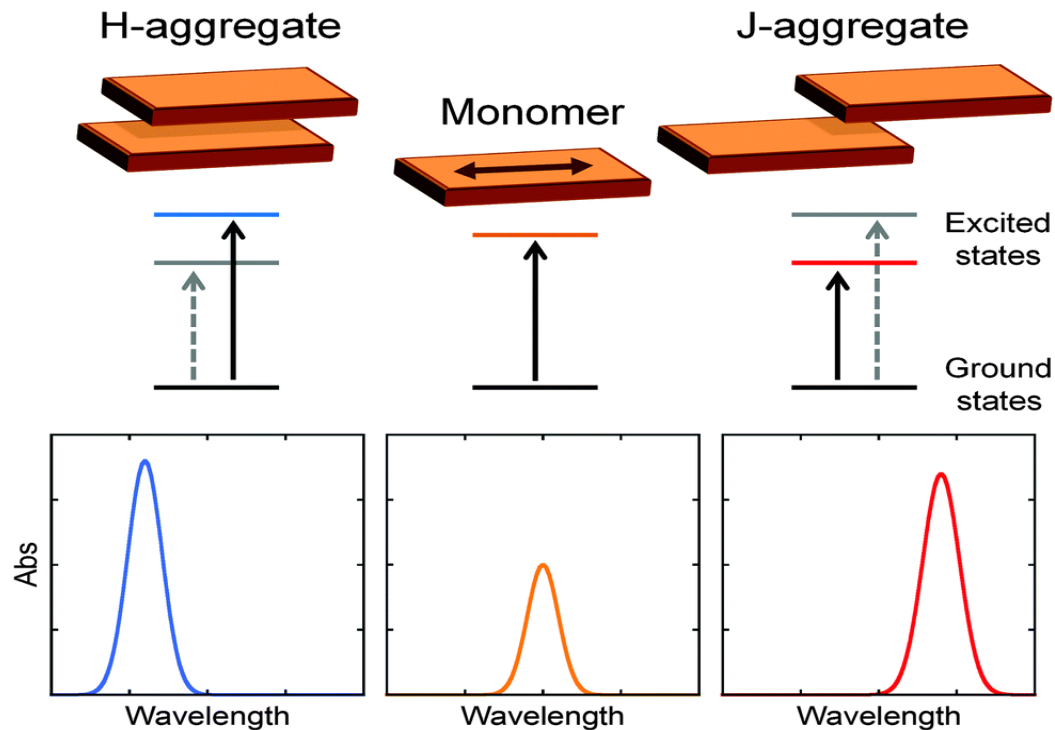

FIG 3: Spectral effects seen in dye aggregates

OBJECTIVES

- To understand the impact of aggregation (dimerization) on the spectra of the molecules

- To calculate the energy and charge transfer on the absorption spectra of the molecules

- To describe the impact of the chosen methods on spectra

Kasha's Exciton Model*

1. Historical theory (1960s). Necessarily very approximate!
2. Assumes a van der Waals (vdW) dimer.
3. Perturbative. Only zero and first order.
4. Point-dipole point-dipole approximation.

**Michael Kasha
(1920-2013)**
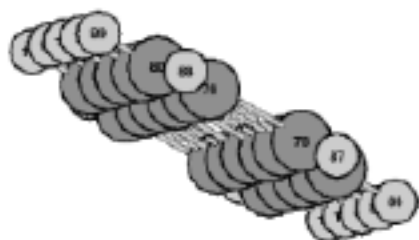
$$\Psi_1^0 \to \Psi_1^I \quad (1)$$

$$\omega = E_1^I - E_1^0 \quad (2)$$

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \hat{V}_{12} \quad (5)$$

$$\Psi_0 = \Psi_1^0 \Psi_2^0 \quad (6)$$

$$\Psi_2^0 \to \Psi_2^I \quad (3)$$

$$\omega = E_1^I - E_1^0 \quad (4)$$

$$\Psi_I = C_1 \Psi_1^I \Psi_2^0 + C_2 \Psi_1^0 \Psi_2^I \quad (7)$$

* **[KRE65]** M. Kasha, H.R. Rawls, and A. El Bayoumi, "The exciton model in molecular Spectroscopy", *Pure Appl. Chem.* **11**, 371 (1965).

Ground-State Energy

$$E_0 = \langle \Psi_1^0 \Psi_2^0 | \hat{H} | \Psi_1^0 \Psi_2^0 \rangle \qquad \text{(1)}$$

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \hat{V}_{12} \qquad \text{(2)}$$

$$E_0 = \langle \Psi_1^0 \Psi_2^0 | \hat{H}_1 | \Psi_1^0 \Psi_2^0 \rangle + \langle \Psi_1^0 \Psi_2^0 | \hat{H}_2 | \Psi_1^0 \Psi_2^0 \rangle + \langle \Psi_1^0 \Psi_2^0 | \hat{V}_{12} | \Psi_1^0 \Psi_2^0 \rangle \qquad \text{(3)}$$

$$E_0 = \langle \Psi_1^0 | \hat{H}_1 | \Psi_1^0 \rangle \langle \Psi_2^0 | \Psi_2^0 \rangle + \langle \Psi_1^0 | \Psi_1^0 \rangle \langle \Psi_2^0 | \hat{H}_2 | \Psi_2^0 \rangle + \langle \Psi_1^0 \Psi_2^0 | \hat{V}_{12} | \Psi_1^0 \Psi_2^0 \rangle \qquad \text{(4)}$$

$$E_0 = E_1^0 + E_2^0 + \langle \Psi_1^0 \Psi_2^0 | \hat{V}_{12} | \Psi_1^0 \Psi_2^0 \rangle \qquad \text{(5)}$$

$$E_0 = E_1^0 + E_2^0 + E_{vdW}^0 \qquad \text{(6)}$$

Excited-State Energy

$$\Psi_I = C_1 \Psi_1^I \Psi_2^0 + C_2 \Psi_1^0 \Psi_2^I \qquad (1)$$

$$\begin{bmatrix} A & B \\ B & A \end{bmatrix} \begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = E^I \begin{pmatrix} C_1 \\ C_2 \end{pmatrix} \qquad (2)$$

$$A = \langle \Psi_1^I \Psi_2^0 | \hat{H} | \Psi_1^I \Psi_2^0 \rangle = \langle \Psi_1^0 \Psi_2^I | \hat{H} | \Psi_1^0 \Psi_2^I \rangle \qquad (3)$$

$$B = \langle \Psi_1^0 \Psi_2^I | \hat{H} | \Psi_1^I \Psi_2^0 \rangle = \langle \Psi_1^I \Psi_2^0 | \hat{H} | \Psi_1^0 \Psi_2^I \rangle \qquad (4)$$

$$\Psi_{\pm}^I = \frac{1}{\sqrt{2}} \left(\Psi_1^I \Psi_2^0 \pm \Psi_1^0 \Psi_2^I \right) \qquad (5)$$

$$E_{\pm}^I = A \pm B \qquad (6)$$

Exciton Splitting

$$A = \langle \Psi_1^I \Psi_2^0 | \hat{H} | \Psi_1^I \Psi_2^0 \rangle \tag{1}$$

$$B = \langle \Psi_1^0 \Psi_2^I | \hat{H} | \Psi_1^I \Psi_2^0 \rangle \tag{2}$$

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \hat{V}_{12} \tag{3}$$

$$A = E_1^I + E_2^0 + \langle \Psi_1^I \Psi_2^0 | \hat{V}_{12} | \Psi_1^I \Psi_2^0 \rangle = E_1^I + E_2^0 + E_{vdW}^I \tag{4}$$

$$B = \langle \Psi_1^0 \Psi_2^I | \hat{V}_{12} | \Psi_1^I \Psi_2^0 \rangle = E_{\text{exciton splitting}} \tag{5}$$

$$E_\pm^I = E_1^I + E_2^0 + E_{vdW}^I \pm E_{\text{exciton splitting}} \tag{6}$$

$$\omega_\pm^I = E_\pm^I - E^0 = \omega_1^0 + \left(E_{vdW}^I - E_{vdW}^0 \right) \pm E_{\text{exciton splitting}} \tag{7}$$

Transition Moments

$$\vec{\mu}^{I0} = \langle \Psi^I | \vec{r} | \Psi^0 \rangle \qquad (1)$$

$$\vec{\mu}_{\pm}^{I0} = \frac{1}{\sqrt{2}} \langle \Psi_1^I \Psi_2^0 \pm \Psi_1^0 \Psi_2^I | \vec{r} | \Psi_1^0 \Psi_2^0 \rangle \qquad (2)$$

$$\vec{\mu}_{\pm}^{I0} = \frac{1}{\sqrt{2}} \left(\vec{\mu}_1^{I0} \pm \vec{\mu}_2^{I0} \right) \qquad (3)$$

$$f_{\pm}^I = \frac{\omega_{\pm}^I}{3} |\vec{\mu}_1^{I0} \pm \vec{\mu}_2^{I0}|^2 \qquad (4)$$

Example: Parallel stacking $\quad \vec{\mu}_{1/2} \perp \vec{r} \qquad (5)$

$$f_+^I = \frac{4}{3} \omega_1^I |\vec{\mu}_1^{I0}|^2 \qquad (6)$$

$$f_-^I = 0 \qquad (7)$$

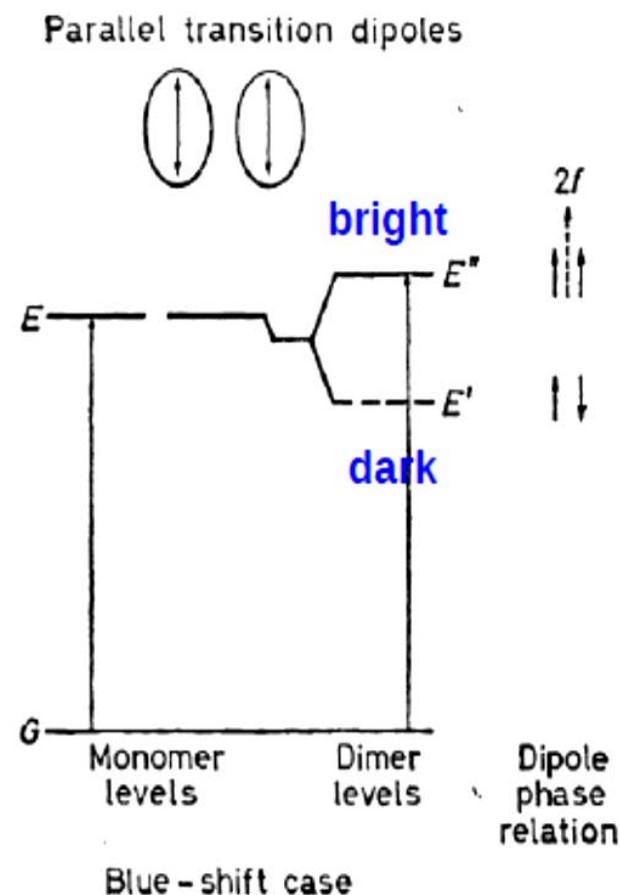Parallel transition dipoles

Fig. 1. Ref. [KRE65]

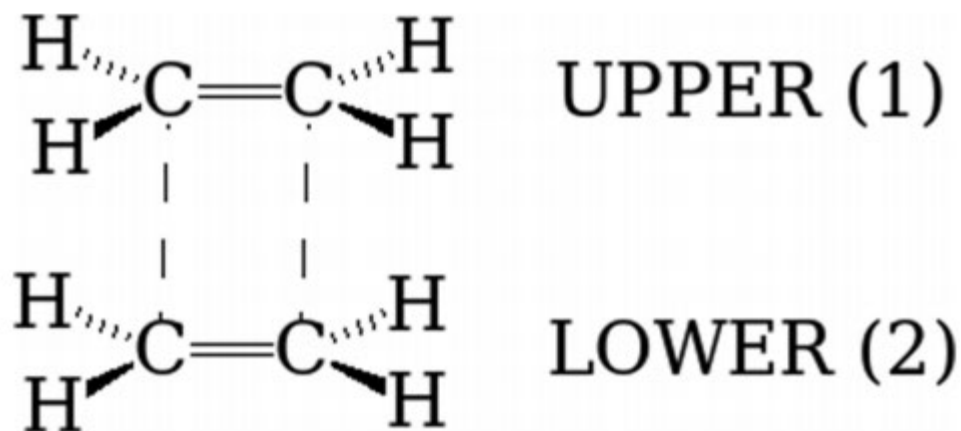# Let's try to understand how this works ... "simply"!

FIG. 1. Two vertically stacked ethylene molecules.

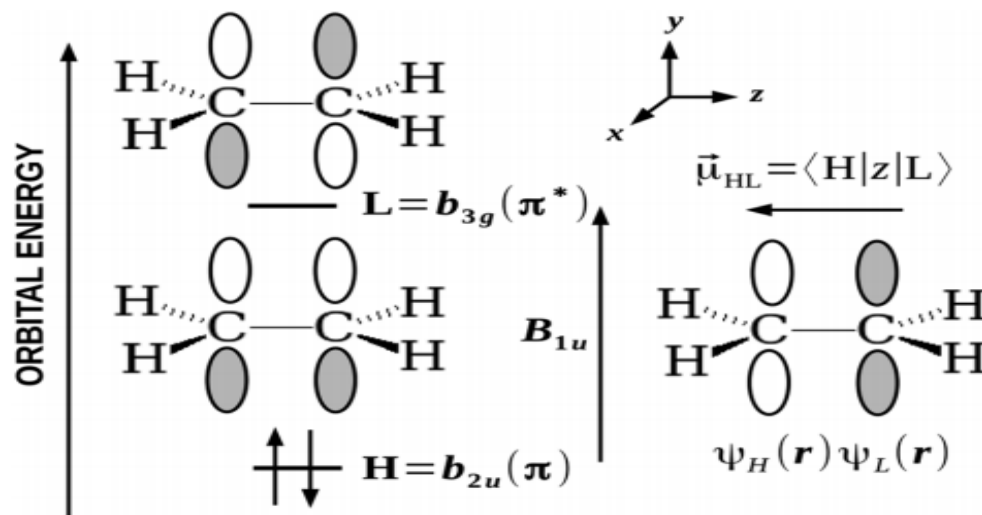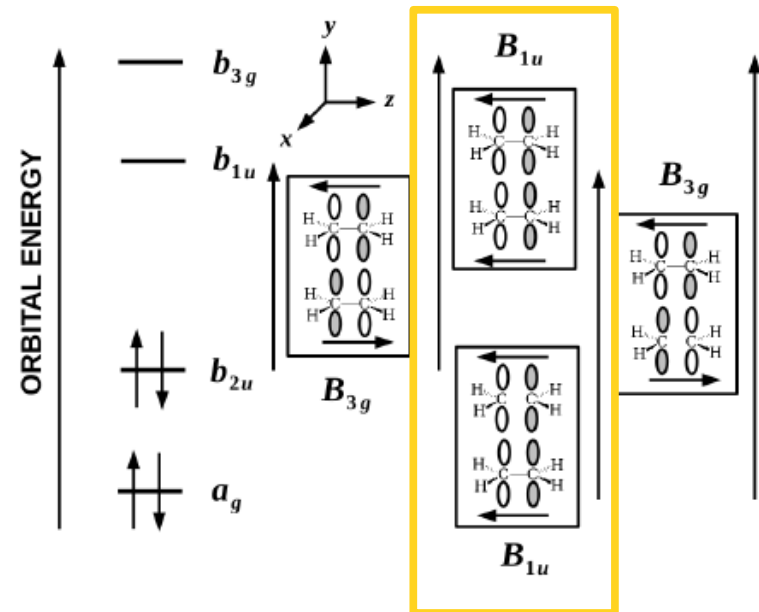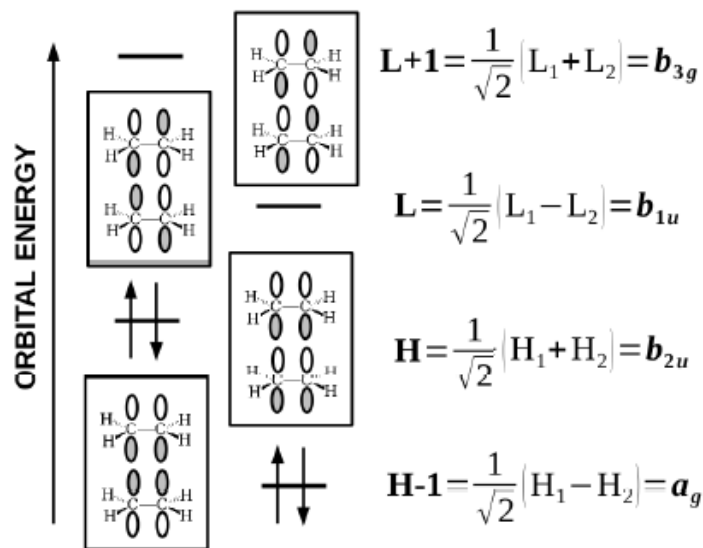FIG. 2. Ethylene highest occupied molecular orbital (H) and lowest unoccupied molecular orbital (L).
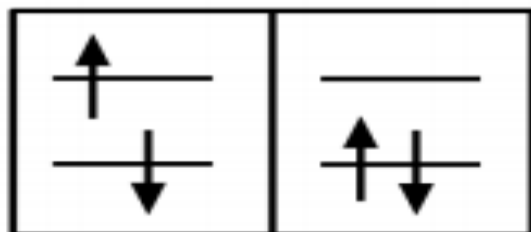
$$\Psi_{B_{1u}} = c_1 {}^1(H, L+1) + c_2 {}^1(H-1, L) \quad (1)$$

$$\Psi_{B_{1u}} = \frac{c_1 + c_2}{\sqrt{2}} ET_{12}^+ + \frac{c_1 - c_2}{\sqrt{2}} CT_{12}^+ \quad (2)$$

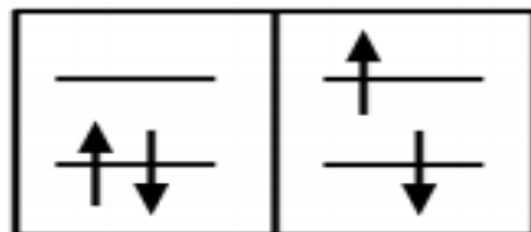$$ET_{12}^+ = \frac{1}{\sqrt{2}} \left[{}^1(H_1, L_1) + {}^1(H_2, L_2) \right] \quad (3)$$

$$CT_{12}^+ = \frac{1}{\sqrt{2}} \left[{}^1(H_1, L_2) + {}^1(H_2, L_1) \right] \quad (4)$$

Let's try to understand how this works … "simply"!
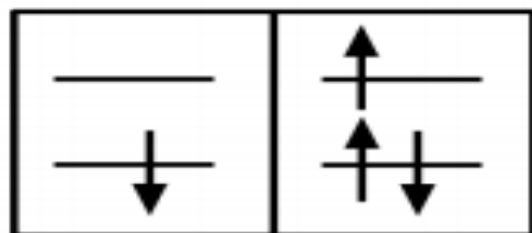
ENERGY TRANSFER (ET)

$^1(H_1, L_1)$

$^1(H_2, L_2)$
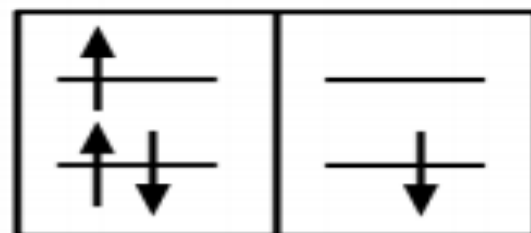
CHARGE TRANSFER (CT)

$^1(H_1, L_2)$

$^1(H_2, L_1)$

COMPUTATIONAL METHODS

Hartree-Fock and Local Spin Density Approximation (LSDA) for all calculations

Time-Dependent Density Functional Theory (TD-DFT) Calculations for the spectrum

Basis set : STO-3G,

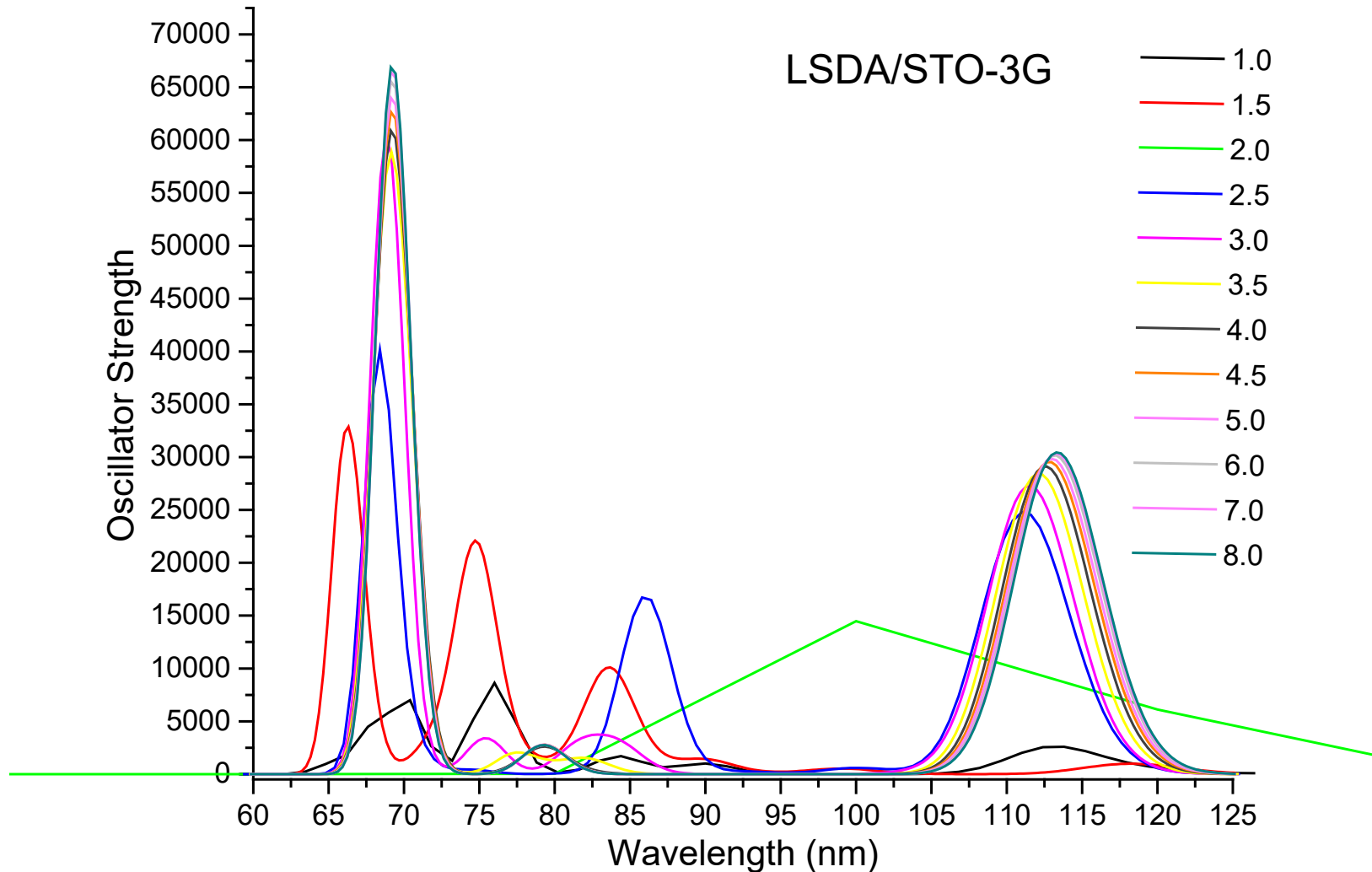Gaussian 09 RevD.01 package is used

Progress of the project

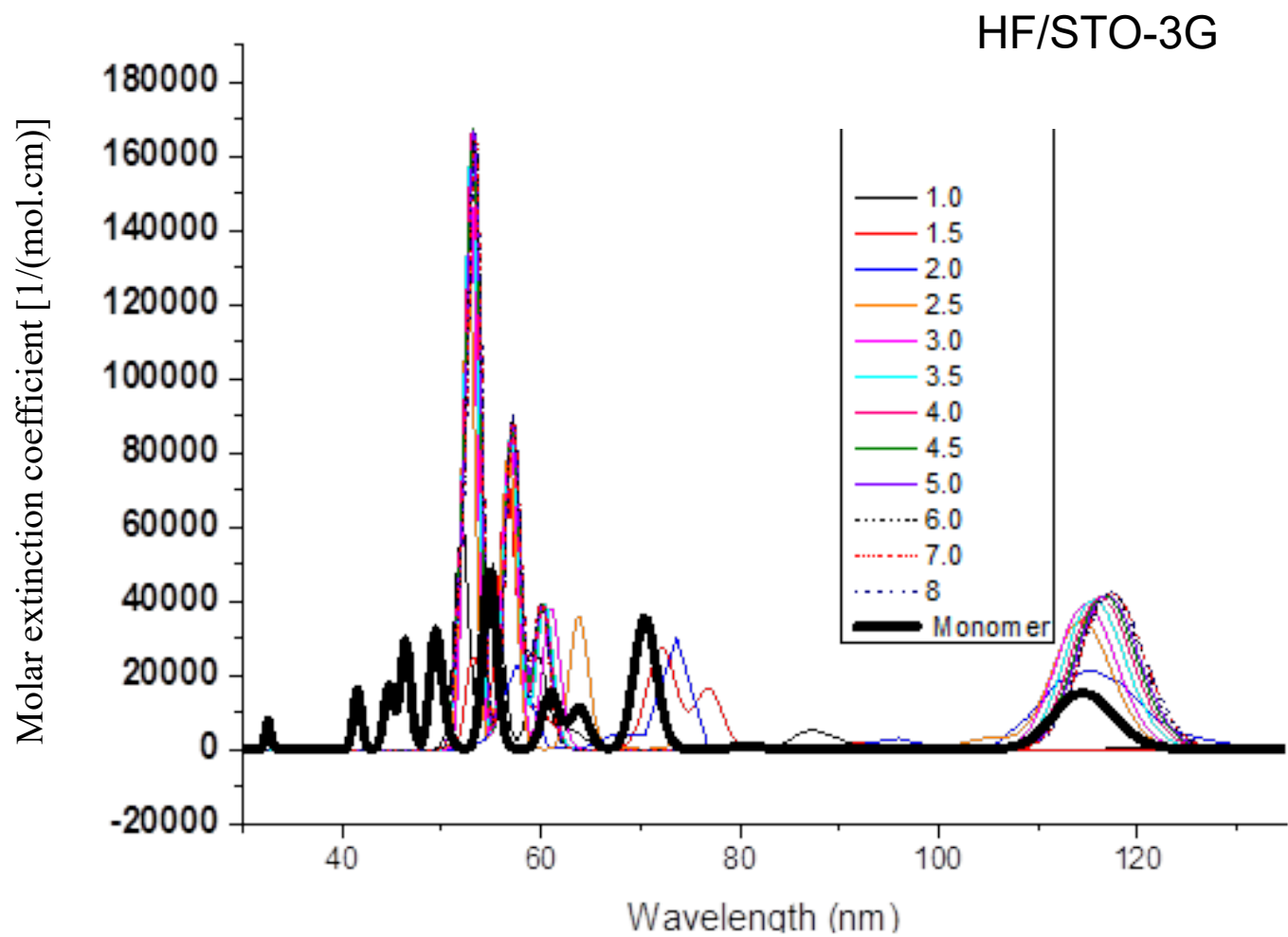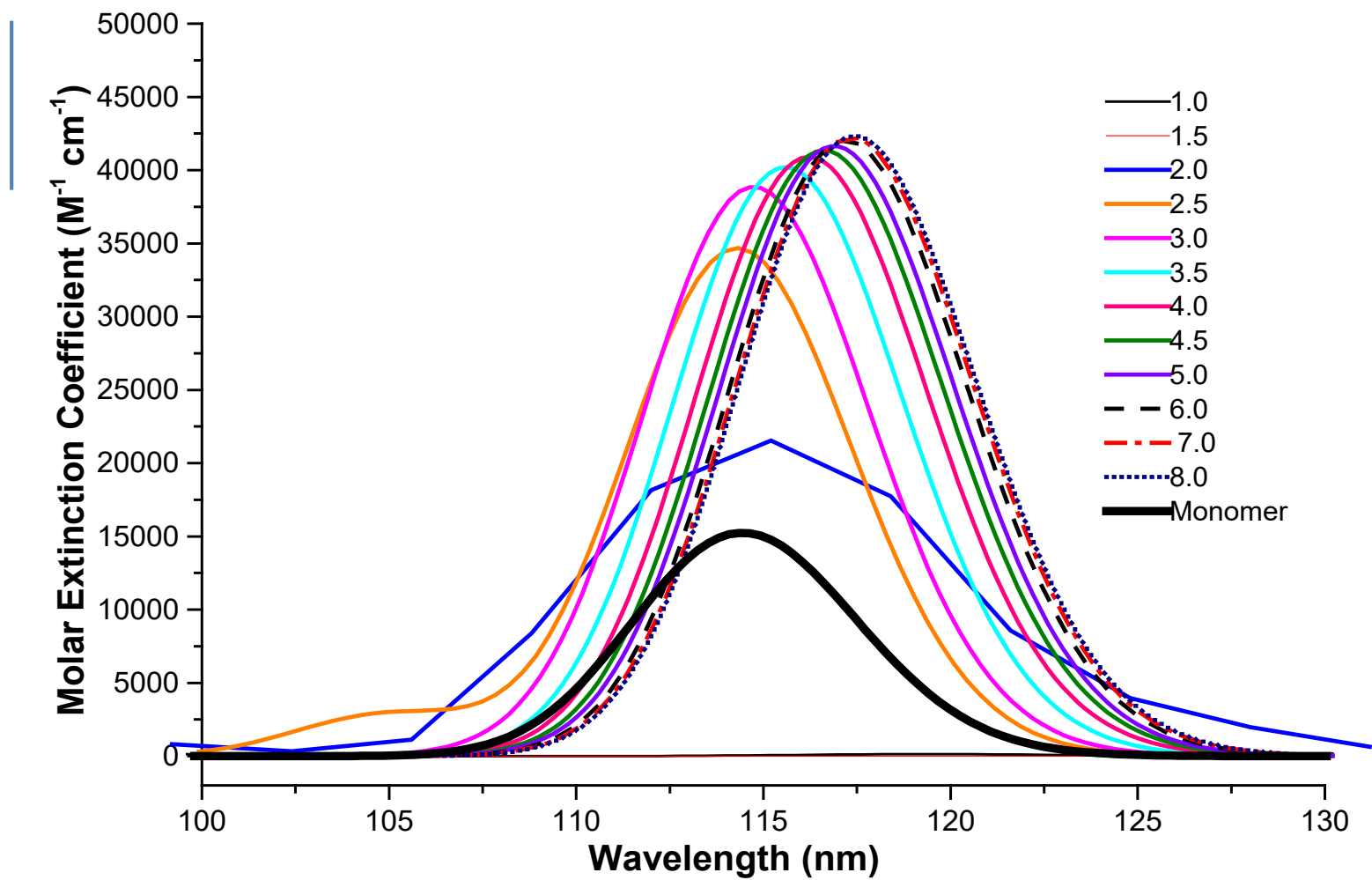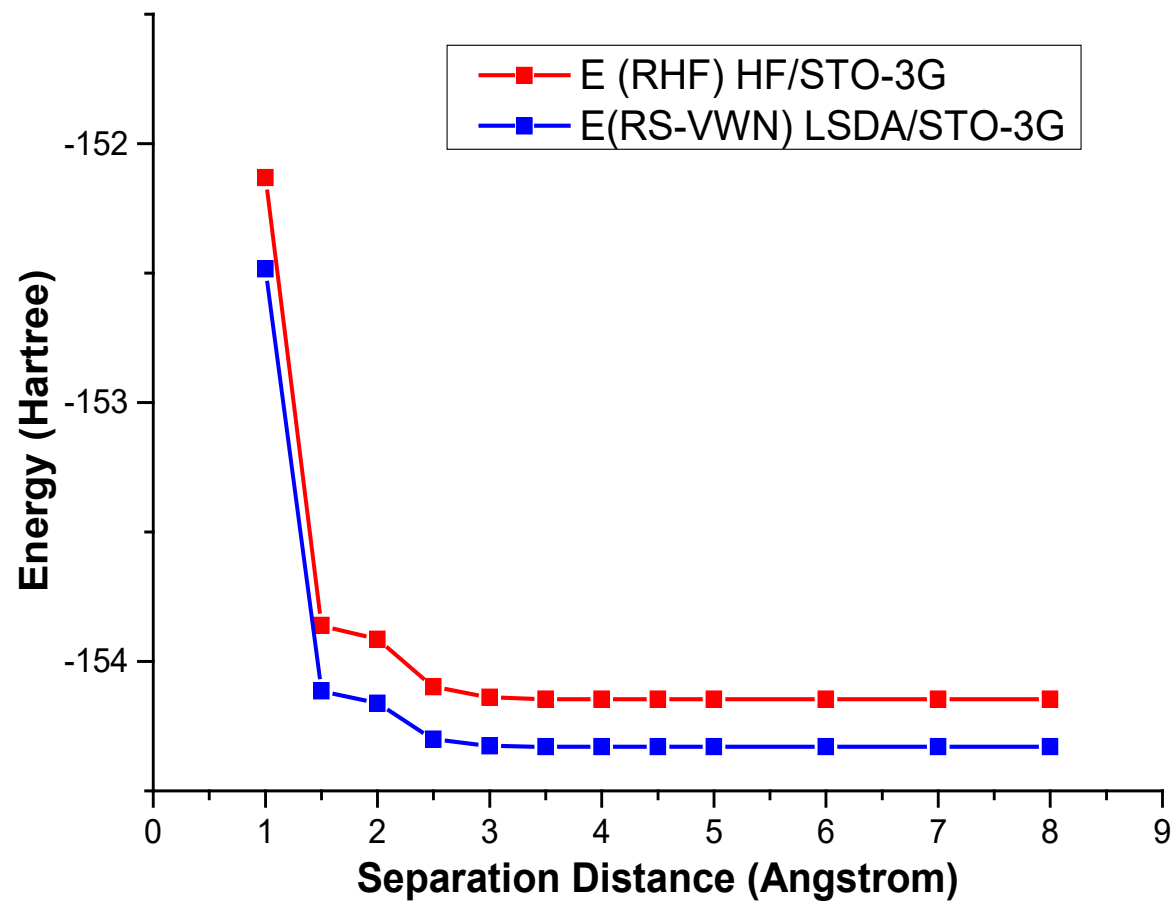**Fig.1 Absorption spectrum at different interplanar distances**

Fig.2 Absorption spectrum at different interplanar distances

Charge Transfer and Energy Transfer AU states

Distance (Å)	State	Excited	LSDA			HF		
			ET	CT	E(eV)	ET	CT	E(eV)
2.5	31AU	15→17 & 16 -> 18	0.070061	0.929939	10.8466	0.070041	0.929959	10.8466
	71AU	15→17 & 16 -> 18	0.93339	0.06661	11.8074	0.933348	0.066652	11.8074
3.5	21AU	15→17 & 16 -> 18	0.000799	0.999201	10.7258	0.000803	0.999197	10.7258
	71AU	15→17 & 16 -> 18	0.999203	0.000797	13.5375	0.999204	0.000796	13.5375
4	21AU	15→17 & 16 -> 18	9.00E-05	0.99991	10.6684	9.19E-05	0.999908	10.6684
	71AU	15→17 & 16 -> 18	0.999912	8.85E-05	14.0704	0.99991	8.98E-05	14.0704
5	21AU	15→17 & 16 -> 18	1	3.66E-07	10.607	1	4.17E-07	10.607
	91AU	15→17 & 16 -> 18	3.60E-07	1	14.807	4.23E-07	1	14.807
8	21AU	15→17 & 16 -> 18	1	0	10.5576	1	0	10.5576
	91AU	15→17 & 16 -> 18	1	0	15.8986	0	1	15.8986

Charge Transfer and Energy Transfer AG states

Distance (Å)	State	Excited	LSDA			HF		
			ET	CT	E(eV)	ET	CT	E(eV)
3.5	11AG	15 → 18 & 16 → 17	0.028399	0.971601	10.2284	0.028395	0.971605	10.2284
	81AG	15 → 18 & 16 → 17	0.973133	0.026867	13.6281	0.973124	0.026876	13.6281
4	11AG	15 → 18 & 16 → 17	0.002426	0.997574	10.3922	0.002423	0.997577	10.3922
	81AG	15 → 18 & 16 → 17	0.997712	0.002288	14.0787	0.997721	0.002279	14.0787
5	11AG	15 → 18 & 16 → 17	0.999993	6.88E-06	10.4722	0.999993	7.21E-06	10.4722
	101AG	15 → 18 & 16 → 17	6.76E-06	0.999993	14.8071	6.66E-06	0.999993	14.8071
8	11AG	15 → 18 & 16 → 17	1	0	10.5253	1	0	10.5253
	101AG	15 → 18 & 16 → 17	1	0	15.8986	1	0	15.8986

CONCLUSION

Method shows both charge transfer and energy transfer for the π to π^* transition in dimers

Below a separation distance of 2.5 Angstroms, the model fails.

At large distance, there is no charge transfer.

FUTURE PLANS

- BSE (Better Salpeter Equation)

- Evaluate the BSE for more geometries

- Test more functionals (especially optimally-tuned range-separated functionals)

- Test for the effect of other basis sets.

□□ □□□□

Thank you