School of Engineering
Institute of Materials
Laboratory of Macromolecular
and Organic Materials

Organic Electronic Materials 2025 Exercise 4 Solutions

1. Explain why the energy of a molecular system in its electronic ground state is always higher than the energetic eigenvalue associated with this state.

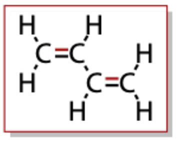
   The energy of a molecular system in its electronic ground state is always higher than the corresponding electronic energy eigenvalue because of vibrational motion.

   When solving the electronic Schrödinger equation (using the Born–Oppenheimer approximation), the nuclei are assumed to be fixed, and the resulting eigenvalue represents the minimum electronic energy for that nuclear configuration.

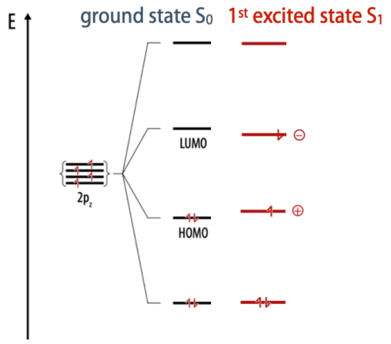
   However, the nuclei cannot be completely at rest due to the Heisenberg uncertainty principle. Even in the lowest vibrational state, the system retains a small amount of vibrational energy, known as the ***zero-point energy****, which is given by:*

$$E_0^{vib} = \frac{1}{2}\hbar\omega$$

2. Draw the MO energy level diagram of butadiene with the electrons and draw the same diagram after promotion of one electron from the HOMO to the next higher orbital upon photon absorption. Why does the wavelength of the absorbed photon not correspond to the HOMO-LUMO gap? Which energy does it correspond to? Draw a transition corresponding to this promotion of electron in a Jablonski diagram. Briefly explain the difference in representation between a Jablonski diagram and a diagram such as the first ones you drew.

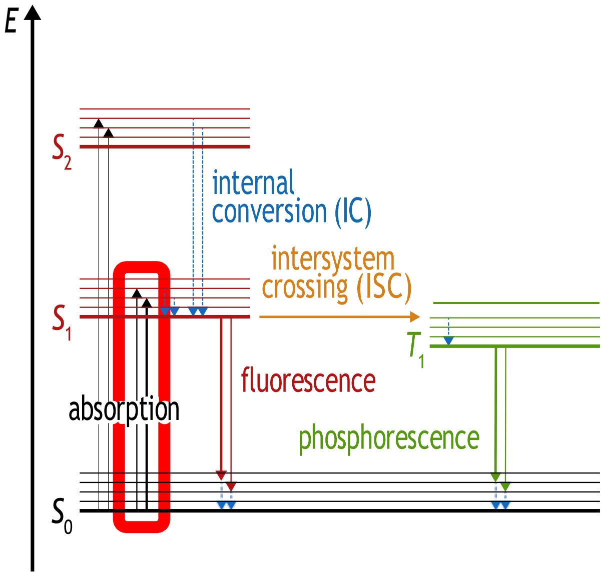


1,3-butadiene



The energy required to excite a molecule to the first excited state does not correspond exactly to the HOMO-LUMO gap because when an electron is excited and leaves a hole behind in the valence band, it interacts with the hole via electrostatic forces, creating a bound electron-hole pair, exciton. The binding energy associated to the exciton reduces therefore the energy required for the transition and it corresponds to the optical gap.

One of the circled transitions on the following Jablonski diagram, or any other one to a vibrationally excited state of the first electronically excited state, corresponds to this promotion of electron.



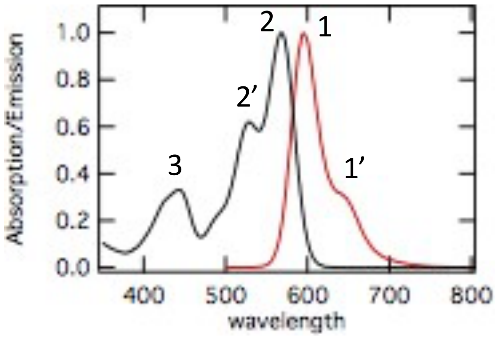
A Jablonski diagram shows the energy level of the whole system where a diagram like the first one shows the energy associated to the different orbitals involved in the system, that is given to the electron in it.

3. What are the electronic, vibronic, and spin conditions for a non-zero probability of an electron to be excited (this probability is related to an associated transition dipole moment)?

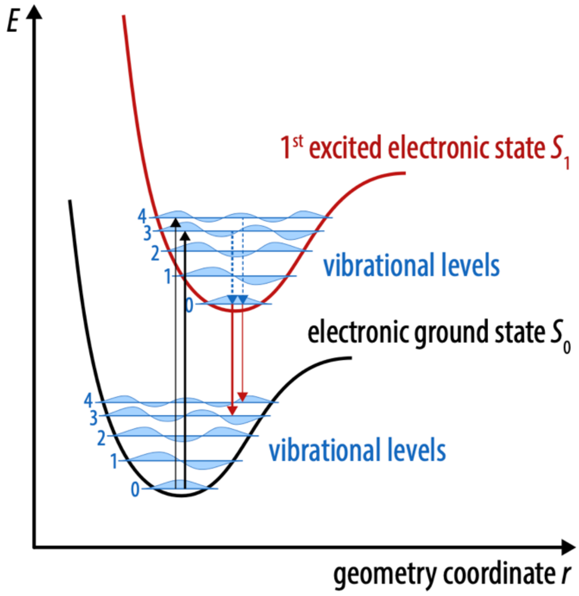
selection rules:

- *(electronic) spatial overlap of the electronic wave functions*
- *(electronic) symmetry may cancel overlapping wave functions (Laporte rule in centrosymmetric systems)*
- *(vibronic) overlap of vibrational wave functions (Frank-Condon overlap)*
- *(spin) $\Delta S=0$ (no change in spin)*

4. The absorption and emission spectra of a tetraphenoxyperylene bisimide are shown below. Which is which? Draw the four transitions associated with the peaks 1, 1', 2 and 2' on a relevant diagram. Explain the difference in wavelength between the peaks 1 and 2. Name both the principle and the rule that lead to this observation. To which transition could the peak 3 correspond to?



Black: Absorption
Red: Emission



2': thin black arrow
2: thick black arrow
1: thick red arrow
1': thin red arrow

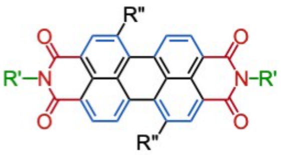
The difference in wavelengths between the peaks 1 and 2, called the Stokes shift, is because the excited state has a different potential energy curve associated to its geometry. Therefore, because of the Franck-Condon principle (vertical transition without geometry changes) and Kasha's rule (fluorescence is observed from the lowest excited state) this shift is observed.

The peak 3 could correspond to an excitation to the second electronic excited state.

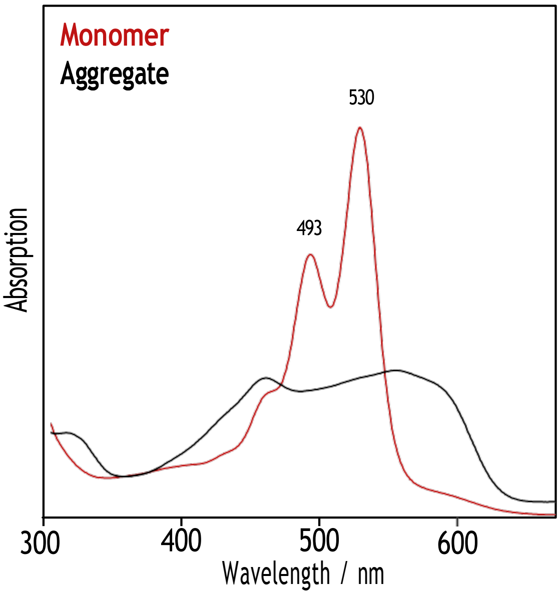
5. Single molecules of naphthalene, anthracene, tetracene and pentacene absorb at 200–300 nm, 250–400 nm, 280–500 nm and 450–600 nm, respectively in solution. What is the reason for this absorption shift?

   By extending the pi-system, delocalization of the electrons is increased and the HOMO-LUMO gap decreases. This can be explained with Hückel theory for LCAO, where ΔE ~ 1/N, where N is number of conjugated carbons.

6. The absorption spectra of a perylene diimide derivative in its monomeric and aggregated form are given below. What can you say about the type of spectroscopic aggregates observed in this case?

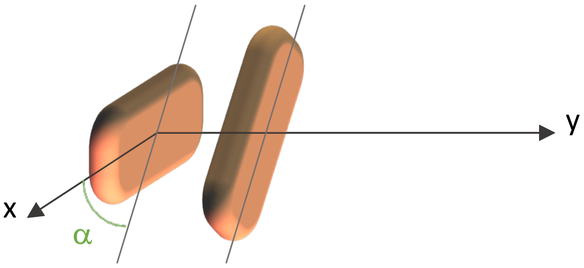


perylene diimide

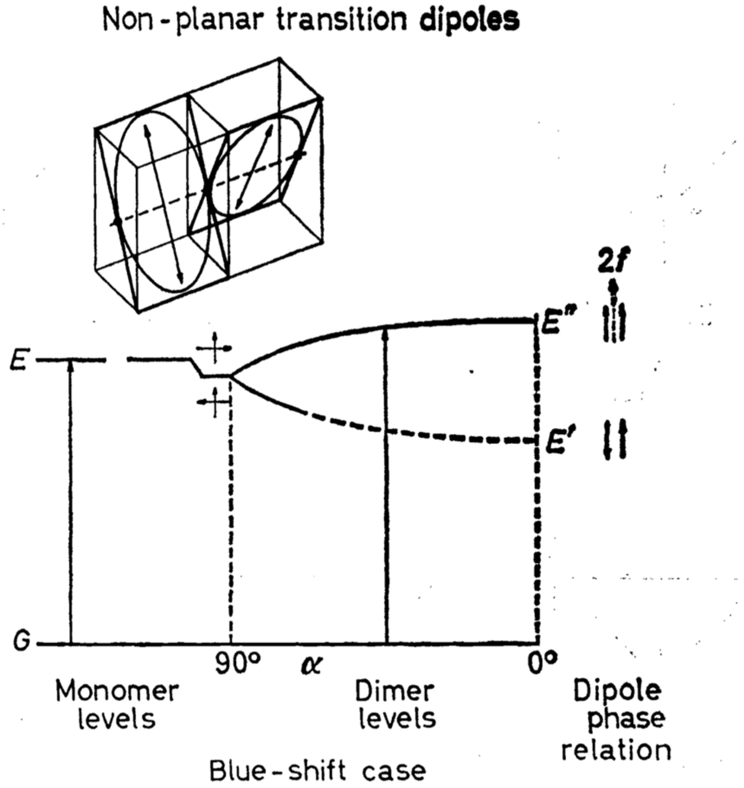


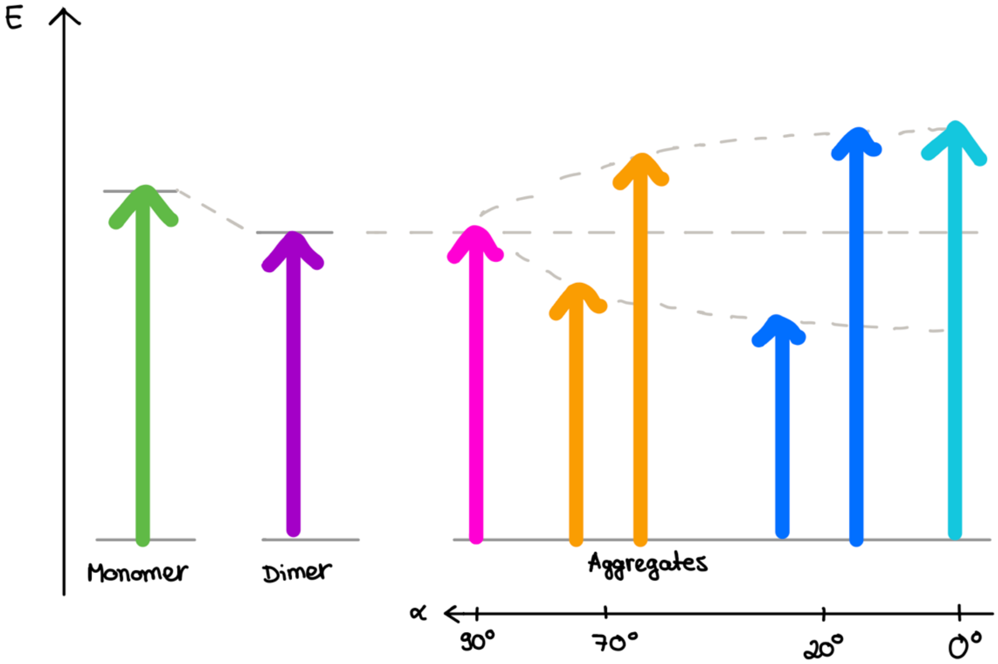
The spectroscopic aggregate observed here is neither a pure H-type nor a pure J-Type. These spectra could be the signature of a spectroscopic aggregates with non-colinear transition dipole moments, leading to a Davydov splitting or, of an 2D aggregates with a H-type excitonic coupling in one direction and a J-type excitonic coupling in the other direction.

7. Kasha, *Pure Appl.Chem.* **1965**, *11*, 371–392: Two perylene diimide derivatives are stacked helically as represented on the figure below. Considering the absorption spectrum of the perylene diimide derivative in its monomeric form in the previous question, sketch the absorption and emission spectra of such a dimer in the cases where α=0°, α≈20°, α≈70° and α=90°.



See slide 189 of the course for the definition of the alpha angle and Davydov splitting + Week 6 Homework (Kasha article) page 379. In the case of the question, we have $\theta = 90°$ because the centers of the molecules are aligned over the y axis. Also see slide 188 about the spectral signatures of H and J aggregates.



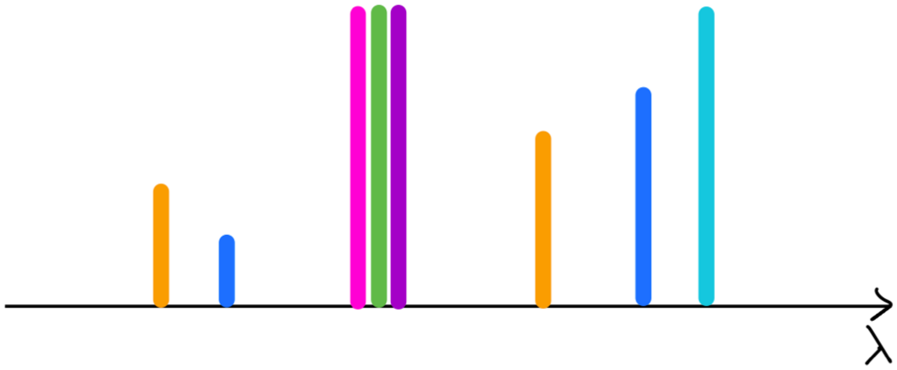


When the transition dipole moments of the two dyes are perpendicular to each other (α=90° case), then the transition dipole moments don't couple at all. The two molecules behave pretty much as isolated molecules. We therefore would not expect a significant spectral change; the absorption behavior is ***almost*** *identical to the absorption of the monomers. The closer α is to 0°, the more constructive the coupling, which means:*

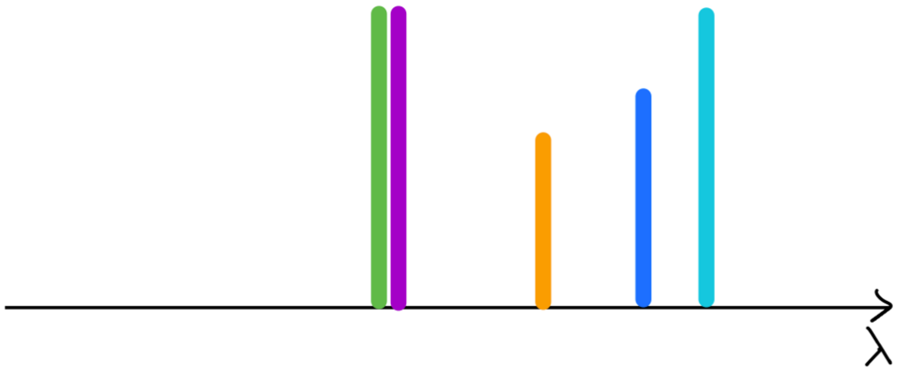
- *Stronger excitonic coupling*
- *Greater red shift*
- *Longer wavelength (higher λ) for both absorption and emission*

In the case of the dimer: there is a slight stabilization of excited states in the dimer phase leading to lower excited-state energy, hence lower E and higher λ in the spectra.
In the case of Davydov splitting, the molecules show "HJ absorption" behavior and a red-shifted J-type emission.

Absorption spectrum:



Emission spectrum: Davydov Splitting



Further Reading Suggestions:

- "Polarons, Bipolarons, and Solitons in Conducting Polymers" Acc. Chem. Res. 1985, 18, 309-315.
- "Mind the Gap", Mater. Horiz. 2014, 1, 17.
- "Electronic Processes in Organic Semiconductors: An Introduction", Anna Kohler, Heinz Bassler ISBN: 978-3-527-33292-2; p.37: selection rules, p.48: absorption, p.98: Jablonski diagram, p. 99-107: Exciton coupling, p.136: Kuhn plots