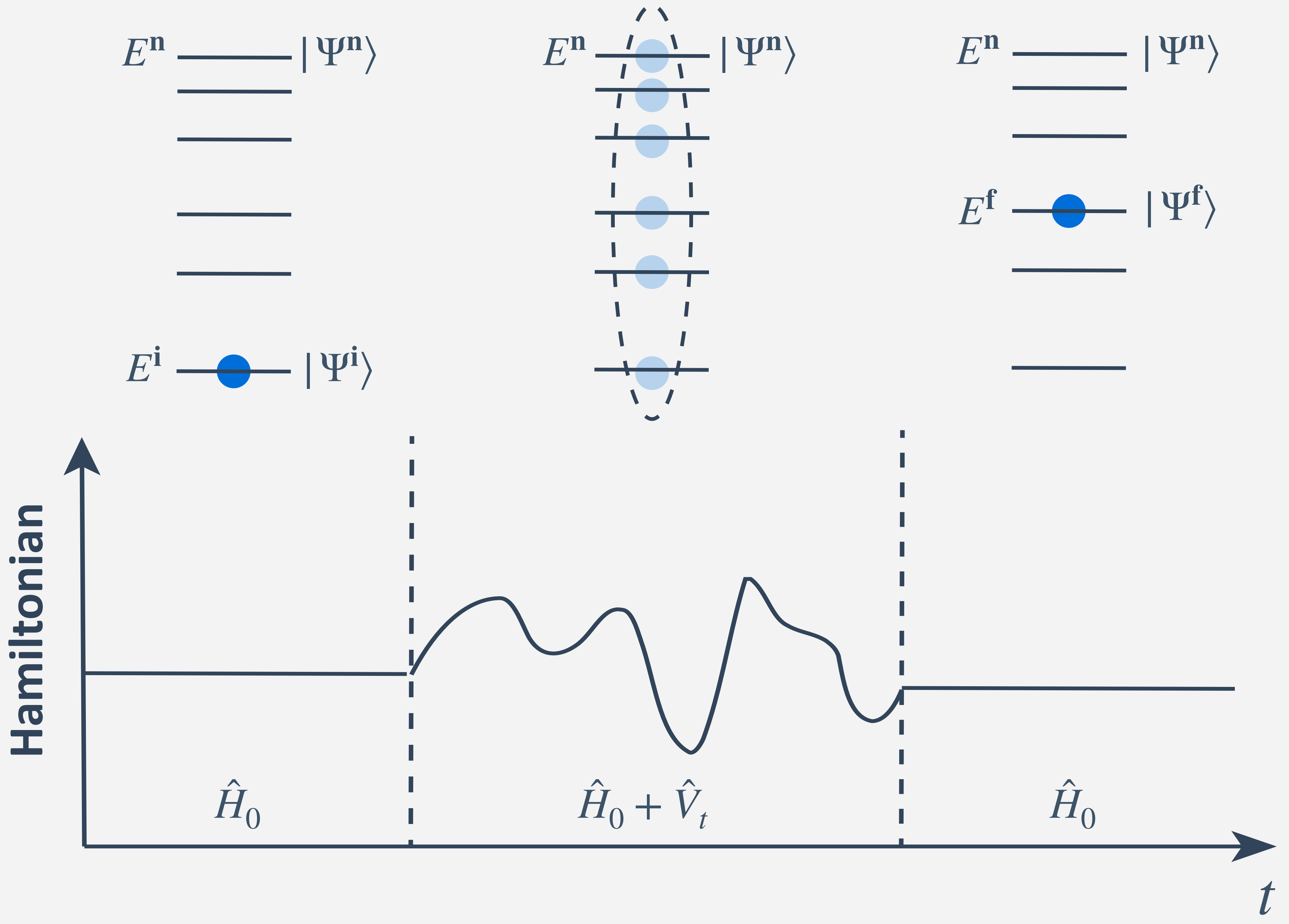
4.3 Exciton Formation and Excitonic Coupling

Temporal Evolution of Perturbed Quantum System

- perturbed wavefunction expressed as Eigenstates of the non-perturbed hamiltonian $\hat{H}_0$

$$|\Psi(t)\rangle = e^{-i\hat{H}_0 t/\hbar}|\Psi'(t)\rangle = e^{-i\hat{H}_0 t/\hbar}\sum^{n} c_n(t)|\Psi^{\mathbf{n}}\rangle$$



- **$c_{\mathbf{f}}(t)$ is the probability of transition to the state $|\Psi^{\mathbf{f}}\rangle$ after exposure to $\hat{V}_t$ during *t***

$$c_{\mathbf{f}}(t) = |\langle\Psi^{\mathbf{f}}|\Psi(t)\rangle|^2 = |\langle\Psi^{\mathbf{f}}|\Psi'(t)\rangle|^2 = |\langle\Psi^{\mathbf{f}}|\Psi^{\mathbf{n}}\rangle|^2 = P_{\mathbf{i}\to\mathbf{f}}(t)$$

Quantum System Perturbed by a Periodic Perturbation

- Schrödinger equation for the perturbed quantum system cannot be solved analytically:

$$i\hbar\frac{d}{dt}|\Psi(t)\rangle = (\hat{H}_0 + \hat{V}(t))|\Psi(t)\rangle \quad \Leftrightarrow \quad i\hbar\frac{d}{dt}|\Psi'(t)\rangle = e^{i\hat{H}_0 t/\hbar}\ \hat{V}(t)\ e^{-i\hat{H}_0 t/\hbar}|\Psi'(t)\rangle$$

- but a solution can be approximated while integrating the equation over the exposure time, particularly in the case of a periodic perturbation $\hat{V}_t = 2\hat{V}cos(\omega t)$:

$$P_{\mathbf{i}\rightarrow\mathbf{f}}(t) = \frac{2\pi t}{\hbar}|\langle\Psi^{\mathbf{f}}|\hat{V}|\Psi^{\mathbf{i}}\rangle|^2\delta(E^{\mathbf{f}} - E^{\mathbf{i}}\ \pm\ \hbar\omega)$$

- as the probability of transition is proportional to t, it is mostly given as probability per unit of time

$$\Gamma_{\mathbf{i}\rightarrow\mathbf{f}} = \frac{2\pi}{\hbar}|\langle\Psi^{\mathbf{f}}|\hat{V}|\Psi^{\mathbf{i}}\rangle|^2\ \delta(E^{\mathbf{f}} - E^{\mathbf{i}}\ \pm\ \hbar\omega)$$

Fermi's Golden Rule

- with the Dirac delta function $\delta(E^{\mathbf{f}} - E^{\mathbf{i}}\ \pm\ \hbar\omega) = 0$ except if $E^{\mathbf{f}} - E^{\mathbf{i}} = \pm\ \hbar\omega$
  - the perturbation acting on the initial state must match a final state
  - the energy difference of final and initial state must match the energy of the perturbation

Interaction of Molecules with Light

- optical electromagnetic radiation can be described as a monochromatic progressive plane wave

$$\overrightarrow{\mathscr{E}}(t) = \mathscr{E}_0(e^{i(kx-\omega t)} + e^{-i(kx-\omega t)})\vec{u}_y$$

- in the approximation of large wavelengths $\lambda \gg a_0$ (Bohr radius):

$$e^{\pm ikx} \approx 1 \quad \Rightarrow \quad \overrightarrow{\mathscr{E}}(t) = 2\mathscr{E}_0 cos(\omega t)\vec{u}_y$$

- the interaction of the light with a molecule is related to a periodic time-dependent perturbation term of the Hamiltonian

$$\hat{V}_t = -\sum_{k}^{particules} Z_k e \overrightarrow{\hat{R}_k} \cdot \overrightarrow{\mathscr{E}}(t) = 2(-\overrightarrow{\hat{\mu}} \cdot \mathscr{E}_0\vec{u}_y)cos(\omega t)$$

- probability of transition from $|\Psi^{\mathbf{i}}\rangle$ to $|\Psi^{\mathbf{f}}\rangle$ under the influence of a optical electromagnetic radiation is given by

$$\Gamma_{\mathbf{i}\to\mathbf{f}} = \frac{2\pi}{\hbar}\mathscr{E}_0^2 |\langle\Psi^{\mathbf{f}}|\overrightarrow{\hat{\mu}}|\Psi^{\mathbf{i}}\rangle \cdot \vec{u}_y|^2 \delta(E^{\mathbf{f}} - E^{\mathbf{i}} \pm \hbar\omega)$$

Electric Transition Dipole Moment

- within the Born Oppenheimer approximation framework, wavefunctions and the electric transition dipole moment $\vec{\mu}_{\mathbf{i}\to\mathbf{f}}$ decompose into be separated vibrational and electronic terms, and the latter further into an electronic orbital, a vibronic, and a spin part:

$$\vec{\mu}_{\mathbf{i}\to\mathbf{f}} = \underbrace{\langle \phi^{\mathbf{e,orb}}_{n_\mathbf{f}} \,|\, \vec{\hat{\mu}}_{\mathbf{e}} \,|\, \phi^{\mathbf{e,orb}}_{n_\mathbf{i}} \rangle \, \langle \phi^{\mathbf{nu}}_{n_\mathbf{f},\nu_\mathbf{f}} \,|\, \phi^{\mathbf{nu}}_{n_\mathbf{i},\nu_\mathbf{i}} \rangle}_{\neq \vec{0} \ \text{ if } \ n_\mathbf{i} \neq n_\mathbf{f}} \, \langle \sigma_\mathbf{f} \,|\, \sigma_\mathbf{i} \rangle + \underbrace{\langle \phi^{\mathbf{nu}}_{n_\mathbf{f},\nu_\mathbf{f}} \,|\, \vec{\hat{\mu}}_{\mathbf{nu}} \,|\, \phi^{\mathbf{nu}}_{n_\mathbf{i},\nu_\mathbf{i}} \rangle \langle \phi^{\mathbf{e,orb}}_{n_\mathbf{f}} \,|\, \phi^{\mathbf{e,orb}}_{n_\mathbf{i}} \rangle}_{\neq \vec{0} \ \text{ if } \ n_\mathbf{i} = n_\mathbf{f}} \langle \sigma_\mathbf{f} \,|\, \sigma_\mathbf{i} \rangle$$

electronic transitions
UV-Vis spectroscopy

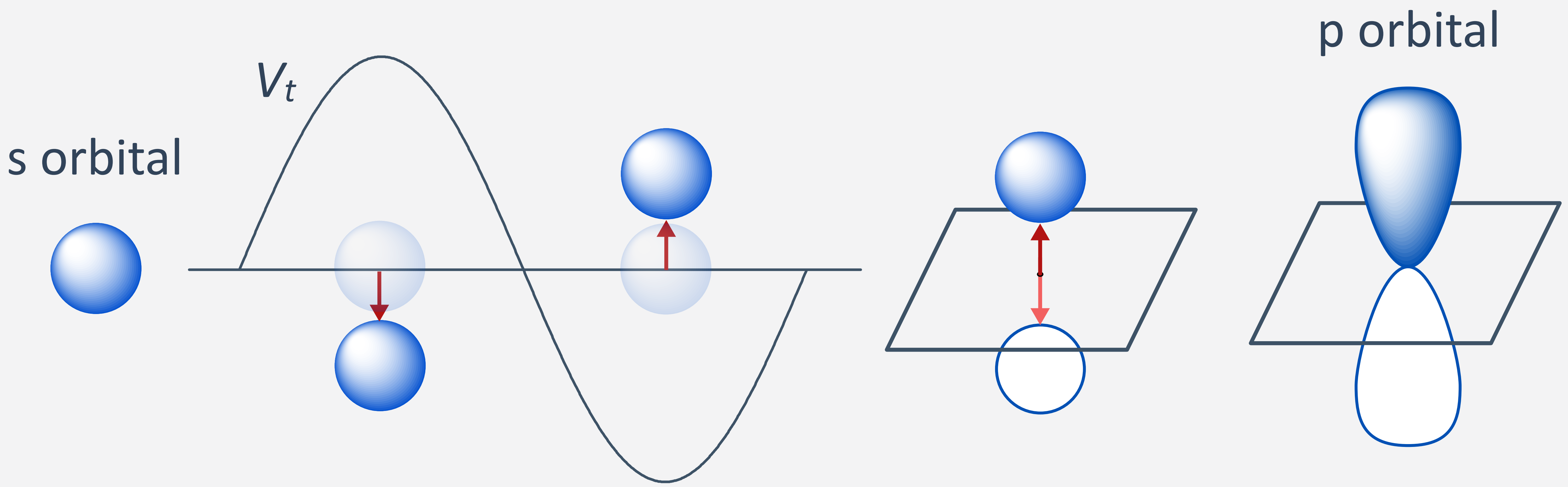
vibrational transitions
Infrared spectroscopy

- **in the case of perturbations by electromagnetic radiation at optical wavelengths**
  - their range of energies is on the order of the electronic level splitting
  - the transition dipole moment can be reduced to its electronic term

Selection Rules for Electronic Transitions

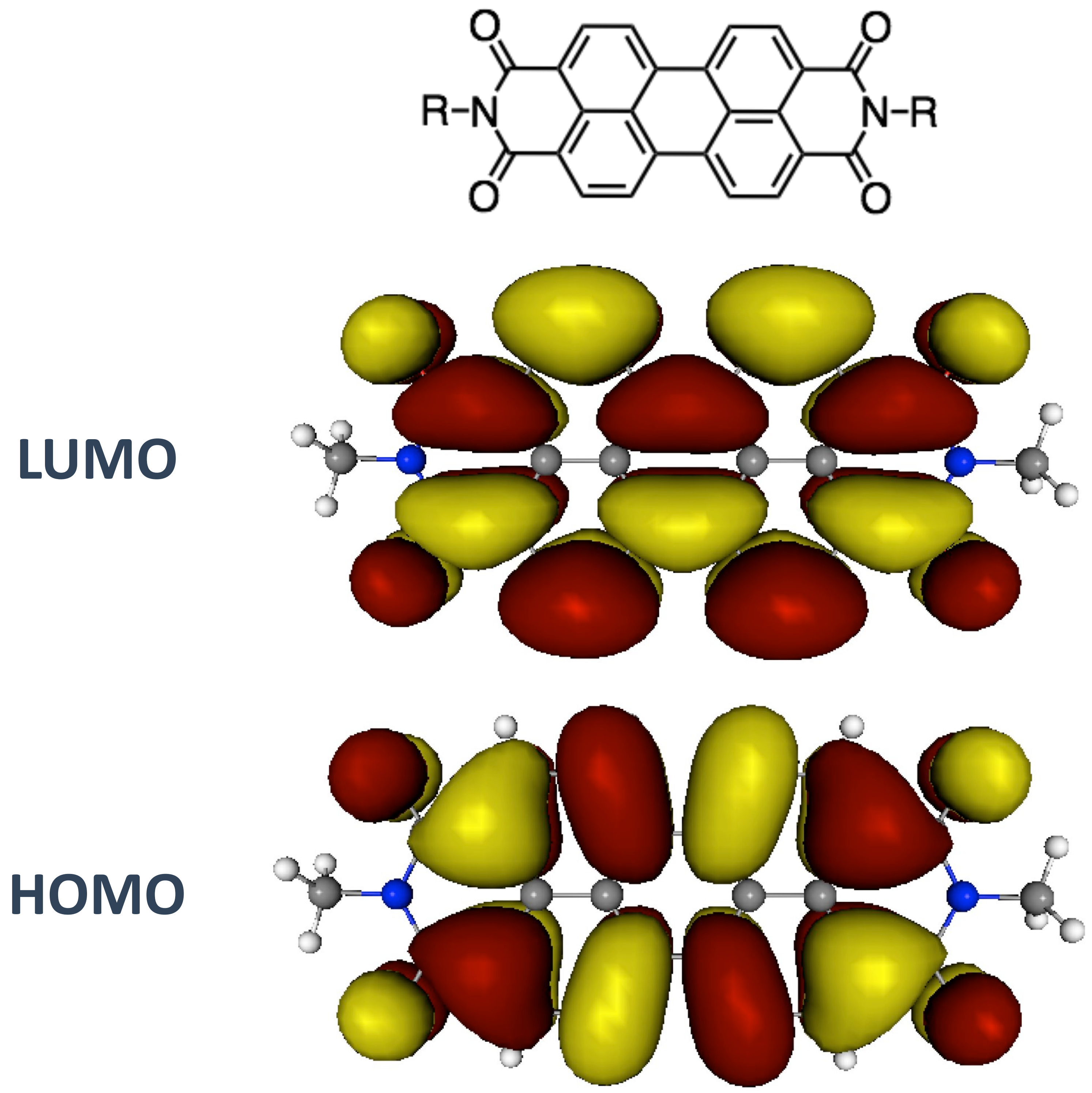
- the allowance of electronic transitions ($n_\mathrm{i} \neq n_\mathrm{f}$) is described by different selection rules derive from the condition

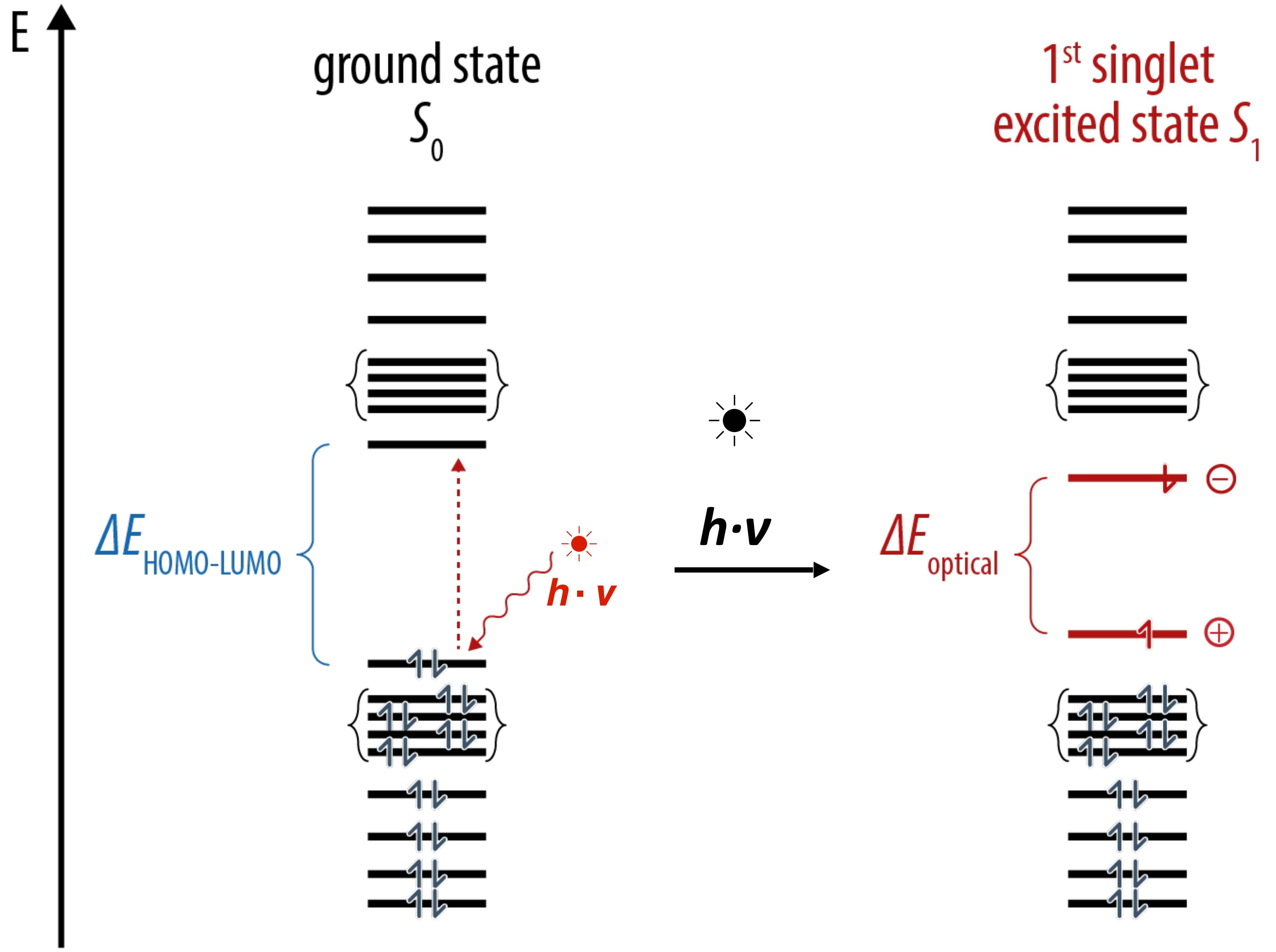
$$\langle \Psi^\mathrm{f} | \overrightarrow{\hat{\mu}} | \Psi^\mathrm{i} \rangle = \langle \phi_{n_\mathrm{f}}^{\mathbf{e,orb}} | \overrightarrow{\hat{\mu}}_\mathbf{e} | \phi_{n_\mathrm{i}}^{\mathbf{e,orb}} \rangle \langle \phi_{n_\mathrm{f},\nu_\mathrm{f}}^{\mathbf{nu}} | \phi_{n_\mathrm{i},\nu_\mathrm{i}}^{\mathbf{nu}} \rangle \langle \sigma_\mathbf{f} | \sigma_\mathbf{i} \rangle \neq \vec{0}$$



- **Laporte Rule: transitions between states of the same parity (u, g) are forbidden (in centrosymmetric molecules)**
- **Frank Condon Principle: overlap of the vibrational wave functions**
- **Spin Selection Rule: the transition occurs without change in spin**

Interaction of light with conjugated molecules

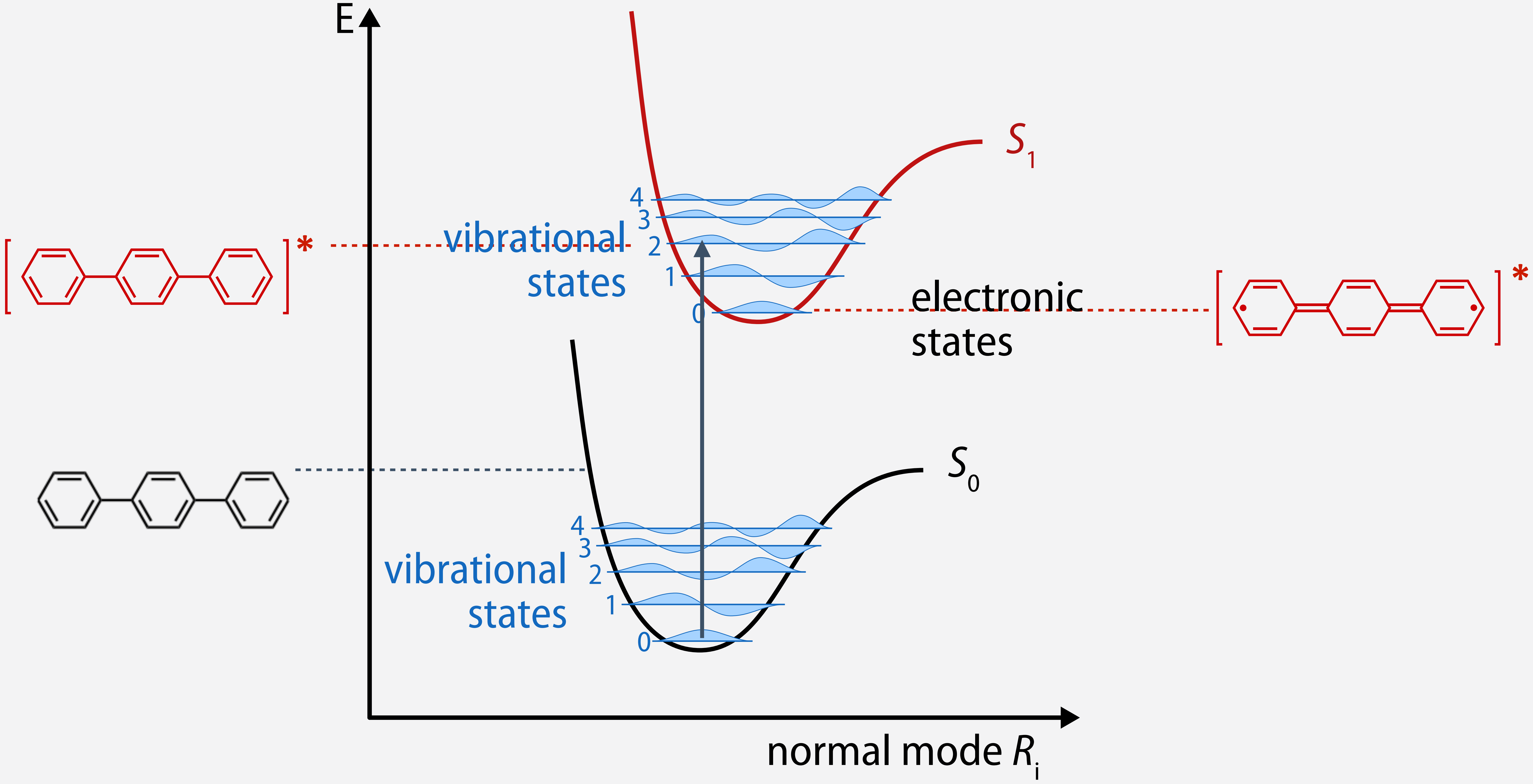




- excitation by light promotes one electron from the HOMO to the LUMO by absorption of photon energy and leads to the **formation of a Frenkel exciton** (bound electron-hole pair)
- excitation must result in **singlet excitons** (a pair of electrons with opposite spins) because of the **spin selection rule**
- because of exciton binding energy, HOMO-LUMO gap ≠ optical transition energy $\Delta E_{\text{optical}}$

Franck-Condon Principle

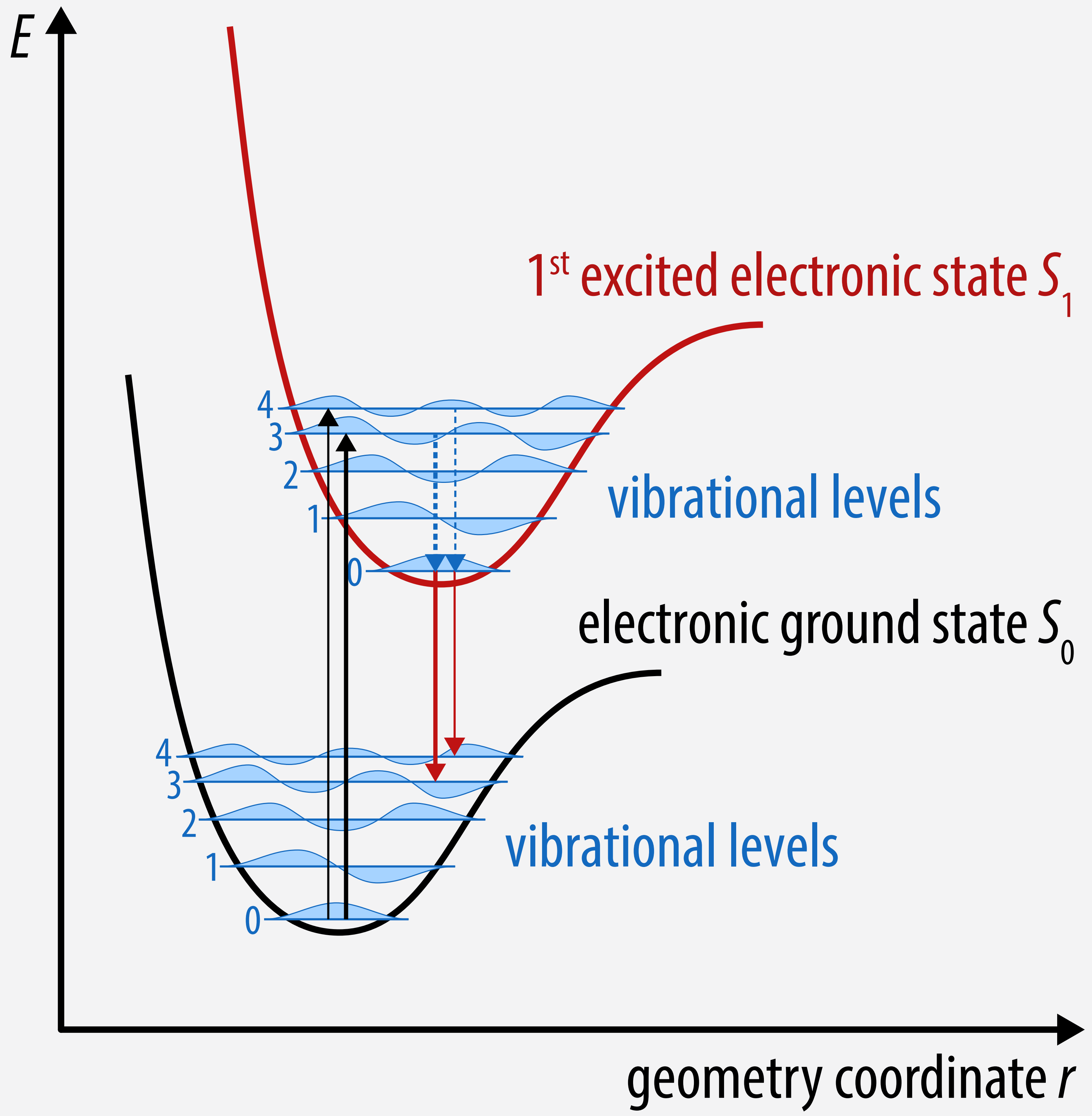
- Franck-Condon principle: fast “vertical” transition (10^{-15} s), without geometry changes (10^{-12} s)

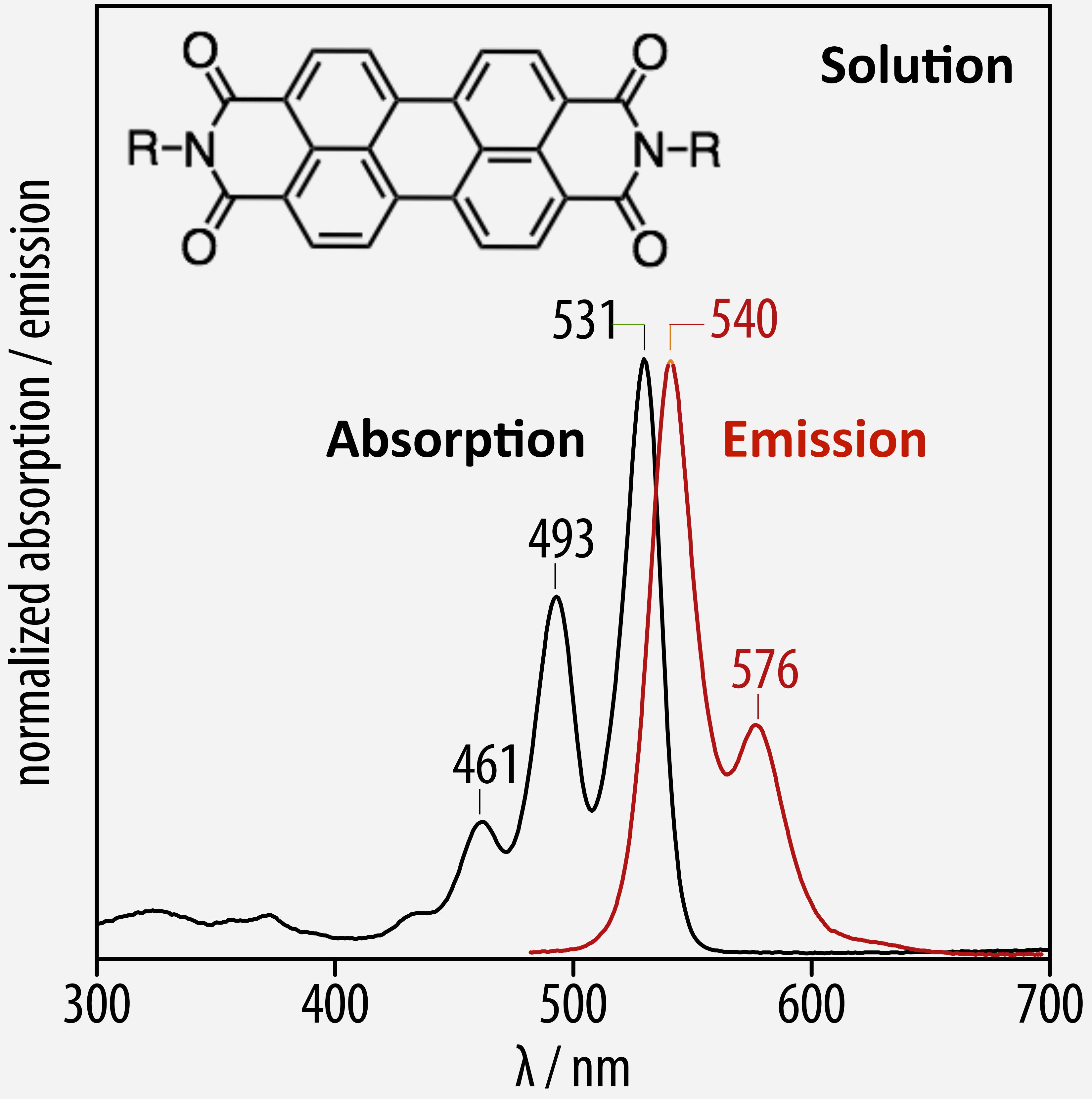


- **excitation to vibrationally excited (“hot”) state of S_1 with bond lengths similar to S_0**
- **subsequent vibrational relaxation results in energy loss as heat**
- **upon relaxation to ground state (same rules apply), photon with lower energy is emitted**

Absorption and Emission Spectra

- emission spectra usually mirror the absorption spectra, shifted to higher wavelength

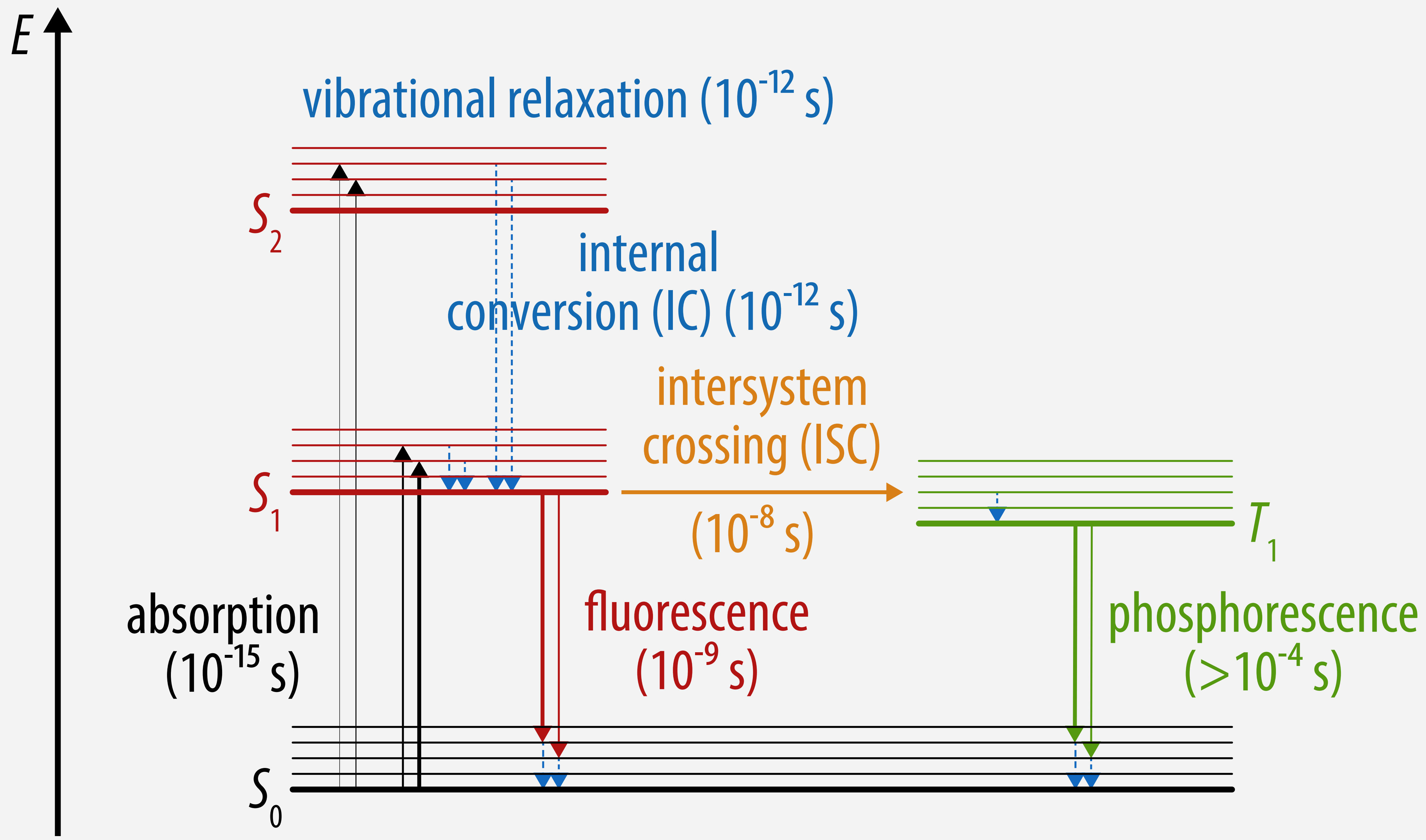




- **Stokes shift is the difference in the wavelengths of highest wavelength absorption and lowest wavelength emission**

Jablonski Diagram

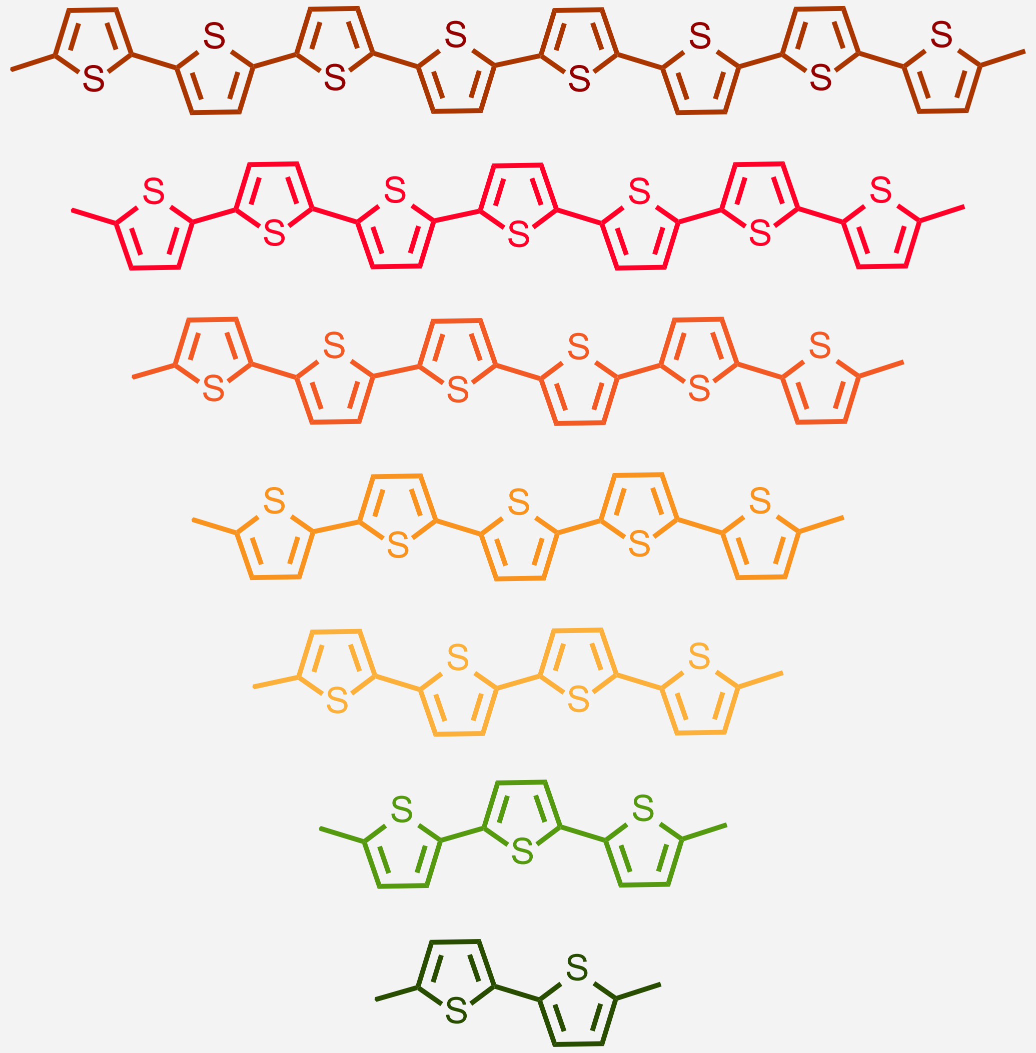
- Jablonski diagram illustrates electronic states and the transitions between them
- internal conversion (IC): non-radiative transition to a state with the same spin multiplicity
- intersystem crossing (ISC): non-radiative transition to a state with a different spin multiplicity

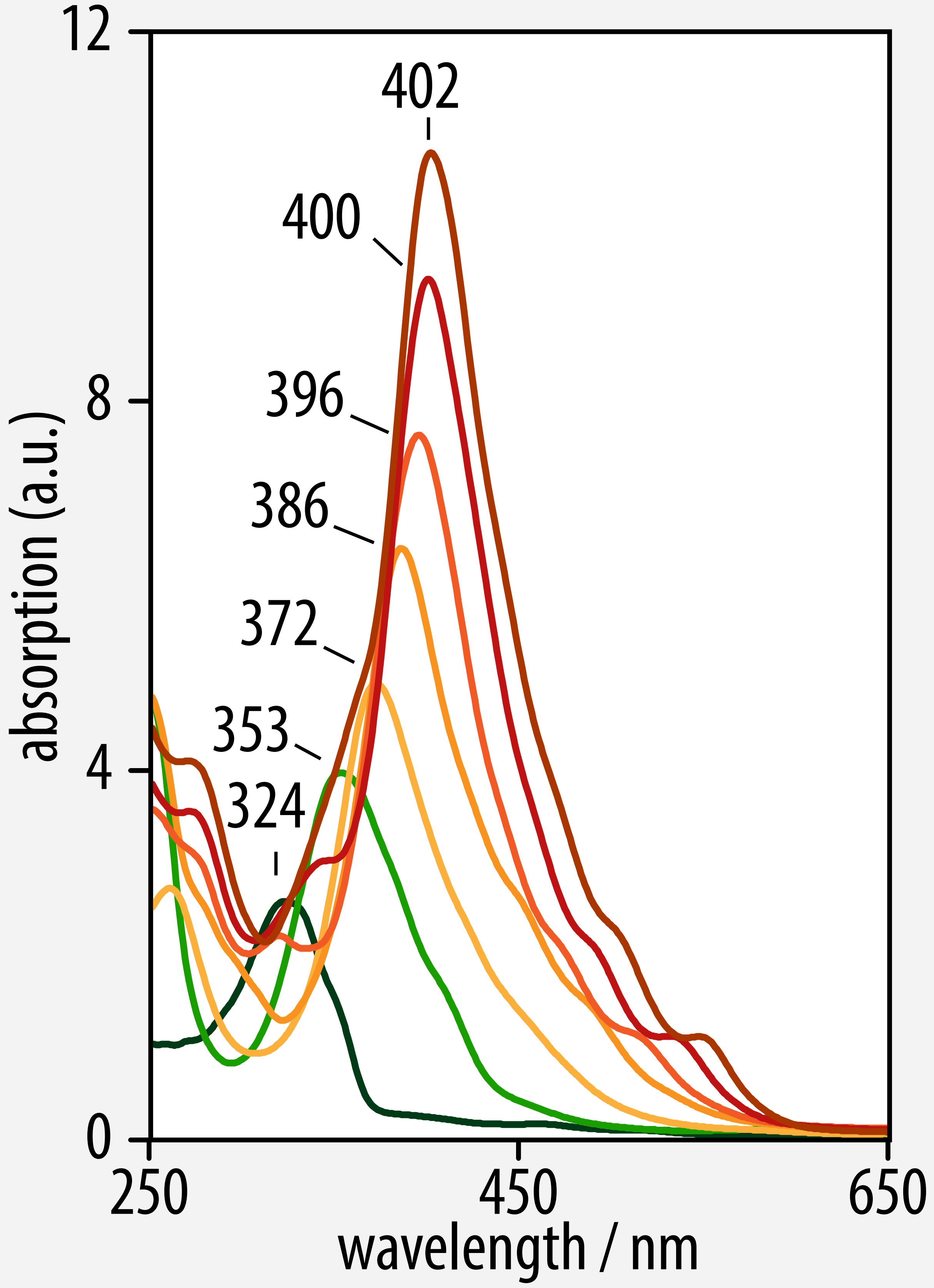


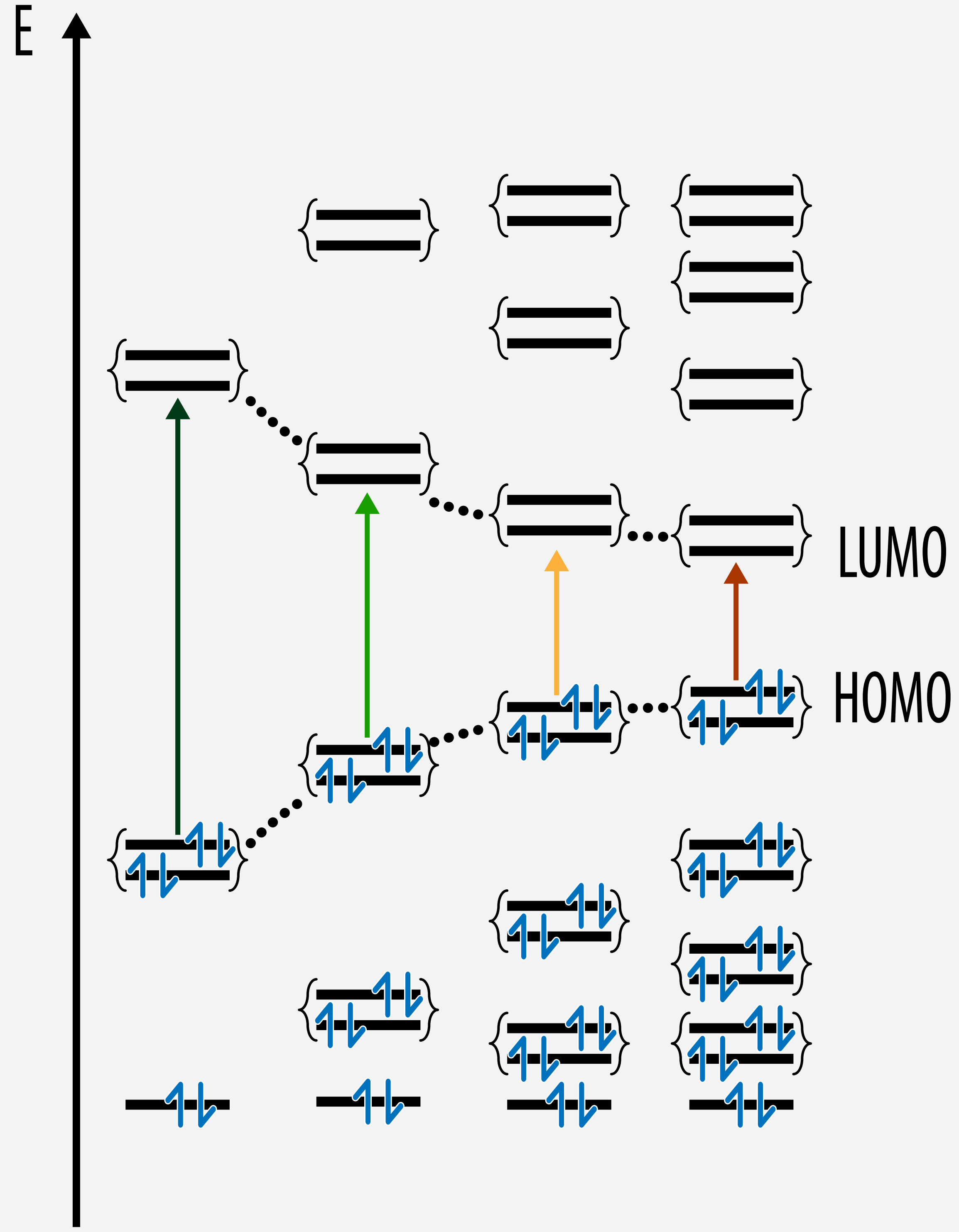
- **time constants of the individual processes determine the deactivation paths**
  - fluorescence is observed from the lowest excited state, as IC is much faster (Kasha’s rule)
  - the much larger time scale of phosphorescence is caused by “spin-forbidden" transition

Optical Gap and Degree of Electronic Delocalization

- with increasing conjugation length the main absorption shifts towards longer wavelength
- intensity increases as transition dipole moment increases



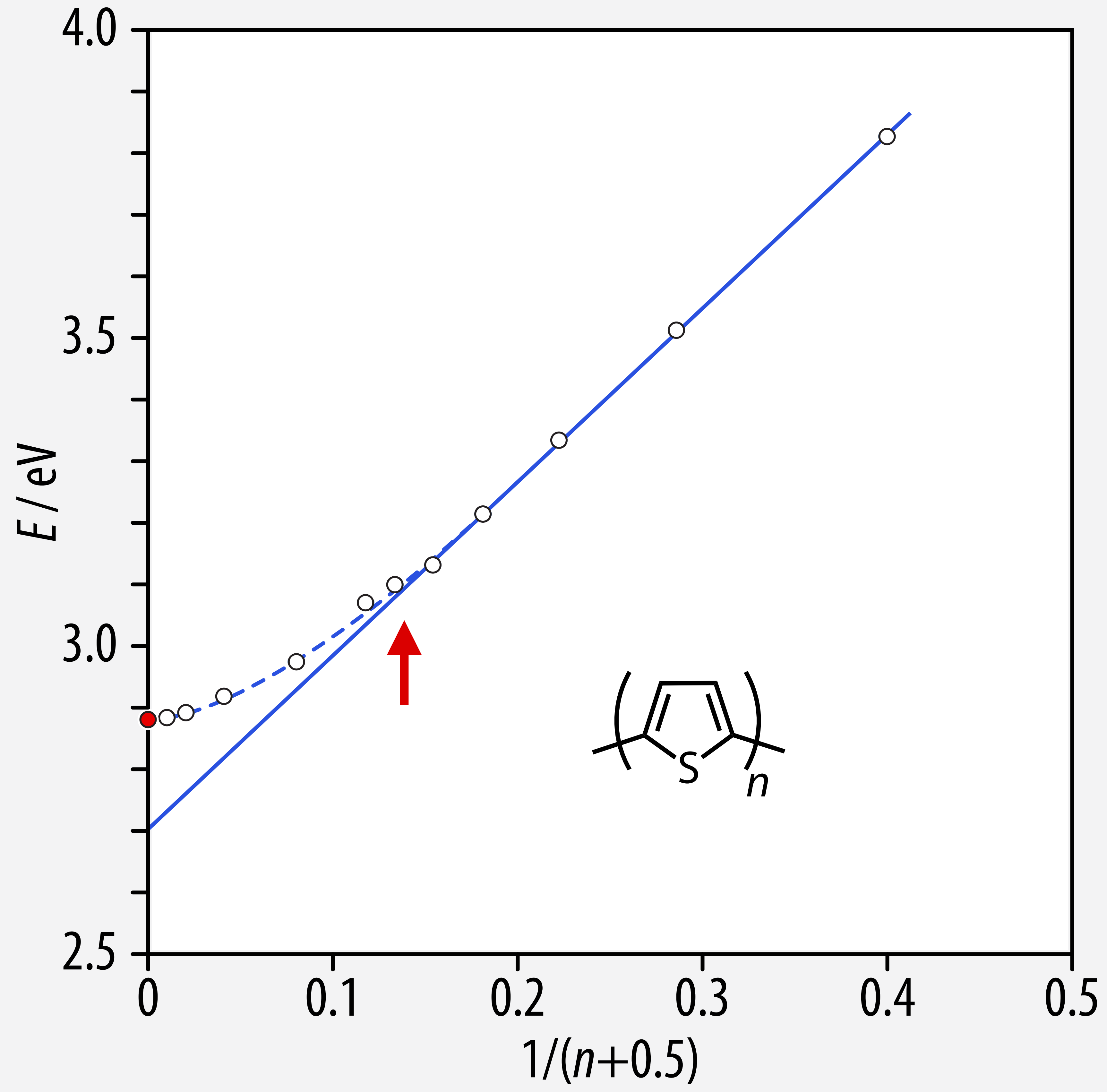


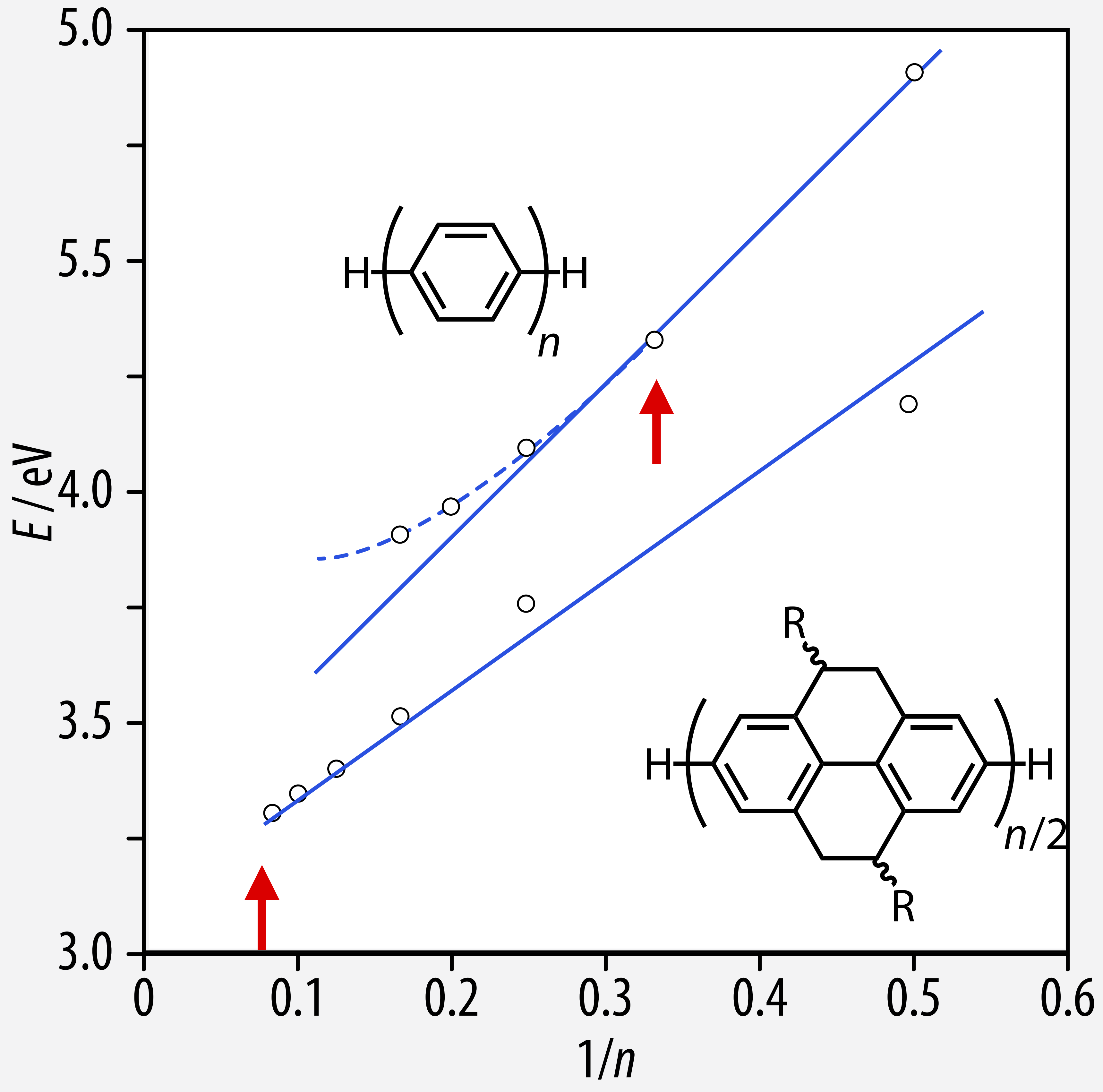


- **the bathochromic shift in the absorption spectra is due to decreasing HOMO-LUMO gaps**

Effective Conjugation Length

- Kuhn plot of transition energy $E = h \cdot c / \lambda$ (in eV) vs. inverse length of the π-system

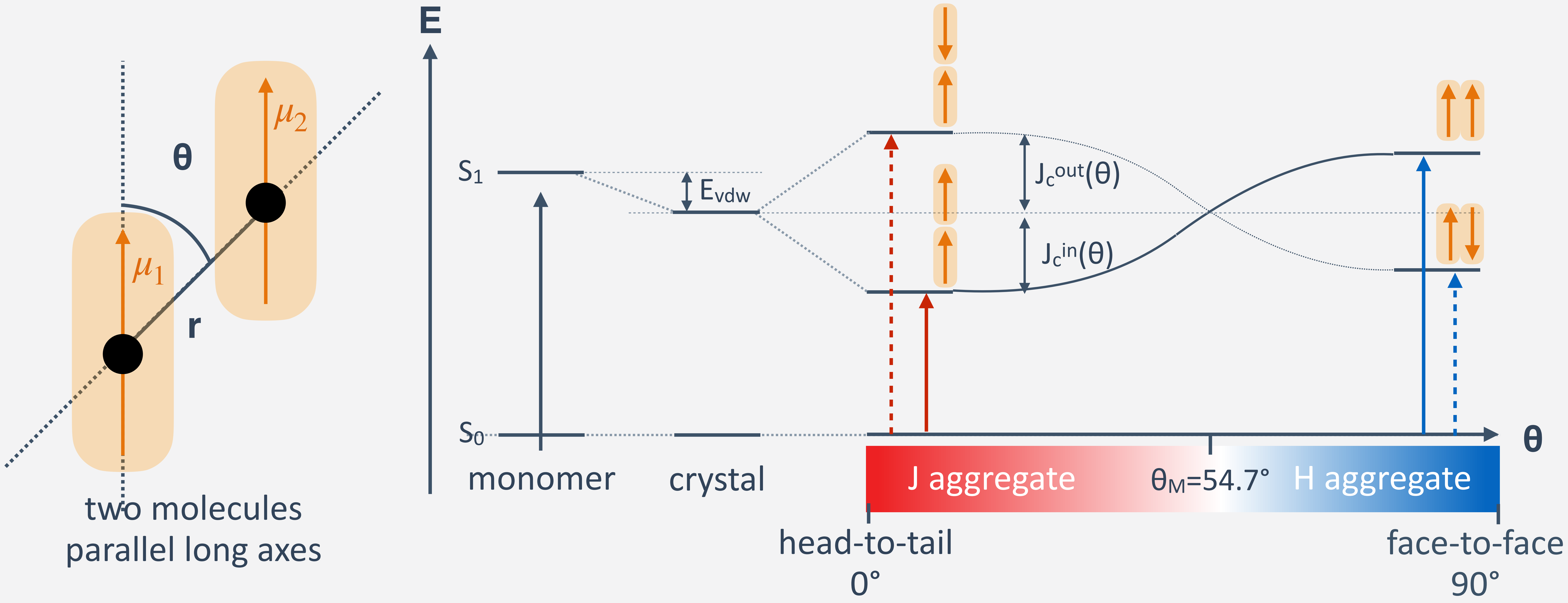




- **with increasing size of the π system, the main absorption shifts towards lower energy**
- **but beyond a critical effective conjugation length, it converges to a finite energy**

"Spectroscopic Aggregates": Excitonic Coupling in Dimers

- excitonic coupling: transition dipole moments of molecules in close proximity interact, which can be treated as a perturbation by a Coulomb potential



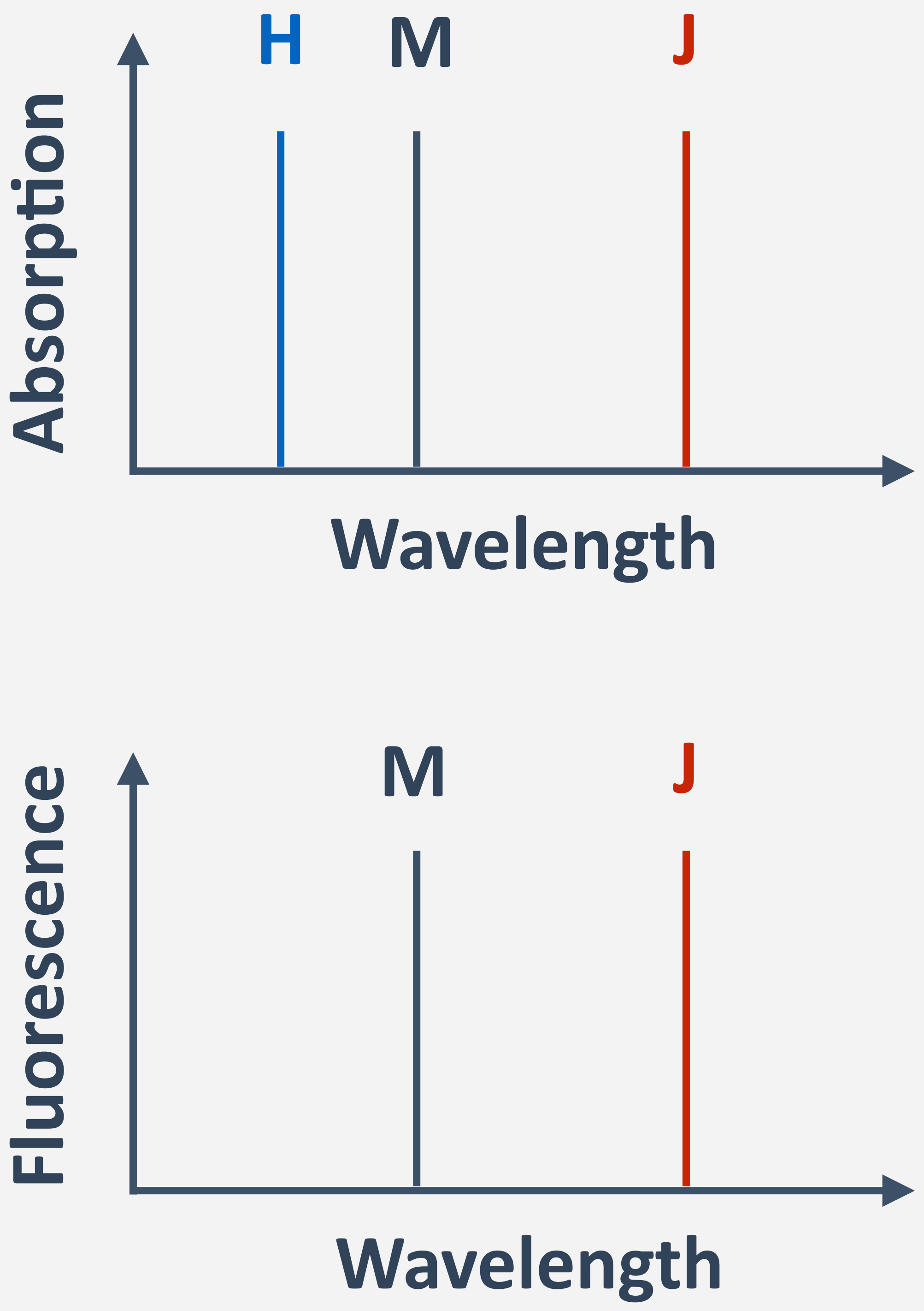
- **excitonic coupling leads to a stabilisation by E_{vdw} of the excited state (solid state red shift)**
- **moreover, a splitting occurs as given by the point-dipole model**

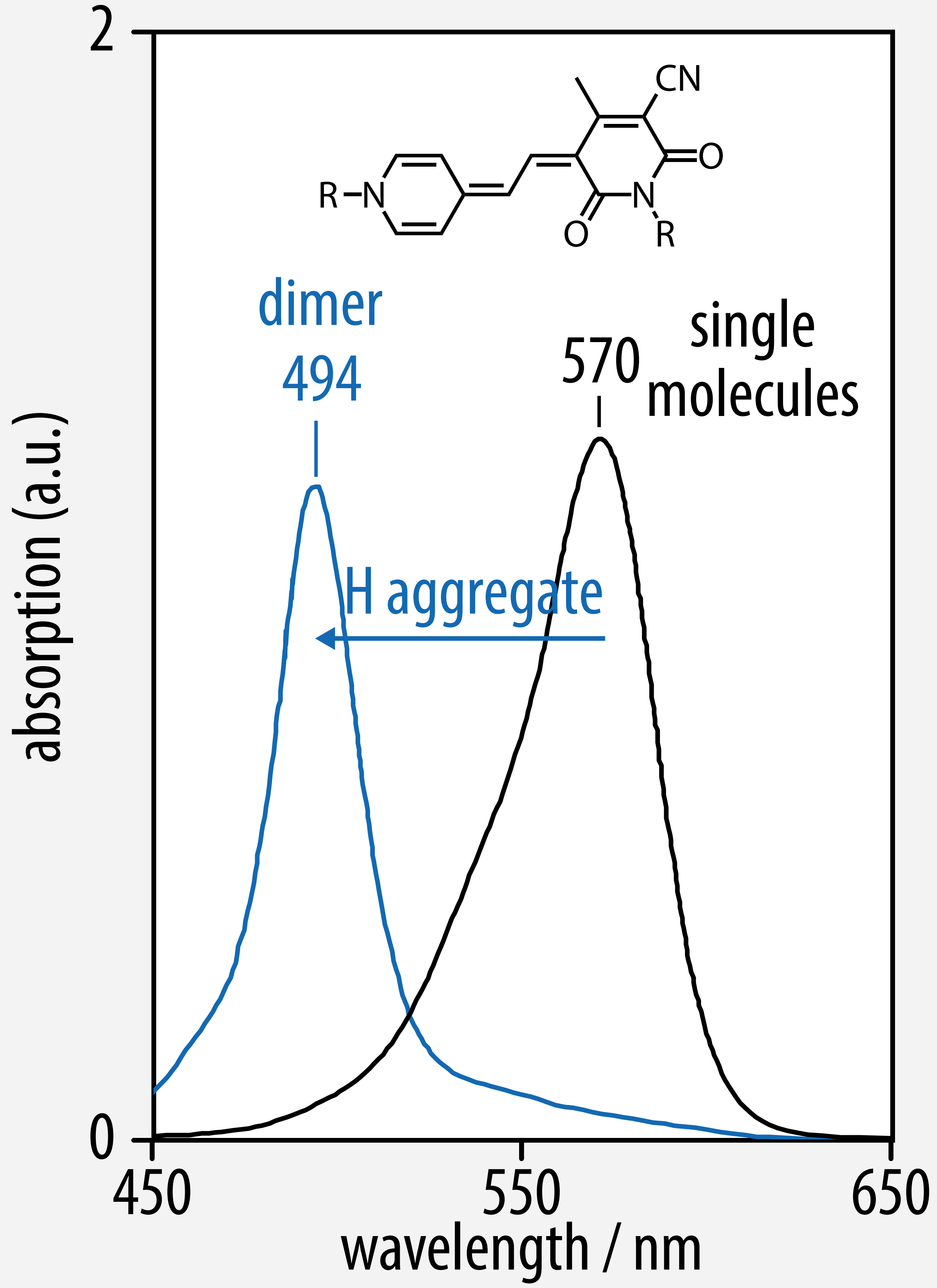
$$J_c = \frac{\vec{\mu}_1 \cdot \vec{\mu}_2}{r^3} - \frac{3(\vec{\mu}_1 \cdot \vec{r})(\vec{\mu}_2 \cdot \vec{r})}{r^5}$$

KEY CONCEPT: see Kasha, *Pure Appl.Chem.* **1965**, *11*, 371–392.

Spectral Signatures of H and J Aggregates

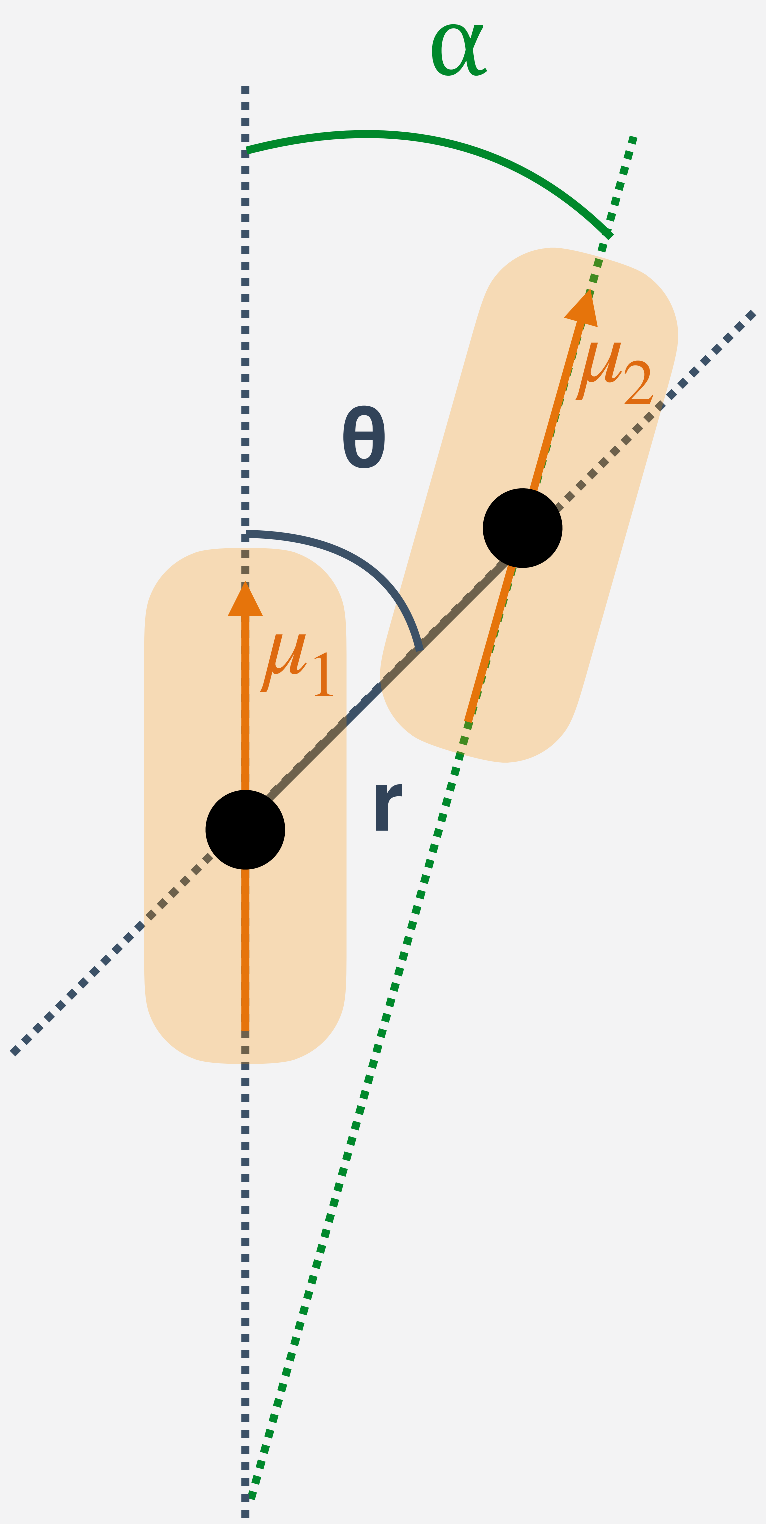
- in J aggregates (after E. E. Jelley), the main absorption and emission bands are shifted to higher wavelengths
- in H aggregates (as in hypsochromic), absorption band is shifted to lower wavelengths, and the emission band vanishes (because Kasha's rule but transition from lowest state is dipole-forbidden)

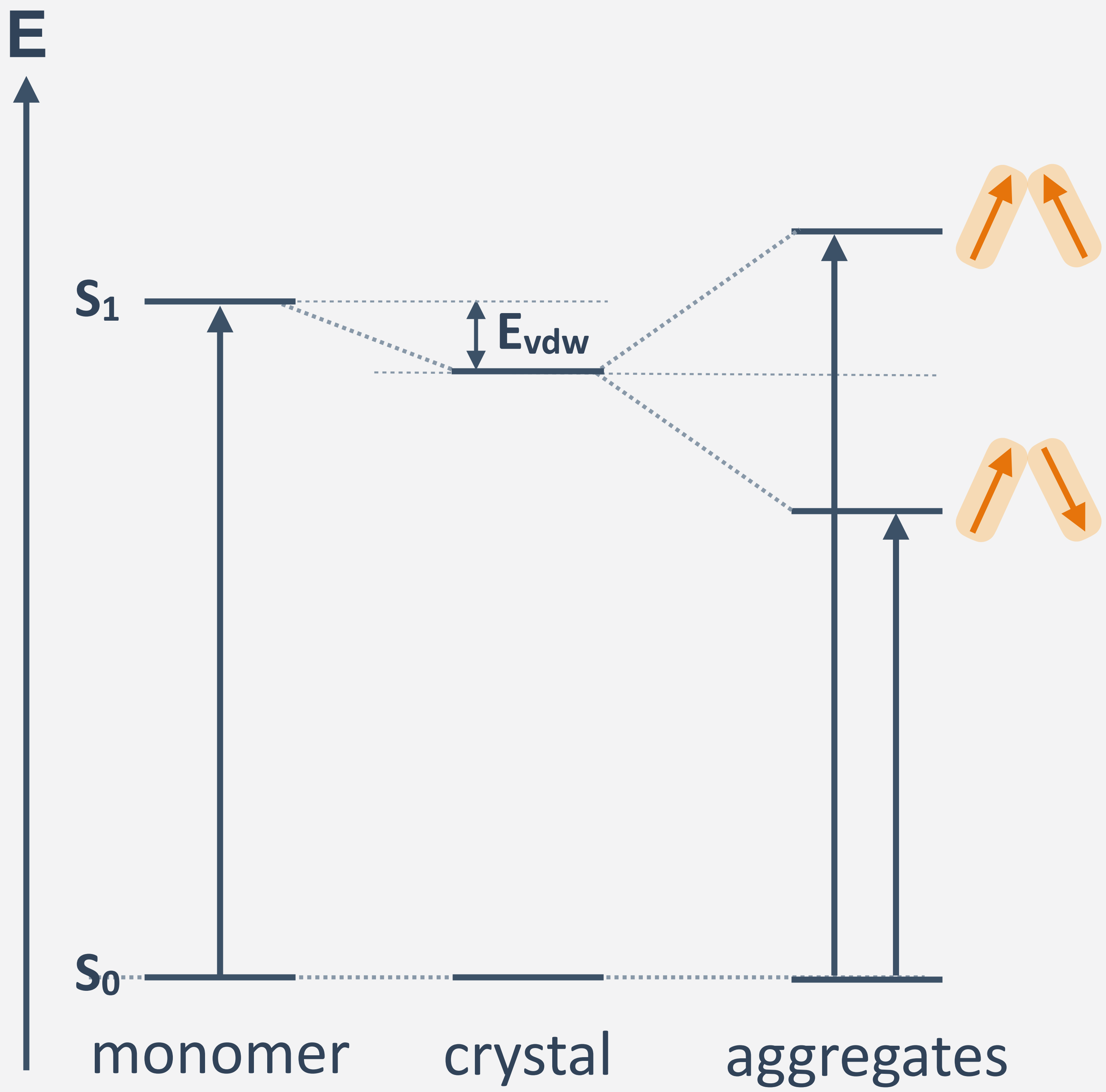




Davydov Splitting

- the general case of excitonic coupling of non-colinear transition dipole moments is often referred to as Davydov splitting
- rotational twist and slipped arrangement make transitions to both states allowed



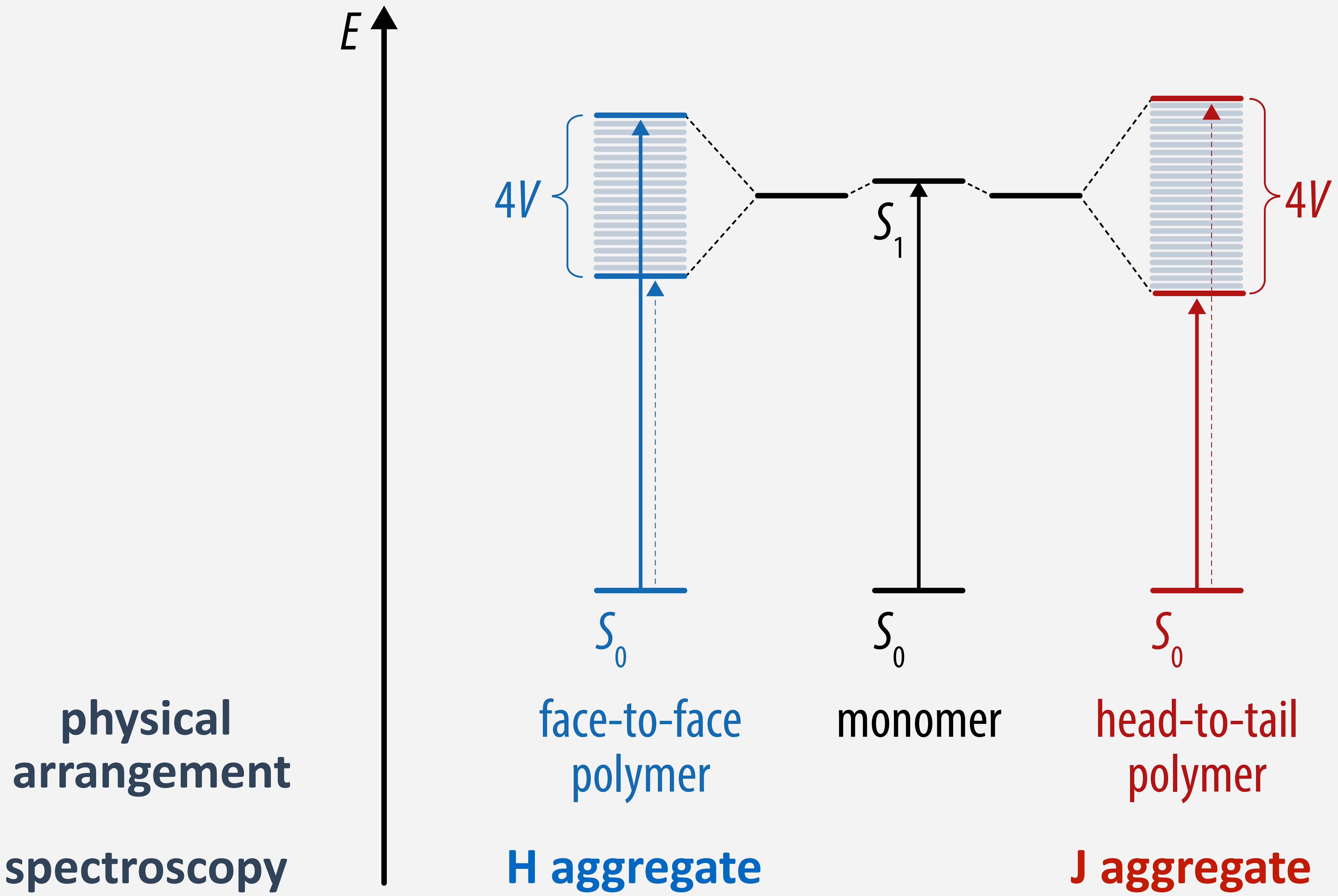


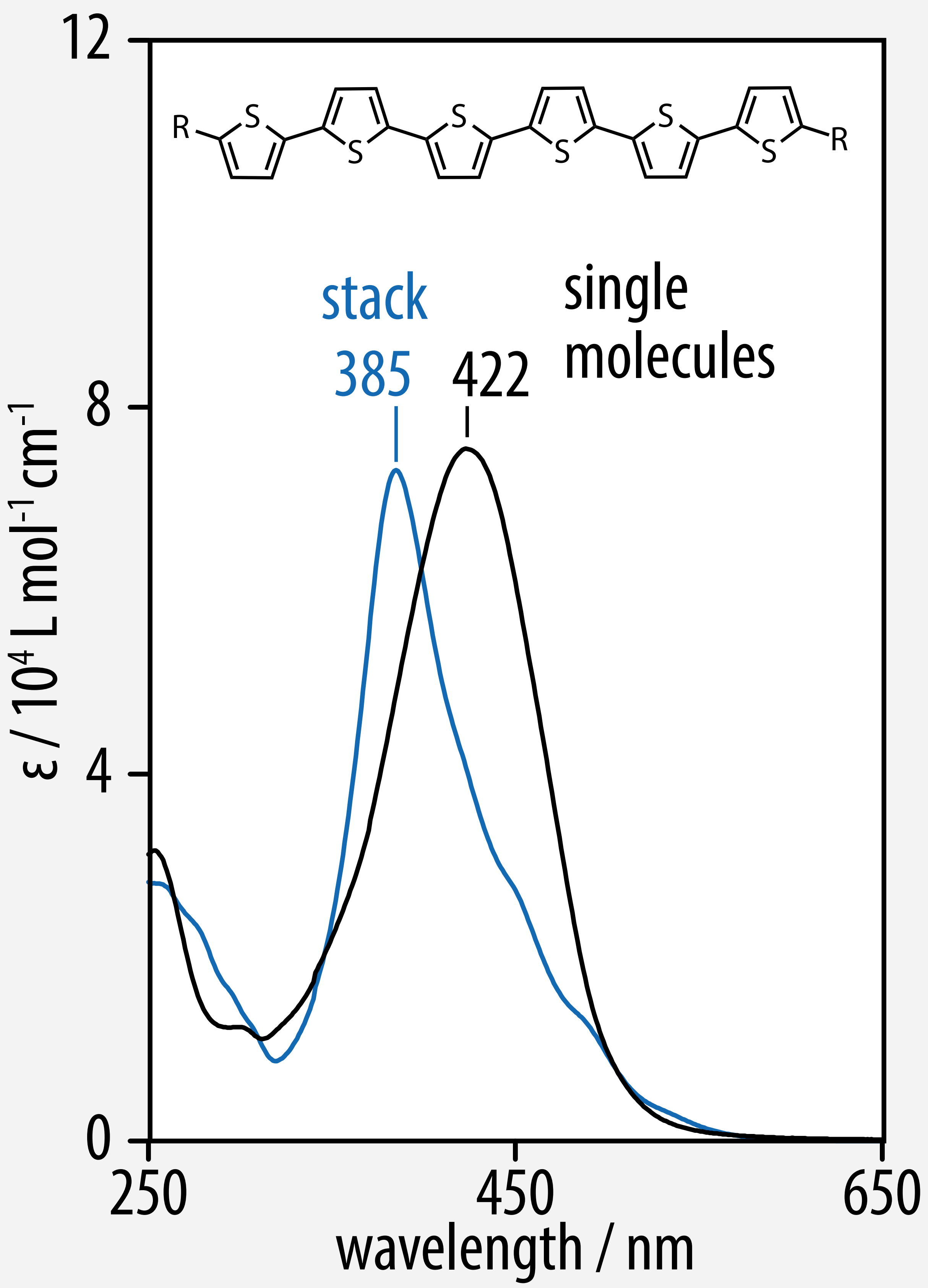
- **molecules show “HJ absorption” behavior and a red-shifted J-type emission**

Kasha, *Pure Appl.Chem.* **1965**, *11*, 371–392.

"Spectroscopic Aggregates": Excitonic Coupling in the Bulk State

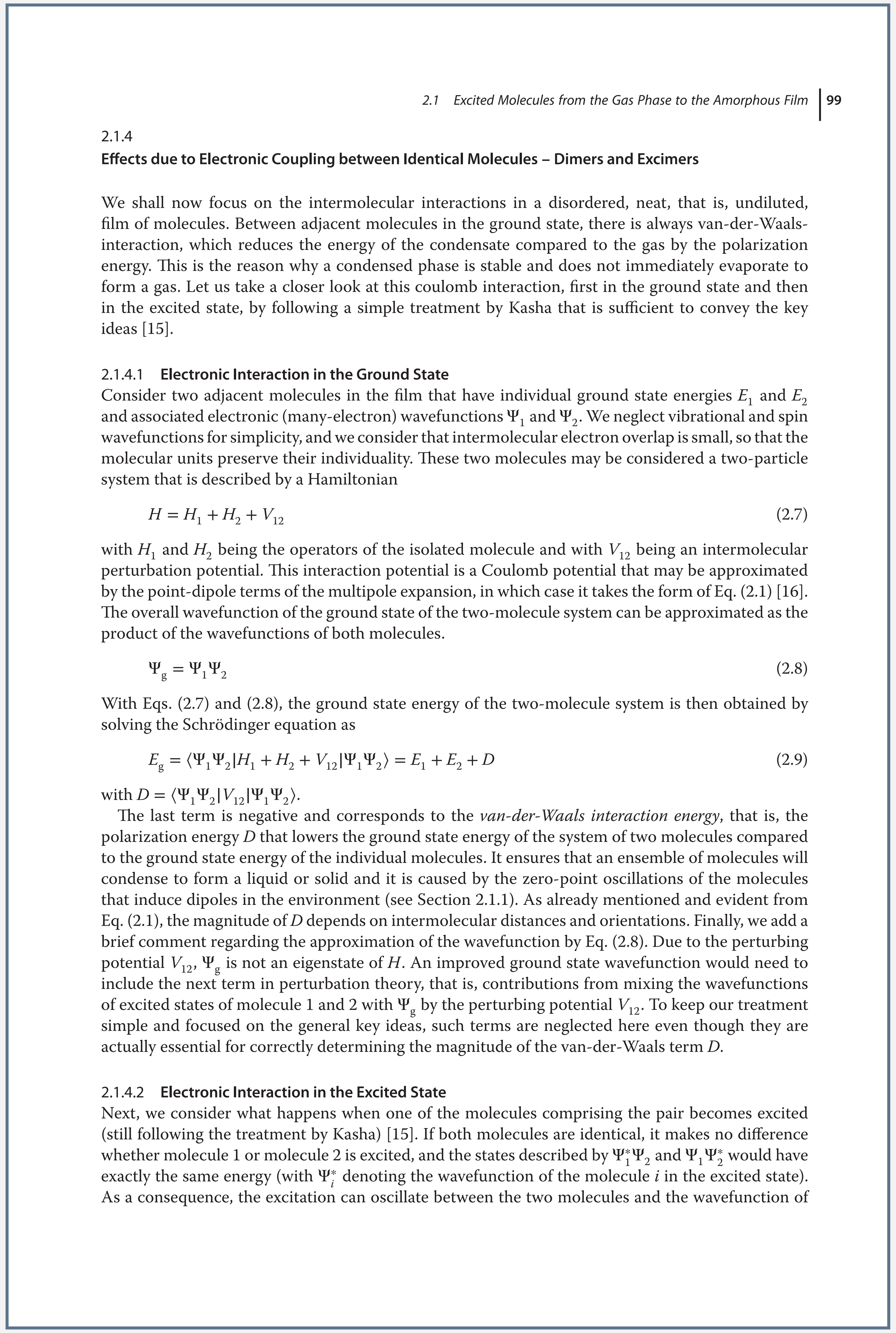
- excitonic coupling with *n* transition dipole moments leads to *n* delocalised excitonic states
- all excitonic states are energetically within the range of 4 J_c





- **magnitudes of transition dipole moments depend on local symmetry (similar to dimer)**

Homework & Reading Assignment



2.1.4
Effects due to Electronic Coupling between Identical Molecules – Dimers and Excimers

We shall now focus on the intermolecular interactions in a disordered, neat, that is, undiluted, film of molecules. Between adjacent molecules in the ground state, there is always van-der-Waals-interaction, which reduces the energy of the condensate compared to the gas by the polarization energy. This is the reason why a condensed phase is stable and does not immediately evaporate to form a gas. Let us take a closer look at this coulomb interaction, first in the ground state and then in the excited state, by following a simple treatment by Kasha that is sufficient to convey the key ideas [15].

2.1.4.1 Electronic Interaction in the Ground State

Consider two adjacent molecules in the film that have individual ground state energies E_1 and E_2 and associated electronic (many-electron) wavefunctions Ψ_1 and Ψ_2. We neglect vibrational and spin wavefunctions for simplicity, and we consider that intermolecular electron overlap is small, so that the molecular units preserve their individuality. These two molecules may be considered a two-particle system that is described by a Hamiltonian

$$H = H_1 + H_2 + V_{12} \tag{2.7}$$

with H_1 and H_2 being the operators of the isolated molecule and with V_{12} being an intermolecular perturbation potential. This interaction potential is a Coulomb potential that may be approximated by the point-dipole terms of the multipole expansion, in which case it takes the form of Eq. (2.1) [16]. The overall wavefunction of the ground state of the two-molecule system can be approximated as the product of the wavefunctions of both molecules.

$$\Psi_g = \Psi_1 \Psi_2 \tag{2.8}$$

With Eqs. (2.7) and (2.8), the ground state energy of the two-molecule system is then obtained by solving the Schrödinger equation as

$$E_g = \langle \Psi_1 \Psi_2 | H_1 + H_2 + V_{12} | \Psi_1 \Psi_2 \rangle = E_1 + E_2 + D \tag{2.9}$$

with $D = \langle \Psi_1 \Psi_2 | V_{12} | \Psi_1 \Psi_2 \rangle$.

The last term is negative and corresponds to the *van-der-Waals interaction energy*, that is, the polarization energy D that lowers the ground state energy of the system of two molecules compared to the ground state energy of the individual molecules. It ensures that an ensemble of molecules will condense to form a liquid or solid and it is caused by the zero-point oscillations of the molecules that induce dipoles in the environment (see Section 2.1.1). As already mentioned and evident from Eq. (2.1), the magnitude of D depends on intermolecular distances and orientations. Finally, we add a brief comment regarding the approximation of the wavefunction by Eq. (2.8). Due to the perturbing potential V_{12}, Ψ_g is not an eigenstate of H. An improved ground state wavefunction would need to include the next term in perturbation theory, that is, contributions from mixing the wavefunctions of excited states of molecule 1 and 2 with Ψ_g by the perturbing potential V_{12}. To keep our treatment simple and focused on the general key ideas, such terms are neglected here even though they are actually essential for correctly determining the magnitude of the van-der-Waals term D.

2.1.4.2 Electronic Interaction in the Excited State

Next, we consider what happens when one of the molecules comprising the pair becomes excited (still following the treatment by Kasha) [15]. If both molecules are identical, it makes no difference whether molecule 1 or molecule 2 is excited, and the states described by $\Psi_1^* \Psi_2$ and $\Psi_1 \Psi_2^*$ would have exactly the same energy (with Ψ_i^* denoting the wavefunction of the molecule i in the excited state). As a consequence, the excitation can oscillate between the two molecules and the wavefunction of

---

THE EXCITON MODEL IN MOLECULAR SPECTROSCOPY

M. Kasha, H. R. Rawls and M. Ashraf El-Bayoumi
Institute of Molecular Biophysics and Department of Chemistry, Florida State University, Tallahassee, Florida

INTRODUCTION

The molecular exciton model has received its most extensive development and application in the field of molecular crystals[1,2]. More recently, numerous applications to non-crystalline molecular composite systems have been made, including van der Waals and hydrogen-bonded dimers, trimers, and higher order aggregates. Another type of composite system has also been investigated, namely the composite molecule consisting of covalently bonded molecular units, with intrinsic individual unsaturated electronic systems so isolated by single bonds that but little or insignificant electronic overlap between units may occur.

It is now well established that in molecular aggregates and in composite molecules, exciton effects may be observed if sufficiently strong electronic transitions exist in the component sub-units. The result of exciton splitting of excited states in the composite molecule may be the appearance of strong spectral shifts or splittings (which may be of the order of 2000 cm^{-1}) of the absorption bands for the component molecules. At the same time, as a consequence of the exciton splitting of the excited state manifold, an enhancement of triplet state excitation may result.

The purpose of this paper is to present a summary of the various type cases for molecular dimers, trimers and double and triple molecules in the description of the molecular exciton strong-coupling model. Then it will be shown by new experimental examples that, even in those cases where no significant exciton effect is observable in the singlet–singlet absorption spectrum for the composite molecule (intermediate and weak coupling cases), the enhancement of lowest triplet state excitation may still be conspicuous and significant.

The ideas which are summarized in this paper have a curious history. Long ago, Kautsky and Merkel[3] demonstrated experimentally that aggregation of dyes facilitated their action as photophysical sensitizers in photochemical reactions, at the same time diminishing their fluorescence efficiency. Kautsky attributed these easily demonstrated effects to enhancement of metastable state excitation in the aggregate dye. There is no doubt today that the metastable state he described is the lowest triplet state of the molecules studied. However, he did not distinguish between intrinsic and enhanced metastable (triplet) state excitation, so his interpretations were largely overlooked. Förster in 1946[4] used the quasi-classical vector model to

Learning Outcomes

- **interaction of light with a molecule can be treated as a time-dependent perturbation in the quantum description**
- **in molecules, absorption of light promotes an electron from the HOMO to the LUMO**
- **absorption band intensity & shape dictated by electronics and geometry**
    - electronic delocalization results in red shift
    - blue/red shift due to intermolecular Coulomb interactions (H/J aggregates)
- **excited state processes are competing with each other**
- **fluorescence is (mostly) from the lowest excited state (Kasha's rule)**