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 excited state for the two-molecule system is a linear combination of both situations, that is,

$$\Psi_E = c_1\Psi_1^*\Psi_2 + c_2\Psi_1\Psi_2^* \tag{2.10}$$

For identical molecules $c_1 = c_2$ and, after normalization, $|c_1| = |c_2| = 1/\sqrt{2}$. However, coupling can be either symmetric or anti-symmetric. Consequently, the excited state wavefunctions are

$$\Psi_{E\pm} = \frac{1}{\sqrt{2}}(\Psi_1^*\Psi_2 \pm \Psi_1\Psi_2^*) \tag{2.11}$$

This is analogous to the two normal modes of two mechanical pendula that are coupled. Inserting Eq. (2.11) into the Schrödinger equation with the Hamiltonian of Eq. (2.7) yields

$$\begin{aligned} E_{E+} &= \frac{1}{2}\langle\Psi_1^*\Psi_2 + \Psi_1\Psi_2^*|H_1 + H_2 + V_{12}|\Psi_1^*\Psi_2 + \Psi_1\Psi_2^*\rangle \\ &= E_1^* + E_2 + \langle\Psi_1^*\Psi_2|V_{12}|\Psi_1^*\Psi_2\rangle + \langle\Psi_1^*\Psi_2|V_{12}|\Psi_1\Psi_2^*\rangle \\ &= E_1^* + E_2 + D' + \beta \end{aligned} \tag{2.12a}$$

and

$$\begin{aligned} E_{E-} &= \frac{1}{2}\langle\Psi_1^*\Psi_2 - \Psi_1\Psi_2^*|H_1 + H_2 + V_{12}|\Psi_1^*\Psi_2 - \Psi_1\Psi_2^*\rangle \\ &= E_1^* + E_2 + \langle\Psi_1^*\Psi_2|V_{12}|\Psi_1^*\Psi_2\rangle - \langle\Psi_1^*\Psi_2|V_{12}|\Psi_1\Psi_2^*\rangle \\ &= E_1^* + E_2 + D' - \beta \end{aligned} \tag{2.12b}$$

E_1^* and $E_2$are the energies of the (non-interacting) molecule 1 in the excited state and the (non-interacting) molecule 2 in the ground state. The third term, D' in Eq. (2.12), is analogous to D in Eq. (2.9). It represents the van-der-Waals interaction (polarization energy) between molecule 1 in the excited state and molecule 2 in the ground state (or vice versa). One may think of it as the coulombic energy of interaction of the charge distribution present in the excited state of molecule 1 with that of molecule 2 in the ground state (analogous to Box 1.4). As outlined in Section 2.1.1, for non-polar molecules, $|D'| > |D|$, and both are negative.

The fourth term, β, gives the resonance interaction energy that determines the splitting between the two levels E_{E+} and E_{E-}. It can be understood as representing the interaction of the overlap charge density (of molecule 1 in the excited state and molecule 2 in the ground state) with either molecule. Analogous to D', the value for β depends on the relative intermolecular distance and orientation. This is, for example, evident when the interaction potential V_{12} is expressed in a point-dipole approximation as in Eq. (2.1). Note however, that β and D' differ in their sensitivity to these parameters. There may well be sizable coulomb interaction between the charge distribution present in the excited molecule 1 with the ground state of molecule 2 (and thus a finite D'), even though poor overlap between the two wavefunctions prevents significant resonance interaction (implying $\beta \approx 0$).

The quantity that is experimentally observed in an absorption or emission spectrum is not the total energy of the system (the two coupled molecules) but rather the transition energy between the system's ground and excited state. It is

$$\Delta E_{\text{total}} = (E_1^* + E_2 + D' \pm \beta) - (E_1 + E_2 + D) \quad = \Delta E_1 + \Delta D \pm \beta \tag{2.13}$$

that is, the excitation energy for molecule 1, shifted by the (negative) difference polarization energy and the resonance energy (Figure 2.12). The degree of the resonance energy β depends on wavefunction overlap and is thus very sensitive to the intermolecular distance.

How do we interpret this result? In order to relate this to the spectra measured in an amorphous thin film or in a concentrated solution, it is helpful to distinguish three cases.

No Noticeable Interaction The intermolecular distance is large enough that the resonance interaction is small and can be neglected, that is, $\beta \approx 0$. In an amorphous film, this case is realized when the mean splitting is small compared to the inhomogeneous broadening, so that the splitting cannot be resolved

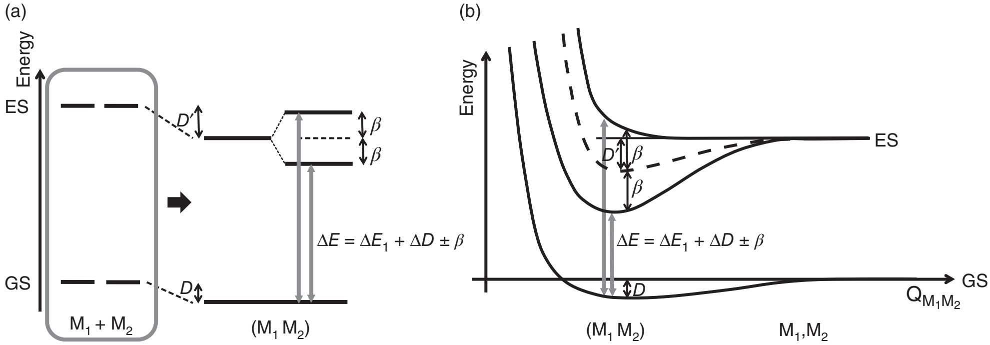

Figure 2.12 Schematic illustrating the effect of electronic coupling between two molecules. (a) Electronic coupling between two molecules M_1 and M_2 takes place both in the ground state (GS) and the excited state (ES). Ground and excited state energies are reduced in the coupled system (M_1M_2) by the polarization energies D and D'. Furthermore, the excited state of the coupled pair splits into two levels separated by a resonance energy β. Transitions between the ground and excited states of the coupled pair, indicated by arrows, take an energy of $\Delta E_{(M1M2)} = \Delta E_{M1} + \Delta D \pm \beta$. (b) The same as in (a), yet plotted as a function of a generalized intermolecular coordinate Q that represents distance and orientation. At large Q, no coupling takes place. As the molecules M_1 and M_2 approach, ground and excited states are stabilized by D and D'. In addition, the excited state level splits into two levels. The lower one stabilizes the pair of molecules. Note that the equilibrium distance of the coupled pair may differ in the ground and excited states.

($\beta \ll \sigma(\Delta D)$). This is the situation that is desired for device applications of organic semiconductors, such as light-emitting diodes (LEDs) and solar cells. This situation can be assisted by synthetic or processing means, for example, by decorating the chromophores with sterically demanding side groups or by using a volatile, low-boiling point solvent so that structural disorder from solution is frozen in quickly during spin-coating a film. The transition energy (Eq. 2.13) for the system then becomes $\Delta E_{\text{total}} \approx \Delta E_1 + \Delta D$, that is, the excitation energy for molecule 1 and the (negative) difference in polarization energies. We have thus recovered the result of Section 2.1.1.

Dimer Formation The second case is that where the resonance interaction is finite and moderate. For singlet excitations, β is typically of the order of several 1000 cm^{-1} ($\approx$100 meV), that is, much smaller than the excited state energies themselves. Two such weakly interacting identical molecules are termed a (*physical*) *dimer*. This is not to be confused with a chemical dimer, where two identical chromophores are joined by a covalent bond. Physical dimers occur frequently in planar, linear π-conjugated chromophores that do not have side chains. Examples include the acenes such as naphthalene, anthracene, tetracene, and pentacene. Typical molecular orientations that favor the formation of a dimer are a sandwich arrangement, where one molecule lies flat on top of another so that the two π-systems can interact well, and a herringbone arrangement. In the latter, one molecule is next to another, yet tilted by about 55° around the long axis, so that the electron-poor H-atoms on the long side of one molecule point toward the electron-rich π-system on the other, with a center of mass distance of about 0.5–0.6 nm (Figure 2.13).

In a dimer, there are two split levels separated by 2β and the transition energies are $\Delta E_{\text{total}} = \Delta E_1 + \Delta D \pm \beta$. As the interaction energy is moderate, the attractive force between the two molecules does not lead to any major changes in the intermolecular distance or orientation. When potential energies of the dimer are plotted as a function of the distance between the two molecules, the minima of the dimer ground state and the dimer excited state differ only little. In consequence, there can be absorption and emission between the dimer ground state and the dimer excited state, provided the transitions have oscillator strength (see below). Both, absorption and emission may well have a vibrational structure (Figure 2.14).

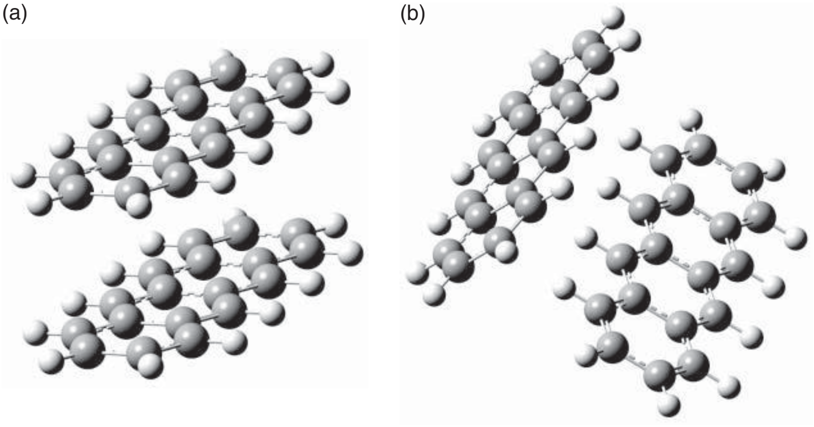

Figure 2.13 Molecular orientations, illustrated qualitatively for tetracene, that are conducive to electronic interaction. (a) Sandwich arrangement, and (b) herringbone arrangement.

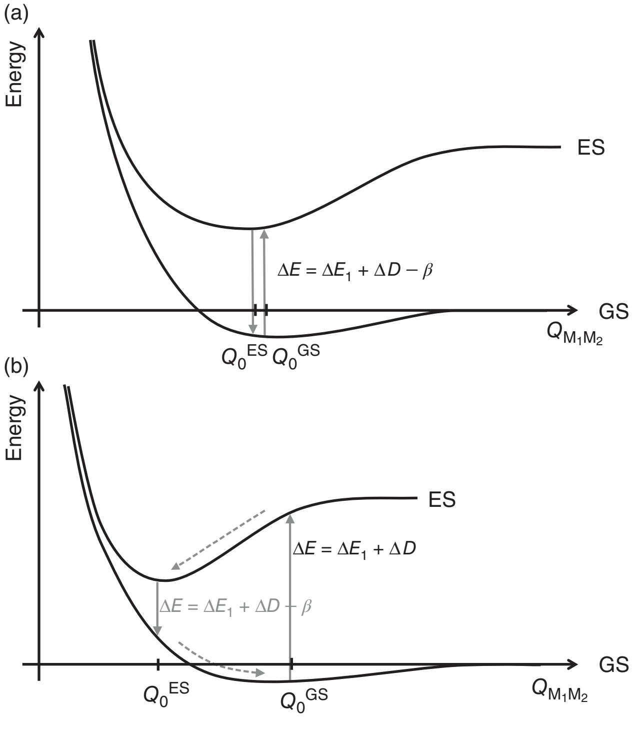

Figure 2.14 Schematic illustrating the difference between dimer and excimer. (a) Dimer formation: The coupled pair (M_1M_2) has a very similar equilibrium distance/orientation in the ground state and in the excited state. Absorption and emission both occur from the coupled pair. (b) Excimer formation: Upon excitation, the coupled pair (M_1M_2) changes its distance/mutual orientation significantly, so that the excited state equilibrium coordinate differs from the ground state one. Absorption takes place at an intermolecular distance/orientation where resonance splitting is not noticeable. The absorption of (M_1M_2) does not differ from that of the individual molecule M_1. Emission occurs from the relaxed geometry of the pair to the repulsive (M_1M_2) ground state. It is followed by geometric reorientation to the (M_1M_2) ground state equilibrium position.

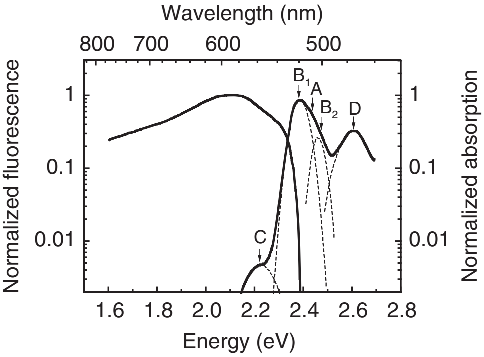

Figure 2.15 Absorption and fluorescence of a disordered film of tetracene. The absorption spectrum (Data from Hesse *et al.* [8].) has been taken at 250 K on a film that was prepared by evaporating on a substrate held at 130 K. The following features are indicted by capital letters: A = center of two dimer 0-0 transitions, B1 (B2) = lower (upper) component of the 0-0 transition of the dimer, C = excimer-like absorption, D = unresolved 0-1 vibrational peaks. The fluorescence spectrum was taken at 130 K. (Data from Peter and Bässler [17].) It shows emission from the lower dimer 0-0 level, indicated by B1, as well as a broad unstructured redshifted emission that is associated with an excimer.

For our model system tetracene, an example for dimer formation can be seen in Figure 2.15. This is a very similar spectrum to the tetracene film spectrum already discussed in Figure 2.5, yet it has been analyzed in more detail. Figure 2.15 shows the absorption spectrum on a logarithmic ordinate scale for a tetracene film that has been vapor deposited on a substrate held at 130 K and that was then warmed up to a temperature of 250 K for recording the spectrum. When the spectrum is analyzed and deconvoluted into Gaussian features, one comes to the following conclusions. First of all, the center of the $S_1 \leftarrow S_0$ 0-0 electronic transition, marked "A" in Figure 2.15, is redshifted from that in MTHF due to the increase in polarization energy when going from a weakly polarizing MTHF to a strongly polarizing tetracene matrix. Further, the $S_1 \leftarrow S_0$ 0-0 transition splits into a doublet with energy separation of 74 ± 6 meV. This doublet cannot be assigned to a molecular vibration. Rather, it indicates that the absorbing entity is a tetracene dimer. The lower and upper components of the dimer are indicated by "B_1" and "B_2" in the figure, respectively. Both of the dimer absorption peaks are inhomogeneously broadened with a standard deviation of $\sigma = 42$ meV (B_1) and 32 meV (B_2). The broadening depends strongly on the preparation conditions. In addition to the two dimer peaks, there is a weak broad absorption feature "C" off-set from the center of the $S_1 \leftarrow S_0$ 0-0 dimer transition. This feature is tentatively assigned to a closer arrangement of the two tetracene molecules that leads to a stronger resonance splitting β, thus having more of an excimer-like character (see below).

Excimer Formation Finally, in the third case, the resonance interaction β may be large enough to cause the two interacting molecules to reorient such as to optimize their interaction. This is the case of an *excimer.* It is common for flat, disk-shaped or elongated π-conjugated chromophores. Classical examples include pyrene and perylene, which pack face-to-face with a small center of mass separation of 0.30–0.35 nm. The excited state energy levels of the excimer are split as given in Eq. (2.12), and the transition energies are $\Delta E_{\text{total}} = \Delta E_1 + \Delta D \pm \beta$, as for a dimer, though with larger values for β. Due to the attractive interaction, the excited state potential is shifted compared to the dimer ground state potential, so that the excited state minimum occurs at an intermolecular distance Q_E where the ground state potential U_G is repulsive ($dU_G(Q_E)/dQ < 0$) and non-bonding ($U_G(Q_E) > 0$) (Figure 2.14b). Emission from the excimer excited state to the excimer ground state does not feature a vibrational structure. Absorption takes place at a larger intermolecular distance and appears therefore identical to that of very weakly coupled molecules, as in case (i). The fact that the excimer can

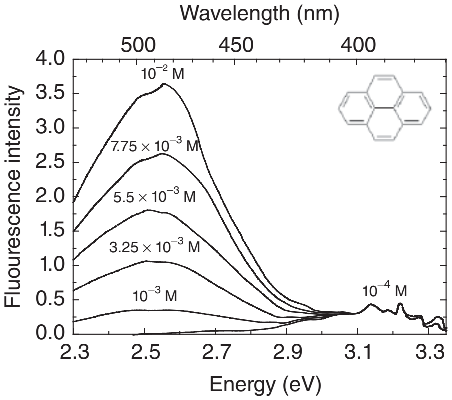

Figure 2.16 The fluorescence of pyrene at various concentrations as indicated in the figure, excited with a mercury vapor lamp, showing emission from the monomer centered around 3.2 eV and from the excimer centered around 2.6 eV. (Data from Birks and Christophorou [19].)

only be observed as a distinct entity in the excited state is the source of its name "excimer = excited dimer."

The occurrence and correct interpretation of excimers has first been reported by Förster in 1955 for pyrene [18] and was later investigated by Birks [19, 20]. An example for the formation of excimers is shown in Figure 2.16. Upon increasing the concentration of pyrene in an ethanol solution, the monomer FL decreases and a broad, vibrationally unresolved, and redshifted emission is observed. Birks denotes the blue emission (at about 3.2 eV) with a letter M and the red emission (around 2.6 eV) with D and he refers to Förster for the interpretation of the spectra by explaining that "M corresponds to the FL of unassociated (monomer) molecules, and D to the FL of transient excited dimers, known as *excimers*, formed by the diffusional association of excited and unexcited molecules. The excimers dissociate on emission yielding the structureless band D. This interpretation [18] has been confirmed by studies of the time dependence of the intensities of M and D as a function of concentration, viscosity, and temperature." The methods mentioned in the last sentence are still used to unambiguously identify an excimer. The sentence "excimers dissociate on emission" requires a clarifying comment. When an excimer returns to its ground state by emission from the excited state at the equilibrium distance Q_0^{ES}, the repulsive ground state potential at Q_0^{ES} implies that the two molecules move apart from each other. In the solid state, such as an amorphous film or crystal, they move until they reach the shallow minimum of the ground state potential at Q_0^{GS}, and then they stay there. After all, most compounds with excimers are not explosives, and many of them yield crystals with a dimer unit cell (see below). In solution, where Förster and Birks conducted their investigation, the stability of the dimer ground state depends on how the shallow van-der-Waals potential minimum (i.e., chromophores pairing up) compares against the energy gained upon solvation (i.e., chromophores surrounding themselves with solvent molecules). In good solvents, the latter wins and therefore, the two molecules separate. For the same reason, in solution, an excimer only forms when an excited molecule collides with an unexcited one.

It is worth stressing that the difference between a dimer and an excimer is not one of fundamental nature but lies only in the strength of the resonance interaction and the concomitant geometric relaxation of the two molecules toward each other. Due to the random morphology in an amorphous film, these three cases can occur in parallel, with some of the chromophores not showing any noticeable splitting and others forming dimers or excimers. A herringbone arrangement prevents further approach upon excitation and thus leads predominantly to dimers, while a sandwich-type packing allows for a high stabilization energy of the pair of molecules and for further mutual approach upon excitation, thus aiding the formation of excimers. Depending on how much the two molecules change their mutual geometry after excitation, there are also borderline cases where the emission shows all the signatures of an excimer emission (structureless, strongly redshifted emission), yet some weak absorption can nevertheless be observed. This is the case for certain molecular arrangements of tetracene, as evident in Figure 2.15.

2.1.4.3 Oscillator Strength of Dimer and Excimer Transitions

We shall now consider the selection rules that apply to electronically coupled molecules. The strength of an electronic transition depends on the transition dipole moment, as detailed in Section 1.4.2. For noninteracting molecules, the transition dipole moments are $\vec{\boldsymbol{\mu}}_1 = \langle \psi_1 | e\vec{\boldsymbol{r}} | \psi_1^* \rangle$ and $\vec{\boldsymbol{\mu}}_2 = \langle \psi_2 | e\vec{\boldsymbol{r}} | \psi_2^* \rangle$. Similarly, the transition moment for the two states of the coupled molecules is given by

$$
\begin{aligned}
\vec{\boldsymbol{\mu}}_\pm &= \langle \Psi_\mathrm{G} | e\boldsymbol{r} | \Psi_{\mathrm{E}\pm} \rangle \\
&= \frac{1}{\sqrt{2}} \langle \Psi_1 \Psi_2 | e\vec{\boldsymbol{r}} | (\Psi_1^* \Psi_2 \pm \Psi_1 \Psi_2^*) \rangle \\
&= \frac{1}{\sqrt{2}} \langle \Psi_1 \Psi_2 | e\vec{\boldsymbol{r}} | \Psi_1^* \Psi_2 \rangle \pm \langle \Psi_1 \Psi_2 | e\vec{\boldsymbol{r}} | \Psi_1 \Psi_2^* \rangle \\
&= \frac{1}{\sqrt{2}} (\vec{\boldsymbol{\mu}}_1 \pm \vec{\boldsymbol{\mu}}_2) \qquad (2.14)
\end{aligned}
$$

Thus, the transition dipole moment to the two states of the coupled molecules results from the vector sum of individual molecules' transition dipole moments. In consequence, it depends on the relative orientation of the two molecules. A few limiting cases are worth highlighting (Figure 2.17).

H-Type Interaction The two molecules are arranged in a coplanar, stacked manner. In this case, the transition dipole moments for lower energy excited states E_- are arranged in a antiparallel manner and add to a total value of zero, while parallel arrangement prevails for E_+ and adds up to a value of 2μ. This has important consequences for the optical spectra. According to Eq. (1.6) in Section 1.4.2, absorption can only occur into E_+, so the absorption spectrum appears hypsochromically (blue) shifted relative to the absorption of the parent molecule. With regard to emission, one needs to keep in mind that excitation energy always relaxes to the lowest excited state (cf. Section 1.4.4), in this case E_-. As transitions from E_- to the ground state of the two coupled molecules carry no oscillator strength, the radiative decay rate k_r is zero and the energy can only be dissipated non-radiatively. The lifetime of E_-, $\tau = 1/(k_\mathrm{r} + k_\mathrm{nr})$, is then determined solely by the nonradiative decay rate k_nr. In real systems, a slight misorientation and/or vibronic coupling in the excited state gives rise to a finite yet weak oscillator strength, so that usually a weak, long-lived emission is observed. Electronically coupled molecules of this category are called *H-aggregates*. As their cofacial arrangement is conducive to a large resonance interaction, they are prone to excimer formation.

J-Type Interaction The two molecules are arranged in a sequential co-linear and parallel manner. The lower-energy state E_- is then realized for a parallel sequence of transition dipole moments that add up to 2μ, while the higher-energy state E_+ is associated with an antiparallel order and a net zero moment. Absorption to and emission from E_- are optically allowed, so that the absorption spectrum is bathochromically (red) shifted with respect to the monomer spectrum, and FL is fast and intense. Molecules coupled in such a manner are referred to as *J-aggregates* or *Scheibe-aggregates.* The "J" derives from Jelley [21] who characterized such coupled molecules that, by the way, were discovered independently at almost the same time by Scheibe [22].

Arbitrary Orientation Very often π-bonded chromophores are oriented in neither of these two limiting ways, but they may be arranged with a variable angle between them. When the orientation of the transition moments of the constituent molecules is arbitrary, the absorption spectrum of the monomer is split into a doublet as both, the lower and the higher energy transition acquire a certain

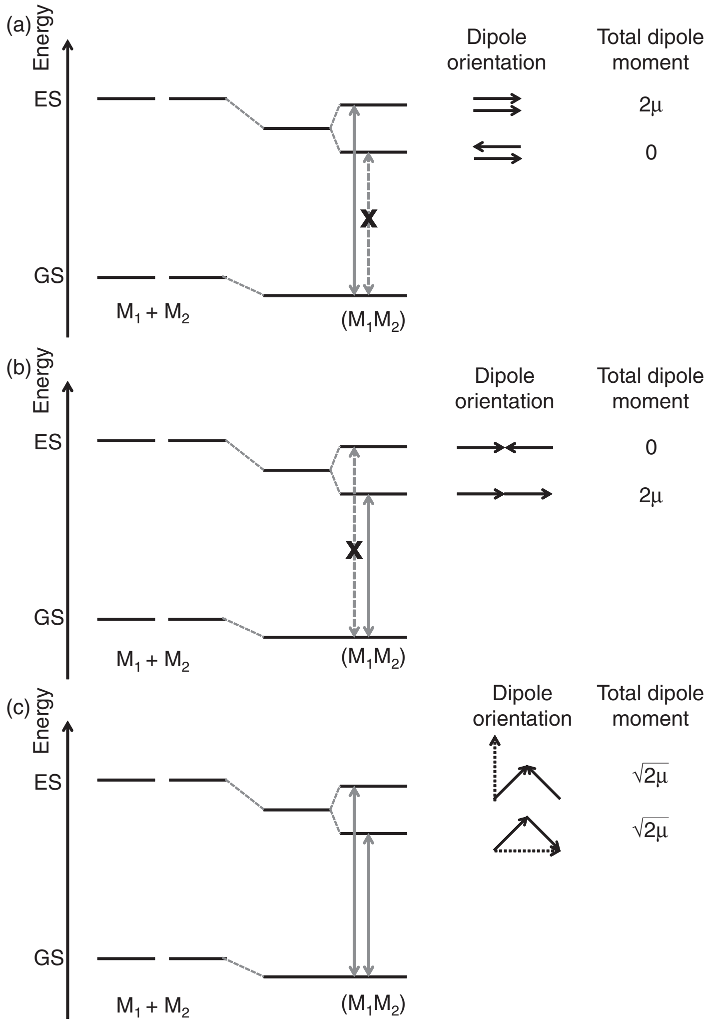

Figure 2.17 Schematic illustration of the ground and excited state energies of two individual molecules and of a pair of electronically coupled molecules for (a) a side-by-side orientation, leading to an H-type interaction, (b) for head-to-tail orientation, leading to a J-type interaction, and (c) for an oblique orientation. The relative orientation of the excited state transition dipoles and possible optical transitions are also indicated, and the modulus of the resulting total dipole moment is also listed.

degree of oscillator strengths. The ratio of the intensities of the components is set by the vectorial sum of the monomer moments, as indicated in Figure 2.17. FL would be emitted from the lower dimer state. FL lifetime is typically one to two orders of magnitude longer than for the monomer. For example, for tetracene, the lower dimer level (B_1 in Figure 2.15) has a lifetime of about 6 ns, comparable to that of the unassociated monomer, while the more stabilized and differently oriented excimer (C in Figure 2.15) has a lifetime of 21 ns, that is, about three to four times as long. For pyrene, in cyclohexane at room temperature, the radiative decay rates for the monomer and the excimer have been determined as 1.5×10^{-6} and 1.2×10^{-7} s^{-1}, respectively, that is, the radiative rate for the excimer emission is a factor of 10 lower [23].

Absorption and FL spectra of pyrene functionalized with flexible promesogenic alkoxy chains will illustrate the great impact that small changes of the mutual orientation of the transition moments of the chromophores in a dimer can have on its spectroscopic properties. The pyrene derivative tetraethynylpyrene is furthermore an example of a compound where emission occurs from an excimer, yet absorption is nevertheless observed. In the condensed state, the tetraethynylpyrene forms a liquid crystalline columnar phase [24]. This is a signature of interchromophoric interaction among the pyrene cores. The FL shows the same general features to that of the parent molecule pyrene. Upon increasing the concentration of the solution, the FL from the monomer, centered at 2.5 eV, decreases and a red-shifted broad emission, centered at 2.0 eV, appears. The latter is also the dominant feature in the thin film emission (Figure 2.18). However, in contrast to pyrene, in this room temperature film FL is very strong with a quantum yield of $(62 \pm 6)\%$. Further, in contrast to the non-functionalized pyrene molecule, the monomer-like absorption spectrum splits into a doublet when changing over from the dilute solution phase to the condensed phase. Analyzing the thin film absorption spectrum shows that it can be composed of two dimer components with 0-0 transitions at 2.38 and 2.76 eV, centered around 2.57 eV with a splitting of $\beta = 0.19$ eV. The existence of almost equally intense doublet feature in absorptions combined with intense, redshifted emission indicates that the absorbing entity is a pair of aligned pyrene derivatives whose transition dipole moments are not parallel, as realized in the conventional pyrene excimer, but form an angle of $70-80°$. Semi-empirical calculations show how the splitting between the two levels depends on the relative orientation of the two pyrene cores (Figure 2.18). For a cofacial arrangement, a perfect H-aggregate is formed with all oscillator strength in the upper state. With an increasing rotation angle between the two pyrene-derivatives, the amount of splitting reduces and the lower state acquires some oscillator strength. For an angle of 90°, the coupling vanishes. The unusually high quantum yield observed for the tetraethynylpyrene excimer is a result of the rotation angle between them. Similarly, it implies that absorption is optically allowed. Note that the large Stokes' shift of 0.32 eV between the lower transition in absorption and emission is the signature of mutual approach of the pyrene molecules after optical excitation. This is a characteristic feature of an excimer. At the same time, the intermolecular equilibrium separation in the ground state is sufficiently close to allow for absorption into the dimer state, with both levels having oscillator strength.

It is worth mentioning that Kasha's simple treatment that we followed here implicitly assumes the point-dipole approximation to be valid. This is the case when the distance between chromophores is large compared to the size of the chromophore, so that the transition dipole moments can be regarded as arising from point dipoles. In condensed phases such as amorphous films, this condition often no longer applies. For a quantum chemical approach that explicitly considers extended charge distributions, we refer to the work of Gierscher and Park [25].

2.1.4.4 Singlet and Triplet Dimers/Excimers

So far we disregarded the spin of the dimer. This is of little relevance for singlet states whose spin is zero, but it is important for triplet states. From Section 1.3.4, we know that the triplet state of a chromophore is offset from the singlet state by the exchange energy Δ that decreases exponentially with increasing distance between the charges comprising the excited state. In a dimer or excimer, the excited state spreads over two adjacent molecules so that the electron and the hole can approximately be considered separated by up to the intermolecular distance. For this reason, the exchange energy of a dimer or excimer, $\Delta_{(M1M2)}$, is reduced compared to the parent monomer. The value of the exchange energy in a dimer or excimer depends on the degree of electron–hole separation. To give a rough orientation, the comparatively large $\Delta_{(M1M2)}$ of about 250 meV reported for sandwich-type carbazole dimers (see below) may be taken as an upper limit, while in the extreme case of electron–hole separation as realized in geminate pairs, exchange energies tend to be only a few millielectron volts and may even be negative [26, 27]. This has an important consequence for the stability of triplet excimers. In (unassociated) chromophores in which the optical transition has a $\pi\pi^*$ character, electron–hole wavefunction overlap is strong, and so the individual chromophore has an exchange energy, Δ_{M1}, on