

## 13. Interacting single molecules

### 13.1. Basic interaction mechanisms

We already had to consider the interactions of an absorbing molecule with the surrounding matrix molecules. These interactions are responsible for, among others, the solvent shift. They arise from Van der Waals (or dispersive) forces and short-range repulsion between molecular electronic clouds, from electrostatic and polarization interactions, from specific effects such as hydrogen bonds, etc. In such interactions, the excitation remains localized on the 'colored' molecule, while the surrounding 'transparent' matrix molecules retain their chemical structure and remain in their ground state.

Interactions between the excited molecule and the matrix can lead to chemical reactions, i.e., photochemistry, e.g.:

- photo-oxidation,
- photoinduced electron transfer, in which the excited molecule can accept or donate an electron,
- proton transfer, the donation or abstraction of a proton by the excited molecule,
- excimer and exciplex formation, the formation of a transiently bound dimer upon excitation of one of the interacting partners. The excimer has a very different geometry from that of the initial pair, but usually reverts to the initial pair after relaxation of the excitation energy. If present, excimer fluorescence presents a very large Stokes shift. Exciplexes are similar complexes between two different molecules.

Let us particularize to systems in which the optical excitation can be shared or exchanged between different molecules. We already considered the case of FRET, energy transfer between a donor and an acceptor, whose excited state lies at lower energy than the donor's. FRET depends on temperature via the dependence of the overlap integral between acceptor absorption and donor fluorescence. For different donor and acceptor, the overlap depends only weakly on temperature, and FRET still takes place at low temperatures. If donor and acceptor are identical, however, the excitation can « jump » back and forth in the pair, or in more extended aggregates or clusters of molecules. If thermal activation is present, transport and diffusion can take

place over large distances: this is hopping exciton transport. At low temperature, the excitation gets trapped in the lowest excited state.

The subject of the present chapter is 'resonant interaction', i.e., the excitonic or coherent effects taking place when two (nearly) identical molecules interact strongly. When two molecules are very close, the electronic clouds overlap so strongly, that the Schrödinger wave equation has to be solved in the whole 'supermolecule'. However, as soon as the coupling gets weaker, it is a good approximation to discuss the new states in terms of molecular states (this is already a good approximation for terrylene, which can be discussed in terms of interacting naphthalene subunits). Two main mechanisms lead to this so-called 'excitonic' coupling (we discussed them as perturbations in the chapter on FRET for Förster and Dexter transfers):

- the direct Coulomb interaction, which can be described as dipole-dipole at large distances, and can be expanded as multipoles of the electron-electron Coulomb interaction between the electrons of the two molecules. The dipole-dipole interaction decays as the inverse cube of the intermolecular distance.
- the exchange interaction, which results from a double exchange of electrons between the two molecules, without change of orbital. This interaction depends on the overlap of the electrons' wavefunctions, and decays exponentially with intermolecular distance. In the case of allowed transitions, and for distances larger than the molecular sizes, the exchange interaction is usually much weaker than the Coulomb interaction. Again, for triplet states, only exchange interactions are spin-allowed. For singlet states, both processes should be considered in principle, but Coulomb interactions are in general stronger.

Neglecting the angular dependence, the dipole-dipole interaction is approximately given by:

$$J \approx \frac{\mu^2}{4\pi\epsilon_0} r^{-3}$$

For an allowed transition (transition moment  $\mu \approx 3 \times 10^{-29} \text{ C} \cdot \text{m}$ ) and a distance of 1 nm, we find

$$J \approx 50 \text{ cm}^{-1}.$$

However, the molecular transitions are spread over a number of vibronic lines. The above calculation is valid only if the interaction is so strong that all vibronic lines

participate in the interaction. If only the zero-phonon lines of the 0-0 participate, the square of the dipole moment (and therefore the interaction) is reduced by the Debye-Waller factor, typically 10 to 30 %. In sections 13.2, 13.3, we will examine two examples where the dipole-dipole interaction is stronger or weaker than the spread of the vibronic structure.

Let us briefly discuss the exciton eigenstates in a dimer, neglecting the coupling to vibrations. The Hamiltonian of the singly excited state of two interacting molecules writes :

$$H = \Delta|A\rangle\langle A| - \Delta|B\rangle\langle B| + J[|A\rangle\langle B| + |B\rangle\langle A|],$$

where  $|A\rangle$ ,  $|B\rangle$  represent one excitation localized on molecule A or B respectively,  $2\Delta$  is the energy splitting of the molecules and  $J$  is their interaction energy. The exciton states  $|1\rangle$  and  $|2\rangle$  are coherent superpositions of states  $|A\rangle$  and  $|B\rangle$ ,

$|1\rangle = \cos\alpha|A\rangle + \sin\alpha|B\rangle$  and  $|2\rangle = -\sin\alpha|A\rangle + \cos\alpha|B\rangle$ , corresponding to eigenvalues :

$$\pm \sqrt{\Delta^2 + J^2},$$

with a mixing angle  $\alpha$  given by :  $\tan 2\alpha = \frac{J}{\Delta}$ .

For large splitting  $\Delta$ , the exciton states are weakly perturbed localized states, whereas for small  $\Delta$  they are in-phase and out-of-phase oscillations equally shared by molecules A and B (see Figure 13.1).

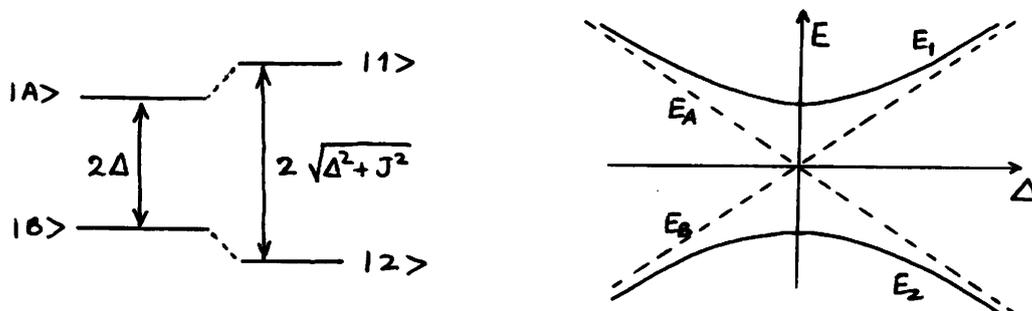
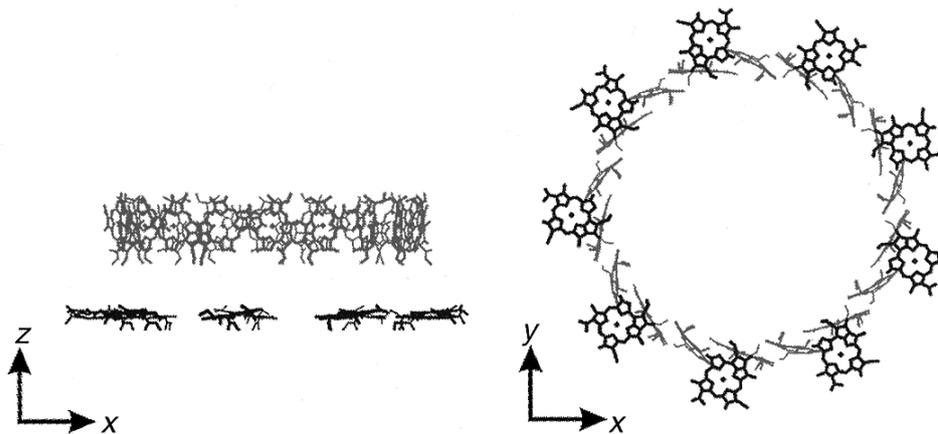


Figure 13.1 : Left : Shift of molecular levels due to exciton coupling. Right : Exciton energies in a pair of molecules as functions of the splitting  $\Delta$ , for a fixed interaction  $J$ . The unperturbed levels are indicated by the dashed lines.

## 13.2. Antenna complex

Here, we discuss a system in which the interaction between the chromophores is strong, and the number of coupled chromophores is rather large (9 or 18). The system is the light-harvesting (or antenna) complex of a bacterium (*Rhodospseudomonas acidophila*). The function of this complex is to collect sunlight and to transfer its energy to the photosynthetic reaction center, where it will be used.



*Figure 13.2 : Positions of the two chlorophyll rings in the LH2 antenna complex. The B800 ring (lower one on the left) is weakly coupled, whereas the interaction is very strong in the B850 ring (upper one on the left). The protein scaffold has been omitted for clarity [from van Oijen et al. Science 285 (1999) 400 ; Copyright 1999 AAAS].*

The structure of the complex has been elucidated by X-ray diffraction : A protein scaffold holds two rings of chlorophyll molecules (chromophores with a porphyrin structure and a complexed magnesium in the center) together. A first ring, with the larger diameter (see Fig. 13.2) contains 9 coplanar, weakly coupled molecules, which absorb around 800 nm (the ring is thus called B800). A second ring, with a smaller diameter, contains 18 molecules with their planes perpendicular to that of the ring, arranged like the blades of a turbine. This system absorbs at 850 nm and is therefore called the B850 ring. The B800 system just collects photons, but the B850 ring is a strongly coupled system in which the excitation is delocalized and hops around at room temperature. This hopping is very important to ensure fast energy transport to other LH2 rings, and eventually to the reaction center (placed in a different complex, also included in a ring of chlorophylls). It is important to note that the shapes of the

spectra of the two rings (B800 and B850) don't differ that much in ensemble experiments. Only the structure and theoretical models gave any indication as to their roles.

The first experiments on single LH2 complexes were published in 1999 by the group of J. Schmidt in Leiden [A. van Oijen et al., *Science* 285 (1999) 400]. Let us summarize their main observations of single LH2's at liquid helium temperature:

- The broad band of the B800 system resolves into about 4-8 sharp lines (see Fig. 13.3), while the B850 system only show 2 or 3 broad bands (see Fig. 13.3);
- All the bands are strongly polarized, which is a current feature in many single-molecule data. The polarizations of the main broad bands in the B850 system are always perpendicular to each other.
- There is a weak sharp line at the red edge of the excitation spectrum of the B850 system (not visible in Fig 13.3).

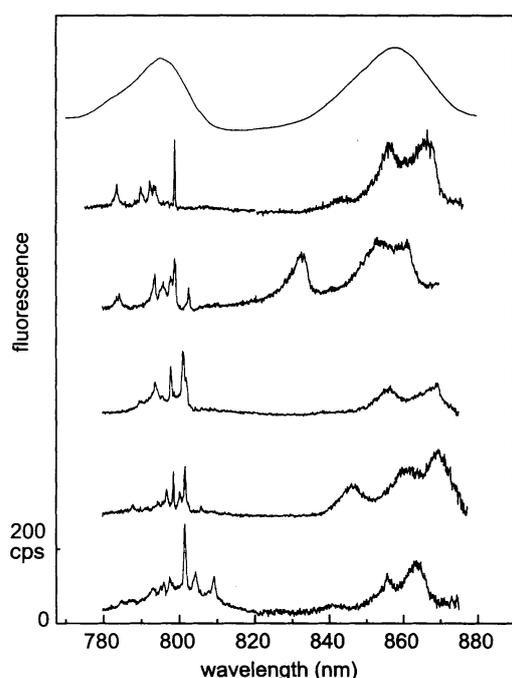


Figure 13.3 : Fluorescence excitation spectra of an ensemble of LH2 complexes (top) and of several individual complexes (below). Although the B800 and B850 bands look similar in the bulk spectra, they differ dramatically in all individuals. Reprinted with permission from van Oijen et al. *Science* 285 (1999) 400 ; Copyright 1999 AAAS.

All these results can be nicely interpreted in the exciton picture.

**B800 ring:** In the case of the B800 ring, the excited states are mainly localized on each chlorophyll, and polarized along each transition moment, with very few interacting pairs. This picture is consistent with weak interactions between the

chromophores, and a large spread of resonance energies,  $\Delta \gg J$ .  $\Delta$  can be estimated from ensemble measurements to about  $125 \text{ cm}^{-1}$ , while the interaction between two point dipoles at the same distance is  $-24 \text{ cm}^{-1}$  (negative for parallel dipoles). This B800 system consists of localized excitons.

B850 ring: A quantum-chemical calculation of the interaction in this case gives  $300 \text{ cm}^{-1}$ , significantly more than the spread of energies, again about  $100 \text{ cm}^{-1}$ . We therefore expect a strong coupling. For a ring of strongly coupled molecules, only three states carry oscillator strength: the  $k = 0$  state (all dipoles oscillate in phase) for the dipole component perpendicular to the ring plane, and the  $k = \pm 1$  states corresponding to a phase rotation of  $2\pi$  on a rotation around the ring, for the component in the plane. For a perfectly circular ring, the latter two states are degenerate.

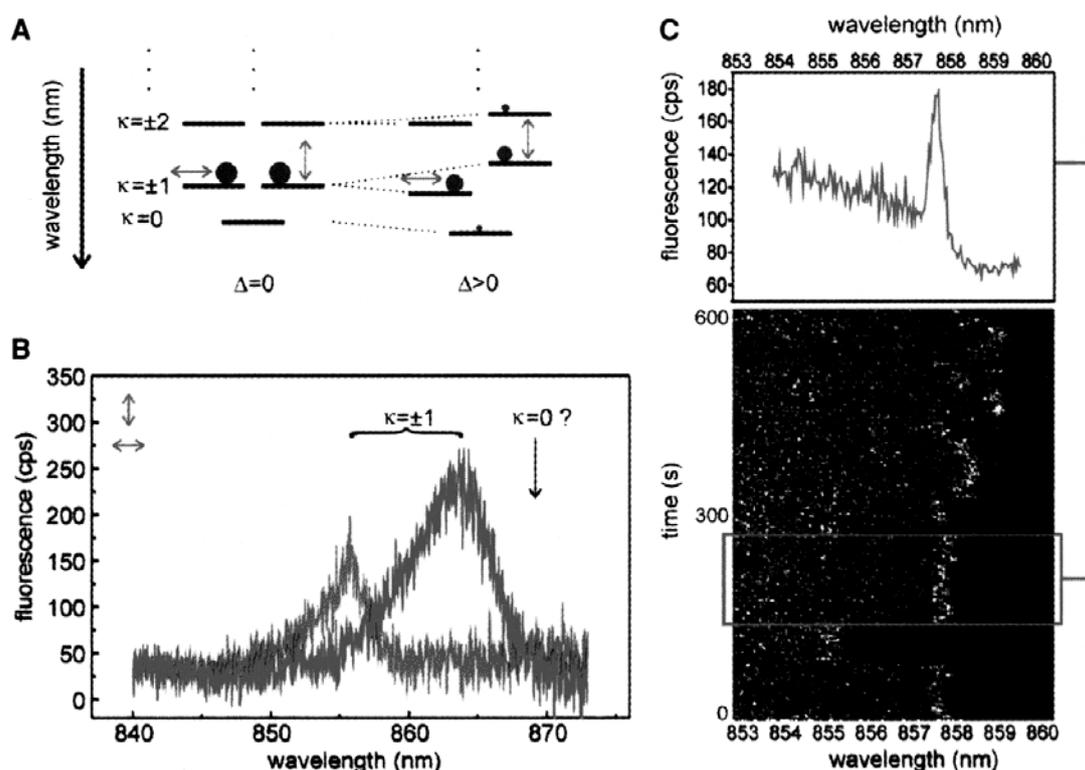


Figure 13.4 : Exciton picture for the B850 system. A : Exciton level diagram for an undistorted complex (left) and for a distorted one (right). B : The two most intense bands are orthogonally polarized. C : The  $k=0$  state appears in time traces, at the red edge of the fluorescence excitation spectrum. It is broadened by spectral diffusion, but can be seen clearly after integration in a time interval where no jumps occur (top). Reprinted with permission from van Oijen et al. *Science* 285 (1999) 400 ; Copyright 1999 AAAS.

Single LH2 rings show two non-degenerate broad bands with perpendicular polarizations, which are attributed to the  $k = \pm 1$  states, split by a deformation of the ring. The breadth of these bands arises from the fast relaxation to the lower-lying  $k = 0$  state. In addition to these broad states, a sharp line found at the red edge of the excitation spectrum, is attributed to the  $k = 0$  state, which appears either via its vertical component, or because of the ring distortion.

### 13.3. Two quasi-resonant molecules

This second example is that of two single molecules studied by Sandoghdar and collaborators [see C. Hettich et al., *Science* 298 (2002) 386]. They doped a p-terphenyl crystal with terrylene and found (by chance) two guest molecules close to each other. They located them by applying a strong electric field via a metal-coated bead on a scanning tip. The dependence of the shift on the 3D position of the tip allowed them to determine the positions of the two molecules in the crystal, about 10 nm apart. Experiments at a higher excitation intensity (see below) show that these two molecules are in fact coupled to one another. The coupling gives rise to shifts of both lines, and to a redistribution of their oscillator strength. The transition dipole moments of the exciton states are given (according to the notations of paragraph 1) by :

$$\vec{\mu}_1 = \cos \alpha \vec{\mu}_A + \sin \alpha \vec{\mu}_B \quad \text{and} \quad \vec{\mu}_2 = -\sin \alpha \vec{\mu}_A + \cos \alpha \vec{\mu}_B .$$

For example, in the case of two parallel and resonant molecules ( $\alpha = \pi/4$ ), one of the states has no oscillator strength, while the other carries twice the oscillator strength of one molecule (the total oscillator strength is always conserved). Those are the subradiant and superradiant states of a pair of atoms, as defined by Dicke. For the molecules of interest here, the coupling was rather weak (about 1 GHz), so that we have to remember that the exciton coupling only applies to the zero-phonon component, as discussed above. Indeed, the two lines show significant differences in their coupling to radiation and spontaneous emission. The coupling modifies the Stark shift of the exciton transitions as compared to that of the molecules, according to the equations of (1). Therefore, the new values for the Stark shifts leads to a new intermolecular distance, now found to be 12 instead of 9 nm.

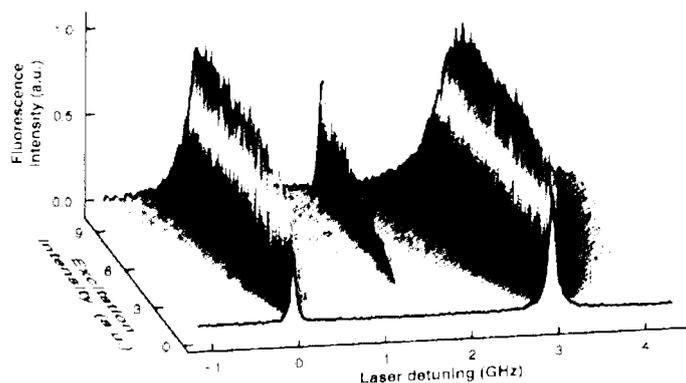


Figure 13.5 : 3D plot of fluorescence excitation spectra of two single molecules for increasing laser intensity (depth coordinate). For high enough intensity, a third line appears in the middle between the two exciton lines of the low-power spectrum. This third line is caused by simultaneous absorption of two photons by the coupled system, towards the doubly excited state. Reprinted with permission from Hettich et al. *Science* 298 : 385 (2002) ; Copyright 2002 AAAS.

We now discuss how the coupling between the molecules was found. When the laser intensity is increased, a new line appears right in the middle of the two saturated lines. The new line is much narrower than the other two, for two reasons :

- i) it is not saturated,
- ii) it is a two-photon effect, in which two laser photons are absorbed simultaneously to give two excitations located on the two molecules.

Solving optical Bloch equations for the coupled system, one sees that the new line appears only when the molecules are coupled, by either of two coupling mechanisms :

- i) the exciton coupling we just discussed,
- ii) a « proximity » coupling, arising from the slight change in excitation energy of molecule A when molecule B is excited. The source of this coupling can be the Van der Waals interaction between the two molecules, or an elastic coupling via a deformation of the lattice (we have seen similar examples in our discussion of two-level systems in spectral diffusion). The measured spectra of the dimer are in full agreement with the simulation, and confirm the existence of the coupling. The exciton coupling gives the dominant contribution, but a careful analysis also shows the existence of a weak proximity coupling.

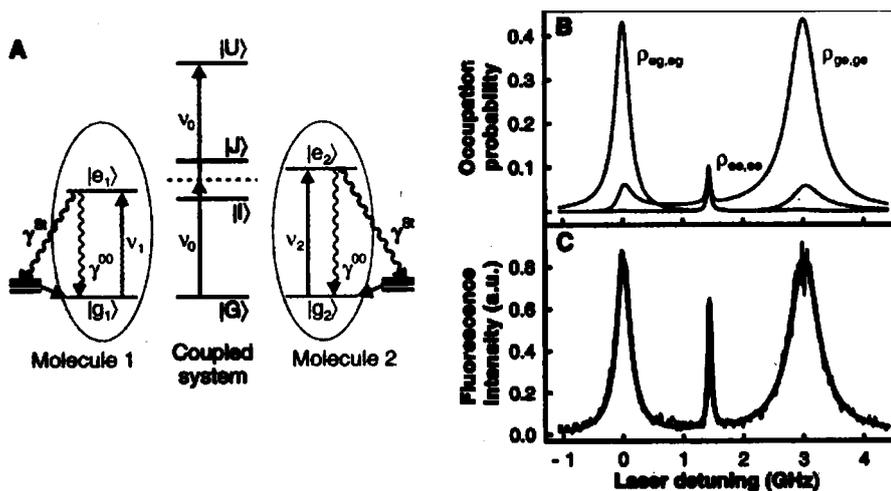


Figure 13.6 : A : Level diagram of the two coupled molecules, with the doubly excited state. C : Observed spectrum with a simulation of the optical Bloch equations. B : Various contributions to the signal from excitation of the two individual molecules. The central line arises from both molecules in equal amounts. Reprinted with permission from Hettich et al. *Science* 298 : 385 (2002) ; Copyright 2002 AAAS.

The discussion of these two coupled molecules is an example of the role of interactions in a molecular system at nanometer scales. By tuning the resonance splitting  $\Delta$  of the uncoupled molecules, for example via an inhomogeneous electric field, or via a local mechanical strain, it would be possible to manipulate the degree of coupling (or of entanglement) of the two excited states. Such manipulations are at the center of quantum computing schemes. Although the present system is probably not well suited to actual computations because of the short lifetimes of the excited state (nanoseconds), it would be a nice model for demonstrations.

#### 13.4. Conjugated polymers

Conjugated polymers contain long chains of alternating single and double bonds. Because of their structure, they can conduct electrons or holes and interact with visible-UV light. They are used in many applications as organic semiconductors, for example light-emitting diodes (OLEDs) or displays. Here, we discuss only briefly their optical properties. A perfect chain without distortion would give rise to perfectly delocalized electron states over the whole chain. However, Peierls showed that a one dimensional chain is unstable with respect to pairing, leading to the opening of a gap in the electron band (Peierls instability). This is the reason why these systems absorb only down above an energy gap, for example around 500 nm for polyenes.

The strong interaction between monomers favors delocalized exciton states, while disorder in the chain due to folding or perturbation by neighboring molecules favors localized states. The competition between these two effects leads to states delocalized over a few monomers (usually 3-10, more at low temperature and in well ordered systems), these collective states are often called chromophores. Exciton transfer between chromophores takes place via exciton hopping and incoherent energy transfer processes similar to FRET. This gives rise to the energy funnel effect, where all excitons created on a chain may be efficiently transferred to the lowest-energy chromophore. The funnel effect explains why often a single chromophore emits in a single conjugated polymer molecule, while all chromophores or monomers absorb. The relaxation of excitations towards the lowest-energy chromophore leads to antibunching (i.e., singlet-singlet annihilation of multi-excited states, until only one excitation remains) and to quenching events responsible for blinking of the emission (while the absorption would not blink).