CHAPTER 1

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1.1 Molecular aggregates

Condensed phase molecular spectroscopy is concerned with the study of molecular energy states. In solids the interaction between the molecules under study and their environment is important. In a molecular crystal this environment consists of identical molecules, which are ordered perfectly. Two situations are important; one can study the molecule of interest as a pure crystal [1,2], in which every molecule is surrounded by identical neighbors, or a as guest molecule in a crystal of a different compound [3]. When comparing the excited state of a molecule in a pure crystal with the excited state of a molecule which is isolated, a striking difference is encountered. The state formed after optical excitation of a single molecule is confined to that molecule. The excited state of a molecule in a pure crystal is often delocalized, which means that not a single molecule is excited, but a whole array of molecules. This type of excitation is called exciton [4].

Molecular aggregates represent a situation intermediary between isolated molecules and pure crystals. As such they offer the opportunity to acquire insight in the processes of localization and delocalization of molecular excited states. The spectroscopy of molecular aggregates has been an important topic in molecular spectroscopy [5].

The interactions of the electronic excited state with the environment can be studied using steady state absorption and emission spectroscopy. An absorption spectrum, for example, gives the position and the linewidth of an optical transition. This linewidth contains a contribution from relaxation (homogeneous linewidth), and a contribution which is caused by the statistical fluctuations of the environment of the different molecules (inhomogeneous linewidth). Stated differently, both static and dynamic interactions determine the steady state optical spectra.

Time resolved spectroscopy gives information about the dynamics of the interaction of the molecule with the host environment. The relaxation of an optically excited molecule consists of two processes: relaxation to other states characterized by a population lifetime $T_1$, and pure dephasing process with a lifetime $T_2$. Examples of the first process are fluorescence and radiationless relaxation. Optical excitation of a molecule can be treated as driving an optical oscillator to a higher energy level. The disturbances of this optical oscillator that change the phase but not the energy state are called pure dephasing. The host environment of the excited molecule is the source of these disturbances. Both static and time resolved spectroscopies of molecular aggregates are the subject of this thesis.

The concept of the molecular exciton dates back to the work of Frenkel [6], and has been applied to many problems in molecular spectroscopy [7]. The coupling of the molecular excited states leads to formation of molecular exciton bands. The oscillator strength is renormalized, and drastic changes occur in the spectrum upon the coupling of the molecules. The simplest molecular exciton is the dimer. Such a dimer state is formed when the electronic excited states of two molecules mix into a plus and a minus combination. An interesting question is whether the dimer state is a true two-molecule state, or a one molecule state that hops from
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molecule 1 to 2 [8]. Dimer exciton bands are formed in isotopically mixed crystals. It turns out that the main factor determining the lineshape is the scattering of the exciton, either by impurities or by crystal phonons [9].

When more than two molecules are coupled together a band of molecular exciton states is formed. Some molecular crystals and molecular aggregates exhibit a strong anisotropy of the coupling between the molecules, leading to low dimensional excitations. The salient feature of one and two dimensional molecular excitons is the projection of the combined oscillator strength of the monomers on just a few exciton states. These particular exciton states acquire a large transition dipole moment. The radiative rate of a transition is proportional to the square of the transition dipole moment, so aggregation leads to very high radiative rates. This effect is called superradiance.

The main part of the studies on molecular excitons in molecular crystals has been done on triplet excitons [10,11]. Triplet states of chromophores generally have small transition moments, whereas singlet excited states couple much stronger to applied optical fields. Molecules in the triplet state are in general not coupled as strongly as in the singlet state. As a result, the triplet exciton bandwidth is generally of the order of a few cm⁻¹, whereas the bandwidth of a singlet exciton can easily be 1000 cm⁻¹. The key parameter determining the delocalization of an exciton in both cases is the ratio of the spread of the site inhomogeneity (σ) to the exciton bandwidth (B). A delocalized triplet exciton can be observed in highly perfect crystals, which have very small site inhomogeneities. Molecular aggregates are not as perfectly ordered as molecular crystals. The strong coupling between units, however, allows for the observation of delocalized exciton states.

The study of singlet excitons is complicated by the fact that the high oscillator strength per unit volume for these transitions in molecular crystals leads to polariton formation upon optical absorption. A polariton is a mixed photon–exciton state which is formed when the coupling of the molecular states to the optical field is very strong. A recent study on naphthalene single crystals [12] shows that their optical properties are indeed governed by polaritons. The transition moment per unit volume in such a pure crystal can be very high. The characteristic length of an excitation process is the wavelength of the exciting light (λexc). The low dimensionality of molecular aggregates leads to a low transition dipole moment per unit volume (∝λexc⁻¹), and polariton formation can be excluded. As such, molecular aggregates offer an unique possibility to study singlet molecular excitons.

1.2 Picosecond lasers

The development of lasers has opened new possibilities for the spectroscopic study of molecules. Using narrow band continuous light sources, lineshapes and thus dephasing can be studied in the frequency domain. Another line in the development of lasers has led to pulsed lasers. Both relaxation and dephasing of collections of optically excited chromophores can be studied in the time domain with the help of pulsed
lasers. Sequences of coherent pulses generate a variety of effects like, for example, coherent Raman scattering [13], and photon echo phenomena [14]. Incoherent dynamics can be probed as well. In this case the laser pulses serve to generate a non-equilibrium population whose relaxation can be followed in time. This relaxation can be monitored by either another laser pulse, as in pump/probe spectroscopy, or by fast electronic detection, as in time resolved photon counting.

The so called continuous wave modelocked laser has supported the development of time resolved spectroscopy. In this laser the gain is modulated at a frequency which is the same as the inverse round trip time of the light. Only during the short period that the gain is larger than one the light will be amplified. The resulting output is a train of pulses at exactly the round trip frequency. The pulse lengths that can be produced depend on the actual gain and loss media in the laser. The pulse lengths vary from 100 picoseconds (1 ps = 10^{-12} second) in acousto-optically modelocked argon-ion lasers to as short as 6 femtoseconds [15] (1 fs = 10^{-15} second) in colliding pulse modelocked (CPM) dye lasers.

Most lasing media have only a limited spectral width where a high gain is found. For example, an argon laser only operates at a number of wavelengths. This poses severe limitations on the applicability of lasers for spectroscopy. The invention of the dye laser has solved this problem. Organic dye molecules and some inorganic systems have very broad emission spectra (>1000 cm^{-1}) and can show laser action in broad ranges. The technical progress in the past three decades since the invention of the laser, has led to lasers that cover most of the ultra-violet, visible and infra-red parts of the electromagnetic spectrum.

1.3 Summary

The subject of this thesis is the spectroscopy and dynamics of molecular aggregates in amorphous matrices. Aggregates of three different molecules were studied. The molecules are depicted in Fig. (1.1). Supersaturated solutions of these molecules show aggregate formation. Aggregation is a process similar to precipitation of a solution. The loss of entropy in such a precipitation process is compensated by the gain in enthalpy. Molecular aggregates in solutions thus represent a metastable thermodynamic state. The organization of aggregates in solution can be fixed by rapid cooling or rapid solvent evaporation.

The molecules were selected because of the dramatic changes occurring in the absorption spectra upon formation of aggregates. The aggregates show absorption bands that are shifted to lower energy by more than 1000 cm^{-1}, with respect to the monomer transition. The dynamics of the optical excitations that are formed after absorption of a photon by these aggregates is the main topic of this thesis.

In Chapter 2 an overview is given of the concept of the spectroscopy of excitons in molecular aggregates. Starting from a description of dimers, the energy level structure of exciton bands is developed. The interaction of the excitons with the lattice modes of the environment, the so-called phonons, is also treated.
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Figure 1.1. From top to bottom: pseudo-iso-cyanine (PIC), a thiapyrilium dye (TPY), and a thiacyanine dye (TD). The first two molecules are charged positively and are accompanied by a negative counter ion. The last molecule is an internal salt.

In Chapter 3 the experimental methods are described. The time scale of the radiative and dephasing dynamics of molecular excitons ranges typically from 1 ps to 100 ps. The dynamics was studied by time resolved fluorescence, pump/probe spectroscopy, and accumulated echo spectroscopy, which have the time resolution that is required. In this chapter the steady state spectroscopy and the preparation of the aggregate samples are described as well.

Chapter 4 deals with the dephasing of PIC aggregates in water/ethylene glycol mixtures. These aggregates exhibit very narrow absorption lines (≈30 cm⁻¹) in solid solution. The dephasing time is related to the
homogeneous width of the transition. At 1.5 kelvin (1.5 K) the homogeneous width is about 1 cm\(^{-1}\). At temperatures of about 100 K the dephasing time is much shorter and the linewidth is determined by this dephasing time.

In Chapter 5 the radiative properties of PIC aggregates are studied. The key result is the observation of a fading of the superradiant effect at higher temperatures. This shows that the radiative coupling of the monomer units is less effective at higher temperatures. Possible reasons for this decoupling are discussed.

The excitations of TPY aggregates that are treated in Chapter 6 differ dramatically from the excitons observed in PIC aggregates. The delocalized excitation is coupled strongly to lattice phonons. A model is proposed that explains the observations in terms of a self-trapping process of the exciton.

Finally, in Chapter 7, a preliminary report is given of results from experiments on aggregates of the thiacyanine dye TD. These aggregates exhibit a number of features that indicate superradiant exciton behavior comparable to PIC aggregates.

References

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