The ultrafast dynamics of aggregate excitons in water
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Document Version
Publisher's PDF, also known as Version of record

Publication date:
1999

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

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Download date: 25-02-2019
1.1 Molecular aggregates

In liquid solutions, absorption spectra of molecules are relatively broad and structureless. This reflects the ultrafast dynamics of the electronic states of the molecules in a liquid environment. In the mid thirties Scheibe [1] and, independently, Jelley [2] discovered that upon increasing the concentration of the dye pseudo-isocyanine (PIC) in water, an unusually sharp absorption band arises, that is redshifted relative to the broad absorption band observed in dilute solutions. Both ascribed the sharp transition to an optical excitation on aggregates of this dye molecule. These aggregates are usually referred to as J-aggregates or, occasionally, Scheibe-aggregates. Scheibe also discovered that J-aggregates of PIC in solution have a distinct tendency to form threads. This property can be used to orient the J-aggregates, whereby the absorption is polarized parallel to the direction of the threads. On the basis of absorption experiments on streaming solutions of PIC aggregates, Scheibe suggested a one-dimensional structure for these aggregates [3].

Many spectroscopic investigations on J-aggregates have been conducted since their first discovery [4-9], most often on PIC (see fig. (1.1)). The special interest in the optical response of aggregates arises from collective effects that are caused by the strong interactions between the molecules within the aggregate [10-12]. The resulting delocalization of the electronic states over many molecules on the chain leads to the formation of collective eigenstates for all molecules in the aggregate, the so called exciton states. These states can be visualized as a coherent movement of an excitation, i.e., a bound electron and hole, over the chain of molecules. Hereby the electrons keep tightly bound to their molecular centres, so only energy is transported. In the one-exciton states, grouped together in the one-exciton band, or Frenkel exciton band, one excitation is shared by all the molecules in the aggregate. But also higher exciton bands exist. These multi-exciton states are important in non-linear optical experiments. For instance, the two-exciton band, in which the molecules on a chain share two excitations, shows up in third-order optical response [13]. When the molecules are modelled as two-level systems, an aggregate can carry in principle as many excitations as there are molecules.

As a direct result of the delocalization of the optical excitations over a certain number of lattice sites in the aggregates structure, aggregates have interesting optical properties, distinctly different from those of the individual molecules that constitute the aggregate. The unusual sharpness of the absorption or J-band is one of these cooperative effects in the optical response. The delocalized exciton states average over the inhomogeneities in the transition frequencies of the individual molecules, resulting in the narrow absorption band. This mechanism is called motional narrowing or exchange narrowing [14]. Another very interesting collective effect is exciton superradiance: an ultrafast radiative decay caused by the fact that the system’s oscillator strength is concentrated primarily in one or a few delocalized eigenstates in an exciton band. It can be observed at low temperatures in glasses [15-18]. Directly related is the possible occurrence of giant optical nonlinearities, caused, again, by the large oscillator strength of a few electronic states [11,12].

Whereas the intermolecular interaction is the driving force for delocalization of the excitation over the entire aggregate, disorder in the single-molecule energies or in the couplings between the molecules tend to localize the excited-state wavefunction on a finite section of the
aggregate [19]. The exciton delocalization range is then determined by the relative magnitude of the intermolecular coupling compared to the energetic disorder, instead of by the real, often much longer, physical size of the aggregate. The delocalization length is important because it determines the (non-) linear optical properties of aggregates. If the aggregates are small compared to their delocalization (or coherence-) length, a size dependence of the optical response can be observed for many aggregates, for instance of optical nonlinearities [20,21], or of the superradiance decay rate [22].

In the past decade, the effects of energetic disorder on the localization of excitation and the corresponding reduction of collective effects in the (non-) linear optical response was extensively studied [14,23-29]. This was usually done for static disorder, neglecting dynamic aspects due to coupling of the excitonic system with a heat bath, which facilitates a theoretical description of the optical response. Assuming a Gaussian distribution of the transition frequencies, many effects of disorder on excitonic properties could be explained [14,26]. This picture in principle only holds for zero-temperature, and accordingly all of that work was done in glassy matrices at, or close to, liquid helium temperatures.

In this thesis, we return to the original circumstances under which aggregates were first discovered: room temperature liquids. The single-molecule energies and intermolecular couplings fluctuate in a random manner and the dynamical aspects of the disorder cannot be ignored [30-32]. Like static disorder, dynamic disorder localizes the excitation. This is a more complicated process than the zero-temperature case, where the localization is fully determined by the balance between the intermolecular coupling and the energetic disorder. Now the time scales, that are associated with the coherent motion of the exciton and with the solvent perturbations, have to be considered as well. For individually solvated molecules the perturbations originating from the surrounding solvent molecules lead to ultrafast dephasing of the optical transitions, which was in recent years extensively studied by a number of ultrafast techniques, such as transient hole burning [33], two- and three-pulse photon echoes [34-41] and chirped four-wave mixing [42,43]. For aggregates, the fluctuations lead to localization of the excitation, optical dephasing of the exciton optical transitions, and (incoherent) propagation of the excitons over the entire physical size of the aggregates. Therefore, the spatial extent of the exciton, the speed of propagation and the optical dephasing of the exciton transitions are all determined by the same physical phenomenon: the coupling of the aggregate energy levels with a heat bath.

The unusual properties of aggregates makes them particularly interesting, both from a fundamental point of view and for (potential) applications in several fields. Materials with a large and fast nonlinear optical response are necessary for future applications in optical devices for communication and information processing, like optical switches in computers [44]. This is an important reason for the strongly increased interest in molecular aggregates in the last decade. Today, due to their strong light absorption, they are widely used as spectral sensitizers on the surface of silver halide microcrystals in photographic materials [45,46]. As such, these aggregates function as antenna systems that collect light for the photographic process. In biology, aggregates are of general interest since most photobiological processes, including photosynthesis, rely on molecular aggregates for energy or charge transfer processes [47]. The aggregates which are investigated in this thesis, can therefore be considered to be model systems for more complex excitonic systems, like light harvesting pigment molecules in natural photosynthetic antenna
systems.

Most of the research on aggregates has been performed on PIC, since this is the dye for which J-aggregation was first observed. In this thesis we investigate a different aggregate, called TDBC, which forms even better defined, stable aggregates in room temperature water solutions. The structure of the molecule is shown in fig. (1.1). In contrast to PIC, TDBC is not sterically hindered and therefore it should have an almost planar structure. It is known to easily form J-aggregates at room temperature \[48\] whereby no dimers or aggregates with a blue-shifted absorption spectrum (H-aggregates) are formed under any condition. This facilitates the interpretation of spectroscopic data. The physical size of the TDBC aggregates which we study, is tens of thousands of molecules. The optical excitations are found to be of much smaller size: as discussed in chapter 3, they are localized on about 15 molecules. The structure of the aggregate is supposed to be linear, which facilitates a theoretical treatment.

1.2 Outline of this thesis

Until recently, the nature of the optical transitions of room temperature aggregates, as well as their dynamics, were not very well known. In this thesis, the level structure and the dynamics of the linear TDBC aggregate in liquid solution is studied on a femtosecond time scale by ultrafast non-linear optical experiments. As a result of the fast advance in femtosecond laser technology \[49-51\], dynamical processes can now be studied on time scales well below 100 femtoseconds. In the experiments outlined in this thesis usually pulses of about 10 femtoseconds were used. Ultrafast pump-probe experiments were performed to provide information on the spatial extent of the excitons. Grating scattering, time-resolved photon counting, and photon echo experiments

![Molecular structures of the monomer dye molecule TDBC used in the investigations described in this thesis (top) and the most investigated dye in literature, known as pseudo-isocyanine or PIC (bottom). The monomers form aggregates when they are dissolved in water. TDBC is the sodium salt of 1,1'-diethyl-3,3'-bis(4-sulfobutyl)-5,5',6,6'-tetrachloro-benzimidazolo-carbocyanine. PIC is the synonym of 1,1'-diethyl-2,2'-cyanine.](image-url)
were employed to characterize the population decay and dephasing dynamics of the excitons under various excitation conditions. The results of all experiments are interpreted in terms of a single model, based on conventional exciton theory for one-dimensional molecular systems, with stochastic fluctuations of the transition frequencies at two, ultrafast time scales.

This thesis is organized as follows: In chapter 2, the femtosecond laser set-up is introduced that was used for the non-linear optical experiments. It also contains some general descriptions of the various time-resolved experiments which were used to explore the aggregate dynamics. Furthermore, the handling and preparation of the aggregates is described.

Chapter 3 provides the background for the discussion and explanation of the experimental results, reported in the other chapters of this thesis. Some aspects of the conventional theory for one-dimensional molecular excitons will be briefly reviewed. It will be explained that the one-exciton band, as well as multi-exciton bands, contribute to the observed nonlinear optical response. A pump-probe experiment is reported, in which the presence of multi-exciton bands clearly shows up. It will be demonstrated that this feature can be used to determine the spatial extent, or the delocalization length, of the excitons.

The rapid motions in liquids lead to ultrafast perturbations of the molecular energy levels. The resulting optical dephasing of the exciton transitions was studied by two- and three-pulse photon echo experiments, which are described in chapters 4 and 5, respectively. Often, fluctuations of electronic energy levels can be separated into a fast part, leading to homogeneous line broadening, and a slow part, leading to what may be called inhomogeneous dynamics. In chapter 4, the results of the two-pulse photon echo experiments on aggregate excitons show that stochastic perturbations of the exciton transition frequencies indeed occur on two distinct time scales. Due to motional averaging, the amplitude of especially the slow fluctuations is strongly reduced compared to those of the individual molecules. For the fast part of the dynamics this averaging process is much less efficient, since these fluctuations occur on a time scale similar to, or even faster than, the motional averaging process itself. A measure of this motional averaging time-scale is the inverse of the intermolecular coupling. A quantitative theory, based on stochastic fluctuations with finite correlation times, is used to explain the observed experimental results. It is argued that the optical dephasing of excitons is directly related to the spatial extent of the excitation on the aggregate chain.

The results of the three-pulse stimulated photon echo experiments are discussed in chapter 5. These experiments are performed in order to probe the fluctuations of the energy levels over a wider range of timescales. Especially information about the slow fluctuations is obtained and this is interesting in view of the fact that exchange narrowing of the exciton absorption spectrum is mainly due to a reduction of the slow fluctuations. Also solvation can be studied in such a three-pulse echo experiment.

In chapter 6, the results of exciton lifetime experiments are presented. The decay of the exciton population density was studied by femtosecond grating scattering and time-resolved single-photon counting. As found before by many other groups [5,6,52,53], the exciton population decays non-exponentially with an excitation intensity dependent rate. This can be adequately explained by a phenomenological model of exciton annihilation, in which the excitons propagate in a random walk-type of way over the aggregate chain. This propagation is induced by the same fluctuations that give rise to the optical dephasing, studied by the photon echo experiments.
experiments. A simple kinetic picture of this process is presented, in which the multi-exciton bands act as doorway states in the annihilation process. For one-dimensional aggregates, spatial self-ordering is predicted, due to the fact that the annihilation process selectively affects those excitons that are close together. Hence, the annihilation reaction is expected to become diffusion-limited on very short time scales. However, this is not observed. At the moment, we can only speculate on the reasons for this behaviour.
References