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COHERENCE DOMAINS IN THE RADIATIVE DYNAMICS OF MOLECULAR AGGREGATES

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Abstract

We present theoretical evidence for the existence of excited- state coherence domains in molecular aggregates. The domain size is a function of exciton-phonon coupling and temperature, and determines the radiative decay rate of the entire aggregate. A series of supporting experiments, involving statistical control of the aggregate physical size, are also proposed.

Keywords: Superradiance, J-aggregates, molecular aggregates, exciton-phonon coupling, fluorescence lifetime, coherence domain

INTRODUCTION

In many practical imaging systems, semiconductors are sensitized to wavelengths below their bandgap energies by photoinduced charge transfer from an adsorbed dye. The high surface concentration needed for appreciable light absorption causes the dye molecules to form aggregates, which consist of regularly arranged dye molecules. In a J-aggregate, the transition dipole moments of adjacent dye molecules interact strongly, resulting in a red-shifted and narrow absorption spectrum compared to that of the monomer.[1-3] The increased cooperativity also leads to an ultrafast radiative decay rate, which has recently been observed in pseudo-isocyanine bromide (PICBr) J-aggregates at low temperature.[2] These observations are attributed to delocalized excited states or excitons. In a rigid aggregate (i.e. no phonons) with dimensions much smaller than an optical wavelength λ, exciton theory predicts that the fluorescence decay rate is equal to $N\gamma$, where γ is the monomer decay rate and N is the number of dye molecules in the aggregate[4]; when the aggregate dimensions are much greater than λ, the decay rate levels off to a constant value, approximately given by $N_\lambda\gamma$, where N_λ is the number of molecules in a volume λ^d where the dimension d is equal to 1 or 2.[5] According to this analysis an optically excited electron in a large J-aggregate adsorbed on a semiconductor surface should most likely return to the electronic ground state while emitting a photon, rather than undergo interfacial transfer, greatly reducing the efficiency of the color photographic process, for example. However, the picture is not complete without considering the effect of temperature. Experimentally, it has been observed that increasing temperature quenches the superradiant behavior,[2] so that even small aggregates display fluorescence lifetimes significantly longer than $(N\gamma)^{-1}$. In this paper, we explore theoretically the nature of aggregate fluorescence and propose a series of supporting experiments.

Previous measurements of the temperature dependent fluorescence decay in J-aggregates[2] and semiconductor quantum wells,[6] and the coherent energy transfer rate in J-aggregate monolayers,[7] have provided evidence for coherence domains consisting of a temperature dependent number N_{eff} ($<N$) of atoms or molecules; in a molecular aggregate, the radiative decay rate is reduced from $N\gamma$ to $N_{eff}\gamma$ at finite

temperature. The domain size, N_{eff}, is a measure of the range of correlations between the molecular polarizations in a uniformly excited aggregate. N_{eff} is a function of the exciton-phonon coupling and the temperature; higher temperatures, or stronger exciton-phonon coupling, result in a smaller N_{eff}, a trend that is consistent with experiment.[2,6,7] In an effectively infinite aggregate such as a macroscopic monolayer, N_{eff} should no longer depend on N and any successful theory must have N_{eff} converging (to a value N^*) as N approaches infinity. We have developed a microscopic theory which predicts a convergent value of N_{eff} in the presence of both acoustic (intermolecular vibrations) and optical (librations) phonon coupling to excitons. In addition, we present an experimental system which can provide evidence of N^* through measurements of the fluorescence radiative decay rate of a J-aggregate adsorbed on an AgBr surface as a function of average aggregate physical size. In section II we outline our theoretical approach and show how N_{eff} scales with N and temperature. In section III, the proposed experiments are described and in the following section, we present a theoretical prediction of the experimental results.

THEORY

Our starting point[8] is a one-dimensional aggregate Hamiltonian (with periodic boundary conditions):

$$H = \hbar\sum_{k=0}^{N-1} \{\omega(k) + i\frac{N}{2}\gamma\,\delta_{k,0}\}\hat{B}_k^\dagger\hat{B}_k + \hbar\sum_{s}\sum_{q=0}^{N-1}\Omega_s(q)\,\{\hat{b}_{qs}^\dagger\hat{b}_{qs} + \frac{1}{2}\} + \sum_{s,k,q}\frac{F_s(k,q)}{\sqrt{N}}\hat{B}_{k+q}^\dagger\hat{B}_k(\hat{b}_{q,s} + \hat{b}_{-q,s}^\dagger) \quad (1)$$

where $\hat{B}_k^\dagger$ ($\hat{b}_{qs}^\dagger$) denotes the Frenkel exciton (phonon) creation operator with wavenumber k (q). (s differentiates between optical and acoustical phonons). The coupling of the electronic excitations to the photon modes results in a superradiant damping,[4] which predicts that the k=0 excitonic coherence decays exponentially with a rate $N\gamma/2$. $\omega(k)$ (= ω_0 - 2Vcos[2πk/N]) and $\Omega_s(q)$ (= $\Omega_{ac}\sin\pi q/N$ for acoustic phonons and = Ω_{op} for dispersionless optical phonons) are the exciton and phonon dispersion relations respectively, where V is the nearest neighbor dipole-dipole interaction energy and $\hbar\omega_0$ is the electronic excited state energy. The sign of V depends on the angle the transition dipole moment makes with the aggregate axis[1]. In J-aggregates V is positive (which we assume in all calculations) so that the k=0 state is at the bottom of the band. The final term in Eq.(1) is a linear exciton-phonon coupling (off diagonal in the site basis[9]), where $F_{ac/op}(k,q)$ is due to the first order change of the electronic coupling as a function of intermolecular separation (acoustic phonons) or molecular orientation (optical phonons). $F_{ac/op}(k,q)$ is equal to an amplitude $F_{ac/op}$ times a factor of order unity which includes the wavevector dependence.[8] (Site diagonal[9] exciton-phonon coupling is not believed to be operative in J-aggregates as evidenced by the lack of an appreciable Stokes shift in the emission spectrum[2]). Based on the Hamiltonian of Eq.(1), a k- space reduced equation of motion is derived for the N exciton populations by truncating an infinite hierarchy of equations of motion (generated by the Heisenberg equation) for all exciton-phonon operators. The truncation is accomplished by factorizing the expectation value of bi-quadratic exciton-phonon operators into the product of the expectation values of the exciton and phonon parts, eventually leading

to a set of N coupled integro-differential equations for the N exciton populations, which are then solved numerically. The fluorescence intensity is directly proportional to the expectation value of the k=0 exciton population[4], i.e. $I_{fl} \sim \langle B^{\dagger}_{k=0}(t)B_{k=0}(t)\rangle$. The resulting time dependent fluorescence decay is generally multiexponential; we therefore define an effective lifetime, τ_{fl} to be the time at which a fraction (1-1/e) of the total number of photons are emitted. The coherence domain size, N_{eff}, is then simply defined as $(\gamma\tau_{fl})^{-1}$.

Figure 1 shows N_{eff} as a function of N when acoustic phonons are present (Ω_{ac} = 0.01V and F_{ac} = 0.01V) at several different temperatures (solid curves). The curves are a result of our numerical procedure. For small values of N the aggregate radiates superradiantly as N increases (N_{eff} = N) but eventually levels off to a value, N^*,which remains constant as N increases. (We have verified the constancy of N^* out to N = 500). Further note that N^* decreases monotonically as the temperature T is increased. These results are consistent with the aforementioned experimental observations and provide firm support for the coherence domain theory. Also in Figure 1, we show a similar plot for the dispersionless optical phonon case (dashed curves, Ω_{op} = 0.01V and F_{op} = 0.01V). As with the acoustic phonon case, the results are consistent with the coherence domain theory, however, there are pronounced oscillations of N_{eff} as a function of N, which appear to damp out when N is large enough. The n^{th} dip in the oscillations corresponds to a resonance condition between the optical phonon frequency Ω_{op} and the frequency difference between the k=0 and k=n exciton. The resonance condition leads to a more efficient population redistribution away from the initially excited k=0 state, resulting in reduced cooperativity and a smaller N_{eff}.

EXPERIMENT

We have found that the physical size of the J- aggregate of 1,1'-diethyl-2,2'-cyanine

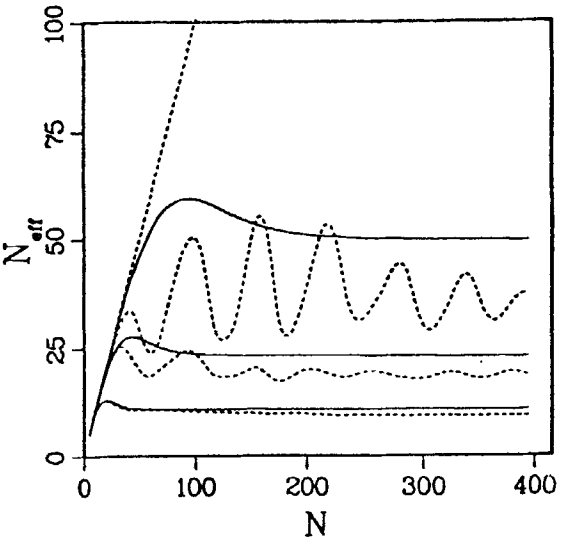

Figure 1 The effective cooperation number, N_{eff}, as a function of aggregate size for acoustic phonons (solid curves) with F_{ac} = 0.01V and Ω_{ac}=0.01V and optical phonons (dashed curves) with the same parameters. Acoustic (optical) curves from top to bottom correspond to $kT/\Omega_{ac(op)}$ = 1 (3.16), 10 (10) and 100 (100). The linear dashed curve is the superradiant limit, i.e., N_{eff} = N.

(PIC) on an AgBr surface can be controlled in a statistical sense by mixing the dye with its 9-aza analog, an ideal diluent dye for PIC aggregates for several reasons. This pair of dyes has been shown to form a solid solution in investigations of mixed single crystals,[10] increasing the probability that the distribution of the dyes in the mixed aggregate will be random. In addition, the electronic transition energies of the two dyes in the mixed J-aggregate are well separated, with the transition of the aza analog occurring approximately 5000 cm^{-1} to the blue.

To demonstrate the control of aggregate physical size, samples were prepared with 1,1'-diethyl-2,2'-cyanine (PIC) paratoluene sulfonate diluted by its 9-aza analog. The mixed J-aggregates were formed on the surface of octahedral AgBr microcrystals of 0.3 mm edgelength by adding methanolic solutions of the dyes to suspensions of the microcrystals in gelatin solution. The suspensions were then coated onto film base and dryed to give the samples used. The total surface coverage of the dyes on the microcrystals was kept constant at approximately 60% of monolayer coverage and the mole fraction of the diluent dye varied from 0 to 0.94. The absorptance spectra obtained for this series of samples are given in Figure 2. Strong evidence for control of aggregate size can be seen in the shift from the familiar 575 nm J-aggregate absorption to a monomer-like 540 nm absorption (corresponding to isolated guest molecules within the azacyanine J-aggregate host) as the concentration of the diluent is increased.

This series of samples will be used to investigate the effect of aggregate physical size on the fluorescence lifetime and quantum yield of PIC J-aggregate. Temperature dependence of these quantities will also be determined. Preliminary room temperature data comparing the fluorescence lifetime of the undiluted J-aggregate and a very dilute, monomer-like sample indicates that the fluorescence lifetime for the aggregate is shortened by a factor of 9.5. If the fluorescence yields for these two samples are the same (an assumption which we are investigating), this shortening yields a value for N_{eff} of 9.5 for the pure PIC aggregate at room temperature.

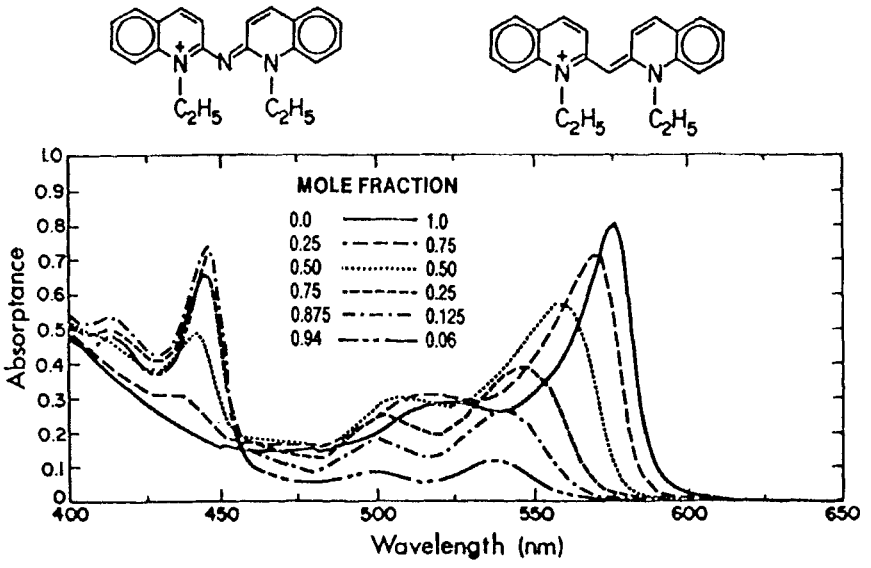

Figure 2 Absorptance spectra for PIC dilution series on AgBr octahedra

RESULTS AND CONCLUSION

In Figure 3, N_{eff} is shown as a function of PIC molefraction, m_J. The continuous solid curve is a numerical result using the probability distribution[11],

$$p(N;m_J) = N m_J^{N-1}(1-m_J)^2 \qquad 0 < m_J < 1 \tag{2}$$

for finding an aggregate of size N on an infinite one dimensional chain containing a molefraction m_J of PICBr and 1-m_J of the inert dye. To calculate the fluorescence signal $I_{fl}(t)$ at molefraction m_J we use:[4]

$$\langle I_{fl}(t)\rangle \propto \sum_{N=1}^{\infty} p(N,m_J)N^2\langle B^{\dagger}_{k=0}(t)B_{k=0}(t)\rangle \tag{3}$$

In Figure 3, time dependent fluorescence signals for N = 1 to 100 were averaged together according to Eq.(2) and Eq.(3) for each value of m_J. Ω_{ac} (= 0.01V) and F_{ac} (= 0.022V) were chosen so that $N^* = 9.5 = N_{eff}$ ($m_J \sim 1$). However, because of a scaling relationship[8], any pair Ω_{ac}, F_{ac} will give the same results as long as the ratio F^2_{ac}/Ω_{ac} is preserved, and $\Omega_{ac} < 0.1$V. In addition, low frequency optical phonons give similar results[8]. The dashed, continuous curve results from using the 240 cm^{-1} optical phonon parameters, used to fit the temperature dependent lifetime data in reference 2 (F_{op} = 0.35V, Ω_{op} = .4V)[12]. Note that $N^* \sim 8.5$ and is in excellent agreement with the value of 9.5 obtained experimentally.

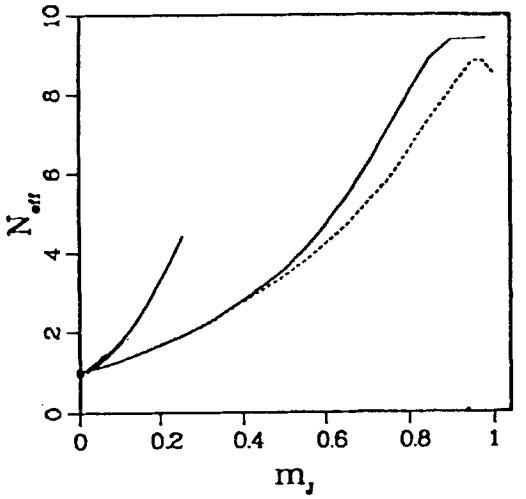

Figure 3 Theoretical predictions for N_{eff} as a function of PIC molefraction m_J at T = 298K. The continuous solid curve is a numerical calculation for a one-dimensional distribution of aggregates with Ω_{ac} = 0.01V and F_{ac} = 0.022V (V=600cm^{-1}); in the dashed curve Ω_{op} = 0.4V and F_{op} = 0.35V. The truncated curve is the result for a two-dimensional aggregate distribution using percolation theory, also with Ω_{ac} = 0.01V and F_{ac} = 0.022V.

We have also calculated the dependence of N_{eff} on m_J using a two-dimensional percolation model. Assuming a square lattice, the distribution function of cluster sizes is:[13]

$$p(N;m_J) = Nm_J^{N-1}D_N(1-m_J) \quad (4)$$

where $D_N(q)$ is the perimeter polynomial, which accounts for the many ways a size N cluster can be realized in two dimensions. The truncated curve in Figure 3 is the result of using the averaging procedure prescribed by Eq.(3) and Eq.(4) using $D_N(q)$ for a square lattice with $N \leq 17$ from reference 13. Because $D_N(q)$ for $N > 17$ is not available, we could safely calculate N_{eff} up to $m_J = 0.25$. In addition, Eq.(4) is only valid when m_J is smaller than the percolation threshold m_J^T, which for a square lattice is $m_J^T = 0.59$. Above the percolation threshold the average cluster size is infinity (for an infinitely large surface, of course), in which case we can safely set $N_{eff} = N^*$.

Figure 3 shows clearly a convergence in the radiative decay rate. The approach to that convergence is a strong function of the m_J dependent aggregate size distribution and the aggregate dimensionality. The system of PIC J-aggregate diluted by its azacyanine analog offers an excellent experimental test of the predictions of convergent behavior given in Fig. 3, since the physical size of the aggregate can be controlled in a known fashion. The percolation model assumes that the site occupation probability is independent of the occupation of neighboring sites, which is a good approximation since the two dye molecules have similar structures. We are now pursuing fluorescence lifetime and relative quantum yield measurements for the PIC aggregate as a function of diluent concentration and temperature. These experiments will yield values for the temperature dependence of the radiative decay rate for aggregates of varying physical size and should give a clear indication of the convergent behavior of N_{eff}.

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