DOI: 10.1002/masy.200551150

Optical Absorption and Photo-Luminescence Spectra of Molecular van der Waals Systems: Frenkel Exciton Resonance Effects

Alexander J. Fleming, Jonathan N. Coleman, Werner J. Blau*

Summary: Applying the principle of conservation of energy, the photo-absorption-luminescence (p-a-l) cycle of resonant Frenkel excitons in aggregates is explained in terms of the p-a-l cycles of isolated molecules. The method employed to measure the Stokes shift of Frenkel Exciton Resonance (FER) systems, derived from our model, is found to differ significantly from that employed currently. Our postulate, that the aggregate v-e transition energy, in the frame of reference of a resonant exciton, decreases as function of the localisation length of the exciton, is demonstrated by the excellent agreement of the model with existing data. This has allowed the determination of the localisation length of resonant excitons from readily available spectra. As the localisation length is a good indicator of the order of a system, this result will be useful in molecular self-assembly (MSA) research. Results from the model suggest that Frenkel exciton resonance is vibrationally modulated, and the collective exciton eigenstate of a resonant Frenkel exciton can couple the v-e manifolds of $2N$ molecules together via the electronic resonance interaction, even in the absence of direct intermolecular vibrational coupling. In essence, we demonstrate that the photo-physics of an exciton that is resonant over many molecules is fundamentally determined by the photo-physics of the isolated molecule just as one would expect.

Keywords: aggregates; axciton; Frenkel; photoluminescence; resonance

Introduction

Optical spectroscopy is a useful tool to investigate molecular aggregation[1,2] and other molecular phenomena. However, its usefulness to date is limited because experimental optical spectra are generally incompatible with the photo-absorption-luminescence (p-a-l) cycle described by the Stokes model for isolated molecules.[3,4] Comparing optical spectra of many similar dye molecules[5] reveals variations that are much better explained by the next step in complexity: the molecular aggregate structure and Frenkel exciton resonance (FER). Taking general examples of molecular optical spectra in solution and solid state, we demonstrate that a conservation of energy model, in the framework of disorder-limited FER, typical of van der Waals aggregates, successfully explains observed trends in molecular optical absorption and photo-luminescence spectra as a function of aggregate morphology order (such as the variation of the vibrational-electronic (v-e) transition energy and the apparently small Stokes shift). FER describes the process whereby one excitation quantum[6,7] is distributed over $2N$ molecules. The ideal conditions for FER are found wherever there exists a collection of identical molecules e.g. solution or solid state samples. It should be noted that in contrast to inorganic crystals, delocalisation does not necessarily involve electron-hole separation. No separation is required for exciton resonance as only the energy of the intra-molecular Frenkel exciton is resonant.[8,9]

Department of Physics, University of Dublin, Trinity College, Dublin 2, Ireland

Theory

By applying the conservation of energy principle, the relationship between the energy losses of an exciton on an isolated molecule, and the energy losses of a resonant exciton on an aggregate, can be determined, regardless of the exact underlying mechanisms involved. We demonstrate that the total energy converted to phonons by a resonant exciton is predetermined by the non-resonant case (including some additional aggregation effects). From this the p-a-l cycle for resonant excitons is constructed, indicating that the current method of measuring E_S is incorrect, in that it significantly underestimates its value. From the model, the observed aggregate v-e transition energy is found to vary as a function of $(2N)^{-1}$. Using published spectra we then calculate $2N$ for various aggregate systems. The good fit of the model to published values of $2N$ and the correlation between predictions of the model and general trends observed indicate the validity of our model.

Take two independent systems: system I where one isolated molecule is in a solvent bath and system A where one aggregate, comprised of $2N$ molecules grouped together (each identical to the molecule in system I), is in a solvent bath. For each system, an idealised photo-luminescence gedankenexperiment is set up where one photon of a given energy is absorbed by the system and the energy of the re-emitted photon is measured. The difference in energy between the absorbed and emitted photons is equal to the total vibrational relaxation (V-R) energy of the molecules in a system, E_S (for this gedankenexperiment molecule-solvent relaxation interactions can be ignored). The absorption of one photon of $\hbar\omega_{00Abs}$ energy by system I promotes an electron from the ϕ_I to $\phi_F{}^*$ molecular electronic state generating one exciton on the isolated molecule (Figure 1b). In the new force-field, the excited molecule then undergoes V-R, releasing excess energy by emitting S_{Abs} phonons of $\hbar\omega_{pAbs}$ energy each during the change of the isolated molecule configuration from the $\phi_F{}^*$ to ϕ_F state. The exciton then decays by changing from the ϕ_F to $\phi_I{}^*$ state by emitting a photon of $\hbar\omega_{00L}$ energy. Again in a new force-field, the molecule emits S_L phonons of $\hbar\omega_{pL}$ energy each during V-R from the ϕ_I^* to ϕ_I state. The Stokes energy balance equation for the p-a-l cycle of an isolated molecule is therefore

$$\underbrace{\hbar\omega_{00AbsI} - \hbar\omega_{00LI}}_{\text{ElectronicEnergy}} = \underbrace{S_{AbsI}\hbar\omega_{pAbsI} + S_{LI}\hbar\omega_{pLI}}_{\text{Vibrational-Electronic Energy}} \quad (1)$$

where the subscripts I represents isolated molecules, Abs refers to absorption, L refers to luminescence, p represents phonons, 0-0 is the phonon transition of an electronic transition and the variable S is the Huang-Rhys (H-R) parameter. The H-R parameter is a measure of the number of phonons involved in the V-R of a molecule.[10,11] With the general assumption that both halves of the p-a-l cycle are symmetrical i.e. $S_I = S_{AbsI} = S_{LI}$, then for system I, $2S_I$ phonons are emitted during V-R (an example of an asymmetrical p-a-l cycle is discussed later). E_S is therefore given by the sum of the v-e relaxation terms for both halves of the p-a-l cycle[12] $E_S = E_{RAbs} + E_{RL} = 2S_I\hbar\omega_{pI}$. For system A on the other hand, the absorption of a photon by the aggregate leads to FER. Resonance will only occur if each of the $2N$ molecules have the same electronic transition energy $\hbar\omega_{00}$. A good review of the physical principles of FER can be found in references.[6–8] The general equations, describing the electronic transition energies of a 1-D resonant one-exciton collective eigenstate, are given by,[6]

$$\text{a)}\,|\Phi_\pm\rangle = \frac{1}{\sqrt{2N}}\sum_{-N}^{+N}|\phi_n\rangle$$

$$\text{b)}\ \hbar\omega_\pm = \left(\frac{1}{2N}\sum_{-N}^{+N}\hbar\omega_{n00I}\right) \pm \beta \quad (2)$$

where $|\Phi_\pm\rangle$ are the symmetric and anti-symmetric exciton eigenstates, $|\phi_n\rangle$ are the basis eigenfunctions of the individual molecules, $\hbar\omega_{\pm}$ are the symmetric and anti-symmetric eigenvalues, $\hbar\omega_{n00}$ is the isolated molecule electronic transition energy of the n^{th} molecule and β is the resonant transfer interaction energy. The one-exciton collective eigenstate in Equation 2a, is the result of a normalised superposition of the individual molecule basis states. In Equation 2b, the eigenvalues for the collective exciton eigenstates are given. The averaging of $\hbar\omega_{n00I}$ leads to a process known as exchange-narrowing[13] that reduces the observed variance in the electronic energy. Variances of the resonance interaction energy term β in Equation 2b and exchange-narrowing of β are not considered here because we are more concerned with V-R. If the aggregate v-e transition energy $\hbar\omega_{pA}$ is different to the isolated molecule v-e transition energy $\hbar\omega_{pI}$, the Stokes energy equation of an aggregate in terms of the experimental observables, ignoring β in Eq. 2b, is given by

$$\begin{aligned}\frac{1}{2N}\sum_{-N}^{+N}\hbar\omega_{00AbsI}-\frac{1}{2N}\sum_{-N}^{+N}\hbar\omega_{00LI}\\ =\sum_{-N}^{+N}S_{AbsA}\hbar\omega_{pAbsA}+\sum_{-N}^{+N}S_{LA}\hbar\omega_{pLA}\end{aligned}\tag{3}$$

where all subscripts have their usual meaning and A represents aggregates. In Equation 2a only the purely electronic energy is normalised as the equation describes a one-exciton state. The lack of a direct intermolecular vibrational coupling in van der Waals systems results in no normalisation of the overall vibrational energy. Therefore, the electronic transition energy is averaged while the v-e relaxation is summed over the contributing molecules (see Figure 1a). The ratio of the aggregate to isolated E_S, R, is included in the

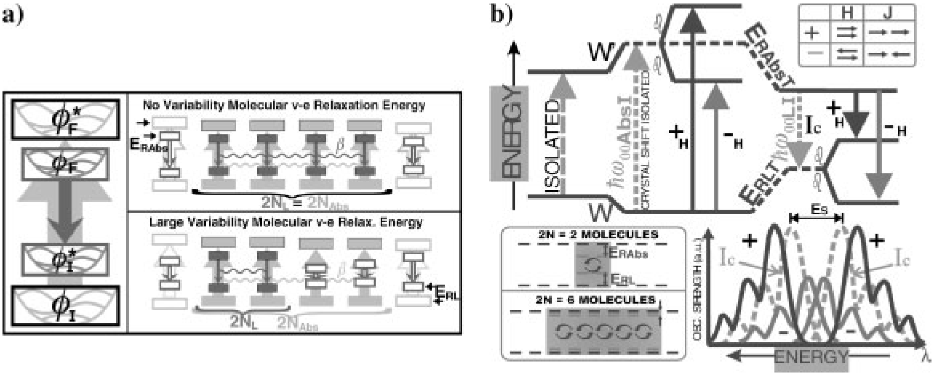


Figure 1.

a) Illustration of how the localisation length 2*N*, for resonant excitons in real systems with fixed (top) and variable (bottom) v-e relaxation energies, depends on how many molecules have the same transition energy. Light grey arrows represent electronic transitions from the ϕ_I to ϕ_F^* states (absorption) and dark grey arrows represent electronic transition from the ϕ_F to ϕ_I^* states (luminescence). Filled arrows represent transitions that are in resonance. Notice how, for the system with variable v-e relaxation $N_L < N_{Abs}$. b) Photo-absorption-luminescence cycle of resonant Frenkel excitons showing how E_S is related to the relaxation of the "crystal shifted" isolated molecule energy levels (I_C). All symbols have their usual meaning. W is the ground state Coulombic interaction or intermolecular ground state binding energy (tends to zero for non-polar molecules), W′ is the excited state-ground state interaction (can be positive or negative). For the electronic transitions in the p-a-l cycle, + is the symmetric and − is the anti-symmetric electronic transition of an H-aggregate (opposite for J-aggregates e.g. $+_H$ transition is re-labelled $-_J$ etc.). An illustration of the non-convoluted optical spectrum of the p-a-l cycle is also given (from transition dipole interactions, the + transition will have most of the oscillator strength). Experimentally, the spectrum is a superposition of the + and − transition (I_C is illustrated but not observed). Often, this superposition, and especially any significant inhomogeneous broadening, will make the v-e peaks un-resolvable. For coincident J absorption and PL, $E_{RAbsT} = E_{RLT} = RS_I\hbar\omega_{pI} = \beta$. The effect of the resonance range 2N on the potential barrier, $2S_A\hbar\omega_{pA}$, between relaxed and un-relaxed molecules that will influence exciton migration is also shown.

expression describing the conservation of the *total vibrational energy*. This is constructed by equating the total V-R energy of Equations 1 and 3, with the usual assumption that the absorption and luminescence processes are symmetric,

$$\begin{aligned} & R2S_I\hbar\omega_{pI} = 2N2S_A\hbar\omega_{pA} \\ & R\tfrac{S_I\hbar\omega_{pI}}{2N} = S_A\hbar\omega_{pA} \end{aligned} \tag{4}$$

This equation describes the inverse scale relationship of the reorganisation energy per molecule for each half of the p-a-l cycle, $S_A\hbar\omega_{pA}$, with respect to the resonance range $2N$ (see Figure 1b). From the expression for the V-R energy per molecule (Equation 4) and using the ratio $k = S_A/S_I$, the *energy per phonon* of system A with respect to system I is

$$\hbar\omega_{pA} = \frac{R}{k}\frac{\hbar\omega_{pI}}{2N} \tag{5}$$

This equation describes the v-e transition energy of the resonant exciton with respect to the v-e transition energy of the isolated molecule for $N \geq 1$ where R/k is the energy partitioning coefficient. If this is the case then Equation 3 becomes:

$$\begin{aligned} &\text{a) } \frac{1}{2N}\sum_{-N}^{+N}\hbar\omega_{00AbsI} - \frac{1}{2N}\sum_{-N}^{+N}\hbar\omega_{00LI} \\ &\quad = \sum_{-N}^{+N} S_{AbsA}\tfrac{R\hbar\omega_{pAbsI}}{2kN} + \sum_{-N}^{+N} S_{LA}\tfrac{R\hbar\omega_{pLI}}{2kN} \\ &\qquad\qquad\qquad\qquad \text{or} \\ &\text{b) } \frac{1}{2N}\sum_{-N}^{+N}\hbar\omega_{00AbsI} - \frac{1}{2N}\sum_{-N}^{+N}\hbar\omega_{00LI} \\ &\quad = R\left(\sum_{-N}^{+N}\tfrac{S_{AbsI}\hbar\omega_{pAbsI}}{2N} + \sum_{-N}^{+N}\tfrac{S_{LI}\hbar\omega_{pLI}}{2N}\right) \end{aligned} \tag{6}$$

Equations 6a and 6b describe the p-a-l cycle of a collective one-dimensional exciton eigenstate localised over $2N$ molecules, in terms of the isolated molecule electronic and v-e transition energies, by taking into account changes to the e-p coupling and other V-R processes via the ratios k and R. By comparing the aggregate p-a-l cycle in Equation 6b with that of the isolated molecule in Equation 1, it is evident that in both cases the total V-R of the exciton is determined in some respect by $S_I\hbar\omega_{pI}$ (to illustrate this, if a resonant exciton could be re-localised onto just one molecule in an aggregate one would expect $2N$-1 molecules to un-relax and 1 molecule to fully relax by an amount equivalent, within a factor R, to the isolated V-R). Therefore from Equation 6, with FER, the individual molecule reorganisation energy $S_A\hbar\omega_{pA}$, given by the normalised v-e relaxation of the isolated molecule, now scales inversely with $2N$, making the experimentally observed E_S invariant with $2N$. An ensemble of aggregates with FER will therefore have a sharp PL, as is observed.

Illustrated in Figure 1b is the p-a-l cycle of a resonant exciton constructed from Equation 6. With charge sharing unfavourable, the electronic transition energies of the collective eigenstates are not permanent energy levels of the system, but momentary levels arising from nearest-neighbour transition dipole interactions during photon absorption and emission. Evident in Figure 1b is the absorption and PL mirror-symmetry of the symmetric and anti-symmetric transitions that often causes aggregate spectra to be mistaken for isolated molecular spectra. Typically, when the absorption symmetric transition is coincident in energy with the PL symmetric transition (anti-symmetric transition for H-aggregates), E_S is incorrectly measured as zero. The lack of a significant solvent relaxation of non-polar aggregated molecules and the mistaken belief that the e-p coupling decreases because the aggregate is a rigid system, akin to inorganic crystals, has fuelled this incorrect idea. For large aggregates, the vast majority of molecules do not lie on the surface, hence the negligible solvent relaxation.[3] From our model and Figure 1b, coincident absorption and PL can only occur when $E_{RabsT} = E_{RLT} = \beta$, where E_{RabsT} and E_{RLT} are the total v-e relaxation summed over 2N for the absorption and luminescence respectively (i.e. $E_S = E_{RabsT} + E_{RLT}$). Therefore,

$$2NS_A\hbar\omega_{pA} = \beta \tag{7}$$

This is often termed J-resonance, however from Figure 1b it is clear that this condition only arises when the crystal shifted isolated molecular electronic states vibrationally relax by an amount equal to β. The condition of J-resonance can be used to calculate $2N$ from Equation 7. For J-resonance $2N = \beta/(S_A\hbar\omega_{pA})$ or using the relationship $S = g^2$, where g is the e-p coupling, $2N = \beta/(g_A{}^2\hbar\omega_{pA})$. This is very similar to a qualitative function[14]f used to describe the v-e properties of resonant excitons $f = \beta/g_A\hbar\omega_{pA}$ (derived from the ratio β/g_A where β is in units of $\hbar\omega_{pA}$). Our equation is quantitative and has similar limits. If β is very small, the molecules in an aggregate are essentially electronically uncoupled, therefore the vibrational properties of the exciton are those of the isolated molecule. If β is very large, compared to $g_A{}^2\hbar\omega_{pA}$, the v-e structure of resonant excitons digresses from that of the isolated molecule. Our model arrives at the same conclusions in a quantitative manner that matches data from the whole spectrum of FER ranges of different molecular van der Waals systems. Therefore a notable result of this model is that for any given β the FER range can assume any value, not only in the case of J-vibrationally assisted resonance (N.B. FER is disorder-limited).

A significant outcome of the model and the p-a-l cycle in Figure 1b is that the method of measuring E_S of an isolated molecule[15] is not correct for aggregates per se. In optical spectra of aggregates, both the symmetric and anti-symmetric transition peaks must be considered and typically both are observable (for polar molecules the permanent dipole-permanent dipole interaction tends to favour one of the transitions). Measuring from the lowest energy absorption peak to the highest energy luminescence peak is incorrect as this ignores the symmetric/anti-symmetric transition of H/J aggregates respectively (see Figure 1b). It creates the false impression that E_S has reduced practically to zero upon aggregation and incorrectly suggests that E_S of the symmetric and anti-symmetric transitions differ by an amount 2β. There is no reason why a dimer should have zero V-R, when as a monomer it significantly relaxes with an appreciable E_S. Our model indicates that experimentally, E_S should be taken as the difference between the average of the symmetric and anti-symmetric absorption transitions and the average energy of the symmetric and anti-symmetric emissive transitions. In this framework, transitions of both symmetries have the same total reorganisation energy (and hence E_S) determined by the underlying relaxation of the isolated molecule energy levels (Figure 1b). Experimentally $\hbar\omega_{pA} = \hbar\omega_{pI}$ is generally not observed (except, as we will show, for systems with $2N \sim 2$ molecules). For large FER range systems, the v-e peaks seem to disappear. From the gedankenexperiment, either S or $\hbar\omega_{pA}$ must decrease with respect to the isolated molecule if resonance is to satisfy the conservation of energy principle. A reduction in S would lead to a decrease of the V-R per molecule, although it does imply that aggregation makes the system more rigid. With FER this is unlikely to be the case. FER is a dipole-dipole interaction that can occur between molecules that are physically not in contact with each other. Instead, it appears that S increases slightly from nearest-neighbour interactions.[6] Therefore to conserve energy $\hbar\omega_{pA} < \hbar\omega_{pI}$. The conclusion that although the observed $\hbar\omega_{pA}$ varies inversely with $2N$, the resonant exciton total V-R, E_S, is fundamentally determined by $S_I\hbar\omega_{pI}$.

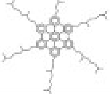
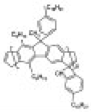
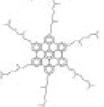
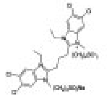
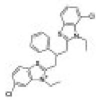
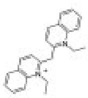
Comparisons to Experiment

To demonstrate changes in $\hbar\omega_{pA}$ as a function of N, the absorption/photo-luminescence-excitation (Abs/PLE) and photoluminescence (PL) spectra of three materials, methyl-substituted ladder-type poly-(para-phenyl) (mLPPP),[16] alkyl-substituted hexa-*peri*-hexabenzocoronene[17,18] (HBC-C8,2) and a Pseudo-Iso-Cyanine dye analogue[19,21] (PICa) were analysed. In Table 1, values of the experimental observables obtained from the spectra and an additional two molecules PIC[22] (Pseudo-Iso-Cyanine) and TBDC[23,24] (another cyanine based dye) are given. According to our model, when aggregation

Table 1.

Name and structure of molecules studied are given. Values obtained from spectra in and the literature are in normal type. For clarity, estimated values are given in italics, and values calculated or corrected are indicated. FER localisation lengths, 2N, calculated from the model (see text) using values in the table, are as expected larger for more ordered aggregates. This trend is confirmed by the decrease in FWHM. The fact that $\beta/S_A\hbar\omega_{pI} \sim 1$ for all molecules suggests that FER is vibrationally modulated. Values of R/k are measured or extrapolated from J-resonant conditions. $FWHM^e$ is the measured full-width-half-maximum of an individual v-e peak, whereas $FWHM^o$ is taken from the overall spectral envelope. As described in the text, for large FER range systems FWHM measurements are unreliable.

Aggregate Order

	$C_{8,2}$ Isolated	mLPPP	$C_{8,2}$ MSA	TDBC	PICa	PIC
						
S_I	0.5	*0.45 – 0.5*	-	0.5	*0.25*	0.25
$\hbar\omega_{pI}$ [eV]	0.16	*0.15*	-	0.17^	*0.19°*	0.19°
S_A	-	0.45 - 0.5	1^{Abs}, 1^{PL}	*0.5*	0.39*(calc)*	~ 0.5
$\hbar\omega_{pA}$ [eV]	-	0.15	0.16^{Abs}, 0.04^{PL}	0.01	*0.01*	< 0.01
E_S=$2N2S\hbar\omega_p$ [eV]	0.16*(calc)*	0.3*(calc)*	0.64*(calc)*	0.22*(calc)*	0.225*(calc)*	-
E_S (Meas.) [eV]	0.36	0.27	0.64	0.22	0.225	-
R/k	-	2	2	1.34	1.52	-
β [eV]	-	0.08	0.135^{Abs} 0.045^{PL}	0.114	0.145	-
$\beta/S_A\hbar\omega_{pI}$	-	1	0.84^{Abs} 1.12^{PL}	1.34	1.52	-
$FWHM^e$ [eV]	~ 0.2^{PL}	~ 0.1	~0.15^{Abs},~0.05^{PL}	*0.05*	*0.05*	*0.01*
$FWHM^o$[eV]	~ 0.3^{PL}	~ 0.25	~0.3^{Abs},~0.1^{PL}	~0.05	~ 0.05	~ 0.01
2*N* (Calc.)	1	~ 2	~2^{Abs}, ~8^{PL}	~ 22	~ 29	~ 40*(Corr.)*
2*N* (Lit.)	-	-	-	15-18	~ *50*	50
Reference	[17]	[16]	[17]	[23,24]	[19-21]	[22]
Comment	HBC-C8,2 Monomer species in solution at 10^{-13} M	Disordered polymer aggregates in solid state	HBC-C8,2 Molecular nanowires in solution at 10^{-6} M that undergo an ordering process in the photo-excited state	J-resonant, ordered mol. aggregate in solution at 10^{-4} M	J-resonant, very ordered mol. aggregate in solid state	J-resonant, very ordered mol. agg. at 1.5K in an ethylene/Glycol glass

begins, system order will increase in many cases. This initial ordering, increments the FER range 2*N* from 1 to 2. The change, from monomer to dimer, is exemplified by exchange-narrowing of absorption and PL peaks, and splitting of isolated absorption and PL peaks into two peaks separated by 2β. From our model, changes to the v-e transition energy can be very small if $R/k \sim 2$; even though an increase of E_S is observed. For example, for mLPPP, $R/k = 2$, therefore from Equation 5, $\hbar\omega_{pA} = \hbar\omega_{pI}$ for $2N = 2$. For $2N > 2$, the following changes are expected: further exchange-narrowing of absorption and PL peaks, a decrease of $\hbar\omega_{pA}$ and no further change to E_S. Therefore, the larger N (for $N \geq 1$), the narrower and closer the v-e peaks become without any change to the aggregate E_S.

The PLE and PL spectra of HBC-C8,2 isolated molecules obtained at 10^{-13} M in toluene are typical of molecular monomer species (including those of TBDC and PIC). These are characterised by inhomogeneously broadened peaks, with $S_I \sim 0.5$, a large $\hbar\omega_{pL}$ (compared to higher concentration aggregated species) and hence an appreciable E_S. As the concentration of HBC-C8,2 molecules is increased from 10^{-13} M to 10^{-6} M, FER leads to splitting of isolated absorption and PL peaks into two peaks separated by 2β, and considerable exchange-narrowing of all v-e peaks. The e-p coupling also increases to $S_A \sim 1$.

As predicted by the model in Equation 5, and particularly noticeable in the PL, is the decrease of $\hbar\omega_{pA}$ with respect to $\hbar\omega_{pI}$ (the same applies to TBDC and PIC). These typical characteristics, together with the mirror-symmetry of the absorption and PL spectra as predicted in Figure 1b, indicate that the species observed are aggregates.

In Table 1, values of the ratio $\beta/S_A\hbar\omega_{pI}$ are given for each molecule. The fact that for all the materials this ratio is $\sim$1 suggests that FER is modulated by the vibrational frequency $\hbar\omega_{pI}$ and e-p coupling of the molecule, in all systems. This is likely to be a characteristic of van der Waals systems in general, perhaps due to the lack of strong intermolecular vibrational modes and weak charge sharing not enabling a faster exciton transfer and hence limiting β. This makes sense when one considers that the molecular electronic energy levels, and thus $\hbar\omega_{00nI}$, are modulated by the nuclear motion via the e-p coupling. From the spectra in references,[21–24] PICa and TBDC are J-resonant resonant systems. J-resonance occurs when $E_{\mathrm{RAbsT}} = 2N\text{-}NS_{\mathrm{A}}\hbar\omega_{\mathrm{pA}} = \beta = RS_{\mathrm{A}}\hbar\omega_{\mathrm{pI}}/k$. Therefore, the resonant exciton is undergoing the usual v-e relaxation associated with an exciton on an isolated molecule; with the exception that g_I increases to g_A and other relaxation processes may make $R > 1$. This demonstrates how the optical properties of an aggregate are fundamentally determined by the optical properties of the isolated molecule. Values of R/k measured (and calculated where possible from J-resonance conditions) are given in Table 1. Values of R/k are much greater than 1 for non J-resonant systems such as mLPPP and HBC-C8,2. This is probably related to secondary effects of FER coupling other intra-molecular v-e relaxation modes to the resonant exciton or to a difference between the sharp boundary FER distribution range used in this model and a more realistic smooth distribution. For polar molecules especially, R/k will be larger than unity due to solvent relaxation interactions contributing to R and not k.

The FER range, $2N$, calculated for each molecule from either measured values of E_S ($E_{SA} = 2N2S_A\hbar\omega_{pA}$) or measured β values using Equation 7, are compared to values of $2N$ published in the literature. PICa, PIC and TBDC are small polar molecules that form ordered aggregates that are well known for their large FER ranges. Polymers, on the other hand, although known to form small aggregates in most solutions have tended to be disregarded for FER, with some exceptions.[25,26] Our model indicates that mLPPP, with optical spectra typical of polymers is in fact forming large aggregates with FER ranges, limited by disorder, to approximately an effective dimer, $2N = 2$. This is a plausible FER range for polymer systems, which usually have many degrees of conformational freedom. If, in general, polymers form highly disordered aggregates with FER ranges $2N \sim 2$, then the frequently observed variation of the relative peak intensities of the fine structure in optical spectra,[16,25] of different samples of the same molecule (without a large variation of $\hbar\omega_{pA}$), can be explained. It is plausible that morphological differences, between samples, could give rise to variations of the relative oscillator strengths of the symmetric and anti-symmetric transitions of aggregates (and their respective v-e progressions). Even if the variance of $\hbar\omega_{00I}$ is small, the FER range can be disorder-limited by variations in β, deriving from the angular dependence of β with the alignment of the interacting molecular electronic transition dipoles. Typically, a variance in the FWHM of peaks in the absorption or PL is observed experimentally. The general trend in the PL is that the lower the peak energy, the broader the FWHM (the opposite for the absorption). The superposition of the v-e peak progressions of the two electronic transitions, implied by this model, will give rise to observed trend (see Figure 1b). This is frequently observed experimentally. HBC-C8,2 is a planar aromatic molecule which forms 1-D molecular nanowires in solution.[17] HBC-C8,2 molecular aggregates therefore have a larger $2N$ than mLPPP, but differ from the others in that they have a calculated localisation length of 2 molecules and a delocalisation length (here, the FER range during PL) of 8 molecules (see Table 1, $\hbar\omega_{pAbsA} > \hbar\omega_{pL}$). This suggests an ordering process of the HBC-C8,2 molecules during the p-a-l cycle. Finally values of $2N$ in Table 1, calculated from the model for TBDC, PICa and PIC (all studied extensively for their FER), are very close to accepted values published in the literature.[27] Therefore, overall, the progression of the optical spectra with respect to $2N$ calculated from the model, compares very favourably with published values of $2N$ and the expected general trends.

Values calculated for $2N$ can be compared with a variable that is independent from this model, such as the change in FWHM resulting from exchange-narrowing (for identical aggregate FER systems the smaller the FWHM the larger $2N$). In Table 1, the trend is that the electronic variance of a single v-e peak (FWHM^{e}) decreases with decreasing $\hbar\omega_{pA}$. This confirms the assumption that $\hbar\omega_{pA}$ scales inversely with $2N$. However, care must be taken when estimating the FWHM, because an ensemble of aggregates can have variances in the aggregate morphology[22] that will lead to additional broadening (this is generally more pronounced in disordered systems such polymers). With an increase of $2N > 2$ the v-e transition energy is observed to decrease more rapidly than the FWHM of each v-e peak. For instance with PIC analogue aggregates this leads to overlapping v-e peaks, making the v-e features less prominent in the spectra. If this is the case, then for systems such as PIC analogue aggregates, the most dominant factor in the overall FWHM of the main absorption or PL peak is roughly $\hbar\omega_{pA}$ and not the variance in electronic transition energy. This would explain why localisation lengths calculated using FWHMs generally give huge overestimates, even though in principle it should work very well. For PIC aggregates, N_{loc} ($2N$ in this letter) is hugely overestimated[28,29] as 1600 molecules compared to its accepted[30,31] value of 50 molecules (from more reliable spontaneous emission rates). The former value is determined from exchange-narrowing: in the weak disorder regime $N_{\text{loc}^*} \sim (\sigma_I/\sigma_A)^2$ where σ is the observed FWHM. If the value $N_{\text{loc}^*} = 1600$ was calculated from FWHM, of which the main contributor was $\hbar\omega_{pA}$ and not the variance in electronic energy, then by comparing this expression to our postulate $\hbar\omega_{pA} \sim (\hbar\omega_{pI}/2N)$, the true value of the localisation length can be extracted $2N \sim (\hbar\omega_{pI}/\hbar\omega_{pA}) \sim (\sigma_I/\sigma_A) \sim \sqrt{N_{\text{loc}^*}}$. Therefore, the corrected localisation length for PIC, using our model, is $2N \sim 40$ molecules; which is very close to the accepted value of 50. This confirms the assumption that overall the PL peaks of PIC and HBC-C8,2 MSA are similar, in that they are both are composed of several closely energetically spaced v-e peaks. This agrees with our conservation of energy argument that the observed aggregate v-e transition energy must decrease as a function of $2N$ for van der Waals systems.

Physically speaking, $\hbar\omega_{pA} < \hbar\omega_{pI}$ may arise during the process of exciton resonance due to a preference of the resonant exciton to couple to lower energy intramolecular vibrational modes. From Equation 4, the total reorganisation energy of the exciton is partitioned over $2N$ molecules. As illustrated in the gedankenexperiment, there are two choices to conserve energy, reduce S or reduce $\hbar\omega_{p}$. In this model, Equation 5 suggests that a resonant exciton can couple to a continuum of vibrational energies $\hbar\omega_{pA}$. However, in reality a molecule will have discreet intramolecular vibrational modes as observed in IR spectra. An exciton therefore has two choices to conserve energy; it can either emit high-energy phonons with very little probability ($\hbar\omega_{pA} \sim \hbar\omega_{pI}$ and $S_A \ll S_I$), or, it can emit low energy phonons with a high probability ($\hbar\omega_{pA} \ll \hbar\omega_{pI}$ and $S_A > S_I$). The latter case is more favourable entropically speaking, and it correlates with our observations that the observed aggregate v-e transition energy decreases as a function of

$(2N)^{-1}$. This agrees with the observed enhancement of low energy vibrational modes of FER systems compared to non-FER systems.[32] In this framework, the discreetness of the intra-molecular vibrational modes available to the resonant exciton may explain the variance in *R*/*k* observed.

Since the FER range is disorder limited, the smaller the resonant exciton v-e transition energy the more ordered a system is. Therefore, in terms of the ordered alignment of molecules in an aggregate the following trend is observed: PIC > TBDC > HBC-C8,2 > mLPPP. This demonstrates that the differences in the v-e structure of optical spectra of these materials arise from differences in the ordering of their systems. Our model also indicates why exciton diffusion by hopping, typical of van der Waals aggregates, is easier in systems where the exciton is resonant over many molecules e.g. in molecular crystals. From Equation 5, the larger *N*, the smaller the V-R of each individual molecule. This decreases the potential energy barrier that exists between a molecule outside the resonance range and its neighbour molecule that is part of the collective exciton eigenstate (as shown in Figure 1b). Thermally assisted hopping, which allows the collective exciton eigenstate to diffuse along an aggregate, is more probable as the potential energy barrier height becomes smaller. Another commonly observed property of aggregates is the reduced PL quantum yield (PLQY) compared to the isolated molecule. In this model, the distributed nature of the collective exciton v-e relaxation, as exemplified by the sum over $2N$ of the individual molecule reorganisation energy in Equation 6, determines that a resonant exciton probes many more molecular vibrational manifolds than an exciton of an isolated molecule. The increased number of non-radiative pathways available to the collective exciton eigenstate in an aggregate reduces the PLQY.[33] This quenching could be a result of dephasing of vibrations in a collective eigenstate, or the larger availability of pre-existing non-radiative pathways originating from the individual molecule.

Conclusions

In this paper, we have shown that although the conservation of energy principle cannot reveal the detailed mechanisms involved with FER, it can clarify how the V-R energy of a resonant exciton is distributed over $2N$ molecules. This approach successfully describes the v-e properties of resonant excitons, and now allows the determination of localisation lengths of resonant Frenkel excitons solely from absorption and PL spectra of aggregates. For J-resonant systems, this has eliminated the need to carry out challenging measurements of FWHMs and spontaneous emission rates from isolated molecules. In fact, solutions of non-polar isolated molecules can be very difficult to prepare, and as our model suggests, many spectra published of non-polar planar aromatic compounds are of aggregates and not isolated molecules. The reason might be that usually samples are prepared for absorption measurements and not PLE or PL, so the lowest concentration explored is $\sim 10^{-7}$ M, which is in general too high.[14] An outcome of the model is that the p-a-l cycle for resonant excitons can now be understood in terms of the v-e relaxation of isolated molecules (the building blocks of the aggregate), thus allowing E_{SA} to be correctly measured. Finally, the model also indicates that FER is perhaps rate-limited or modulated by the e-p coupling and vibrational frequency of the isolated molecule. Interpreting all optical spectra of polymers, small molecules, polyaromatic hydrocarbons and bio-molecular assemblies in terms of an effective resonance range will also enable a more complete understanding of the photophysics of organic materials. In light of the above, other measurements derived from optical spectra may have to be reviewed. For instance, measurements of exciton binding energies calculated from the band gap peak of the absorption and photocurrent spectra may, if mistaken for the isolated molecule, give an overestimate. The correct peak to measure from is in fact the crystal shifted isolated molecule transition energy.

[1] I. Baraldi, M. Caselli, F. Momicchioli, G. Ponterini, D. Vanossi, *Chem. Phys.* **2002**, *275*, 149.

[2] X. Chen, Q. B. Xue, K. Z. Yang, Q. Z. Zhang, *Thin Solid Films* **1996**, *286*, 232.

[3] For example, zero E_S is often reported for polymers eventhough the calculated E_S, from the Huang-Rhys parameter and vibrational-electronic (v-e) transition energy, is clearly non-zero.

[4] M. Fox, *Optical Properties of Solids*, Oxford Press **2001**.

[5] U. Brackmann, *Lambdachrome Laser Dyes*, Lambdaphysik **1994**.

[6] M. Pope and C. E. Swenberg, *Electronic Processes in Organic Crystals and Polymers*, Oxford Science Publications **1999**.

[7] D. P. Craig, S. H. Walmsley, *Excitons in Molecular Crystals*, Benjamin **1968**.

[8] A. J. Stone, *The Theory of Intermolecular Forces*, Oxford **1996**.

[9] It is worth noting that excitons can also be in resonance over large distances e.g. Föster energy transfer.

[10] N. Verdal, J. T. Godbout, T. L. Perkins, G. P. Bartholomew, G. C. Bazan, A. M. Kelley, *Chem. Phys. Lett.* **2000**, *320*, 95.

[11] E. J. W. List, J. Partee, J. Shinar, U. Scherf, K. Müllen, E. Zojer, K. Petrisch, G. Leising, W. Graupner, *Phys. Rev. B* **2000**, *61*, 10807.

[12] G. C. Schatz, M. A. Ratner, *Quantum Mechanics in Chemistry*, Prentice Hall **1993**.

[13] E. W. Knapp, *Chem. Phys.* **1984**, *85*, 73.

[14] M. Hoffmann, Z. G. Soos, *Phys. Rev. B*, **2002**, *66*, 24305.

[15] The correct way to measure E_S for an isolated molecule is from the 0-0 vibronic peak of the absorption peak to the 0-0 vibronic peak of the luminescence.

[16] D. Hertel, H. Bässler, U. Scherf, H. H. Hörhold, *J. Chem. Phys.* **1999**, *110*, 9214.

[17] A. J. Fleming, J. N. Coleman, A. B. Dalton, A. Fechtenkötter, M. D. Watson, K. Müllen, H. J. Byrne, W. J. Blau, *J. Phys. Chem. B*, **2003**, *107*, 37.

[18] A. Fechtenköter, N. Tchebotareva, M. Watson, K. Müellen, *Tetrahedron* **2001**, *57*, 3769.

[19] D. G. Lidzey, J. Wenus, D. M. Whittaker, G. Itskos, P. N. Stavrinou, D. D. C. Bradley, R. Murray, *J. of Lumin.* **2004**, *110*, 347.

[20] D. G. Lidzey, D. D. C. Bradley, M. S. Skolnick, S. Walker, *Synth. Met.* **2001**, *124*, 37.

[21] E. O. Potma, D. A. Wiersma, *J. Chem. Phys.* **1998**, *108*, 4894.

[22] Proc. Enrico Fermi Sch. Phys., *Organic Nanostructures: Science and Applications*, IOS Press, Course CXLIX, p. 150.

[23] H. Fidder, Ph.D. Thesis, University of Groningen **1993**.

[24] H. Fidder, D. A. Wiersma, *J. Phys. Chem.* **1993**, *97*, 11603.

[25] M. Knupfer, J. Fink, E. Zojer, G. Leising, U. Scherf, K. Müllen, *Phys. Rev. B* **1998**, *57*, 8.

[26] K. Kemnitz, N. Tamai, I. Yamakazi, N. Nakashima, K. Yoshihara, *J. Phys. Chem.* **1986**, *90*, 5094.

[27] Calculated by comparing spontaneous emission rates of solutions of aggregated and isolated molecules.

[28] S. de Boer, D. A. Wiersma, *Chem. Phys. Lett.* **1990**, *165*, 45.

[29] S. De Boer, K. Vink, D. A. Wiersma, *Chem. Phys. Lett.* **1987**, *137*, 99.

[30] M. Schreiber, Y. Toyozawa, *J. Phys. Soc. Jpn.* **1982**, *51*, 1528.

[31] H. Fidder, J. Knoester, D. A. Wiersma, *J. Chem. Phys.* **1991**, *95*, 7880.

[32] (19) H. Kano, T. Kobayashi, *J. Lumin.* **2002**, *100*, 269.

[33] A. Yu. Nollau, M. Hoffman, K. Floreck, T. Fritz, K. Leo, *J. Appl. Phys.* **2000**, *87*, 7802.