I. INTRODUCTION

In a series of papers, the “coherent exciton scattering” (CES) approximation was applied with some success to calculate the absorption and circular dichroic spectra of a variety of aggregates of dye molecules. According to their structure, such aggregates exhibit continuous J- or H-band absorption (see e.g. Refs.1–4) and the CES approximation, working directly with the continuous vibronic absorption profile, is able to reproduce both types of bandshape in detail. The CES approximation includes intra-molecular vibrations explicitly and coupling to other modes only implicitly by working with the continuously-broadened experimental spectra. Over the years there have been many other approaches to the inclusion of vibronic effects on aggregate spectra, see for example Refs.7–15.

The CES approximation is a mean-field type of approximation in which the exact monomer Green function, involving both electronic and vibrational degrees of freedom, is replaced by its average in the vibrational ground state. This allows the aggregate bandshape to be expressed in terms of the monomer absorption bandshape; the only fit parameter being the inter-monomer electronic interaction $V$. If $G(E) = (E - H_M - V + i\delta)^{-1}$ is the aggregate Green operator at energy $E$ and $g(E) = (E - H_M + i\delta)^{-1}$ that of the non-interacting monomers, one has the identity

$$G = g + gVg$$

where $H_M$ is the sum of monomer Hamiltonians and $V$ is the electronic interaction operator between monomers. The CES approximation corresponds to replacing the exact monomer Green operator $g$ by $\langle g \rangle$, where $\langle \ldots \rangle$ denotes the aggregate vibrational ground state average. Then

$$\langle G \rangle = \langle g \rangle + \langle gVg \rangle$$

becomes

$$\langle G \rangle = \langle g \rangle + \langle g \rangle V \langle g \rangle$$

when $V$ is assumed to be independent of vibrations. Eq. (3) has symbolically the solution

$$\langle G \rangle = \frac{1}{1 - \langle g \rangle V} \langle g \rangle.$$  (4)

However, the physical content of the CES approximation is best seen by iterating Eq. (3) in a Born series, i.e.

$$\langle G \rangle = \langle g \rangle + \langle g \rangle V \langle g \rangle + \langle g \rangle V \langle g \rangle V \langle g \rangle + \ldots$$  (5)

If the matrix element $G_{nm} = \langle \pi_n | G | \pi_m \rangle$, where $| \pi_n \rangle$ is a state in which monomer $n$ is excited electronically with all other monomers in their ground electronic state, is taken, then Eq. (5) becomes

$$\langle G_{nm} \rangle = \langle g_n \rangle \delta_{nm} + \langle g_n \rangle V_{nm} \langle g_m \rangle + \sum_{n'} \langle g_n \rangle V_{nm'} \langle g_{n'} \rangle V_{n'm} \langle g_m \rangle + \ldots$$  (6)

This shows that whenever electronic excitation is handed on from one monomer to another, the monomer which desexcites goes back into its ground vibrational state. This is the essential ingredient in the CES approximation.

The CES approximation has been used successfully to describe the detailed lineshape of various measured aggregate spectra1–4 in the intermediate and strong coupling regime. Following Simpson and Peterson16 the strong and weak coupling regimes are defined by the conditions $V > \Delta$ or $V < \Delta$ respectively, where $\Delta$ is the width of the monomer absorption spectrum. One speaks about intermediate coupling when $V \approx \Delta$.

In some ways, the CES approximation performs better than it ought to, in that in its original formulation17,18 it involves only the (zero temperature) aggregate ground state, represented as a simple product of monomer vibrational ground states. However in the cases to which it has been applied, measurements were made at room temperature in a variety of solvents which also interact with the dye molecules. The origin of the success of CES in this more general context may lie in the recent demonstration12 that its essential structure (Eq. (1)) is
retained when the average $\langle \ldots \rangle$ is extended to include finite temperature and averages over site solvent interactions. This question of temperature and solvent effects on J-aggregate spectra has been studied extensively both experimentally\textsuperscript{20} and theoretically\textsuperscript{21}. In the theoretical work a purely electronic Hamiltonian was used for the aggregate but coupling to phonons of the surroundings were considered to show that temperature effects can be included successfully in this model. Here, since the CES method includes such effects implicitly, coupling to phonons of the surrounding will not be considered explicitly. Rather, we will include the intra-monomer vibrations and compare the results of the CES approximation with those of a direct diagonalisation of the aggregate vibronic Hamiltonian.

Although the original derivation\textsuperscript{17,18} suggests that the CES-approximation is applicable to strong coupling, in Ref.\textsuperscript{22} it was claimed that it should only be valid for weak coupling. Our subsequent comparison with experimental results\textsuperscript{17,18} indicates validity for both strong and intermediate coupling. To further throw light on these questions, in this work we generalise this notation to define an aggregate vibronic state in which monomer $n$ is in the excited electronic state and all others in the ground electronic state with vibrational quantum number $\alpha_i$ for monomer $i$. This generalised basis is written

$$|\pi_n, \nu_n \rangle = |\pi_n \rangle |\alpha_1 \rangle \cdots |\beta_n \rangle \cdots |\alpha_N \rangle$$

i.e. $\nu_n$ denotes the sequence of vibrational quantum numbers $(\alpha_1 \ldots \beta_n \ldots \alpha_N)$. Note that this simple product basis is a BO basis for the aggregate as a whole. However, the inter-monomer interaction mixes these basis states to give no BO separation of the total aggregate eigenfunctions. In this chosen basis the matrix elements of the aggregate Hamiltonian are

$$\langle \pi_n, \nu_n | H_A | \pi_m, \nu_m \rangle = \epsilon^{\nu_n} \delta_{nm} \delta_{\nu_n, \nu_m} + V_{nm} \langle \beta_n | \tilde{\alpha}_n \rangle \langle \alpha_m | \tilde{\beta}_m \rangle \prod_{i=1}^{N} \delta_{\alpha_i, \tilde{\alpha}_i}$$

with

$$\epsilon^{\nu_n} \equiv \epsilon^{\alpha_1} + \cdots + \epsilon^{\beta_n} + \cdots + \epsilon^{\alpha_N}. \quad (11)$$

Here $\epsilon^{\beta_n}$ is the energy of monomer $n$ in the vibrational state $|\beta_n \rangle$ of the excited electronic state and $\epsilon^{\alpha_i}$ that of monomer $i$ in the vibrational state $|\alpha_i \rangle$ of the electronic ground state. The quantum numbers $\tilde{\alpha}_n$ and $\tilde{\beta}_m$ are elements of the sequence $\nu_m$. The Franck-Condon (FC) factor $\langle \alpha_n | \beta_n \rangle$ denotes the overlap of vibrational state $\beta_n$ of the excited electronic state with vibrational state $\alpha_n$ of the ground electronic state.

The eigenstates and eigenenergies of the aggregate are defined by

$$H_A |\Psi_l \rangle = E_l |\Psi_l \rangle. \quad (12)$$

We designate by $|\pi, 0 \rangle$ the absolute vibronic aggregate ground state i.e.

$$|\pi, 0 \rangle = \prod_{i=1}^{N} |\chi_i \rangle |\alpha_i = 0 \rangle. \quad (13)$$

Then the aggregate absorption cross-section energy dependence is given by the absorption strength

$$A(E_l) = |\langle \pi, 0 | \vec{E} \cdot \vec{D}_A |\Psi_l \rangle|^2 \quad (14)$$

where $\vec{E}$ is the light polarisation vector and the aggregate dipole operator $\vec{D}_A$ is the sum of monomer operators.
The dipole transition matrix element appearing in Eq. (15) can be simplified to give
\[
\langle n, \nu | \tilde{D}_n | \pi_m, \nu_m \rangle = \alpha_n = 0 \langle \chi_n | \tilde{D}_n | \phi_n \rangle \delta_{nm} \delta_{\nu_m, (0 \ldots \beta_n \ldots 0)}.
\] (16)

Consistent with our assumption that \( V \) is independent of vibrations, we make the Condon approximation that \( \tilde{D}_n \) is independent of vibrations so that the dipole transition matrix element of monomer \( n \) is
\[
\langle \alpha_n | \chi_n | \tilde{D}_n | \phi_n \rangle \delta_{nm} \delta_{\nu_m, (0 \ldots \beta_n \ldots 0)}.
\] (17)

The absorption strength Eq. (14) then reduces to
\[
\mathcal{A}(E) = \left| \sum_{n, \beta_n} \tilde{\delta}^* \tilde{D}_n | \alpha_n = 0 \rangle | \pi_n, (0 \ldots \beta_n \ldots 0) \rangle | \Psi_i \rangle \right|^2.
\] (18)

The aggregate (stick) spectrum is then given by
\[
\mathcal{A}(E) = \sum_j \mathcal{A}(E_j) \delta(E - E_j).
\] (19)

The dimension of the basis Eq. (14) and therefore the number of terms in the summation Eq. (19) depends on the number of vibrational states taken into account. If all monomers have \( n_v \) vibrational states of the ground electronic state and \( n_e \) vibrational states of the excited electronic state, the dimension is given by
\[
\dim = N \cdot n_e \cdot n_v^{N-1}.
\] (20)

Therefore the number of absorption sticks is already large (about 10000) for an aggregate of ten monomers with two vibrational states in each electronic state. Note that the dimension depends crucially on the number \( n_v \) of vibrational states of the electronic ground state.

In the special case that we assume that all \( N \) monomers are identical and arranged in a circle, the dimension of the matrix to be diagonalised can be reduced by a factor \( N \) using a transition to a delocalised excitonic basis rather than the localised basis Eq. (14). For simplicity we specialise \( V \) to nearest-neighbour coupling. How the delocalised states are constructed is illustrated first by considering the simple case of a cyclic trimer \( (N = 3) \). The excitonic basis consists of states \( | k, \nu_1 \rangle \), with \( k = 2 \pi / 3, 4 \pi / 3, 2 \pi \), which are simply a superposition
\[
| k, \nu_1 \rangle = \frac{1}{N} \left[ e^{ik} | \pi_1, (\beta_1, \alpha_2, \alpha_3) \rangle + e^{2ik} | \pi_2, (\alpha_3, \beta_1, \alpha_2) \rangle + e^{3ik} | \pi_3, (\alpha_2, \alpha_3, \beta_1) \rangle \right]
\] (21)

of the three possible shifts of the \( | \pi_1, \nu_1 \rangle \) state along the cyclic aggregate. In general, for a cyclic \( N \)-mer the excitonic basis \( | k, \nu_1 \rangle \) is
\[
| k, \nu_1 \rangle = \frac{1}{\sqrt{N}} \sum_{n=1}^N e^{ikn} S_{n-1} | \pi_1, \nu_1 \rangle,
\] (22)

with \( k = 2 \pi j / N, j = 1, \ldots, N \) and where \( S_m \) is a shift operator shifting both the electronic and vibrational excitation on the aggregate by \( m \) monomers to a higher monomer index \( i' = i + m \), i.e.
\[
S_m | \pi_1 + m, (\alpha_{N+1-m} \ldots \beta_1 \ldots \alpha_{N-m}) \rangle.
\] (23)

The action of \( S_m \) is also illustrated in Fig. 1.

Denoting by \( W \equiv V_{n,n+1} \) the nearest-neighbour interaction between the monomers and defining
\[
C = \begin{cases} W & \text{for } N = 2 \text{ (dimer)} \\ 2W & \text{for } N > 2 \end{cases}
\] (24)

the matrix elements of \( H_A \) in the exciton basis Eq. (22) are
\[
| k, \nu_1 \rangle H_A | j, \tilde{\nu}_1 \rangle = \left[ e^{\nu_1 \delta_{\nu,\tilde{\nu}}} + e^{-ik C / 2} \langle \beta_1 | \tilde{\alpha}_2 \rangle \langle \alpha_N | \tilde{\beta}_1 \rangle \prod_{i=2}^{N-1} \delta_{\alpha_i,\tilde{\alpha}_{i+1}} \right. \\
\left. + e^{ik C / 2} \langle \beta_1 | \tilde{\alpha}_N \rangle \langle \alpha_2 | \tilde{\beta}_1 \rangle \prod_{i=2}^{N-1} \delta_{\alpha_{i+1},\tilde{\alpha}_i} \right] \delta_{kj}.
\] (25)

Note that \( \nu_1 = (\beta_1, \alpha_2, \ldots, \alpha_N) \). From Eq. (25) one sees that \( H_A \) is diagonal in the exciton \( k \) basis i.e. the eigenvalue problem
\[
H_A | \Psi_{k\lambda} \rangle = E_{k\lambda} | \Psi_{k\lambda} \rangle
\] (26)

can be solved separately for each \( k = 2 \pi / N, \ldots, 2 \pi \) with \( \lambda = 1, \ldots, n_v \cdot n_e \cdot n_v^{N-1} \) \( (n_v \) and \( n_e \) are the numbers of vibrational states taken into account in the ground and excited electronic state of each monomer, see Eq. (20)). The absorption strength (see Eq. (18) from the aggregate ground state \( | \pi, 0 \rangle \) to the eigenstate \( | \Psi_{k\lambda} \rangle \) is given

\[
\mathcal{A}(E) = \left| \sum_{n, \beta_n} \tilde{\delta}^* \tilde{D}_n | \alpha_n = 0 \rangle | \pi_n, (0 \ldots \beta_n \ldots 0) \rangle | \Psi_i \rangle \right|^2.
\] (18)
by

$$\mathcal{A}(E_{k\lambda}) = \frac{1}{N} N |\mathcal{E}|^2 \sum_{n=1}^{N} e^{iQ_n} d_n|^2 \times \sum_{\beta_1=0}^{\alpha_1=0} \langle\alpha_1 = 0|\beta_1\rangle \langle k, (\beta_1, 0 \ldots 0)|\Psi_{k\lambda}\rangle^2.$$  (27)

The first factor on the r.h.s. is the effective electronic dipole moment of the aggregate in exciton state $k$ and depends upon the aggregate geometry. In the simplest case where all monomer dipoles are parallel, this factor reduces to $N |\mathcal{E} \cdot \vec{d}|^2 \delta_{k,2\pi}$. In this case, to calculate the absorption spectrum, only the block $k = 2\pi$ of the Hamiltonian matrix (25) needs to be diagonalised and the stick spectrum is given by (see Eq. (19))

$$\mathcal{A}(E) = \sum_{\lambda} \mathcal{A}(E_{2\pi,\lambda}) \delta(E - E_{2\pi,\lambda})$$  (28)

with

$$\mathcal{A}(E_{2\pi,\lambda}) = N |\mathcal{E} \cdot \vec{d}|^2 \sum_{\beta_1=0}^{\alpha_1=0} \langle\alpha_1 = 0|\beta_1\rangle \langle k, (\beta_1, 0 \ldots 0)|\Psi_{2\pi,\lambda}\rangle^2.$$  (29)

Calculations of the aggregate spectrum from Eq. (29) using the eigenfunctions and eigenenergies from direct diagonalisation of the aggregate Hamiltonian will be presented and referred to as DD calculations.

In the following discussion the absorption strength is given in arbitrary units. All energies, including $\sigma$ and $\Delta$ are given in units of $\hbar \omega$.

**B. The monomer spectrum**

All that is required to specify the vibrational shape of the monomer spectrum and carry through the calculation of the aggregate spectrum are the monomer Franck-Condon factors between vibrational states of upper and lower electronic states (for the definition see the discussion after Eq. (11)). Hence the calculations can be made for arbitrary ground and excited state BO potential surfaces. However, to conform with a large body of work, particularly using the second quantisation formalism, we will consider here that upper and lower potentials are both harmonic of the same curvature, with a shift $\mathcal{Q}$ of the minimum of the upper surface w.r.t. the minimum of the lower. Here $Q$ is the vibrational coordinate giving rise to a single dominant vibrational progression in the monomer spectrum. Despite its simplicity this model gives a surprisingly good fit to the spectra of a large variety of organic molecules. It has the advantage that the FC factors can be calculated analytically and the monomer spectrum obtained in a simple analytic form.

Denoting the harmonic vibration frequency by $\omega$ and defining the Huang-Rhys factor by

$$X = \frac{\omega}{2\hbar Q}$$  (30)

the absorption strength of the monomer from the ground state (where $\alpha = 0$), which is of relevance to the CES approximation, is

$$\mathcal{M}(E) = \frac{1}{\beta!} X^{\beta} e^{-X} \delta(E - \beta \hbar \omega).$$  (31)

The width (standard deviation) of the monomer spectrum in this case of a Poissonian distribution is given by

$$\Delta = \sqrt{X \hbar \omega}.$$  (32)

Examples of monomer spectra for various values of the parameter $\Delta$ are shown in Fig. 2. As is well-known, for small $X$, i.e. small $\Delta$, the Poisson distribution gives only one dominant peak (Fig. 2(a)) but becomes progressively more Gaussian as $X$ increases and the progression broadens.

**C. The CES approximation**

It is clear from the discussion of the introduction that the CES approximation is equivalent to performing the diagonalisation of section II A in a basis in which in the ground electronic state only the ground vibrational state is included. Then transfer of excitation to or from a monomer must proceed through this state as can be seen from the expansion (6) of the CES approximation. However the effect of the CES approximation on the absorption lineshape is better illustrated by the form (4). The imaginary part of the monomer function $\langle g(E) \rangle$ is proportional to the monomer absorption strength Eq. (31). Once $\text{Im}(g) \equiv g_i$ is determined, the real part can be calculated from the Kramers-Kronig dispersion relation. Then the aggregate absorption strength can be calculated from $\text{Im}(G)$, where $\langle G \rangle$ is given by expression (4).
Nevertheless (poles) H band spectra. At the aggregate absorption energies the function $1/g_n$ lines (representing different coupling strength strength) poles (and hence there is absorption) where the coupling sign and magnitude of $g_n$. Ref. $\langle g_n \rangle ≡ g_n$. As discussed in detail in Eq. (25) is $n_g \cdot n_e^{N-1}$ and computer time for diagonalisation therefore escalates, particularly as $n_g$ increases. However all DD spectra have been checked for convergence and the cases presented have a minimum 95% overlap with the spectra with $n_g$ and/or $n_e$ increased by unity. For all spectra shown, we have used $n_e = 9$. In Fig. 4 our convergence criterion is illustrated for an typical example.

There are three parameters deciding the shape of the aggregate spectrum, namely, the coupling strength $C$, the monomer spectral width $\Delta$ and the size $N$ of the aggregate. In the comparisons presented, representative points in this 3-dimensional space are chosen. To some extent parameters $C$ and $\Delta$ can be combined into the Simpson-Peterson (SP) parameter $|C|/\Delta$, where strong coupling has $|C|/\Delta > 1$ and weak coupling $|C|/\Delta < 1$. Although this is a very rough measure, it will emerge that, for $N \gg 2$, the CES approximation is good for both weak and strong coupling and only may have problems in the intermediate positive regime. Similarly, it has been shown that the CES approximation is not good for dimers ($N = 2$), since electronic excitation is trapped indefinitely on just two monomers (see Ref. 22). This con-

| Energy [ℏω] | Absorption [arb. u.] |
|-------------|---------------------|
| 0           | 0                   |
| 1           | 0                   |
| 2           | 0                   |
| 3           | 0                   |
| 4           | 0                   |

FIG. 4: Illustration of the convergence criterion for the aggregate absorption. a) $n_g = 1$ (solid) and $n_g = 2$ (dashed). The overlap is 68%. b) $n_g = 2$ (solid) and $n_g = 3$ (dashed). The overlap is 81%. c) $n_g = 3$ (solid) and $n_g = 4$ (dashed). The overlap is 90%. b) $n_g = 4$ (solid) and $n_g = 5$ (dashed). The overlap is 95%. Used parameters are $N = 4$, $C = 1.2$, $\Delta = 0.8$, $n_e = 9$.

III. NUMERICAL RESULTS

All calculations, both direct diagonalisation (DD) and CES calculations yield stick spectra. The CES results in fact were obtained from the DD calculation by restricting to the ground vibrational state only (i.e. $n_g = 1$), but it was checked that the results agreed with those obtained from Eq. (23). To facilitate comparison of CES and DD results the calculated stick spectra have been convoluted with a narrow Gaussian of standard deviation $\sigma = 0.1 \pm$. As can be seen in Fig. 2 this width is small enough to clearly resolve the individual peaks of the monomer absorption spectrum.

The dimension of the Hamiltonian matrix (see Eq. (25)) is $n_e \cdot n_g^{N-1}$ and computer time for diagonalisation therefore escalates, particularly as $n_g$ increases. However all DD spectra have been checked for convergence and the cases presented have a minimum 95% overlap with the spectra with $n_g$ and/or $n_e$ increased by unity. For all spectra shown, we have used $n_e = 9$. In Fig. 4 our convergence criterion is illustrated for an typical example.

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FIG. 3: Monomer function $1/g_n$ as a function of energy $E$. The width of the monomer spectrum is $\Delta = 0.8$. The absorption strength at each pole is indicated by the size of the circle. The dashed horizontal lines are for energies $C = -1.5$ and $C = 1.2$.

$$A(E) = \sum_l \left( \frac{\partial g_n^{-1}}{\partial E} \right)^{-1}_{E=E_l} \delta(E - E_l).$$

This shows that the absorption strength at a particular pole is inversely proportional to the slope of $g_n^{-1}$ at that point. Hence only the poles where $g_n^{-1}$ has gradient in the order of unity absorb appreciably and these points are denoted by circles in Fig. 3. One also notes that in the CES approximation the number of poles is limited by the number $n_e$ of vibrational states included on the upper potential irrespective of the number $N$ of monomers considered.
clusion is reinforced by the results presented here, except in the case of weak coupling.

In considering these comparisons, two sum rules satisfied by both DD and CES spectra should be kept in mind. One is that the total absorption strength of any spectrum is equal to that of the monomer (first sum rule SR1) and secondly that the mean energy of the spectrum (first moment) is shifted from that of the monomer by exactly the coupling energy C (second sum rule SR2).

Since the CES result is independent of N, it is logical to present comparisons of DD spectra with CES for fixed values of C and Δ and see at which N the CES approximation becomes adequate.

Although we have performed calculations for monomer spectra with X, defined in Eq. (30), ranging from X = 0 to X = 2, in this work we will focus on the case X = 0.64, i.e. Δ = 0.8ℏω. This value of X is representative of those found for the dominant vibrational progression of many organic dyes.

1) Strong negative coupling

This case is the classic case of the formation of a J band. Representative spectra are shown in Fig. 5 (for SP ≈ 6). The values of ng indicated on the figures are those used in the calculation of the DD spectra. The results presented are for C = −5 but we have checked that there is no change in the shape of the spectra for C < −5. The monomer spectrum for this case is given in Fig. 2(c). As N increases, essentially only one strong peak on the low-energy side of the monomer band appears, whose mean energy is shifted by C from the monomer mean energy. In Fig. 5(d) (N = 8) one sees that the CES approximation is in good agreement with the DD result. As a result of the sum rules, the small peak near E = −3.5 in the DD spectrum causes its J band to be slightly less intense and shifted to slightly larger negative energy than the CES J band peak. On the dispersion curve of Fig. 3 one sees the origin of the J band as due to the single pole at negative energy split off from the monomer band. This pole carries all the oscillator strength. For the other poles the g_r−1 curve is almost vertical, giving vanishing absorption according to Eq. (33).

2) Intermediate negative coupling

Here we choose C = −1.5 so that SP ≈ 2, all other parameters being as in Fig. 5. From Fig. 6 one notes that now the CES approximation has small subsidiary peaks. As can be seen from Fig. 3 these are due to additional poles in the monomer region acquiring some oscillator strength. Nevertheless the CES spectrum is dominated by the isolated-pole J-band peak. Although the peaks in the region of monomer absorption are different in the DD calculation, these contributions diminish with increasing N such that for N = 8 there is again very good agreement between CES and DD results.

3) Weak negative and weak positive coupling

Here C = −0.2, SP = 0.25 (Fig. 7) and C = +0.3, SP ≈ 0.38 (Fig. 8), all other parameters being taken as in Fig. 5.

In the case of weak coupling the DD spectrum does not change with N for the case Δ = 0.8 and so only the dimer case N = 2 is shown in Fig. 7 and Fig. 8. Here there is excellent agreement, both in position and magnitude between DD and CES results. This is perhaps remarkable when one remembers that the DD results represent a convolution over up to about 10000 individual eigenvalues, whereas the CES spectrum arises from only the four main contributing poles for C = −0.2 and for C = +0.3, respectively.

To summarise, we have shown that, for aggregates of length N ≥ 6, the CES results, i.e. including only the ground vibrational state in the electronic ground state, agree well with DD calculations where several vibrational states are included, for all negative coupling strength and for weak positive coupling. For weak negative or positive coupling the CES method gives good results even for the dimer N = 2.

The case of strong positive coupling is not shown, since if there were a strong shift to higher energies the absorption would overlap higher electronic bands and our model would break down.

There remains the most interesting case of interme-
4) Intermediate positive coupling

Note first that from Fig. 8 one sees that for intermediate positive coupling, the aggregate poles in the CES approximation lie in the region of monomer absorption and their strength and location then is very sensitive to the coupling strength \( C \). In the following we consider the case \( C = 1.2 \) (i.e. a SP parameter of 1.5). In Fig. 8 the CES result for this case is illustrated (intersection of upper dashed horizontal line). In Fig. 9 a comparison of CES and DD spectra is shown.

One notes no good agreement of CES and DD results in this case, except to say that the dominant absorption is in the same spectral region for both methods. Indeed in this case the DD results themselves vary significantly with the \( N \) value and no convergence with \( N \) is seen, in contrast to the case of intermediate negative coupling shown in Fig. 6.

One must remember that the curves of Fig. 8 are calculated, in all cases, first as stick spectra and then convoluted with a Gaussian whose width is chosen arbitrarily as \( \sigma = 0.1 \). This width is considerably less than that typical of room–temperature solvent spectra. Hence in Fig. 8 the same data as in Fig. 9 is shown convoluted with a Gaussian of \( \sigma = 0.3 \) width. Then one sees that, for \( N \geq 4 \), there is a much better, although still not exact agreement between CES and DD results. Hence, even when averaged over a broad energy region, the CES method would appear not to perform well for the H-
band case of intermediate positive coupling. However, in Ref. we showed that the CES method gives excellent agreement, even in some fine details, with measured H-band spectra. Important is that in Ref. the measured monomer spectrum, rather than a calculated Poissonian stick spectrum, was used as input to the CES method. As we show now, it appears that this is crucial in order to obtain agreement with measured aggregate spectra.

a) The measured monomer spectrum of Pinacyanol from Ref. and is shown in Fig. (a) (dotted line), is fitted to a stick Poissonian distribution with each peak broadened by the same Gaussian. This fitted spectrum is also shown in Fig. (a) (solid line). Taking $X$ and $\omega$ from the fitted monomer stick spectrum, the stick spectrum of the aggregate is calculated using the DD method. Then each peak is convoluted with the same Gaussian as used in the monomer spectrum. The coupling strength $C$ has been optimised to obtain a best fit and the overall calculated spectrum shifted by exactly the shift $S = 480\text{cm}^{-1}$ used in Ref. for the dye concentration considered. The DD result for $N = 5$ and $n_g = 5$ is shown in Fig. (b) and is in reasonable agreement with experiment, except for a large discrepancy in the peak around 16,500cm$^{-1}$.

b) The fitted continuous monomer spectrum of Fig. (a) is used as input in the CES calculation of the aggregate spectrum, again with $C$ optimised and with $S = 480\text{cm}^{-1}$. Now, Fig. (c), there is reasonable agreement in the peak position and respective heights but the peaks appear too narrow. This probably arises from the too-low absorption of the monomer fit in the region around 19,000 cm$^{-1}$ (see Fig. (a)), leading to a too-low absorption in the same region of the aggregate spectrum (as explained already, the local aggregate absorption depends on the monomer absorption in the same locality).

c) From Ref., the measured monomer spectrum is used as input to the CES calculation of the aggregate spectrum. The result is shown in Fig. (d), where one notes excellent agreement with the measured aggregate spectrum.

IV. CONCLUSION

In its original form the CES approximation is equivalent to the assumption that each monomer possesses only a ground vibrational state in the electronic ground state. Hence, in the aggregate only this state is involved when electronic excitation is transferred be-
tween monomers. Here the validity of this approximation has been tested by comparing CES spectra with those obtained from direct diagonalisation (DD) of the aggregate vibronic Hamiltonian with a sufficient number of vibrational states in the electronic ground state to ensure convergence. For negative values of the inter-monomer coupling energy, leading to a shift of the aggregate absorption to lower energies, good agreement of the CES spectra with DD spectra has been obtained for all negative coupling strengths, so long as the aggregate size \( N \) exceeds 4 or 5 monomers. This success is probably due to the fact that for negative coupling, even intermediate values, a single dominant J-band peak splits off from the monomer region and carries most of the oscillator strength. As shown in Fig. 3, this mechanism of J-band formation is well-described by the CES approximation.

In the weak coupling regime, both negative and positive, the CES result agrees excellently with DD results since there is no strong mixing of monomer vibronic transitions. In fact for weak coupling CES and DD results agree even for the dimer \( N = 2 \). The success of CES in weak coupling can be understood as follows. For weak coupling one can truncate the Born series of the exact equation (2) to include the interaction \( V \) only in lowest order, i.e.

\[
\langle G \rangle = \langle g \rangle + \langle gVg \rangle + \cdots \tag{34}
\]

Then one can show that, without any further approximation, the second term of the r.h.s. can be written

\[
\langle gVg \rangle = \langle g \rangle V\langle g \rangle. \tag{35}
\]

Thus to lowest order in \( V \) the exact equation (34) is identical to the CES result Eq. 3.

Only for intermediate coupling, where the aggregate H-band absorption is shifted into the region of strong monomer absorption, do CES and DD results not agree, except qualitatively under low resolution. This raises the question as to why the CES method applied previously \( ^2 \) produces very good agreement with measured H-band spectra. The answer has been shown to be that the procedure of calculating aggregate spectra using stick spectra with only one vibrational mode pro monomer taken into account and then fitting to a measured continuous spectrum by convoluting with Gaussians, is not a good strategy. A good reproduction of aggregate H-band spectra is only obtained in the CES method when the experimental monomer spectrum is used. Presumably this is because the DD model includes only one vibrational mode per monomer and does not contain any influence of dissipation from the environment; the eigenvalues are discrete. When continuous experimental monomer spectra are used, such effects are included implicitly and the only assumption of the CES method in its generalised form \( ^2 \) is that such dissipative effects act in the same way on both monomer and aggregate spectra.

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