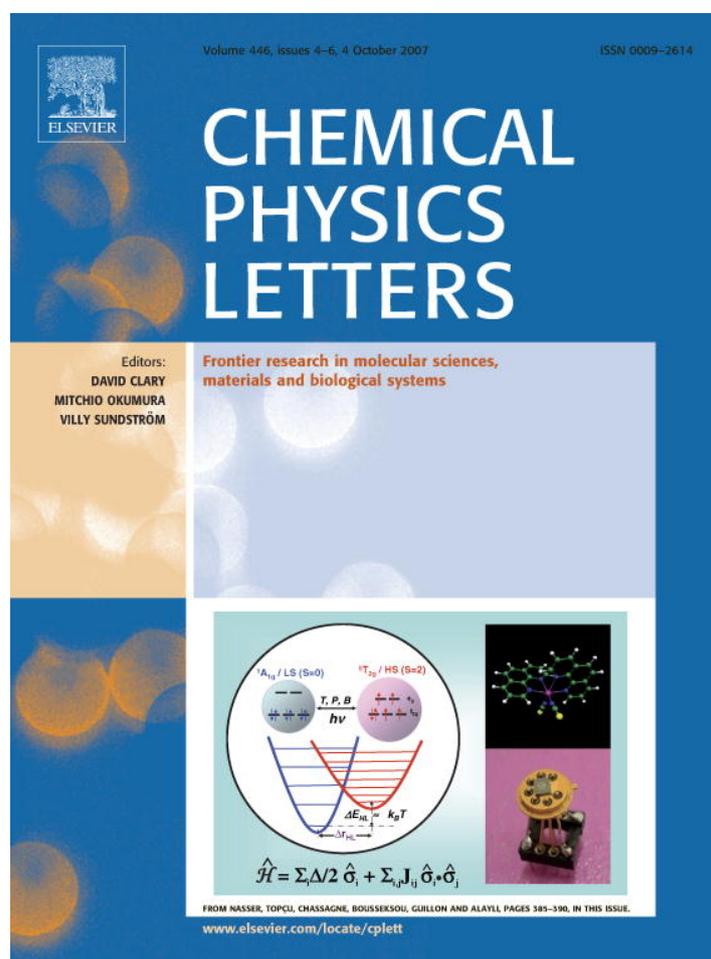


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The shape of the J-band of pseudoisocyanine

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Abstract

We show that, within the coherent exciton scattering (CES) approximation, both the measured exponential band-tail and the detailed shape of the J-band region of the absorption spectrum of pseudoisocyanine aggregates can be reproduced with high accuracy, using only a single free parameter. Our numerical studies confirm analytical results that the J-band width depends crucially on the monomer absorption strength in the energy region where the J-band peak occurs.

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Upon aggregation many organic dyes show a remarkable change in the absorption spectrum. Whereas the spectrum of non-interacting monomers is very broad and shows a vibrational progression (see Fig. 1), the absorption spectrum of the aggregated dyes shows a very narrow red-shifted absorption peak where no vibrational structure is visible. This peak was called the J-band or Scheibe-peak after Jelley [1] and Scheibe [2,3] who independently discovered this phenomenon in 1936 when they investigated the dye pseudoisocyanine (PIC). Other aggregates exhibiting a J-band are commonly referred to as J-aggregates [4].

Such excitonic aggregates have been investigated intensely over the last 70 years, not only because of the striking change in absorption, reflecting the coherent excitation of many monomers, but also in connection with many technical applications, e.g. as a sensitising agent in photography [5] or to measure membrane potentials [6]. They are also promising candidates for the construction of artificial light harvesting units [7,8].

Although besides PIC there exist many dyes that aggregate and exhibit a J-band, PIC still is probably the one most studied. In recent years cryo-TEM measurements have revealed that the PIC aggregates form rod-like structures with a length of up to several 100 nm and with a

diameter of the order of some nm [10,11]. It was shown that the light absorbed by the J-band is polarised parallel to the rods [12,4]. In addition there is a broad blue-shifted absorption band, commonly called the H-band, which is polarised perpendicularly to the rod long-axis. However, in spite of all the studies performed there remain a lot of open questions, e.g. the precise arrangement and spacing of the PIC-monomers in the aggregate is still not determined, although there is evidence [10,11,13,14] that cylindrical/helical structures are formed.

Scheibe attributed the J-band to a ‘communal’ electronic state of the aggregate and in 1938 Franck and Teller [15] interpreted it in terms of the exciton theory of Frenkel [16]. In this theory, although the monomers in the aggregate are weakly bound in the electronic ground state, upon electronic excitation they interact via transition dipole–dipole forces. This interaction leads to the formation of exciton states where the excitation is delocalised over several monomers. Despite this correct interpretation of the origin of the J-band itself, no detailed explanation of the extreme vibrational narrowing of the J band was advanced. Qualitatively, this was explained in 1957 by Simpson and Peterson [17] who identified strong and weak electronic coupling according to the ratio of the inter-monomer electronic coupling strength, which we call C to the vibrational width σ of the monomer absorption band. Strong coupling corresponds to C/σ much greater than unity and weak

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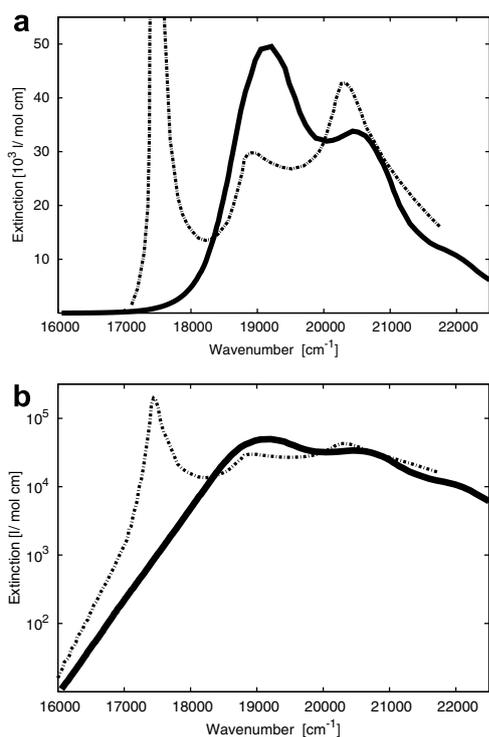


Fig. 1. Measured absorption spectra of monomeric (solid line) and aggregated (dashed line) PIC from Ref. [9]: (a) plotted on a linear scale and (b) plotted on a semi-logarithmic scale.

coupling to the ratio much less than unity. The J-band appears in the strong coupling limit.

Since then, there have been several theoretical approaches put forward to explain the detailed line-shape of the continuous J-band [18–25]. Historically the first approach [26] was the coherent exciton scattering (CES) approximation [27,28] which allows one to treat intramolecular vibrations and various kinds of disorder in an approximate way. The CES approximation is a theory in which one works directly with the continuous vibronic spectra of both monomer and aggregate. The basic idea of the CES approximation is to use the absorption spectrum of the non-interacting monomers to calculate the absorption spectrum of the aggregate, with the electronic coupling energy C between the monomers as a free parameter. Following Simpson and Peterson, the narrowing of the J-band is attributed [27] to the fact that, as the coupling strength C increases, an individual monomer spends less time (of the order of \hbar/C) on the upper potential curve before the vibrational wavepacket is transferred to the next monomer in a resonant Condon vertical transition. Hence there is no time for clear vibrational structure to develop in the excited electronic state and a narrow J-band results. In weak coupling, the typical vibrational period (of the order of \hbar/Δ) on the upper potential curve is much less than the electronic excitation transfer time and broad vibrational structure can be seen i.e. there is no narrow J-band. Later [29], the narrowing was called exchange or motional narrowing, although attributed to an averaging over varia-

tions in the monomer transition energies, rather than arising from the absence of intra-molecular vibration in the excitonic state as in the CES theory. In a modified form the CES transform was used by Knapp et al. [23] to calculate the spectral shape of both the J-band and the blue-shifted H-band of PIC. These authors assumed a Gaussian form for the monomer absorption bands. As we will see later, this assumption, although a good overall fit to the main monomer absorption spectrum, does not reproduce all spectral features satisfactorily. Nevertheless, this was the first attempt to compare directly measured and theoretical aggregate spectra.

More recently [30,31,13], we have shown that one obtains very good agreement between the aggregate spectrum calculated within the CES approximation and measured spectra of PIC, not only for the narrow red-shifted J-band but also the broad, blue-shifted H-band. To obtain this agreement it was necessary to use the measured monomer spectrum as input but then with only a single free parameter, the coupling energy C , for each band. In Ref. [32] it was shown that, for strong coupling, where C is larger than the monomer bandwidth, the line-shape (and in particular the width) of the J-band depends crucially on the precise shape of the absorption spectrum of the monomers in the low-energy wing of the monomer absorption, where the J-band is located. Explicit demonstration of this is the main aim of this Letter. Already in Refs. [31,32], within the CES theory, we have shown analytically that a Lorentzian form of the monomer spectrum leads to the same Lorentzian form of the aggregate spectrum, with the same width, irrespective of the coupling strength C . That this CES result is correct is supported by the results of numerical diagonalization of the J-aggregate Hamiltonian with energies distributed according to a Lorentzian [32]. For a Gaussian monomer lineshape, the CES analytical prediction [28,32] is a J-band which narrows as $C^2 \exp(-C^2/2\sigma^2)$ where σ is the width of the monomer spectrum. A monomer spectrum exhibiting the typical Urbach [33] exponential decay, with decay constant k , gives an aggregate spectrum whose width also narrows exponentially as $C^2 \exp(-k|C|)$ with increasing $|C|$. Furthermore, one can show that, ultimately, far in the wings of the spectrum, the aggregate spectrum will assume exactly the form of the monomer spectrum.

The calculation of the aggregate absorption spectrum in CES approximation is done in the following way: denoting by $g(E)$ the (energy-dependent) Green operator of the non-interacting monomers, the imaginary part of g is related to the monomer absorption spectrum \mathcal{A}_{Mon} by

$$\mathcal{A}_{\text{Mon}}(\omega) \propto -\text{Im}\langle g(E) \rangle \quad (1)$$

where the brackets $\langle \dots \rangle$ denote an integration over the initial vibrational state and various statistical averages [32] and $E = E_0 + \hbar\omega$ where E_0 is the monomer ground state energy and ω the photon frequency.

In the following we assume a cylindrical/helical arrangement of the monomers in the aggregate. Although the

assumption of a cylindrical geometry is not necessary (see the general expression derived in Ref. [32]), this geometry is suggested by the results of cryo-TEM measurements [10,11]. Also, using a cylindrical geometry, a very good agreement between theoretical and experimental circular and linear dichroism spectra was obtained [13]. Then the aggregate absorption spectrum $\mathcal{A}_{\text{Agg}}^{\parallel}$ for light polarised parallel to the long cylinder axis in CES approximation is given by

$$\mathcal{A}_{\text{Agg}}^{\parallel}(\omega) \propto -\text{Im} \frac{\langle g(E) \rangle}{1 - C_{\parallel} \langle g(E) \rangle} \quad (2)$$

where C_{\parallel} is the constant geometry-dependent coupling energy between the monomers, which is given to good approximation by the dipole–dipole interaction between one monomer and all others [30]. As shown in Ref. [13], for light polarised perpendicular to the cylinder axis, which is absorbed in the H-band region, one finds the same dependence as given in Eq. (2) but with an energy C_{\perp} which differs in general from C_{\parallel} . Since in this work we are interested in the J-band (and not in the H-band) we will only discuss the contribution $\mathcal{A}_{\text{Agg}}^{\parallel}$ which we assign to the J-band.

Since the detailed spacing and transition dipole strength of the monomers in the cylindrical aggregate is unknown we use C_{\parallel} in Eq. (2) as a fit parameter. Note that for a given value of the energy shift C_{\parallel} the line-shape of the aggregate absorption spectrum is completely determined over the whole spectral region. The real part of $\langle g \rangle$ which is needed in Eq. (2) can be calculated from the imaginary part via a Kramers–Kronig transformation.

Our previous comparisons of measured spectra to CES predictions [30–32,13] were made over a broad spectral region where it is not easy to see the extent of the precise agreement between theory and experiment around the narrow J-band. Here we will compare directly with higher resolution measurements [9] specifically emphasising the band-tail and the J-band regions.

In the case of PIC the monomer and aggregate spectra have been measured with high-resolution by Kopainsky et al. [9] and are shown in Fig. 1 on both a linear and a semi-logarithmic plot. The monomer and aggregate spectra on the low-energy side have been measured to energies much lower than the energy of the J-band. An exponential behaviour which can be seen in Fig. 1b is evident in both spectra and the slopes appear to be converging in agreement with the prediction of the analytic CES approximation quoted above.

Some comments are in order regarding the experimental results. The linear plot of the aggregate spectrum, concentrating on just the J-band region, has been measured with a high-resolution of 7 cm^{-1} and is taken from the original Letter of Kopainsky et al. [9]. However, the semi-logarithmic plot in that Letter does not appear to be accurately drawn in the J-band region. Therefore we use the more accurate semi-logarithmic plot given in Ref. [23] and attributed to the measurements of Kopainsky et al. There is also

a slight discrepancy in absolute normalisation between the accurate linear data and the semi-logarithmic plot. However, when we bring the latter onto the same scale as the former, there is perfect agreement in the J-band shape which is of primary interest here. The aggregate spectrum calculated from the monomer spectrum of Fig. 1 in CES approximation using a single fit parameter $C_{\parallel} = 1930 \text{ cm}^{-1}$ is shown in Fig. 2a on a semi-logarithmic scale. There is good agreement over four orders of magnitude of the absorption strength, except above 17550 cm^{-1} . In particular the low-energy exponential tail is well-reproduced, which was not the case in the comparison of Knapp et al. [23]. As will be shown below, this is almost certainly due to the assumption in that paper of a Gaussian tail for the monomer spectrum. In Fig. 2b the region around the J-band (17200 cm^{-1} to 17600 cm^{-1}) is magnified and CES theory compared to the high-resolution data of Kopainsky et al. plotted on a linear scale which emphasises the accurate shape of the J-band. Here, there is also excellent agree-

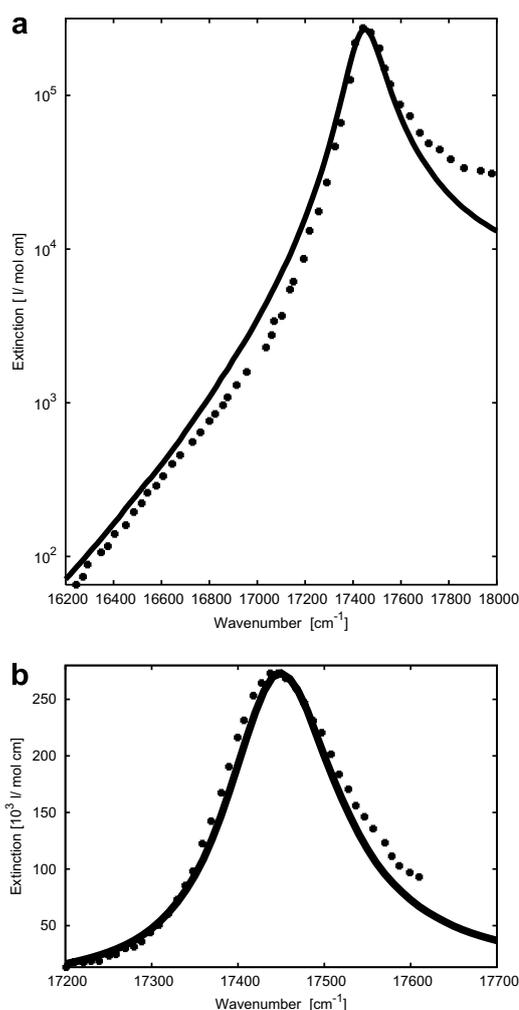


Fig. 2. (a) Semi-logarithmic plot of the J-band. Dots are the measurement (taken from Ref. [23]). Solid line: calculated J-band with $C_{\parallel} = 1930 \text{ cm}^{-1}$. (b) High-resolution plot of the J-band. Dots are the measurement (taken from Ref. [9]). Solid line: calculated J-band with $C_{\parallel} = 1930 \text{ cm}^{-1}$. Note the difference in the wavenumber range compared to (a).

ment. Only in the region above 17550 cm^{-1} does there begin to be a discrepancy between theory and experiment. However, this is due to the onset of H-band absorption (the measurements are with unpolarised light), which is not taken into account here.

To emphasise further that it is the monomer absorption in the J-band region that decides the shape of the J-band

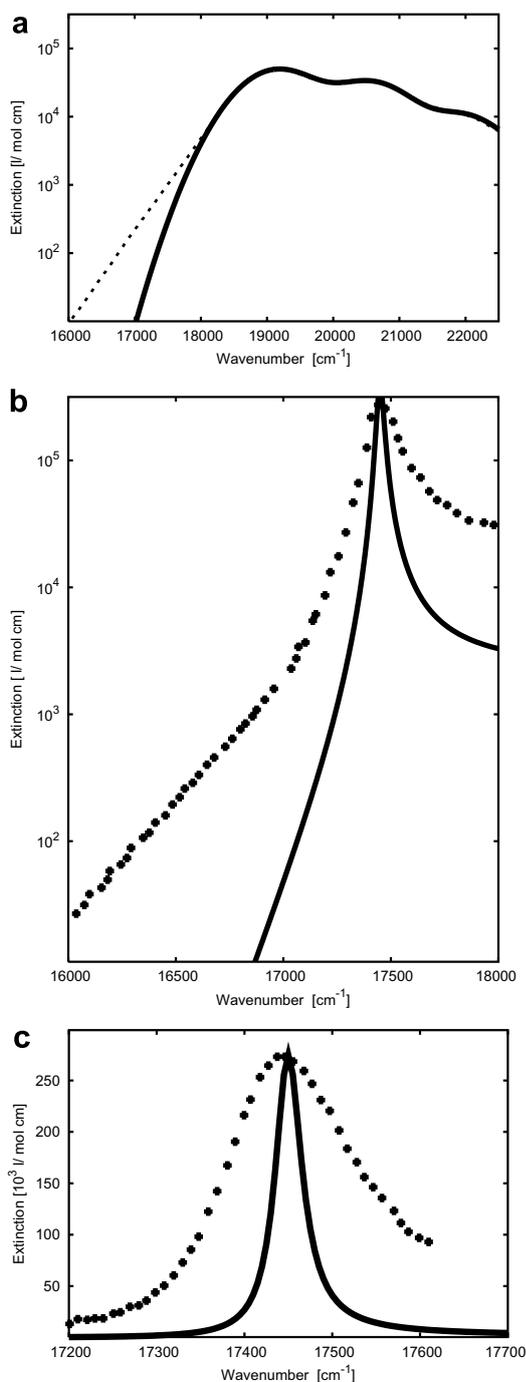


Fig. 3. (a) Dashed line: the measured monomer spectrum from Ref. [9], solid line: the fitted theoretical spectrum, assumed to consist of a vibrational progression where each peak is convoluted with a Gaussian. The parameters used are given in Ref. [34]. (b) and (c) Dots: experimental aggregate spectra as in Fig. 2a and b. Solid line: the calculated aggregate spectrum using the theoretical monomer shape from (a) and $C_{\parallel} = -1980\text{ cm}^{-1}$.

and the shape of the band-tail, we have made calculations in which the monomer spectrum of Fig. 1a is fitted to a sum of three Gaussian peaks, rather than using directly the measured spectrum of Fig. 1b. From Fig. 3a one sees that, although the region of strong monomer absorption is well-reproduced, the Gaussian tail falls off much more rapidly than the experiment, i.e. the Gaussian form is not a good fit to the experimental monomer spectrum in the wings. However it is precisely this region which, according to our CES theory, decides the shape of the J-aggregate spectrum in the same region. As seen in Fig. 3b, this assumption of a Gaussian tail leads to an aggregate spectrum whose band-tail also decreases much more rapidly than experiment. This is probably the explanation of the wrong behaviour of the aggregate band-tail calculated in Ref. [23]. More importantly perhaps, one notes from Fig. 3b and c that the predicted J-band is much narrower than in the experiment. This is completely in line with the approximate analytic result that the width of the J-band decreases as $C^2 \exp(-C^2/2\sigma^2)$ for an assumed Gaussian monomer spectrum. Hence, to obtain the aggregate spectrum over a broad region, it is essential to use a monomer spectrum which is accurate over the whole spectral region.

In principle the temperature dependence of the J-band shape and the aggregate Urbach tail could be calculated also in CES approximation. Unfortunately, although there have been temperature-dependent measurements of the monomer spectra required [35], they are not presented with sufficient resolution in the band-tail region for such calculations to be made. Such data would be highly desirable to further test the CES approximation as formulated in Ref. [32].

In summary, we have shown that the CES theory can reproduce reliably in high-resolution the detailed shape of the J-aggregate vibronic spectrum in both the exponential band-tail and the J-band spectral regions, using only a single fit parameter, the energy of the inter-monomer electronic coupling. Although the monomer absorption in this region is small, its shape and magnitude is crucial in deciding the shape of the aggregate spectrum, in agreement with analytical results of the simple CES theory.

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