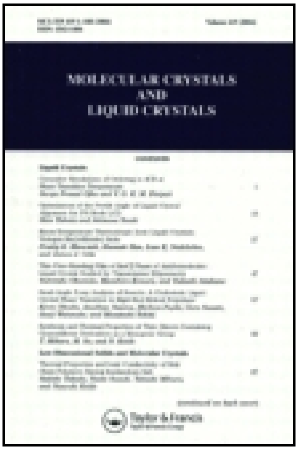

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Strong and Weak Exciton-Phonon Coupling in Molecular Crystals

M. D. Clarke [a] , D. P. Craig [a] & L. A. Dissado [a]

[a] Research School of Chemistry, Australian National University, P.O. Box 4, Canberra, A.C.T., 2600, Australia

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Strong and Weak Exciton–Phonon Coupling in Molecular Crystals

M. D. CLARKE, D. P. CRAIG, and L. A. DISSADO

Research School of Chemistry, Australian National University, P.O. Box 4, Canberra, A.C.T.2600, Australia

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The coupling cases for exciton–phonon interaction in molecular crystals are analysed with the help of three quantities: (i) the exciton bandwidth, related to the exciton transfer rate between molecules, (ii) the dispersive interaction between excitons and phonons, related to the rate of excitation interchange between phonons and excitons, and (iii) the phonon frequencies, related to the rate at which the phonon motions, and lattice structure, respond to changed lattice forces produced by molecular excitations. Cases intermediate between extreme weak coupling (exciton transfer faster than both lattice relaxation and exciton–phonon interchange) and extreme strong coupling (excitation locked on one site by lattice relaxation) are distinguished, and their spectral characteristics discussed.

INTRODUCTION

The coupling of crystal excitons to intra-molecular vibrations in a rigid lattice is described as weak or strong coupling according to the ratio of the progression-forming molecular frequency or frequencies, ω_{mol}, to the exciton bandwidth M calculated from the free molecule integrated spectral intensity. In weak coupling ($\hbar\omega_{\text{mol}} < M$) each molecule is excited for so short a time that its nuclei are unable to relax to a new equilibrium structure. Electronic and nuclear motions are for practical purposes uncoupled: the exciton bandwidth remains that for the whole of the free molecule transition moment, and the associated excitation transfer integral M_{if} between sites i and f is

$$M_{if} = \langle if' | V_{if} | i'f \rangle \tag{1}$$

the prime denoting the excited electronic state. In strong coupling ($\hbar\omega_{\text{mol}} > M$) the excitation transfer time is long enough for intramolecular relaxation, and each progression member acts individually according to its proportion of the total oscillator strength, giving a vibronic exciton bandwidth in this proportion. This is equal to the bandwidth calculated for M times a Franck–Condon factor $\langle G0|nv|\rangle^2$ for the overlap of the zero-quantum level in the ground state with the v-th quantum level in the n-th electronic state. The corresponding excitation transfer integral is

$$\langle G0|nv\rangle^2 M_{if} \tag{2}$$

To this consideration of weak and strong coupling to intramolecular vibrations there has to be added that of the coupling to external molecular motions, namely lattice phonons. The theory of the coupling to external modes has been developed by a number of authors.[2–9] In this paper we discuss the limiting cases in relation to the quantities they depend on, namely exciton bandwidth, lattice frequencies, and coupling constants between excitons and molecular motions.

In typical organic crystals composed of molecules that are not too large, say of molecular weight of a few hundred a.m.u., the internal frequencies appearing in progressions are usually higher than the highest lattice frequencies. Typically the acoustic phonons lie in the frequency range 0–50 cm^{-1}, and the translational optic and librational phonons in the range 50–150 cm^{-1}. Thus if the transfer integral (2), i.e. after allowing for the influence of intramolecular vibrations, is in this case less than 150 cm^{-1} there can be lattice relaxation at the excited site, and site-to-site transfer is a process in which lattice motion as well as electronic excitation is involved. Such clothed excitons have reduced transfer rates, and transfer integrals reduced from (2) by a further factor, loosely described as the Franck–Condon factor for the lattice vibrations. Relaxation can only occur if there is coupling between excitons and phonons, and its magnitude in relation to bandwidth and phonon frequencies must be taken into account.

Following this argument, the molecular excitations forming excitons in the crystal will be taken to be the elementary vibrational-electronic (vibronic) excitations of the isolated molecule. Each has a characteristic excitation energy ε and transition dipole moment $\mathbf{d}$ from the ground state.

EXCITON–PHOTON COUPLING

A Hamiltonian for the set of coupled molecular excitations and lattice phonons allowing for lattice distortion due to molecular excitation has been given before.[1] Taking the molecular excitation in site representation and the phonons as delocalised, we have

$$H = H_{\mathrm{ex}} + H_{\mathrm{ph}} + H^{1}_{\mathrm{ex-ph}} + H^{2}_{\mathrm{ex-ph}} \tag{3a}$$

$$H_{\mathrm{ex}} = \sum_{n}\left[\left(\varepsilon + \sum_{m}{}' D_{nm}\right)B_n^{\dagger}B_n + \sum_{m}{}' M_{nm}B_n^{\dagger}B_m\right] \tag{3b}$$

$$H_{\mathrm{ph}} = \sum_{\mathbf{q}s} b_{\mathbf{q}s}^{\dagger}b_{\mathbf{q}s}\hbar\omega_s(\mathbf{q}) \tag{3c}$$

$$H^{1}_{\mathrm{ex-ph}} = \sum_{s\mathbf{q}}\sum_{nm}{}'\left[B_n^{\dagger}B_m e^{i\mathbf{q}\cdot\mathbf{n}}F_{nm}(\mathbf{q}s) + B_n^{\dagger}B_n e^{i\mathbf{q}\cdot\mathbf{n}}\chi_s(\mathbf{q})\right]\phi_{\mathbf{q}s} \tag{3d}$$

$$H^{2}_{\mathrm{ex-ph}} = \sum_{s\bar{\mathbf{q}}}\sum_{nm}{}'\left[B_n^{\dagger}B_m F_{nm}(\bar{\mathbf{q}}s) + B_n^{\dagger}B_n\chi_s(\bar{\mathbf{q}})\right]\phi_{\bar{\mathbf{q}}s} \tag{3e}$$

where

$$\phi_{\mathbf{q}s} = b_{\mathbf{q}s} + b^{\dagger}_{-\mathbf{q}s} \tag{4}$$

Here the $B^{\dagger}$, B, $b^{\dagger}$, b are creation and annihilation operators for their respective particles. M_{nm} is the exciton exchange interaction between sites n and m, D_{nm} the dispersion interaction, and $F_{nm}(\mathbf{q}s)$ and $\chi_s(\mathbf{q})$ the exciton–phonon coupling functions for the exciton exchange (resonance) and dispersion interactions respectively. The Hamiltonian may be transformed to a delocalised operator with relations (5)

$$B_n^{\dagger} = N^{-1/2}\sum_{\kappa} B_{\kappa}^{\dagger}\exp(-i\boldsymbol{\kappa}\cdot\mathbf{n}); \quad B_n = N^{-1/2}\sum_{\kappa}\exp(i\boldsymbol{\kappa}\cdot\mathbf{n})B_{\kappa} \tag{5}$$

and is given by

$$H_{\mathrm{ex}} = \sum_{\kappa} E(\boldsymbol{\kappa})B_{\kappa}^{\dagger}B_{\kappa} \tag{6a}$$

$$H^{1}_{\mathrm{ex-ph}} = N^{-1/2}\sum_{s\kappa\mathbf{q}} B_{\kappa+\mathbf{q}}^{\dagger}B_{\kappa}\{F_s(\boldsymbol{\kappa},\mathbf{q}) + \chi_s(\mathbf{q})\}\phi_{\mathbf{q}s} \tag{6b}$$

$$H^{2}_{\mathrm{ex-ph}} = N^{-1/2}\sum_{s\kappa\mathbf{q}} B_{\kappa}^{\dagger}B_{\kappa}\{F_s(\boldsymbol{\kappa},\bar{\mathbf{q}}) + \chi_s(\bar{\mathbf{q}})\}\phi_{\bar{\mathbf{q}}s} \tag{6c}$$

together with (3c). The two forms are identical if the problem is solved exactly. For approximate solutions however the first is based on localised molecular excitation as best zero-th approximation, and the second on delocalised excitation.

Of the various terms in the Hamiltonian, D_{nm} is the change of dispersion interaction between molecules at sites n and m when one of them is raised to an electronic upper state. D_{nm} underlies the change is lattice stabilisation energy, due to a different molecular polarisability in the excited state, and is the source of the change in the transition energy of the molecules in a crystal from the gas phase. M_{nm} is the resonance interaction causing excitation initially on site n to transfer to site m at a rate $\sim\Delta E/\hbar\ s^{-1}$. In the absence of any coupling of excitons to phonons, the exact Hamiltonian is the sum of

(3c) and (6a), the exciton part of the total energy being given by (7), the exciton energy $E(\boldsymbol{\kappa})$

$$E(\boldsymbol{\kappa}) = \varepsilon + \sum_m D_{0m} + \sum_m{}' e^{i\boldsymbol{\kappa}\cdot\mathbf{m}} M_{0m} \tag{7}$$

The coupling between excitons and phonons given by (6b) and (6c) depends on coupling functions $F_s(\boldsymbol{\kappa}, \mathbf{q})$ and $\chi_s(\mathbf{q})$. The former gives the coupling arising from the dependence of the resonance interaction M_{nm} on the relative displacement of the molecules n and m, according to (8),

$$\begin{aligned} F_s(\boldsymbol{\kappa}, \mathbf{q}) &= \sum_m e^{i\boldsymbol{\kappa}\cdot\mathbf{m}} F_{0m}(\mathbf{q}s) \\ &= \sum_{jm} \left[\frac{\hbar}{2I_j\omega_s(\mathbf{q})}\right]^{1/2} e_s^j(\mathbf{q}) \left\{\frac{\partial}{\partial R_0^j} + e^{i\mathbf{q}\cdot\mathbf{m}} \frac{\partial}{\partial R_m^j}\right\} e^{i\boldsymbol{\kappa}\cdot\mathbf{m}} M_{0m} \end{aligned} \tag{8}$$

where $e_s^j(\mathbf{q})$ is the j-th component of a unit vector in the direction of the displacement in the $\mathbf{q}$ mode of the s branch, R_m^j being such a displacement at lattice site m: $j = 1, 2, 3$ are translational displacements and $j = 4, 5, 6$ rotational displacements. Strictly, translations and rotations cannot in general be separated in this way, but we assume that for most $\mathbf{q}$ values the motion will be dominantly one or the other. I_j is the mass coefficient for the motion of the $s\mathbf{q}$ mode. The factor (9) is thus the root mean square amplitude

$$\left[\frac{\hbar}{2I_j\omega_s(\mathbf{q})}\right]^{1/2} = \gamma_j(s\mathbf{q}) \tag{9}$$

of the zero point vibration of the $s\mathbf{q}$ mode. This coupling term transfers excitation between lattice sites together with emission or absorption of a phonon.

In the basis of localized excitations with hamiltonian (3) this term can be seen as causing the transfer of local deformation together with the transfer of the exciton. From the form of the delocalized hamiltonian (6) one sees that this transfer is accompanied by a scattering of the excitation between exciton states of different $\boldsymbol{\kappa}$. For librational phonons its magnitude is of the order of M_{0m} multiplied by $\gamma_j(s\mathbf{q})$,^{2} or ~0.01 of M_{0m}. It is usually small compared to the resonance transfer term. When the phonons are translational the coupling is at least an order of magnitude smaller.

The second type of coupling is by the dispersive term (10),

$$\chi_s(\mathbf{q}) = \sum_{jm} \gamma_j(s\mathbf{q}) e_s^j(\mathbf{q}) \left\{\frac{\partial}{\partial R_0^j} + e^{i\mathbf{q}\cdot\mathbf{m}} \frac{\partial}{\partial R_m^j}\right\} D_{0m} \tag{10}$$

which describes the change in lattice energy of an excited molecule due to lattice vibrations affecting the relative positions of molecules at the excited site and throughout the crystal. A non-zero value implies that the excited molecule is not at its equilibrium position in the lattice and for that reason $\chi_s(\mathbf{q})$ is sometimes called a strong coupling term causing excitation localisation. However in the delocalized representation in (6b) it appears as a scattering term similar to $F_s(\boldsymbol{\kappa}, \mathbf{q})$. In molecular crystals $\chi_s(\mathbf{q})$ can vary from a value close to M_{0m} to two orders of magnitude less, and a range of patterns of behaviour is found.

The detailed nature of the exciton–phonon coupling by the scattering mechanism (6b) can be followed by seeing how wave functions for excitons and phonons are coupled by $H^1_{\text{ex-ph}}$. The exciton wave function can be written

$$\Phi(\boldsymbol{\kappa}) = N^{-1/2} \sum_n e^{i\boldsymbol{\kappa}\cdot\mathbf{n}} \sigma_n \tag{11}$$

where

$$\sigma_n = (\phi'_n/\phi_n) \prod_{r=0}^{N-1} \phi_r \tag{12}$$

and ϕ_n and ϕ'_n are ground and excited molecule wave functions at site n. The complete exciton–phonon wave functions are

$$\Phi(\boldsymbol{\kappa})\Psi(\mathbf{q}) \tag{13}$$

where $\Psi(\mathbf{q})$ is the product of individual harmonic oscillator wave functions in each of the normal modes, all in their zero-point states except that in mode $\mathbf{q}$, which will be taken to be in its first quantum level. General phonon wave functions, allowing for any desired excitations in the modes, can be used but give nothing new for the present argument. Thus

$$\Psi(\mathbf{q}) = \psi^0(0) \ldots \psi^1(\mathbf{q}) \ldots \tag{14}$$

the superscript denoting the quantum state of the oscillator. The symbol $\Psi^{(0)}$ means the empty state where all oscillators are in their lowest levels. The pairs of states coupled by the operator as written in (6b) are

$$\left.\begin{array}{ll} \Phi(\boldsymbol{\kappa}+\mathbf{q})\Psi(-\mathbf{q}); & \Phi(\boldsymbol{\kappa})\Psi^{(0)} \\ \Phi(\boldsymbol{\kappa}+\mathbf{q})\Psi^{(0)}; & \Phi(\boldsymbol{\kappa})\Psi(\mathbf{q}) \end{array}\right\} \tag{15}$$

Bearing in mind the definition (11) a typical term in the matrix element of exciton-exchange coupling (8) arising from the upper pair in (15) is

$$N^{-1}\langle e^{i(\boldsymbol{\kappa}+\mathbf{q})\cdot\mathbf{m}} \sigma_m \Psi(-\mathbf{q}) | F_s(\boldsymbol{\kappa}, \mathbf{q}) | \sigma_0 \Psi^{(0)} \rangle \tag{16}$$

which, according to expression (8), is the coupling of exciton exchange between sites 0 and m to the excitation of one quantum of a phonon of wave vector $-\mathbf{q}$.

A typical term in the matrix element of the dispersive coupling (10) is

$$N^{-1}\langle e^{i\mathbf{q}\cdot\mathbf{m}} \sigma_m \Psi(-\mathbf{q}) | \chi_s(\mathbf{q}) | \sigma_m \Psi^{(0)} \rangle \tag{17}$$

This gives the coupling produced by the excitation of the molecule at site m between the exciton and a one-quantum phonon transition in mode $-\mathbf{q}$. This coupling, according to (10), occurs because the dispersion interaction between an excited molecule at site m and other molecules is changed by the relative molecular motion in the phonon modes.

The term in $H^2_{\text{ex-ph}}$, expression (6c), appear only when the crystal properties, expressed in lattice dimensions and molecular orientations, are different in the excited state from those in the ground state. The normal modes of the lattice calculated for the ground state do not necessarily apply to the excited state, but to an acceptable approximation the changes can be confined to shifts in the origins of certain of the normal coordinates, denoted by a bar over the mode index referring to those coordinates ($\bar{\mathbf{q}}$). $H^2_{\text{ex-ph}}$ gives the change in energy of the excited molecule due to the lattice displacements, in terms of an altered resonance interaction and lattice energy. The dispersion-displacement coupling will necessarily lower the energy of the excited molecule while the resonance-displacement coupling may either raise or lower it.

The eigenvalues for a system in which there is one exciton only can be obtained by removing the interaction terms from the Hamiltonian to produce a diagonal form. This can be carried out for the delocalised form of the Hamiltonian (6) by means of two canonical transformations.[1] The first transformation removes the coupling terms (6c). The transformed operators are obtained in terms of the old operators as

$$\left.\begin{aligned} b_{s\bar{\mathbf{q}}} &= \tilde{b}_{s\bar{\mathbf{q}}} - \sum_{\boldsymbol{\kappa}} \tilde{B}^{\dagger}_{\boldsymbol{\kappa}} \tilde{B}_{\boldsymbol{\kappa}}\, \Lambda^*(\boldsymbol{\kappa} s\bar{\mathbf{q}}) \\ B_{\boldsymbol{\kappa}} &= \exp\left(\sum_{s\bar{\mathbf{q}}} \{\Lambda^*(\boldsymbol{\kappa} s\bar{\mathbf{q}})\tilde{b}_{s\bar{\mathbf{q}}} - \Lambda(\boldsymbol{\kappa} s\bar{\mathbf{q}})\tilde{b}_{s\bar{\mathbf{q}}}\}\right)\tilde{B}_{\boldsymbol{\kappa}} \end{aligned}\right\} \tag{18}$$

with

$$\Lambda(\boldsymbol{\kappa} s\bar{\mathbf{q}}) = N^{-1/2}\{\chi_s(\bar{\mathbf{q}}) + F_s(\boldsymbol{\kappa}, \bar{\mathbf{q}})\}/\hbar\omega_s(\bar{\mathbf{q}}) \tag{19}$$

and transformed exciton energy

$$\begin{aligned} E'(\boldsymbol{\kappa}) = \varepsilon + \sum_m D_{0m} - N^{-1} \sum_{s\bar{\mathbf{q}}} \{|F_s(\boldsymbol{\kappa}, \bar{\mathbf{q}})|^2 + |\chi_s(\bar{\mathbf{q}})|^2\}/\hbar\omega_s(\bar{\mathbf{q}}) \\ + \sum_m e^{i\boldsymbol{\kappa}\cdot\mathbf{m}}\Bigg[1 - 2N^{-1} \sum_{s\bar{\mathbf{q}}} \frac{\chi_s^*(\bar{\mathbf{q}})}{\hbar\omega_s(\bar{\mathbf{q}})} \sum_j e_s^j(\bar{\mathbf{q}})\gamma_j(s\bar{\mathbf{q}}) \\ \times \left\{\frac{\partial}{\partial R_0^j} + e^{i\bar{\mathbf{q}}\cdot\mathbf{m}} \frac{\partial}{\partial R_m^j}\right\}\Bigg] M_{0m} \end{aligned} \tag{20}$$

The second transformation is an approximate one for the purpose of removing the $H^1_{\text{ex-ph}}$ coupling term. The phonon operators have a similar form to (18) and are

$$\left.\begin{aligned}\tilde{b}^\dagger_{s\mathbf{q}} &= \tilde{b}^\dagger_{s\mathbf{q}} + \sum_{\boldsymbol{\kappa}} \tilde{B}^\dagger_{\boldsymbol{\kappa}+\mathbf{q}} \tilde{B}_{\boldsymbol{\kappa}} \beta(\boldsymbol{\kappa}, s, \mathbf{q}) \\ \hat{b}_{s\mathbf{q}} &= \tilde{b}_{s\mathbf{q}} - \sum_{\boldsymbol{\kappa}} \tilde{B}^\dagger_{\boldsymbol{\kappa}-\mathbf{q}} \tilde{B}_{\boldsymbol{\kappa}} \bar{\beta}(\boldsymbol{\kappa}, s, -\mathbf{q})\end{aligned}\right\} \tag{21}$$

with

$$\beta(\boldsymbol{\kappa} s\mathbf{q}) = \frac{N^{-1/2}\{F_s(\boldsymbol{\kappa}, \mathbf{q}) + \chi_s(\mathbf{q})\}}{E'(\boldsymbol{\kappa}) - E'(\boldsymbol{\kappa} + \mathbf{q}) + \hbar\omega_s(\mathbf{q})} \tag{22}$$

$$\bar{\beta}(\boldsymbol{\kappa} s\mathbf{q}) = \frac{N^{-1/2}\{F_s(\boldsymbol{\kappa}, \mathbf{q}) + \chi_s(\mathbf{q})\}}{E'(\boldsymbol{\kappa}) - E'(\boldsymbol{\kappa} + \mathbf{q}) - \hbar\omega_s(\mathbf{q})} \tag{23}$$

The transformed exciton operators cannot be expressed in simple form. To second order they are

$$\begin{aligned}\hat{B}_{\boldsymbol{\kappa}} = \tilde{B}_{\boldsymbol{\kappa}} &- \sum_{s\mathbf{q}} \{\beta(\boldsymbol{\kappa} - \mathbf{q}, s\mathbf{q})\tilde{b}_{s\mathbf{q}} + \bar{\beta}(\boldsymbol{\kappa} - \mathbf{q}, s\mathbf{q})\tilde{b}^\dagger_{s-\mathbf{q}}\}\tilde{B}_{\boldsymbol{\kappa}-\mathbf{q}} \\ &+ \tfrac{1}{2}\sum_{s\mathbf{q}} \{\beta(\boldsymbol{\kappa} - \mathbf{q}, s\mathbf{q})\tilde{b}_{s\mathbf{q}} + \bar{\beta}(\boldsymbol{\kappa} - \mathbf{q}, s\mathbf{q})\tilde{b}^\dagger_{s-\mathbf{q}}\} \sum_{s'\mathbf{q}'} \{\beta(\boldsymbol{\kappa} - \mathbf{q} - \mathbf{q}', s'\mathbf{q}')\tilde{b}_{s'\mathbf{q}'} \\ &+ \bar{\beta}(\boldsymbol{\kappa} - \mathbf{q} - \mathbf{q}', s'\mathbf{q}')\tilde{b}^\dagger_{s'-\mathbf{q}'}\}\tilde{B}_{\boldsymbol{\kappa}-\mathbf{q}-\mathbf{q}'} - \cdots\end{aligned} \tag{24}$$

$$\begin{aligned}\hat{B}^\dagger_{\boldsymbol{\kappa}} = \tilde{B}^\dagger_{\boldsymbol{\kappa}} &+ \sum_{s\mathbf{q}} \{\beta(\boldsymbol{\kappa} s\mathbf{q})\tilde{b}_{s\mathbf{q}} + \bar{\beta}(\boldsymbol{\kappa} s\mathbf{q})\tilde{b}^\dagger_{s-\mathbf{q}}\}\tilde{B}^\dagger_{\boldsymbol{\kappa}+\mathbf{q}} \\ &+ \tfrac{1}{2}\sum_{s\mathbf{q}} \{\beta(\boldsymbol{\kappa} s\mathbf{q})\tilde{b}_{s\mathbf{q}} + \bar{\beta}(\boldsymbol{\kappa} s\mathbf{q})\tilde{b}^\dagger_{s-\mathbf{q}}\} \sum_{s'\mathbf{q}'}\{\beta(\boldsymbol{\kappa} + \mathbf{q}, s'\mathbf{q}')\tilde{b}_{s'\mathbf{q}'} \\ &+ \bar{\beta}(\boldsymbol{\kappa} + \mathbf{q}, s'\mathbf{q}')\tilde{b}^\dagger_{s'-\mathbf{q}'}\}\tilde{B}^\dagger_{\boldsymbol{\kappa}+\mathbf{q}+\mathbf{q}'} + \cdots\end{aligned} \tag{25}$$

Higher order terms have exponential numerical coefficients, each coefficient conserving psuedomomentum through sequential phonon processes. On limiting (24) and (25) to first order the diagonal form of the Hamiltonian is given by

$$\hat{H} = \sum_{\boldsymbol{\kappa}} \hat{B}^\dagger_{\boldsymbol{\kappa}} \hat{B}_{\boldsymbol{\kappa}}\{E'(\boldsymbol{\kappa}) + \Delta(\boldsymbol{\kappa}, \mathbf{q})\} + \sum_{s\mathbf{q}} \hbar\omega_s(\mathbf{q})\hat{b}^\dagger_{\mathbf{q}}\hat{b}_{\mathbf{q}} \tag{26}$$

where

$$\begin{aligned}\Delta(\boldsymbol{\kappa}, \mathbf{q}) = N^{-1} \sum_{s\mathbf{q}} |F_s(\boldsymbol{\kappa}, \mathbf{q}) + \chi_s(\mathbf{q})|^2 &\left[\frac{\bar{v}_s(\mathbf{q})}{E'(\boldsymbol{\kappa}) - E'(\boldsymbol{\kappa} + \mathbf{q}) + \hbar\omega_s(\mathbf{q})}\right. \\ &\left.+ \frac{\bar{v}_s(\mathbf{q}) + 1}{E'(\boldsymbol{\kappa}) - E'(\boldsymbol{\kappa} + \mathbf{q}) - \hbar\omega_s(\mathbf{q})}\right]\end{aligned} \tag{27}$$

Here $\bar{\nu}_s(\mathbf{q})$ are the thermal average populations of phonons of wavevector $\pm\mathbf{q}$.

THE COUPLING CASES

The roles of the two interaction terms can now be clearly seen. The *lattice-displacement* coupling terms ($H^2_{\text{ex-ph}}$) depress the molecular excitation energy from its undisturbed level and alter the resonance interaction as in $E'(\boldsymbol{\kappa})$; they are also responsible for a phonon progression in absorption.[3] The *scattering* coupling ($H^1_{\text{ex-ph}}$) introduces an energy shift through the real part of $\Delta(\boldsymbol{\kappa}, \mathbf{q})$. The imaginary part of $\Delta(\boldsymbol{\kappa}, \mathbf{q})$ is to be regarded as a damping giving a finite width to the transformed levels.

The delocalized basis underlying expression (26) for the crystal energies is an acceptable approximation to the correct solution only if the perturbation series in (24) and (25) is rapidly convergent. At the least this requires the inequality (28) to hold for all $\mathbf{q}$ for which β and $\bar{\beta}$ have to be evaluated.

$$1 > |\beta(\boldsymbol{\kappa}s\mathbf{q})|, \qquad |\bar{\beta}(\boldsymbol{\kappa}s\mathbf{q})| \tag{28}$$

We can exclude modes $\mathbf{q}$ giving denominators ~ 0 and treat them as damping terms which can be dealt with in a series of single and multiple scatterings, so long as (28) applies for other modes.

The quantities in β and $\bar{\beta}$ are the coupling functions F_s and χ_s, the exciton band level separations, and the phonon frequencies. Their relative sizes determine whether (28) is obeyed. We shall analyse the various cases with the help of this criterion.

We define two parameters. M is the free exciton band width for the vibronic transition. It is the largest value that is taken by any of the quantities $E(\boldsymbol{\kappa} + \mathbf{q}) - E(\boldsymbol{\kappa})$, which differ from $E'(\boldsymbol{\kappa} + \mathbf{q}) - E'(\boldsymbol{\kappa})$ in the denominators of β and $\bar{\beta}$ by small corrections produced by the energy shifts given in expression (20). M is four times the nearest neighbour resonance transfer interaction if we confine ourselves to those interactions only. It gives the excitation transfer lifetime away from a given molecule according to $\tau_{\text{tr}} \sim \hbar/|M|$. The second parameter, X_s, is the average of the dispersion interaction over phonon modes of branch s. $F_s(\boldsymbol{\kappa}, \mathbf{q})$ is neglected as far as the criteria are concerned since it is usually much smaller than M. In a rough way X_s is associated with a "coupling lifetime" for the degradation of an exciton into mixed exciton-phonon states, according to $\tau_{\text{cpg}} \sim \hbar/|X_s|$. The magnitude of the parameters M and X_s will be related to a fixed phonon frequency ω_s. For librational modes, which are assumed dispersionless, ω_s is the $\mathbf{q} = 0$ optical frequency, and for acoustic modes it is the maximum acoustic frequency. The time for phonon motion through one radian is $\tau_{\text{ph}} \sim \hbar/\omega_s$. We now distinguish three cases depending on the magnitude of M.

Case i) $|M|/\omega_s > 1$. Exciton transfer faster than phonon motion. Here the perturbation series in (24) and (25) converge if

$$|X_s|/|M| < 1 \tag{29}$$

i.e. if exciton transfer is faster also than exciton loss to coupled exciton–phonons (weak coupling limit). Otherwise the delocalised picture (26) is not valid. The problem must then be solved by returning to the Hamiltonian in the site representation (1) and treating the exciton–phonon dispersion coupling terms as the major perturbation on the molecular excitation, before including the resonance transfer integral.[4] The resulting crystal states are those of completely localised excitation at a distorted lattice site. It has been shown[5] that in this case the two types of solutions are mutually exclusive, the excitation either being completely delocalised with lattice normal coordinates unaltered, or localized so strongly that there is an origin shift in all coordinates. This situation can be seen in the following way. After coupling of a single exciton $\boldsymbol{\kappa}$ to a number of exciton–phonons $\boldsymbol{\kappa} + \mathbf{q}$, the transfer integral applicable to each one of them is a small fraction of the total M. The transfer rate in each is then small compared with ω_s and localization is the result.

In summary, in the delocalised case, an instantaneously created localised mode can be regarded as lying within the exciton band into which it spontaneously decays. In the case of localization a completely delocalized band exists at higher energy. Localized excitation can, by thermal activation, be raised to the band, out of which it drops into a localized state at another site, thus having undergone site-to-site transfer.

We note that the transformation of Hochstrasser and Prasad,[6] is a special case of that given here and in Ref. 1, applying to the $\boldsymbol{\kappa} = 0$ exciton at absolute zero. It does not generate a phonon progression unless $|M|/\omega_s$ is less than unity, which removes it from consideration in case i).

Case ii) $|M|/\omega_s < 1$. Exciton transfer slower than phonon motion. Delocalization is possible only if coupling to phonons is very weak; and accordingly we find that the perturbation series converges if

$$|X_s|/\omega_s < 1 \tag{30}$$

where the coupling lifetime is long compared with the time for phonon motion. Otherwise the crystal states have the localised form described under case i). These are best derived from the Hamiltonian (3) in the site representation. However here, by setting the exciton dispersion to zero, we find an exact form of the second canonical transformation.

The excitation operators (24), (25) now become identical to those of Fischer.[7]

$$\hat{B}_{\kappa} = N^{-1/2} \sum_{\kappa'} \sum_{n} \exp\left[-i(\boldsymbol{\kappa} - \boldsymbol{\kappa}') \cdot \mathbf{n} - \sum_{\mathbf{q}s} e^{i\mathbf{q}\cdot\mathbf{n}} \chi_s(\mathbf{q}) \{ \hat{b}_{s\mathbf{q}} - \hat{b}^{\dagger}_{s-\mathbf{q}} \} / \omega_s(\mathbf{q}) \right] \tilde{B}_{\kappa'}$$

$$\hat{B}^{\dagger}_{\kappa} = N^{-1/2} \sum_{\kappa'} \sum_{n} \exp\left[i(\boldsymbol{\kappa} - \boldsymbol{\kappa}') \cdot \mathbf{n} + \sum_{\mathbf{q}s} e^{i\mathbf{q}\cdot\mathbf{n}} \chi_s(\mathbf{q}) \{ \hat{b}_{s\mathbf{q}} - \hat{b}^{\dagger}_{s-\mathbf{q}} \} / \omega_s(\mathbf{q}) \right] \tilde{B}^{\dagger}_{\kappa'} \tag{31}$$

It must be remembered however that the exciton dispersion has already been assumed zero, and thus the excitation is completely localised.

Toyozawa has shown[5] that for the following two cases of fast exciton coupling to exciton–phonons,

$$|M|/\omega_s < 1, \qquad |X_s|/\omega_s > 1$$

and

$$|X_s|/\omega_s > |M|/\omega_s > 1$$

the crystal states lowest in energy are fully localised with displacement of all normal coordinates, the resonance transfer interaction serving only to mediate the thermally activated hopping process. The delocalised picture (26) thus fails in this case.

Transitions to the localised states have phonon sidebands arising from the site interaction in (3d) with intensities of the form, for the m-th member

$$\exp\left\{ -\frac{|X_s|^2}{\omega_s^2}(2\bar{\nu}_s + 1) \right\} \left[\frac{|X_s|^2}{\omega_s^2}(\bar{\nu}_s + 1) \right]^m \Big/ m! \tag{32a}$$

or

$$\exp\left\{ -\frac{|X_s|^2}{\omega_s^2}(2\bar{\nu}_s + 1) \right\} \left[\frac{|X_s|^2}{\omega_s^2}\bar{\nu}_s \right]^m \Big/ m! \tag{32b}$$

the latter applying to transitions involving thermally activated levels of the ground state (hot bands).

Where there is slow exciton–phonon coupling, $|X_s|/\omega_s < 1$, (expression (30)) the perturbation series converges and delocalization is the correct picture. If in addition $|X_s| < |M|$ and exciton transfer is fast localization is self-evident, inasmuch as M becomes the largest perturbation in hamiltonian (3). However when

$$1 > |X_s|/\omega_s > |M|/\omega_s \tag{33}$$

it might be expected that, since $|X_s|$ is the largest perturbation, the crystal states should be localised. This range, in which both molecule-to-molecule transfer, and exciton coupling to the exciton–phonon system are slower than phonon response, namely,

$$|X_s|/\omega_s < 1, \qquad |M|/\omega_s < 1 \tag{34}$$

has been identified by Toyozawa[5] as an intermediate range in which both displacement-localisation and delocalisation are possible simultaneously. The delocalised entities are excitons partially clothed with lattice displacements. In the case of (33) the localised states on which M acts as a perturbation have the maximum intensity in the zero phonon level ($m = 0$ in (32)). The state with maximum intensity is the state with least lattice displacement and in this case it is the lowest crystal state. Thus the resonance transfer interaction acts on an excited molecule with little local disturbance as described in Ref. 2. The conditions $|X_s|/\omega_s < 1$, $|M|/\omega_s < 1$ are also those under which the coupling term $H^1_{\text{ex-ph}}$ in (6) causes intensity transfer to phonon sidebands,[3] and we may proceed to a result similar in form to Hochstrasser and Prasad's[6] for the intensity. If we give the β and $\bar{\beta}$'s of (24) and (25) the common forms

$$\beta \sim \frac{X_s}{\omega_s - M}; \qquad \bar{\beta} \sim \frac{X_s}{\omega_s + M} \tag{35}$$

with the averaged coupling in the numerators and the maximum value of the exciton band level separations in the denominators, exact expressions for (24), (25) are found as given in (31)[7] with the replacement of X_s/ω_s by

$$\frac{X_s\omega_s}{\omega_s^2 - M^2} \tag{36}$$

The phonon progression now has an intensity factor

$$\frac{|X_s|^2\omega_s^2}{(\omega_s^2 - M^2)^2} \tag{37}$$

thus *increasing* the intensity of the sidebands. The effect is small ($\sim 4\times$) because of the restriction (34), and we think that this is why it cannot be seen, rather than explaining it by the small widths of exciton bands in molecular crystals.[8] When the widths are large enough to make an appreciable affect in (37) we are in case i) conditions where the approximations leading to (37) do not apply and the delocalised picture has no phonon sidebands.

A third case can usefully be distinguished. It applies widely to singlet transitions in molecular crystals, and it can be regarded as a sub-case of ii) for low frequency acoustic modes.

Case iii) $|M| \approx \omega_s$

Where, in addition $|X_s| > |M|$, the perturbation expansion fails, indicating that the crystal states must be treated as localized states. Where $|X_s| < |M|$

we have the intermediate range[5] of delocalization accompanied by some lattice displacement. From the formal point of view, after removing from the expressions (24) and (25) the phonon modes responsible for damping, there may still be some modes for which the denominators of β and $\bar{\beta}$ are small enough to prevent convergence of the perturbation series. These modes must be removed and treated as a perturbation on the site excitation energy. This causes a shift in equilibrium position of the excited molecule and identifies those modes as being the $\bar{\mathbf{q}}$ modes of $H^2_{\text{ex-ph}}$. Their effect is to reduce the resonance transfer integral through a Franck–Condon[4,7] factor and to introduce a phonon progression into the absorption spectra through the $H^2_{\text{ex-ph}}$ term.[3] Under these conditions (26) retains validity as long as these modes are removed from the sum of $\Delta(\boldsymbol{\kappa}, \mathbf{q})$ and the reduced form of the resonance transfer integral is used.

Yarkony and Silbey[9] have investigated this situation. They show that for a given magnitude of $|M|$, the lattice displacement decreases from its maximum possible value on reducing $|X_s|$, but that some displacement is always present together with delocalisation. For a given magnitude of $|X_s|$. increasing M reduces the distortion. These results may be given the following physical interpretation. Those molecular crystals in which an excited molecule has a different equilibrium position to the same molecule in the ground state, will undergo structural change to an extent allowed by the time of residence of excitation on any one molecule in relation to the time constants of the lattice displacements, the residence time being $\tau \sim \hbar/M$. The anthracene crystal[10] appears to be an example, with a small lattice structural change, so that the Franck–Condon factor is close to unity and Equation (26) applies without change.

Phonon progressions, when observable in these systems, are determined by $H^2_{\text{ex-ph}}$ through (32). The exciton bandwidth is not expected greatly to affect intensities. This result can be seen from the delocalised form of $H^1_{\text{ex-ph}}$ which places absorption intensity[3] at

$$E'(\boldsymbol{\kappa} + \mathbf{q}) + \hbar\omega_s(\mathbf{q}) \qquad \boldsymbol{\kappa} = 0$$

and

$$E'(\boldsymbol{\kappa} + \mathbf{q}) - \hbar\omega_s(\mathbf{q}) \qquad \boldsymbol{\kappa} = 0 \tag{38}$$

as well as at the optical level $E'(\boldsymbol{\kappa} = 0)$. When the bandwidth is much smaller than $\omega_s(\mathbf{q})$ as in case (ii) these positions lie at the phonon sidebands of $E'(\boldsymbol{\kappa} = 0)$ and contribute to their intensity. When the band width is large they can lie close to $E'(\boldsymbol{\kappa} = 0)$ itself leading to an absorption width through the exciton damping term, and otherwise constitute the energy shift $\Delta(\boldsymbol{\kappa}, \mathbf{q})$.

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