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Triplet Exciton States of Molecular Crystals

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1.1 INTRODUCTION

The triplet states of molecules form bands in molecular crystals and the study of the states of these exciton bands yields information about the wavefunctions of the molecular excited states, spin-dependent interactions, and the interactions between molecules in the crystal. The molecular singlet states that can be reached by electric dipole transitions when there are full shell ground states form singlet exciton bands in the molecular crystal in which the energy spread of the states is determined by the extent to which the intermolecular potential V can induce the excitation energy to move from one molecule to another. If the excitation (*) is located on molecule 1, the energy associated with excitation exchange from $\phi_1*\phi_2 \ldots$ to $\phi_1\phi_2* \ldots$ is

$$\langle \phi_1* \phi_2 | V | \phi_1 \phi_2* \rangle$$

This is the so-called Coulomb interaction and its evaluation can either be based on a multipole expansion of the potential or on an explicit computation starting from a knowledge of the molecular wavefunctions[1]. In the former case the excitation exchange interaction is understood to be caused by 'through space' interactions between molecular transition multipoles. Such interactions vanish identically for pure triplet states and the Coulomb contribution to the triplet exciton band is only recovered to the extent that the singlet states having transition multipoles with the ground state are spin-orbit mixed with the triplet. On the other hand, there is an additional contribution to the excitation exchange interaction for triplets (and singlets) if the indistinguishability of crystal electrons is taken into account[2-4]. The energy associated with the transfer of excitation from $A(\phi_1*\phi_2 \ldots)$ to $A(\phi_1\phi_2* \ldots)$ is

$$\langle A(\phi_1* \phi_2) | V | \phi_1 \phi_2* \rangle$$

where A is the operator antisymmetrising the crystal wavefunction to *intermolecular* electron exchange. This quantity does not vanish for pure triplet excitation and it is termed the *electron* exchange interaction. There have been many attempts to calculate the energy spread of the triplet exciton band states and an important object of optical experiments on crystals is to investigate the validity of these calculations and hence the correctness of the critical features of the assumed wavefunctions.

On the assumption that there is no relative motion of the molecules in the lattice, the wavefunction $\phi \sim \phi(x, Q)$ is quite closely a Born–Oppenheimer product state that depends on both the electronic (x) and nuclear coordinates (Q) for a molecule. Thus the excitation exchange interaction can be approximated as the product of an electronic interaction at a fixed nuclear configuration times a nuclear position dependent integral or Franck–Condon overlap factor. The excited states of the crystal, on the other hand, are not Born–Oppenheimer states unless the excitation exchange interactions are so large as to separate the band states, that mix with one another when the nuclei have kinetic energy, by much more than molecular vibrational frequencies[5,6]. Since the electron exchange interaction is usually quite small it is customary to observe splittings (of molecular states) that are very much

less than molecular vibrational frequencies; hence the triplet excitons are generally not describable as Born–Oppenheimer states. Instead they are superpositions of the form:

$$A(\phi_1{}^* \phi_2 \ldots) \pm A(\phi_1 \phi_2{}^* \ldots) + \ldots$$

such that each molecular Born–Oppenheimer level forms its own exciton band of states in the crystal, the exciton bandwidth being determined by the electronic part of the interaction and a vibrational overlap factor for the particular molecular vibronic state.

1.2 TRIPLET STATES OF MOLECULAR CRYSTALS

When considering the properties of quasi-stationary states of aggregates of excited triplet states of molecules having singlet ground states, it is first necessary to consider the effects of three interactions: the total spin–spin dipolar coupling (H_D), the total spin–orbit coupling (H_{so}), and the intermolecular coulomb potential (V). The splitting of the three triplet sublevels (fine-structure) of a space-fixed molecule is determined by the part of (H_{so} + H_D) for that molecule, and the probability of the excitation jumping with characteristic time τ between molecules is determined by matrix elements of V. If the fine-structure splitting is large compared with $\hbar/\tau$, then each spin sublevel forms its own exciton band[7] or localised state with characteristic spin quantisation determined by the form of the eigenstates of (H_{so} + H_D) for each molecule plus smaller effects of (H_{so} + H_D) between different molecules. In the limit of large excitation transfer matrix elements the observed fine-structure is now a property of a delocalised state and the spin-quantisation is determined by the nature of the anisotropy of V. Both of these situations occur in practical systems, the former in dilute chemically or isotopically mixed crystals, and the latter in neat molecular crystals. There may be molecular crystals for which the former or an intermediate case arises, but none of these interesting cases have yet been characterised. Typical fine-structure splittings are ca. 0.1 cm^{-1}, whereas commonly observed excitation exchange splittings are in the range 1 cm^{-1} or greater. Of course, whenever splittings are apparently absent there arises the opportunity for an intermediate coupling situation.

In the Frenkel exciton approximation the excitation transfer matrix elements for a triplet state are determined by matrix elements of V between single molecule eigenstates of H_0 + H_{so} + H_D, where H_0 is the spin-free molecular Hamiltonian. In this form the Frenkel basis states contain singlet and triplet components and the excitation transfer matrix elements may be both long-range, through the singlet components, and short-range through the triplet components. It is frequently assumed that the long-range effects can be neglected and indeed this may be a satisfactory picture for molecules without heavy atoms, strong spin–orbit interactions or nearby states, but perhaps not in these instances. There is a direct long-range effect between excited triplet states through the total H_D that will contribute very slightly to the energy, though perhaps more significantly to spin–lattice relaxation, but in most theory related to conventional spectroscopic measurements it is

usually assumed that the crystal contains only one exciton or excited state. The interactions between excitons has been studied in detail[8] but will not be dealt with here.

Different eigenstates of $H_0 + H_{so} + H_D$ for each molecule, and also for different molecules, are coupled by V to give also the second-order (with respect to $H_0 + H_{so}$) crystal field effects. Because the fine-structure axes of molecules at different sites may not coincide, the crystal field coupling of different orbital states of $H_0 + H_{so} + H_D$ can modify the magnetic axes of a triplet state and introduce optical spectral intensity into transitions to spin substates that might not otherwise be observed[9]. These effects work both in dilute mixed crystals and in neat crystals, but they are not yet well characterised either by optical or e.p.r. spectroscopy.

The states of neat crystals are characterised by an exciton band index k that measures the number of nodes per unit length (cm^{-1}) in the exciton wavefunction. The $k = 0$ state of a cyclic lattice corresponds to the band state with no nodes and it is the energy region $E(k) \approx E(0)$ that is exposed by conventional optical spectroscopy. Other band states may be caused to appear if the lattice is disturbed by vibrations, defects or impurities. The latter two flaws are probably responsible for the inhomogeneous contribution of *ca.* 0.5–3.0 cm^{-1} to the linewidth of most organic solid state spectra. Bandstates other than those in the region $k = 0$ can be artificially exposed by studies of band-to-band transitions[10,11] (see below) and spectra of heavily doped isotopic mixed crystals[12-14] in which the crystal structure is maintained but there is energy disorder. For triplet states not having very strong spin orbit coupling and for which the transfer matrix element is large compared with spin-splittings, the energy dispersion is given by simple formulae that depend on the crystal structure and number of molecules per unit cell. Not many of these formulae have been tested against experiment and their validity is based on the expectation that a restricted Frenkel limit[15] will apply to triplet excitons. It is also the expectation for triplet states having small H_{so} that their crystal states may be described in the weak vibronic coupling limit in which the transfer matrix element is small compared with the molecular vibrational spacings. Then the excitation transfer parameter β_v of a vibronic state is related to β_1, for the Born–Oppenheimer electronic state, through its Franck–Condon Factor F_v for transitions to the zero-point level of the ground state: that is $\beta_v = F_v \beta_1$. An important implication for spectroscopy is that the parameters of $E(k)$ for each vibronic state must be known before molecular excited state vibrational frequencies can be measured. Molecular vibrational levels in a crystal with weak coupling usually imply the set of levels that would arise if no excitation transfer were occurring, although few such data exist.

1.2.1   The effects of the crystal field

Molecules in solids, be they in mixed crystals or neat crystals, are constrained by the intermolecular interactions with neighbouring molecules to adopt equilibrium configurations whose symmetries are environmentally deter-

mined. Although the actual molecular states can at best be classified in terms of site symmetry group representations, it has become customary to discuss spectra in terms of idealised symmetry groups that refer to the equilibrium disposition of the nuclei in an isolated space-fixed molecule. The implicit assumption behind this procedure is that the crystal field perturbations induce only slight mixing of the idealised wavefunctions. For a triplet state the expectation values for a property may become different in each of the spin substates due to crystal field effects, and if interference can occur amongst the property amplitudes — such as in a Zeeman effect experiment — the results may become even more noticeably different from those of the unperturbed system[9]. The crystal field can mix states having different molecular spin orientation because the spins are quantised by H_D and all molecules in the crystal do not have the same orientation. Thus even in mixed crystals the guest triplet level substates will display properties inappropriate to the ideal symmetry[9]. An extreme example of this is the external heavy atom enhancement of the intensity of singlet–triplet transitions. The conclusion from this discussion is that selection rules involving spin-operators, such as optical transitions permitted through spin–orbit mixing, are expected to be modified by crystal field effects and an appropriate symmetry group for both space and spin states is that of the crystal site. The site symmetry of a guest in a chemically mixed crystal will also depend on distortions of the lattice by the guest molecule.

1.2.2 Singlet–triplet optical transitions

When considering triplet states of molecules interacting with radiation it is appropriate to start with eigenfunctions of the Hamiltonian $H_m + H_D + H_{so}$, where H_m is a Born–Oppenheimer electronic Hamiltonian whose eigenstates are the ϕ_e having species Γ_e in the point groups of the nuclear configurations specified in the function ϕ_e: each eigenstate of $H_m + H_D + H_{so}$ is a spin-electronic state $\phi_e \sigma$ having a definite symmetry species in this point group, but the spin is not an eigenstate of H_D. In the harmonic approximation the vibrational wavefunctions F_{ev} can be symmetry classified in the point group of the equilibrium nuclear configuration to species Γ_v^0. For a given $\Gamma_e \times \Gamma_v^0$ the species of the three triplet substates are $\Gamma_e \times \Gamma_v^0 \times \Gamma_\sigma$ where σ assumes the species of the three axial vectors. The eigenfunction, however, cannot be written as a product ψ_{evs} of the vibronic and a spin part, but is instead

$$\psi_{ev\sigma} = \sum_{e',v',s} c(ev\sigma \mid e'v's)\, \psi_{e'v's}; \ \Gamma = \Gamma_e \times \Gamma_v^0 \times \Gamma_\sigma$$

where s includes the eigenstates of H_D — σ_x, σ_y and σ_z — as well as the singlet spin function s. The intensity of an electric dipole transition from ψ_{000} to an excited state $\psi_{ev\sigma}$ for light plane polarised in the space-fixed direction α is obtained from:

$$\boldsymbol{\alpha} \cdot \langle \psi_{000} \mid e\boldsymbol{r} \mid \psi_{ev\sigma} \rangle =$$

$$c(000 \mid 000)\, c(ev\sigma \mid 000)\, \mu_{00;00} \cdot \boldsymbol{\alpha} \tag{1.1a}$$

$$+\ c(000 \mid ev\sigma)\, c(ev\sigma \mid ev\sigma)\, \mu_{ev;\, ev} \cdot \boldsymbol{\alpha} \tag{1.1b}$$

$$+ \sum_{e'',i'} c(000 \mid 000) \, c(ev\sigma \mid e'v'0') \mu_{00;e'v'} \cdot \mathbf{a} \tag{1.1c}$$

$$+ \sum_{e'',i'\sigma'} c(000 \mid ev\sigma') \, c(ev\sigma \mid e'v'\sigma') \mu_{ev;e'v'} \cdot \mathbf{a} \tag{1.1d}$$

$$+ \sum_{e'',i'} c(000 \mid e'v'\sigma) \, c(ev\sigma \mid ev\sigma) \, \mu_{ei;e'i'} \cdot \mathbf{a} \tag{1.1e}$$

$$+ \sum_{e'v'\sigma'} \sum_{e''v''} c(000 \mid e'v'\sigma') \, c(ev\sigma \mid e''v''\sigma'') \mu_{e'v';e''v''} \cdot \mathbf{a} \tag{1.1f}$$

The first two terms (1.1a) and (1.1b) are those involving the permanent dipole moments of ground and excited states[16]; the term (1.1c) describes the contribution from singlet–singlet transition amplitudes due to spin–orbit coupling with singlets; terms (1.1d) and (1.1f) only occur beyond second order; in term (1.1e) the source of transition amplitude is the triplet–triplet absorption. The ordinary Herzberg–Teller coupling between states of the same spin is included by expanding the wavefunctions ϕ_e and $\phi_{e'}$ about an equilibrium nuclear configuration, and in a categorisation introduced by Albrecht[17] the transitions that are due to the parts linear in the displacement are named vibronic-spin–orbit terms. The symmetry of the vibrational coordinates that can appear in the spectrum are restricted to those for which $\Gamma_v^0 = \Gamma_e^0 \times \Gamma_{e'}^0 \times \Gamma_{e''}^0 \times \Gamma_\sigma^0$ (if they exist[18]) in the point group of the equilibrium configuration where $\Gamma_{e'}^0$ is the species of some state other than $\phi_{e'}^0$ to which there is a dipole transition from ϕ_0^0. Since Γ_e^0 and Γ_σ^0 are understood to be specified by the problem, the possible values of Γ_v^0 are readily tabulated. Common forms for (1.1) are obtained by using approximate sum-rules over vibrational states, and first-order perturbation theory[19].

1.2.3 The $k = 0$ states of a triplet Frenkel exciton[22]

As discussed above, the exciton bands of molecular solids are dependent not only on the matrix elements of the intermolecular potential as in spinless states of crystals but also on the internal magnetic interactions between unpaired spins and between spin and orbital motion. Since the energies depend on all these interactions it is not obvious, *a priori*, how to choose the principal directions of the fine structure tensor. The spin quantisation axes or planes are dependent on the excitation jump time and the molecular fine structure energies. The linewidths for low temperature crystal electronic (zero-phonon) spectra are usually in the range 0.3–3.0 cm^{-1} at 4.2 K. Many molecular crystals show no factor-group splitting, so in these cases the zero-field splitting and the intermolecular interactions are both less than the line-width and it is no longer obvious whether the triplet level will behave in external fields as a dilute mixed crystal or as an exciton.

We consider the general case of a crystal having n molecules ($\mu, \nu, \ldots, n$) per unit cell. These molecules are interchanged by certain of the factor-group symmetry operators, $R_\mu, R_\nu, \ldots$, etc., with R_μ as the identity. The spatial eigenfunctions $\mid i \rangle$ for a crystal excited state are readily constructed for $k = 0$ in terms of the n site functions $\mid \mu \rangle, \mid \nu \rangle, \ldots, \mid n \rangle$

$$\mid i \rangle = n^{-1/2} \sum_R \chi_i(R) R \mid \mu \rangle$$

$$R\mu \mid \mu \rangle = \mid \mu \rangle; \quad R\nu \mid \mu \rangle = \mid \nu \rangle; \text{ etc.}$$

The irreducible representations of the factor group are labelled by the index i. $\chi_i(R)$ is the matrix of the operator R in the irreducible representation i. The effect of the rotation operators (R) on the site functions is as shown. For a triplet level we can follow the same procedure as above but utilise the zero-field spin states of the site functions as the basis. Thus for spin component α $(= x, y$ or z, chosen to coincide with the principal axes of $\langle H_D \rangle$ of a molecule at one of the sites) we have

$$| i\alpha \rangle = n^{-1/2} \sum_R \chi_i(R) R | \mu_a)$$

where $| \mu_a)$ is an μ-site triplet state having a spin function σ_α ($\alpha = x_\mu, y_\mu$ or z_μ), with $S_\alpha \sigma_\alpha = 0$. There are n representations i (where n is the order of the interchange group) and three spin possibilities for each, so there are $3n$ different states $| i\alpha \rangle$. If there were no interactions between the sites, then the energy of $| i\alpha \rangle$ would not depend on i. The matrix of the Hamiltonian containing V (the intermolecular potential) and the fine structure interaction in the $| i\alpha \rangle$ basis is now readily written down using only symmetry:

$$\langle i\alpha | V + H_D | j\gamma \rangle$$
$$= \{ \sum_R \chi_i(R) V_{\mu;R\mu} \langle \sigma_\alpha\mu | \sigma_\gamma R\mu \rangle - D_{\alpha\alpha}\delta_{\alpha\gamma} \} \delta_{ij}$$

All of the $(3n)^2$ matrix elements are obtained from this formula. The $3n \times 3n$ is already blocked by symmetry into n 3×3 matrices, one for each factor-group representation. The elements that lend physical insight are those involving the excitation exchange interaction $V_{\mu;R\mu}$ between molecules at μ sites and those at $R\mu$ sites. The effect of this interaction on the energy levels depends critically on the spin alignment in the two sites. In general the quantity $\langle \sigma_\alpha\mu | \sigma_\beta R\mu \rangle$ is not zero; it represents the projection of an α spin of the μ site on to a β spin of the $R\mu$ site. It follows that if $V_{\mu;R\mu}$ is large, and if $\langle \sigma_\alpha\mu | \sigma_\beta R\mu \rangle$ is non-zero for some α, β, $R\mu$, then a new set of principal axes for spin arise — namely the triplet exciton principal axis system. $D_{\alpha\alpha}$ is a principal value of the fine structure tensor for the direction α in the molecule. When $D_{\alpha\alpha}$ is small compared with the matrix elements of V, the triplet exciton picture described by Sternlicht and McConnell[7] is recovered. In this limit the intermolecular interaction is large enough to ensure that in zero-field the triplet spins are quantised with respect to crystallographic symmetry directions. An application of this theory to the case of crystals having two molecules per unit cell is given in the appendix of Ref. 22. The detailed band structure, its spin properties and the energy transfer processes will depend in the projections of the spin quantisation planes of one molecule on those of another and on the anisotropy in the matrix elements of the intermolecular potential.

1.2.4 Properties of triplet magnetic substates

For the purposes of conventional optical spectroscopy of solids the splitting of the spin states of the vibronic level $\phi_e F_{ev}$ can be described by a spin Hamiltonian

$$H_I \quad \mu_B \ H_\alpha g^{(v)}_{\alpha\beta} S_\beta \ \vdots \ S_\alpha D^{(ev)}_{\alpha\beta} S_\beta$$

where H_α is the α-component of a laboratory magnetic field, $g^{(ev)}{}_{\alpha\beta}$ is the g-tensor for the given vibronic level factor, μ_B the electronic Bohr magneton and S_α the operator for the electron spin. The effect of H_{so} in mixing states of $H_m \cdot H_D$ having different spin accounts for the difference between g_e and the $g^{(ev)}{}_{\alpha\beta}$. $D_{\alpha\beta}$ is an element of the fine structure tensor that is determined in theory by spin spin interactions (H_D) and second order spin orbit (H_{so}) energy shifts of the states $\phi_e F_{ev} \sigma$:

$$D^{(ev)}_{\alpha\beta} \quad F_{ev} \ D^{(e)}_{\alpha\beta}(R) \ \vdots \ F_{ev}$$

where $D^{(e)}{}_{\alpha\beta}(R)$ is the calculated value of $D_{\alpha\beta}$ at nuclear configuration R in Born–Oppenheimer electronic state ϕ_e, and F_{ev} are the anharmonic oscillator solutions to the Born–Oppenheimer nuclear motional equation, so that:

$$D^{(ev)}_{\alpha\beta} \quad D^{(e)}_{\alpha\beta}(R_0) \cdot \left[\frac{\partial D_{\alpha\beta}}{\partial R_\mu}\right]_0 \ F_{ev} \ R_\mu \ F_{ev} \ + \tfrac{1}{2} \left[\frac{\partial^2 D_{\alpha\beta}}{\partial R_\mu^2}\right]_0$$
$$\times \ \langle F_{ev} | R_\mu^2 | F_{ev} \rangle \ + \ \ldots$$

The various derivatives of D should often be amenable to a simple theoretical evaluation: for example, if these tensor elements are due to spin–spin interaction they may be calculated from a point charge model and using constant spin densities to obtain an explicit dependence on the nuclear coordinates. Such calculations are needed in order to understand the temperature dependence and isotope effects on zero-field splittings. In the harmonic approximation only the even terms remain. The variation of spin density with R finds a description in conventional vibronic coupling theory in which wavefunctions are understood to be expandable in terms of R dependent superpositions of the complete set of equilibrium electronic distributions. In cases where the two electronic states are nearby or there is a near degeneracy, a rather strong dependence of all spin dependent properties on the nuclear motion is expected.

In a discussion of the optical properties of space oriented triplet states in high magnetic fields it is useful to work with the spin basis functions σ_α, σ_β, σ_γ corresponding to the achievable space-fixed directions α, β, γ, such that $S_\alpha\sigma_\alpha = 0$, $S_\alpha\sigma_\beta = i\sigma_\gamma$, etc.; then assuming $g\beta H \gg | \ D \ |$, the off-diagonal couplings through $S_\alpha S_\beta D_{\alpha\beta}$, etc., can be treated using perturbation theory. For a magnetic field along α, the spin wavefunction of the unshifted line ($m_s = 0$) is:

$$\sigma_\alpha \quad \sum_i \sigma_i \ \langle \sigma_i | \sigma_\alpha \rangle \quad \sum_i \sigma_i \cos \theta_{\alpha i}$$

in terms of the molecular frame axes $i \quad x, \ y$ and z. The lines shifted by $\pm g\beta H$ correspond to the spin-states:

$$2^{-1/2} [\sigma_\beta \ \pm \ i\sigma_\gamma] \quad 2^{-1/2} \sum_i \sigma_i [\cos \theta_{i\beta} \pm i \cos \theta_{i\gamma}]$$

Electronic transitions from an equilibrated distribution of molecules in these spin states, say to a ground state $| 0v0 \rangle$, have transition amplitudes [via equations (1.1)] determined by which molecular axis components of the

spin can couple with singlet states that can interact with the radiation field. For example, if only one molecular component state i radiates, the ratio of intensity in transitions from $m_s = -1$ and $m_s = 0$ is:

$$I_{-1}/I_0 = [1 - \cos^2 \theta_{iz}/2 \cos^2 \theta_{iz}] \exp (g\beta H/kT)$$

For low-temperature absorption spectra the Boltzmann factor is unity. If more than one i-state is involved there is interference amongst the component amplitudes. The Zeeman spectra of separated branch crystal states ($k = 0$) are simpler in practice since α, β and γ can be chosen parallel to the principal magnetic axes of the triplet exciton just by orienting a crystal in the magnetic field. Since the crystal spin states are superpositions of the σ_i's for different molecules, even in the absence of external fields the intensity pattern of the transitions to the $k = 0$ levels of different branches depends on which terms in equations (1.1) are operative in the molecule. Thus the radiative power of electronic transitions to the various molecular spin states can be determined directly from the field free absorption spectra of crystals that display a Davydov splitting[20-22]. When there is no Davydov splitting the various branches overlap within the optical resolution and the patterns of the optical spectra in magnetic fields revert to those expected for dilute mixed crystals.

Optical spectroscopy is also useful for determining the ordering of zero-field substates[22], and is most useful for this purpose when one component of $D_{x\beta}$ is much larger than the others, in which case its energy relative to the other two can be obtained to an accuracy of $ca.$ 0.04 cm^{-1} even if the spectral linewidth is $ca.$ 1 cm^{-1}. At intermediate high fields, when $g\beta H \approx 10 \cdot D$, the relative intensity of transitions to the nearly $m_s = \pm 1$ states for field orientation H_γ ($\gamma = x, y$ or z) provides the sign and approximate magnitude of the zero-field splitting, from:

$$\frac{I_{+1}}{I_{-1}} = [\{1 + \Omega(H_\gamma)\}/\{1 - \Omega(H_\gamma)\}]$$

where the $\Omega(H_\gamma)$ are given by $[\Delta E_\gamma/(4g\beta H_0 \cdot 2D_{\gamma\gamma})]$ for an energy separation of ΔE_γ between the α and β spin substates. The errors involved in this method are large and despite earlier optimism it is not recommended unless D is large or unless it is just the sign that is needed. Of course, this technique can be applied to higher excited vibronic states for which conventional e.p.r. or optically detected magnetic resonance is not yet possible.

Many details of the radiative and non-radiative properties of the substates of the zero-point vibrational level of the lowest triplet are known from optically detected magnetic studies of crystals and mixed crystals at low temperature. This field grew considerably[23] after the innovative work of van der Waals[24] showing how the independent radiative properties of the substates can be obtained by cooling crystals to the point where the spin-lattice relaxation is slowed down relative to radiative lifetimes. Subsequent microwave studies have contributed to the spectroscopic assignments of both the emitting states and the vibrational levels of the ground state. The vibrational assignments can be made from $\Gamma_i^0 - \Gamma_e^0 = \Gamma_{e'}^0 - \Gamma_0^0$ since σ and e are often both identified by the experiment assuming the observed radiative power derives from spin-orbit coupling. Of course, information about radiative coupling mechanisms is readily and quickly obtained from optical

Zeeman effect studies of absorption or luminescence transitions on the basis of this same assumption.

1.2.5 Electric field effects on triplet states in solids[22,25]

In the first approximation a uniform external electric field does not mix different eigenstates of the spin Hamiltonian $\langle H_D + H_{so} \rangle$. The complete contribution to the energy due to field sources outside the crystal is

$$H_\epsilon = -e\varepsilon_\mu r_\mu - e\,(\nabla_\mu\varepsilon_\nu)\,r_\mu r_\nu$$

It has not yet proved possible to obtain *laboratory* field gradients large enough to bring out effects due to the quadrupole moments of excited states, although the non-uniform fields of charges from nearby molecules undoubtedly contribute to spectral shifts in solid state spectra. The energy shift of a spectral line due to the field ε_α at the molecule is:

$$\Delta E = -\varepsilon_\mu\,\Delta\mu_\mu - \tfrac{1}{2}\,\varepsilon_\mu\,\varepsilon_\nu\,\Delta\alpha_{\mu\nu} + \ldots$$

Thus electric dipole moment and polarisability changes occurring on excitation may be measured by optical spectroscopy. In centrosymmetric crystals there can be no net energy change linear in the field, but a splitting is observed: one half of the molecules in a given state have their energies raised and the other half are stabilised by an equivalent amount. The perturbation H_ε also mixes states that have different parity, thereby providing a means of discovering otherwise unseen states. Fields up to *ca.* 10^6 V cm^{-1} can be achieved in molecular crystals and energy shifts of at least *ca.* 10^{-3} cm^{-1} can be measured by means of modulation techniques. Thus dipole moment changes of as little as 10^{-4} D and polarisability changes as little as *ca.* 3×10^{-24} cm^3 can be measured[25].

The states of the crystal spin Hamiltonian may be severely modified by the presence of a uniform electric field in the crystal. This is readily seen by considering the states of just two molecules related by symmetry (i.e. physically identical) but not having equivalent orientations in the laboratory frame. When the excitation exchange interaction exceeds the fine structure splitting, the spin is quantised along symmetry directions common to both molecules and the fine structure constants are different from those in the molecular principal axis system even if there are no spin-dependent interactions between molecules. Now imagine an electric field to be directed along a laboratory axis that intersects the molecules differently, e.g. the field may be nearly parallel to the dipole moment (*er*) of one molecule but nearly perpendicular to the dipole moment of the other. If *ere* exceeds the excitation exchange interaction then the system becomes essentially that of two nearly isolated molecules and a measurement of the fine structure constants would yield principal axes and values typical of those for the isolated molecule. The effective excitation exchange interaction becomes $\langle V \rangle^2 / |\,ere\,|$ and the molecular fine structure pattern is slightly perturbed. In a crystal the effect of the electric field will be to isolate not an individual molecule but translationally equivalent sets of molecules. Thus the electric field will alter the effective topology of the energy transfer in the crystal.

1.2.6 Luminescence spectra

An important aspect of the spectroscopy of triplet states in crystals is the recognition that the inequalities regarding the excitation exchange interactions and the fine structure constants do not necessarily apply uniformly over the triplet exciton band. Time reversal symmetry requires the degeneracy of exciton levels at specific values of k in the first Brillouin zone[26], so for most three-dimensional molecular crystals the spin quantisation scheme will vary with the k-state. The property is not important for the study of $k \approx 0$ absorption spectra, but it is important for luminescence work because during the lifetime of the molecular excited state there is usually ample time for scattering into a range of k-states, some of which may be close to the zone boundary or other point where the branches are degenerate in the absence of magnetic forces. In luminescence spectra such processes occur with a relative probability determined as well by the density of exciton states at these special points in the zone.

   At finite temperatures and weak exciton–phonon interactions the luminescence can manifest the various thermally accessible k-states of the excited electronic level, owing to the possibility of transitions on to the k-states of vibrational exciton levels of the ground state. Accordingly, at finite temperatures there are lineshape and linewidth variations expected for luminescence transitions involving different ground vibrational states.

1.3   SINGLET–TRIPLET TRANSITIONS OF CRYSTALS OF AROMATIC HYDROCARBONS

1.3.1 Benzene

Benzene is expected to have two triplet states at lower energy than the lowest singlet state: $^3E_{1u}$ is calculated to be in the region just to lower energy than $^1B_{2u}$ of the isolated molecule, and $^3B_{1u}$ is expected in the near ultraviolet around 3400 Å. The well known condensed phase phosphorescence spectra of benzene presumably marks the $^3B_{1u}$ state, whereas the O_2-perturbed crystal spectra of Colson and Bernstein[27] most likely display the $^3E_{1u}$.

1.3.1.1 Crystal structure and selection rules

Benzene crystals are orthorhombic, *Phca*, with four centrosymmetric molecules per unit cell[28]. One of the three inequivalent C—H directions is nearly parallel to the b-axis. Since the site symmetry is C_i, all degenerate states are crystal field split into the site representations A_g or A_u. The spatial factor group states for the A_u site state are the B_{1u} (a), B_{2u} (b), B_{3u} (c) and A_u type representations of the D_{2h} factor group[29]. There are therefore twelve spin–orbit states, obtained from the spatial representations (orbital part) after multiplying by the triplet spin representations b_{1g}, σ_a; b_{2g}, σ_b; and b_{3g}, σ_c. Of these 12 states, transitions to nine are allowed in the electric dipole approximation, whereas transitions to the states A_u (σ_a), A_u (σ_b) and A_u (σ_c)

are forbidden. In this notation the spin-state is designated in parenthesis after the direct product of the spatial and spin parts of the factor group state[22] (i.e. the factor group spin–orbit state). As was discussed earlier, these wavefunctions are appropriate whenever the intermolecular interactions leading to exciton exchange are large compared with the splitting of the molecular spin substates at zero magnetic field. One must consider the spin-splittings to be those for a molecule at a crystal site (i.e. C_i symmetry) in the absence of excitation exchange interactions; thus both the D and E spin Hamiltonian parameters must exist in the case of the benzene crystal triplet states.

1.3.1.2　The benzene $^3B_{1u}$ state

The factor group states of the $^3B_{1u}$ state of benzene have been observed by Burland, Castro and Robinson[30] by means of high-resolution phosphorescence excitation spectroscopy. Prior to that work no absorption attributable to the $^3B_{1u}$ state of benzene had been observed other than diffuse oxygen induced absorption[27,31]. The Franck–Condon allowed portion of the spectra of C_6H_6 and C_6D_6 (i.e. the part that would be missing in the gas phase) shows a splitting in the crystal of each vibronic level into at least four transitions. Such a pattern is expected on theoretical grounds if the D and E parameters are very small (see e.g. Ref. 32) compared with the excitation exchange interactions; since the 0–0 transition (at 29 674 cm^{-1} for C_6H_6 and 29 851 cm^{-1} for C_6D_6) is split into four components ranging from -8.1 cm^{-1} to $+6.0$ cm^{-1} from the centre of the band, there is little doubt that this inequality is realised.

The polarisation of the singlet–triplet absorption of the benzene crystal is consistent with an out-of-plane transition moment[33]. If it is assumed that

Table 1.1　Partitioning of intensity amongst the benzene $^3B_{1u}$ exciton states

Spatial state	Spin–orbit factor group state	Relative intensities for three polarisations*			Total intensity %
		I_a	I_b	I_c	
	A_u (σ_a)	0	0	0	
B_{1u}	B_{3u} (σ_b)	0	0	0.0115	3.9
	B_{2u} (σ_c)	0	0.0277	0	
	B_{3u} (σ_a)	0	0	0.1885	
B_{2u}	A_u (σ_b)	0	0	0	46.7
	B_{1u} (σ_c)	0.2785	0	0	
	B_{2u} (σ_a)	0	0.0211	0	
B_{3u}	B_{1u} (σ_b)	0.0130	0	0	3.4
	A_u (σ_c)	0	0	0	
	B_{1u} (σ_a)	0.2124	0	0	
A_u	B_{2u} (σ_b)	0	0.0013	0	46.1
	B_{3u} (σ_c)	0	0	0.2471	

*The relative intensity for a transition to a substate $\Gamma(\sigma_i)$ is given by $\cos^2\theta_{xi}\cos^2\theta_{yi}$ where θ_{xi} is the angle between the x-axis (the polarisation direction, perpendicular to the molecular plane) and the polar axis of the crystal that transforms like Γ. θ_{yi} is the angle between y and i. These angles are obtained from crystallographic data by choosing the z-axis as the C—H direction nearly parallel to b.

the effect of the crystal field is to open up intramolecular spin–orbit coupling pathways that are forbidden in D_{6h} symmetry and that the 'effective' molecular symmetry for such pathways is D_{2h} (with axes as defined in the mixed C_6H_6 and C_6D_6 crystal experiments described below), then the intensity distribution and Zeeman effects of the factor group components can be theoretically predicted[20] from the crystal structure. The predictions, given in Table 1.1, are that there should be observed four transitions (assuming small unobservable spin-splittings), two of which (the B_{2u} and A_u factor group bunches) have about equal strength and carry about 93 % of the total intensity. These predictions involve restriction of spin–orbit coupling to all but the σ_y state of the benzene triplet; if coupling to σ_z is also permitted (in a D_{2h} model the z-axis is taken through the atoms) the additional effect is felt in the B_{1u}, B_{3u} and A_u factor group bunches to about the same extent; thus there is a clear prediction from this analysis that the A_u factor group bunch of states give the most intense transition from the ground state. For a proper analysis there are more subtle effects of interference amongst transition amplitudes, but their inclusion will require a knowledge of the phases of the spin–orbit coupling induced transition moment amplitudes. Unfortunately there have been no spectroscopic assignments for the benzene triplet factor group states since no Zeeman effect work has been done on the Franck–Condon allowed part of the spectrum. From figure 4(a) of Ref. 30 it appears as if the lowest energy factor group component is the most intense and the next one, near the band centre, is just slightly less intense. The remaining lines appear considerably weaker. If the lowest energy line were assigned to the A_u bunch, then the ordering of the states would be inverted from that predicted by recent theoretical calculations by Craig and Sommer[24], so there remains considerable uncertainty in the status of the benzene crystal lowest triplet state that may only be resolved by e.p.r. or Zeeman effects of the zero-point level exciton. Table 1.1 predicts definitive polarisation and Zeeman behaviour that can be readily used to assign all the component states as long as direct spin–orbit coupling within each molecule is causing the intensity of the singlet–triplet transition of the exciton.

The portion of the spectrum that is Franck–Condon forbidden shows no factor group splitting, as expected, and since the zero-field splitting parameters of the triplet spin Hamiltonian are not known for any vibronically excited states of benzene, the proper spin coupling scheme for these levels is not known. The transition 8_0^1 dominates the spectrum, with $\nu_8' = 250 \text{ cm}^{-1}$, $\nu_8'' = 1600 \text{ cm}^{-1}$, and Burland, Castro and Robinson[30] associate the drop in frequency with the predictions of van der Waals, Berghuis and de Groot[32] regarding the involvement of ν_8 in a pseudo Jahn–Teller coupling of the $^3B_{1u}$ and $^3E_{1u}$ states.

The Zeeman effect of the 8_0^1 absorption of the benzene crystal[33,35] has confirmed the assignment of the doublet at $0 + 230 \text{ cm}^{-1}$ to two components of an e_{2g} vibration (presumably ν_8). The scheme of Figure 1.1 describes the Zeeman effect of 8_0^1 with a magnetic field down the b-axis of the benzene crystal. The molecular axis (x, y, z) designations for the spins are appropriate in this case because the spin splittings are less than the linewidths. Other transitions, such as 6_0^1 (at $0 + 575 \text{ cm}^{-1}$), have been studied by means of the Zeeman effect[33,35-37] and it is clear that the equilibrium
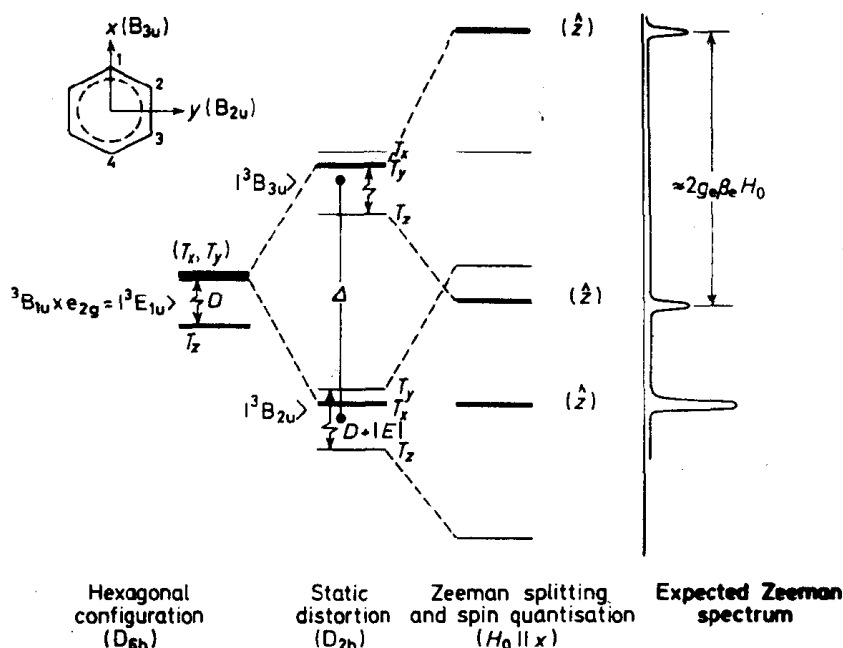
Figure 1.1 Scheme of states for the level involving one quantum of v_8' (e_{2g}) in the $^3B_{1u}$ state of benzene in the presence of a magnetic field along the $b(x)$ axis

symmetry of $^3B_{1u}$ benzene in the benzene crystal is not higher than D_{2h}. The splittings of the e_{2g} modes that occur in the $^3B_{1u}$ state also occur in the $^1B_{2u}$ state of the benzene crystal[38], although to different extents. However, the C—H direction nearly parallel to the b-axis is a principal molecular axis for both $^1B_{2u}$ and $^3B_{1u}$; these splittings are thought to manifest the asymmetry of the crystal field. The distorting effect of what is probably a similar crystal field is also evident in the (spatially non-degenerate) zero-point level of the $^3B_{1u}$ state from e.p.r.[39], ENDOR[40], optical[41] and optically detected magnetic resonance[42] studies of the phosphorescent state of C_6H_6 at low temperatures. Hutchison and Goncalves[40] have shown that in the zero-point vibrational level of C_6H_6 ($^3B_{1u}$) in a C_6D_6 host the symmetry manifested is at most C_i, consistent with site symmetry, although magnetic resonance[39,40] and optical[41] data are consistent with an approximate 'quinoidal' structure in which two nearly parallel bonds are longer than the remaining four.

1.3.1.3   The benzene $^3E_{1u}$ state

Colson and Bernstein[27] identified an oxygen-sensitive absorption of the benzene crystal at ca. 2700 Å which they attributed to $^3E_{1u} \leftarrow {}^1A_{1g}$. Because $^3E_{1u}$ has orbital angular momentum, the additional terms $B_\alpha L_\alpha$ and the crystal field effect must be included in the Hamiltonian used to describe the spin states of the crystal in the presence of a magnetic field. There are expected to be two potential curves along the v_8 coordinate due to a Jahn–
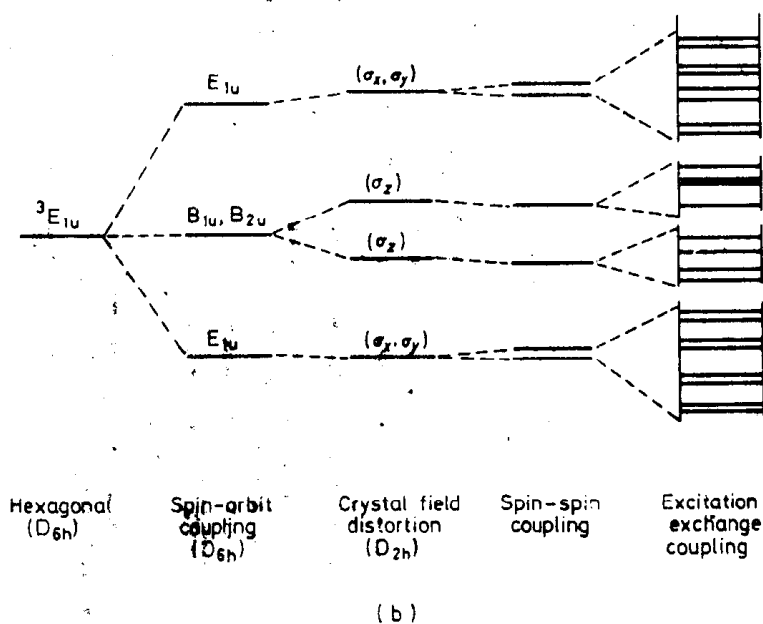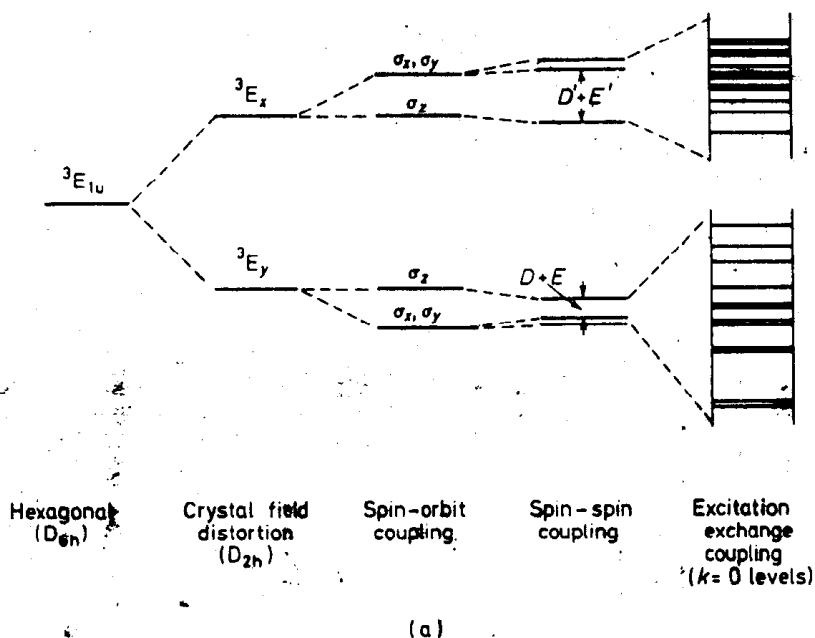
Figure 1.2 The effect of crystal field mixing and spin–orbit coupling on the fine-structure of triplet exciton levels of benzene in $^3E_{1u}$. (a) Crystal effects dominate. Only the $k = 0$ levels of the exciton bands are shown. All $k = 0$ levels will show a first-order Zeeman effect at fields for which $g\beta H$ exceeds the fine structure split-tings. (b) Spin–orbit coupling dominates. Only the $k = 0$ levels of the bands are shown. Note that only two of the bunches of states will exhibit a first-order Zeeman effect

Teller effect[32,43,44] and these are inequivalent in the crystal field since the site symmetry does not contain a reflection plane. Thus there is a site splitting into two sets that are each subject to excitation exchange interactions. In addition, the $^3E_{1u}$ spin multiplets are determined by first-order spin–orbit coupling as well as spin–spin and second-order spin–orbit interactions in rather a similar fashion to a $^3E''$ state of D_{3h} symmetry[45]. There are therefore 24 states associated with the zero-point level of $^3E_{1u}$ in the benzene crystal and 48 with each level involving a degenerate vibration. Theory[44] predicts a very small Jahn–Teller effect for the $^3E_{1u}$ state, and the expected states of the crystal are shown in Figure 1.2 for the case when the crystal field splitting exceeds the factor group splitting of the levels. For this case the fine structure splitting, assumed small compared with the excitation exchange interaction, is different in those factor group states arising from different crystal field components because of the symmetry allowed spin–orbit interaction through L_z. Evidence that the crystal field splitting will be significant is obtained from the aforementioned observation of splittings of the e_{2g} vibrational states of both $^1B_{2u}$ and $^3B_{1u}$. The conceivable situation with spin–orbit interactions exceeding all other effects is also sketched in Figure 1.2. Colson and Bernstein[27] located two very broad transitions at 36 947 and 37 496 cm^{-1} for C_6H_6 which they ascribed to a $^3E_{1u} \leftarrow {}^1A_{1g}$ molecular transition. The presence of a triplet state of benzene corresponding to the Colson–Bernstein system was confirmed using phosphorescence excitation, and a magnetic sensitivity of the absorption was observed[33,36] as a line broadening in a Zeeman effect experiment at $H_b = 105$ kg.

1.3.2 Naphthalene

The lowest triplet state of the naphthalene crystal corresponds to the $^3B_{2u}$ molecular state with the spatial wavefunction transforming like the short in-plane polar vector. The crystal symmetry is $P2_1/a$ with two centrosymmetric molecules per unit cell[46]. All molecular u-states become A_u site states, and each A_u site state maps on to the representations A_u and B_u of the C_{2h} factor group. The spin functions of the crystal transform like the a_g and b_g (σ_a^*, σ_c^*) representations of the factor group, so transitions to all six of the triplet exciton states are allowed, those of type A_u (σ_t) being polarised along the b-axis and those of type B_u (σ_t) polarised perpendicular to b.

All six of the states of the factor group have been observed in the Zeeman effect experiments[47]. The A_u and B_u bunches of states were first observed by Hanson and Robinson[48]; later polarisation measurements by Castro and Robinson[49] using phosphorescence excitation gave results consistent with the overall pattern of intensities predicted from theory[20]. The Zeeman results are not in perfect agreement with the calculation (see Table 1.2) based on only one radiative state (σ_y) presumably because of the weak radiative power of at least one other substate of the molecule, but the agreement is qualitatively correct and the assignments of the spatial parts of the lowest triplet exciton states of the crystal are secure. The high-resolution photoexcitation spectrum of the naphthalene crystal[49] exposes the vibrational structure of the first triplet. The strong Franck–Condon allowed part of the spectrum