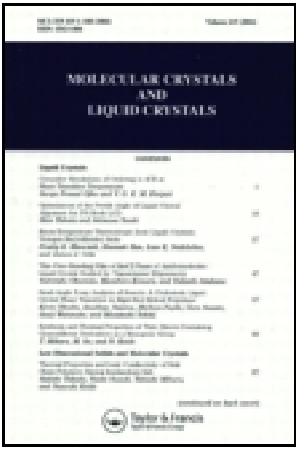

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Triplet Exciton Dynamics in Hexachlorobenzene Single Crystals

G. A. George [a] [b] & G. C. Morris [a]

[a] Department of Chemistry, University of Queensland, St. Lucia, 4067, Queensland, Australia

[b] Department of Supply (Aust.) Student

To cite this article: G. A. George & G. C. Morris (1970): Triplet Exciton Dynamics in Hexachlorobenzene Single Crystals, Molecular Crystals and Liquid Crystals, 10:1-2, 115-135

To link to this article: http://dx.doi.org/10.1080/15421407008083490

Molecular Crystals and Liquid Crystals. 1970. Vol. 10, pp. 115–135

Printed in Great Britain

Triplet Exciton Dynamics in Hexachlorobenzene Single Crystals

G. A. GEORGE‡ and G. C. MORRIS

Department of Chemistry
University of Queensland
St. Lucia, 4067
Queensland, Australia

Received December 4, 1969

Abstract—The singlet–singlet excitation spectrum of triplet exciton phosphorescence for pure single crystals of hexachlorobenzene is reported and compared with the direct absorption spectrum. The observed antibatic behaviour is explained by a mechanism of diffusive random walk of the triplet exciton with surface quenching. No singlet exciton dominated rate processes were detected. The measured diffusion coefficient $D_{c^*c^*}$ perpendicular to the *ab* plane was 2.4×10^{-5} cm^2 sec^{-1}. The diffusion coefficient for charge carriers was measured to be 10^{-2} cm^2 sec^{-1}. The mobilities of these charge carriers were $\mu_+ = 1.2$ cm^2 V^{-1} sec^{-1} and $\mu_- = 0.96$ cm^2 V^{-1} sec^{-1}. The temperature dependence of $D_{c^*c^*}$ was studied. There was no evidence for long-range trap-to-trap migration of the exciton. Above 115 °K no temperature dependence of the mean free path was observed. From the measured spectral band width of the polarized absorption spectrum the mean exciton scattering time was calculated as 2.4×10^{-14} sec. The combined coulombic and exchange interaction energy of the triplet excited molecule and its nearest neighbour along the c^* direction was 1 cm^{-1}.

1 Introduction

In the study of energy transport phenomena in molecular crystals, the triplet exciton has assumed an important role. As a mobile neutral excited state of the crystal, the triplet exciton may be used to probe, by diffusion and annihilation experiments, the nature of both the scattering mechanism and the intermolecular electronic interactions. These latter determine the triplet exciton band structure in a molecular crystal and, in the one electron

---

‡ Department of Supply (Aust.) Student

approximation, consist of coulombic interactions, exchange interaction, and an additional contribution from configuration interactions of the triplet exciton state with charge transfer exciton states. In aromatic crystals, the electron exchange interactions (of the order 5–15 cm^{-1}) provide the dominant contribution to the total triplet interaction energy.[1]

These relatively small electron exchange interactions between adjacent molecules in the crystal determine the rate of migration of the triplet exciton. Two models to describe the exciton motion have been used. In the coherent motion band model, the mean free path of the exciton is much greater than the lattice spacing. The exciton migration length is limited only by exciton-phonon or exciton-defect scattering. In the diffusive motion random walk model the strong scattering leads to a mean free path of the order of a lattice spacing. Which of the two extreme models best describes the triplet exciton migration in aromatic crystals cannot be decided on the basis of measurements of diffusion coefficients as pointed out by Avakian *et al.*[2] But since the mean free path of the triplet exciton is typically much less than a lattice spacing, the strong scattering model is appropriate for these crystals.

The haloaromatics provide an interesting case. The coulomb interactions arising from the intramolecular spin-orbit coupling between the triplet state and the perturbing singlet states will provide an important contribution to the triplet interaction energy. This will decrease the radiative lifetime and so reduce the number of transfers of triplet excitons per radiative lifetime.‡ It will also reduce the extent of the bimolecular reaction—triplet–triplet annihilation which can give rise to delayed fluorescence. The observation of delayed fluorescence of anthracene following direct triplet excitation led to intensive study of the triplet

‡ The long triplet exciton radiative lifetime (on the order of seconds for aromatic crystals) results in a large number of transfers ($\sim 10^{10}$) per radiative lifetime. In contrast, for singlet exciton states, coulombic terms dominate and result in intermolecular interaction energies of the order 10^2 to 10^4 cm^{-1}. But the short radiative lifetime ($\sim 10^{-5}$ sec) limits the number of transfers per radiative lifetime to about 10^5.

exciton migration processes in this crystal.[3] Triplet exciton diffusion coefficients and mean free path lengths, triplet exciton annihilation processes and exciton band structures have been determined by space intermittency techniques,[4] triplet surface quenching[5,6] methods and spectroscopic methods.[2] In all cases the delayed crystal fluorescence has been used as a passive probe. Very few studies have been carried out on crystals other than anthracene. A severe disadvantage in the use of anthracene and other simple aromatics is that triplet emission cannot be readily studied directly. The triplet–triplet annihilation responsible for the characteristic delayed fluorescence reduces the phosphorescence quantum yield to less than 10^{-4}.[7] However, addition of a heavy atom, such as a halogen to the carbon skeleton reduces the triplet exciton radiative lifetime by a factor of 10^4.[8] Triplet exciton phosphorescence spectra from halogenated benzene single crystals can be more readily observed and have been reported for pure crystals at 4 °K.[9,10]

We have investigated triplet exciton migration in single crystals of hexachlorobenzene by surface quenching of phosphorescence. The absence of triplet–triplet annihilation allows use of a simple treatment to obtain $D_{c^*c^*}$, the diffusion coefficient perpendicular to the *ab* plane, from the excitation spectrum of crystal phosphorescence. We are also able to explain the observed phosphorescence excitation spectrum by a mechanism of diffusive random walk of the triplet exciton with surface quenching and obtain the magnitude of the interaction energy between the excited molecule and its nearest neighbour along the c^* direction.

2 Experimental

Light from a 1600 V.A. Xenon lamp was filtered through 5 cm of water and a Dow Corning CS7-54 broad band pass filter and monochromated by a Spex 1702 scanning spectrometer (0.75 m Czerny Turner, dispersion 11 Å/mm). A low photon flux ($<10^{11}$ photons cm^{-2} sec^{-1}) was maintained by diffusely focusing exciting light on the crystal.

Emitted phosphorescence from the front face of the crystal was detected through a CS5-74 filter by an E.M.I. 6256S photomultiplier, amplified and displayed. D.C. Electrometer amplification or phase sensitive detection were employed. Phosphorescence could also be separated from scattered light and fluorescence by a single blade 25 Hz chopper (giving excitation and observation periods of 20 m sec) and small monochromator (Jarrell Ash 0.25 m Ebert, dispersion 32 Å/mm). Triplet decay was measured using either chopping or single switching, the photomultiplier output being displayed on a Tektronix 561A C.R.O. and photographed.

The spectral distribution of the source, excitation optics and monochromator were obtained using either a sodium salicylate coated plate as a quantum counter[11] or a calibrated thermopile Hilger-Schwarz type (1 μV/μW). Absorption spectra were obtained photoelectrically using the Spex spectrometer. Corrections to constant photon flux, calculation of absorption coefficients and plotting of corrected spectra were carried out by computer.

Crystals were cleaved from melt grown chemically purified and zone refined hexachlorobenzene (HCB)[10]. Sample purity was checked by the melting curve, mass spectrum and emission spectrum at 4 °K. No impurities could be detected.‡

Thin crystals for absorption were obtained by fusing the melt between Spectrosil discs. Lonsdale[12] reported (001) to be a good cleavage plane for HCB. Secondary cleavage occurs along (100) and $(10\bar{2})$. The predominant cleavage in our melt grown crystals was found from X-ray oscillation photographs to be (001) i.e. the *ab* face is developed.§ All studies were carried out on sample cleaved parallel to this plane.

---

‡ Sample purity is critical in all energy transfer studies. The possibility of C—Cl bond scission occurring in HCB under UV irradiation has been considered in view of the low C—Cl bond energy (66.5 kcal/mole). There has been no evidence found for any change in the spectroscopic properties before and after prolonged irradiation with photon energies used in these experiments.

§ We thank Mr. R. Seccombe for the X-ray study of cleaved HCB crystals.

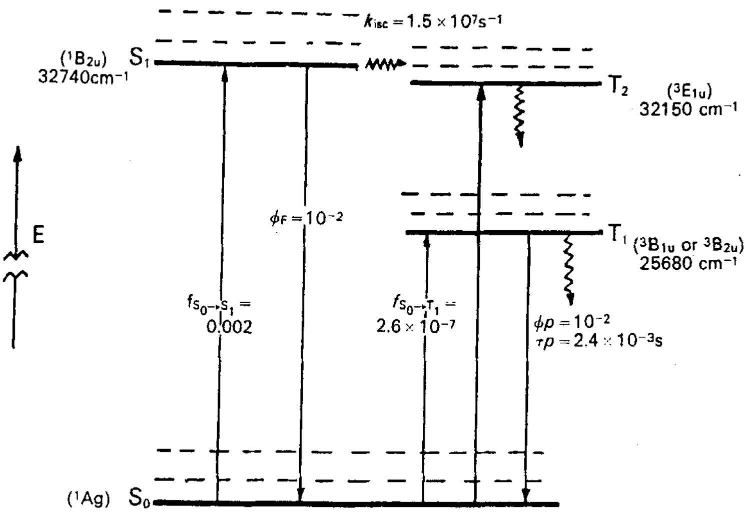

Figure 1. Total state diagram for hexachlorobenzene single crystals.

Liquid helium and liquid nitrogen cryostats were used. Temperature of the crystal could be controlled from 90 °K to 300 °K by a stream of cold nitrogen.

3 Results and Discussion

The properties of the low-lying electronic excited states of the hexachlorobenzene crystal are summarised in Fig. 1[10]. Direct population of the first triplet exciton band is seen to have a low probability ($f \simeq 2.6 \times 10^{-7}$). However it is possible to utilise the more sensitive technique of phosphorescence excitation to obtain the transition energy and vibration structure[13] for the $S_0 \to T_1$ transition. High resolution studies of the triplet state of aromatic molecular crystals have recently been achieved with this technique.[14] The intensity of phosphorescence was proportional to the absorption coeffcient for the process $S_0 \to T_1$.

In the absence of total absorption of the exciting light by the sample, the phosphorescence excitation spectrum is also directly related to the absorption spectrum for $S_0 \rightarrow S_1$ excitation. Such a direct relationship holds as long as intersystem crossing does not occur preferentially from a higher lying vibrational level of S_1 to the triplet manifold.[15]

The $S_0 \rightarrow S_1$ excitation spectrum of the phosphorescence of a thick crystal of HCB does not show this direct relationship. In Fig. 2 is shown the unpolarized absorption spectrum of a 0.5 mm thick crystal of HCB at 7 °K. Also shown is the unpolarized absorption spectrum at 20 °K as reported by Pesteil *et al.*[16] The origin region is omitted because the complexity of the phonon structure built on the origin in the excitation spectrum at the lower temperature makes the comparison of the spectra less obvious. As indicated in the diagram, there is an almost perfect " antibatic " relationship between absorption and excitation spectra (i.e. maxima in absorption intensity corresponding to minima in emission intensity and vice versa).

Antibatic behaviour of the unpolarized fluorescence excitation spectrum of anthracene crystals has been reported by several authors.[17, 18, 19] It has been generally agreed that this arises from singlet exciton diffusion with partial or complete surface quenching.

We suggest that the processes leading to the observed phosphorescence excitation spectrum can be explained by a mechanism of diffusive random walk of the triplet excitons with surface quenching.

3.1. The Exciton Diffusion Equation

Bimolecular processes are unimportant at low light intensities in HCB. This is expected because the free molecule triplet lifetime is short ($\sim 2 \times 10^{-2}$ s). Supporting experimental observations are:

(i) I_p, the measured phosphorescence intensity, shows a first power dependence on the exciting light intensity.

(ii) Non-exponential decay at short times from excitation shut off cannot be observed.

(iii) No delayed fluorescence can be detected under conditions where it would be observable if T–T annihilation occurred.

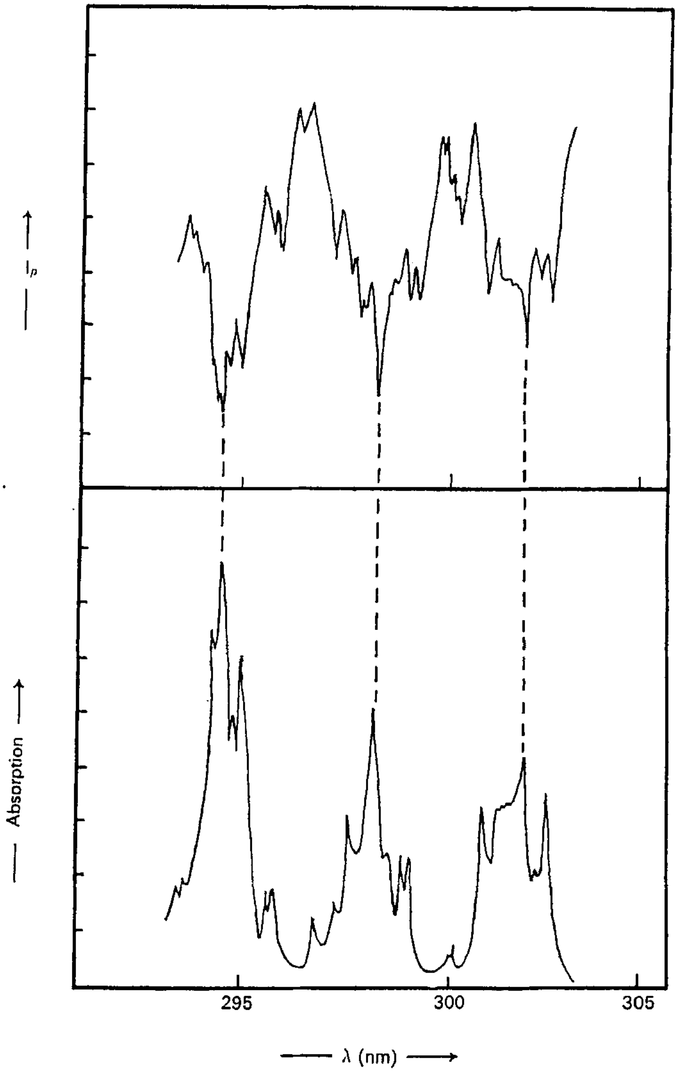

Figure 2. Part of the vibration progression of the optical absorption spectrum (lower curve) at 20 °K and of the phosphorescence excitation spectrum at 7 °K of a hexachlorobenzene single crystal. The transition origin region (3055 Å) is not shown. Dotted line indicates correspondence of maxima in the optical absorption spectrum with minima in the phosphorescence excitation spectra.

The exciton diffusion equation may be simplified in one dimension[20, 21] to

$$\frac{\partial n}{\partial t} = -\beta n + k\alpha I_0 \exp(-\alpha x) + D\frac{\partial^2 n}{\partial x^2} \tag{1}$$

$$= 0 \text{ in the stationary state,}$$

where $n(x)$ is the triplet exciton concentration at depth x, $\beta = 1/\tau_p$ = unimolecular rate constant, k = a constant related to the intersystem crossing quantum yield $S_1 \rightarrow T_1$, α = absorption coefficient in the singlet exciton region, D = diffusion coefficient in the x direction, I_0 = incident photon flux.

The general solution is

$$n(x) = \frac{k\alpha I_0}{\beta - D\alpha^2}\exp(-\alpha x) + A\exp[(\beta/D)^{1/2}x] + B\exp[-(\beta/D)^{1/2}x] \tag{2}$$

The resultant exciton distribution is sensitive to the boundary conditions chosen.[21, 22]

We next consider two extreme sets of boundary conditions which may occur.‡

(i) Complete exciton quenching at the surface of an effectively infinite crystal. (In the singlet absorption region of a thick crystal, the penetration depth $1/\alpha$ is small, so the crystal may be regarded as semi-infinite.)

This leads to

$$\left.\begin{aligned} A &= 0 \\ B &= \frac{-k\alpha I_0}{\beta - D\alpha^2} \end{aligned}\right\} \tag{3}$$

$$n(x) = \frac{k\alpha I_0}{\beta - D\alpha^2}[\exp(-\alpha x) - \exp(-(\beta/D)^{\frac{1}{2}}x)] \tag{4}$$

‡ A situation intermediate between these two extremes in the boundary conditions may well be expected to be operative. Borisov and Vishnevskii[17] assumed that the rate of annihilation is proportional to the concentration of excitons at the surface. This leads to the condition $D(dn/dx) = gn(0)$ where g is an annihilation rate constant. We have chosen to consider only the extreme boundary conditions as they lead to simple relations between I_p and α. It is found that to within experimental error these can explain the observed spectra (Eq. (9)).

(ii) Exciton reflection at the surface.

This leads to

$$\left.\begin{aligned} A &= 0 \\ B &= \frac{-k\alpha^2 I_0}{\beta - D\alpha^2}\left(\frac{D}{\beta}\right)^{1/2} \end{aligned}\right\} \tag{5}$$

$$n(x) = \frac{k\alpha I_0}{\beta - D\alpha^2}\left[\exp(-\alpha x) - \alpha\left(\frac{D}{\beta}\right)^{1/2}\exp(-(\beta/D)^{1/2}x)\right] \tag{6}$$

The integrated phosphorescence intensity I_p, detected by the photomultiplier will be $I_p = K\int_0^\infty n(x)\,dx$, where K is an instrumental and geometrical constant.

Use of the random walk result, that $D = \frac{1}{2}\Delta^2\beta$ (where Δ is the triplet exciton diffusion length), leads to

$$\text{Condition (i)} \qquad I_p = \frac{KkI_0}{\beta(1 + 2^{-1/2}\alpha\Delta)} \tag{7}$$

$$\text{Condition (ii)} \qquad I_p = \frac{KkI_0}{\beta} \tag{8}$$

Boundary condition (ii) predicts I_p to be independent of α. Boundary condition (i) leads to the relation

$$\frac{I_0}{I_p} = \frac{\beta}{Kk}(1 + 2^{-1/2}\alpha\Delta) \tag{9}$$

i.e. the phosphorescence intensity is inversely related to the absorption coefficient.

In Fig. 3 are shown corrected absorption (A) and excitation spectra (B) for *ab* sections of HCB at temperatures of 77 °K and 155 °K. A plot of I_0/I_p vs α is shown for $T = 155$ °K in Fig. 4.

The experimental observations clearly support the use of boundary condition (i)—at least over the range of α and I_0/I_p used in our experiments.

From Eq. (9) above, $\Delta = 2^{\frac{1}{2}}$ (slope/intercept), where Δ applies to diffusion perpendicular to the *ab* plane. The results for temperatures from 77 °K to 210 °K are summarised in Table 1. Above

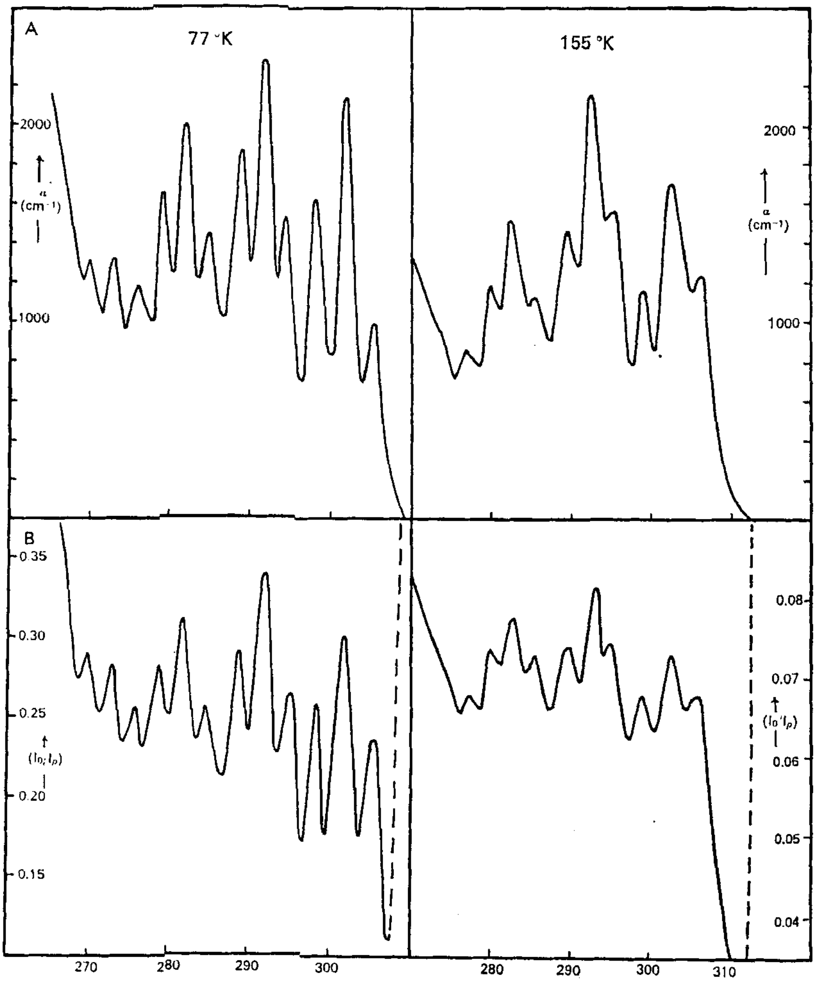

Figure 3. (A). The optical absorption spectrum of hexachlorobenzene single crystals at 77,155 °K; (B) The phosphorescence excitation spectra of hexachlorobenzene single crystals at 77,155 °K.

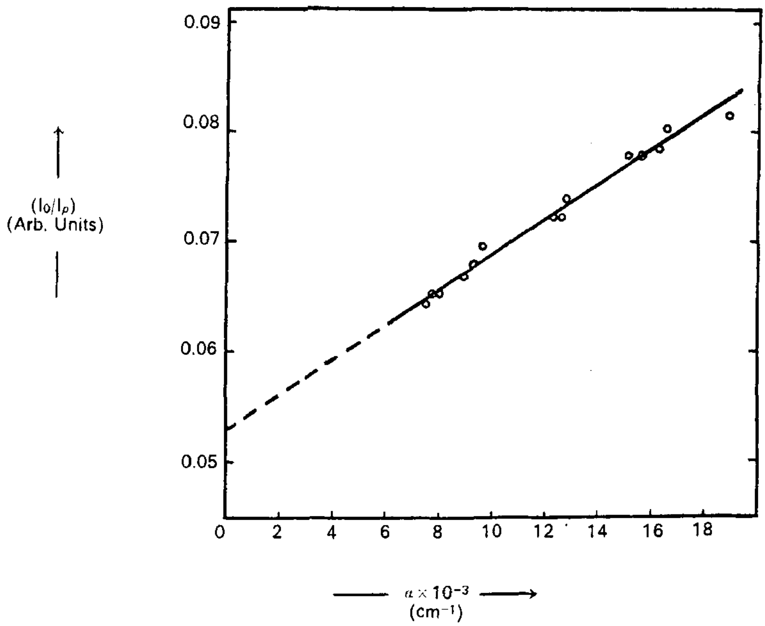

Figure 4. The dependence of I_0/I_p on absorption coefficient for absorption in the singlet exciton region for hexachlorobenzene single crystals at 155 °K. I_0/I_p is the ratio of incident light intensity to phosphorescence light intensity.

TABLE 1 Temperature dependence of the triplet exciton diffusion length, triplet lifetime and phosphorescence excitation maximum in hexachlorobenzene single crystals.

T (°K)	Δ (μ)	τ_p (m sec)‡	$\bar{\nu}_{\max}$ (cm^{-1})§	$\alpha_{\max}$ (cm^{-1})‖
77	8.1 ± 1.5	non exp.	32310	47
95	5.6 ± 1	non exp.	32215	44
115	4.5 ± 1	2.5	32115	44
155	3.0 ± 1	2.4	—	—
190	3.1 ± 1	2.4	—	—
210	4.2 ± 1	2.5	31695	38
265	—	—	31450	40

‡ See Fig. 6. § See Fig. 5(a). ‖ See Fig. 5(b).

the latter temperature, broadening of the vibronic bands prevent an accurate analysis. Taking an averaged value of Δ of 3.6 μ above 115 °K and a lifetime of 2.4 ms (see later) the observed diffusion coefficient $D_{c^*c^*}$ was 2.4×10^{-5} cm^2 sec^{-1}.

3.2. Diffusion of Singlet Excitons and Charge Carriers

The above values of Δ and D are consistent with those expected on the basis of the results for triplet exciton motion in pure aromatic crystals.[23] It is feasible, however, that the antibatic behaviour could result from a singlet exciton dominated rate process although this would imply a singlet diffusion length about 100 times larger than that observed in other crystals e.g. anthracene. Studies of fluorescence excitation spectra of HCB crystals with adsorbed quinine sulphate failed to indicate any singlet dominated process. Since singlet exciton surface quenching can be readily detected by using an adsorbed dye[19] or similar sensitizer[20] on the face of the crystal, we note the lack of experimental support for any singlet dominated process in our triplet diffusion experiments.

It has been suggested from work on anthracene crystals that surface quenching processes used to measure triplet exciton diffusion lengths and diffusion coefficients may in fact measure the migration of charge carriers.[24] It has recently been shown that triplet exciton annihilation can produce charge carriers. Delayed fluorescence then results from electron-hole recombination.[25] Under these conditions the relationships between the triplet exciton distribution and the delayed fluorescence which had been deduced from a direct annihilation mechanism may not hold. Williams and Adolph,[6] however, reported no effect of an electric field on the measured triplet exciton diffusion length in anthracene. It would appear that the probability that charge carriers could be dominating a monomolecular process (i.e. phosphorescence) seems remote. Also, the diffusion coefficient measured in our experiments (2.4×10^{-5} cm^2 sec^{-1}) is much smaller than a typical diffusion coefficient for holes and electrons in anthracene crystals. However, as the value of the diffusion coefficient for charge carriers in HCB has not been reported, we have measured it at room temperature with the crystal in dry air using the Kepler flash technique.[26] Apparatus used was that of Johnston and Lyons.[27] All glass in the system was replaced by synthetic silica. Mobilities obtained for a 1 mm thick *ab* oriented HCB crystal were $\mu_+ = 1.2$ cm^2 V^{-1} sec^{-1}; $\mu_- = 0.96$ cm^2 V^{-1} sec^{-1}. These mobility values lead to a diffusion coefficient perpendicular to the *ab* plane of 10^{-2} cm^2 sec^{-1} (using the Einstein relation[28]). We note that this value is 10^3 larger than the diffusion coefficient measured above.

It is concluded that the results obtained are consistent with triplet exciton migration and surface (or effective surface[21]) quenching.

3.3. THE EXCITATION SPECTRUM MAXIMUM AND THE SINGLET EXCITON ABSORPTION EDGE

The phosphorescence excitation spectrum shows a maximum intensity (corresponding to minimum I_0/I_p in Fig. 4) at wavelengths in the tail of the first singlet exciton absorption band. As shown in Fig. 5(A) this maximum broadens and shifts to lower energy with increase in temperature. In Fig. 5(B) the temperature dependence of the absorption coefficient at the singlet absorption edge has been plotted. The curves illustrate that the absorption follows Urbach's Rule and converge on an energy corresponding to the $S_0 \rightarrow S_1$ pure electronic transition energy. This behaviour has been reported for anthracene.[29] The energies corresponding to the maxima in the excitation spectra at these temperatures are marked on Fig. 5(B). These are summarised in Table 1 in which it is seen that within experimental error, these maxima correspond to an absorption coefficient of about 40 cm^{-1}. This value does not vary greatly from crystal to crystal over the restricted range of thicknesses studied (0.5 mm to 2.0 mm).

We are unable to relate this penetration depth to any physical quantity in the exciton diffusion process. It could correspond to the depth at which excitons can contact the quenching region in their life-time. The absorption coefficient of 40 cm^{-1} corresponds

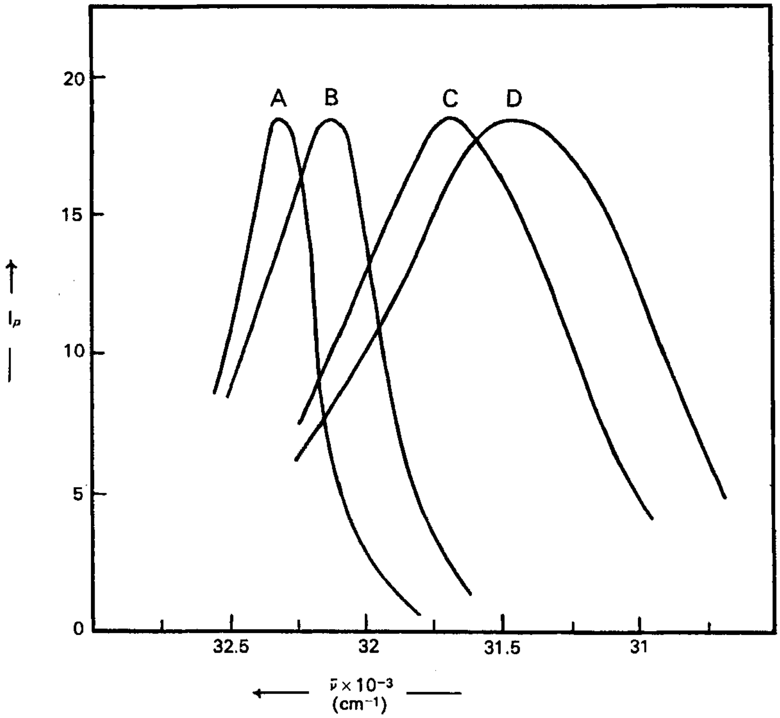

Figure 5(a). Variation of the phosphorescence excitation spectrum for hexachlorobenzene single crystals with temperature at photon energies less than that for the optical transition $S_0 \rightarrow S_1$. Note that the maximum of the phosphorescence intensity shifts to lower energies with higher temperature.

to a penetration depth of 250 μ. This value is of the same order of magnitude as the value (75 μ) which Williams and Adolph[6] have associated with the distribution depth of quenching sites for triplet excitons in cleaved anthracene. Such a value seems very large to us. Certainly in a real crystal many types of imperfections exist e.g. molecular displacements, site vacancies, crystal compressions and so forth. The effect these can have on the optical absorption has been discussed elsewhere.[30] Such imperfections should give rise to exciton traps but we are unable to ascertain

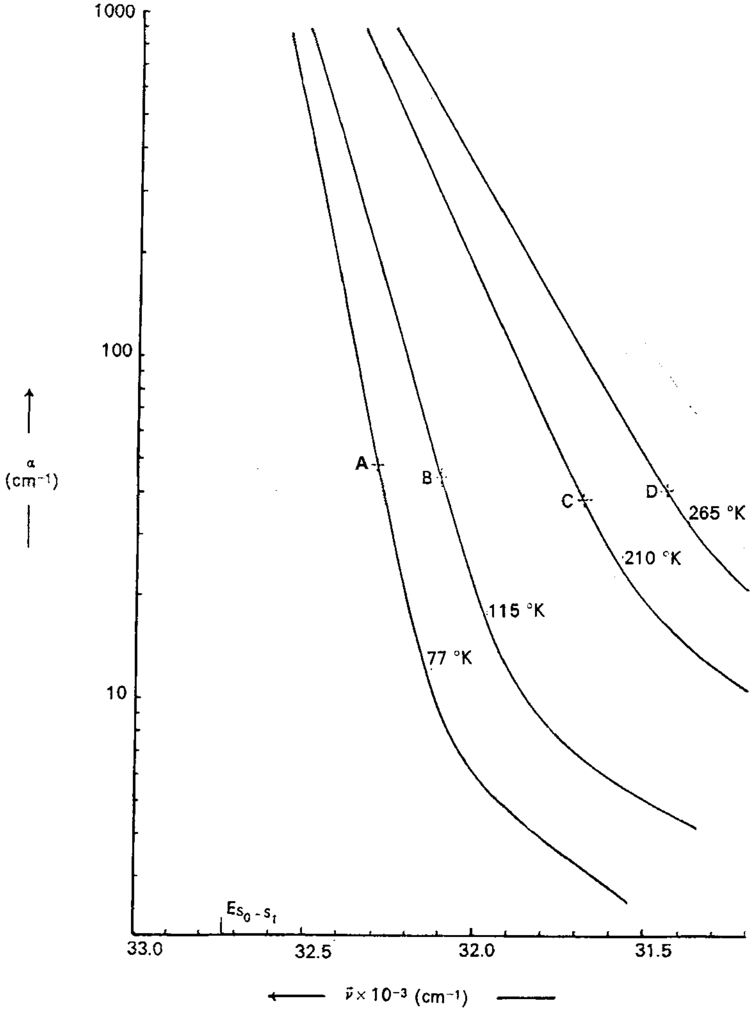

Figure 5(b). The temperature dependence of the absorption edge for the optical transition to the first exciton band in hexachlorobenzene single crystals at various temperatures. $E_{s_0 \rightarrow s_1}$ represents the transition 0—0 band origin. *A*, *B*, *C*, *D* correspond to the energies of the maxima in the normalized phosphorescence spectra of Fig. 5(A).

any relationship between the depth of such traps or the mean distance between them and the value of 40 cm^{-1} (with its corresponding penetration depth of 250 μ) measured from our experiment. While this value cannot be formally related to the triplet exciton diffusion length because of the indefinite limits of integration in this region where the crystal is not effectively infinite, it may indicate that the diffusion length in the absence of surface quenching for the triplet excitons would be ~250 μ. However this leads to an unusually large value of the diffusion coefficient—$1.5 \times 10^{-1}\ \text{cm}^2\ \text{sec}^{-1}$. But we wish to emphasize that this does not invalidate our application of the diffusion equation in the intense absorption region, leading to a diffusion length of ~3–4 μ, as the boundary conditions are then well defined.

Ern[31] has recently measured the anisotropy of the diffusion tensor for anthracene and concluded that $D_{aa} \simeq D_{bb} \gg D_{c^*c^*}$ i.e. migration of triplet excitation energy occurs predominantly in the *ab* plane (equivalent to the *bc* plane of HCB). However, surface quenching experiments on anthracene[5,6] had led to the conclusion that $D_{c^*c^*} \simeq D_{aa}$. This raises severe doubts about the validity of surface quenching experiments. Certainly, the boundary conditions play an important part in the results obtained. We have chosen only the region of intense absorption where the boundary conditions should be well defined. This may overcome some of the possible shortcomings of the surface quenching method.

3.4. TEMPERATURE DEPENDENCE OF THE DIFFUSION COEFFICIENT

Theoretically, the diffusion coefficient is predicted to be temperature dependent for two separate reasons.[1]

(i) The crystal lattice will be expected to contract on cooling so the interaction energies will increase. D will increase.

(ii) The phonon population will alter and the extent of exciton phonon scatter will decrease with decreasing temperature. D will increase.

The experimental diffusion length, Δ, at different temperatures is shown in Table 1. Observed triplet decay curves at selected temperatures are shown in Fig. 6.

It is noted that the region where Δ increases (77–100 °K) is also that where phosphorescence decay becomes non-exponential. The non-exponential behaviour results in an uncertainty in the unimolecular (radiationless) rate constant β. Since $D = \frac{1}{2}\Delta^2\beta$ in the random walk approximation this corresponds to an uncertainty in the diffusion coefficient. There is no proof that D is, in fact, temperature dependent even though Δ does alter with temperature.

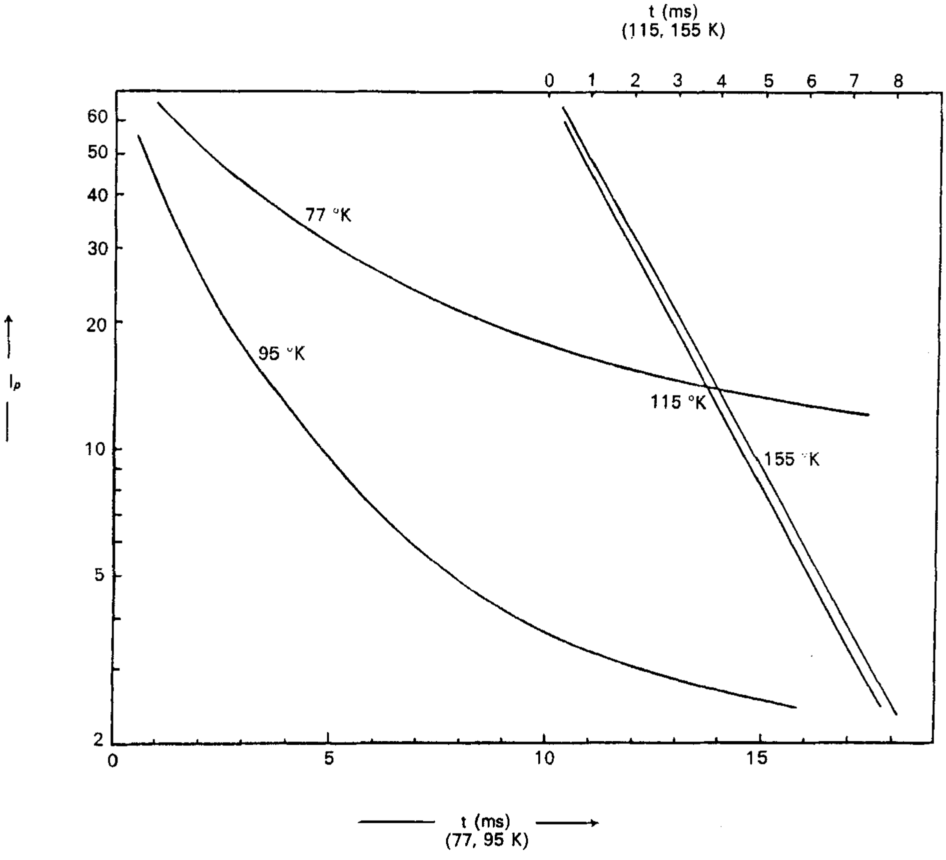

Figure 6. Time decay of the phosphorescence of hexachlorobenzene single crystals at various representative temperatures.

As T is decreased, the bimolecular T–T annihilation probability will increase and will lead to non-exponential triplet decay. However, the non-exponential decay observed here is not explicable in terms of a bimolecular process occurring at short times. It is explicable in terms of deviations from exponential decay at times greater than the exponential half-life. Impurity or defect trapping of excitons is a possible reason for this deviation. There does not seem any evidence for long range trap-to-trap migration of the type observed by Sternlicht *et al.*[32] Such a trap-to-trap migration would require a decrease in D with decreasing temperature.

The only other experimental observation of temperature dependence of the diffusion coefficient has been by Durocher and Williams[33] for anthracene. They observed a decrease with decreasing temperature of the diffusion coefficient both in and perpendicular to the *ab* plane. This is contrary to the theoretical predictions for a pure molecular crystal and our observations in HCB. Avakian *et al.*[2] have emphasised the uncertainty in triplet migration processes at low temperatures. They suggest that the complicated trapping processes could indicate that the simple diffusion equation is no longer applicable. The onset of non-exponential decay in HCB is probably indicative of the breakdown of the simple treatment. We have found no temperature dependence of Δ within experimental error, above ~115 °K (see Table 1).

3.5. INTERMOLECULAR INTERACTION ENERGIES

The crystal structure of hexachlorobenzene is monoclinic, $P_{2_1/c}$, with two molecules per unit cell.[34, 35] Our studies have been confined to *ab* crystal sections because thick crystals can be readily cleaved for excitation studies and also thin samples prepared for absorption spectra. The region of greatest molecular overlap occurs between equivalent molecules along the *b* axis, and inequivalent molecules along the *c* axis. We have studied migration of excitation perpendicular to the *ab* plane, i.e. along the c^* axis.

Triplet exciton migration in simple aromatics has been considered to occur primarily through intermolecular exchange interaction. The coulombic terms in the limit of negligible spin-orbit interactions will be zero. This leads to typical exchange integrals of $\sim 5\ \mathrm{cm}^{-1}$. In HCB the intermolecular overlap integrals will be greatest along the *c* axis (interaction between equivalent and inequivalent molecules). Because of the large separation of 8 Å between molecules at (0, 0, 0) and $(0, \frac{1}{2}, \frac{1}{2})$ in HCB the electron exchange interaction energy will be smaller than the corresponding interaction energy in the *ab* plane of anthracene. This assumes that only nearest neighbour interactions are important when considering exchange energies. In haloaromatics, unlike simple aromatics, spin orbit coupling cannot be neglected. Second order spin-orbit vibronic interactions couple $\pi\pi^*$ transitions to the $S \leftrightarrow T$ transition.[36] This would be expected to bring a substantial coulombic term into the total interaction matrix and enhance the rate of triplet exciton migration in the halo-aromatic.

To obtain some estimate of the triplet interaction energy of HCB along c^*, we follow the work of Avakian *et al.*[2] for anthracene. They have estimated the diffusion coefficient in the *ab* plane from the Davydov splitting in the first triplet region and the $S_0 \rightarrow T_1$ absorption band width.

The component of the diffusion tensor in the c^* direction $D_{c^*c^*}$, is given by

$$D_{c^*c^*} = \tau_s \langle \mathbf{v}_{c^*}^2 \rangle \tag{10}$$

where τ_s is the exciton scattering time and $\mathbf{v}_{c^*}$ the exciton velocity operator along c^*. τ_s is the time an exciton originally created in the $\mathbf{k} \approx 0$ state remains in the state before being scattered out of it. It corresponds to the relaxation time provided it is a constant for all values of $\mathbf{k}$ within the band. τ_s can be approximated as $\hbar/2\Gamma$ (the lifetime of the $\mathbf{k} \approx 0$ state) where Γ is the half-width of the absorption band assumed Lorentzian for the transition $S_0 \rightarrow T_1$ using light polarized along the c^* axis. This is obtained by measuring the band shape of the polarized absorption spectrum (by phosphorescence excitation) for a section cleaved perpendicular to the *ab* cleavage plane i.e. the bc^* face.

Thus $\langle v_{c^*}^2\rangle$ can be calculated from the measured values of $D_{c^*c^*}$ and Γ. Since

$$|\langle v_{c^*}^2\rangle|^{\frac{1}{2}} \simeq \hbar^{-1}|\beta'|c^* \tag{11}$$

the triplet interaction energy β' may be estimated. β' are the transfer matrix elements governing the coherent transfer of triplet excitation from one excited molecule to a near neighbour.

A full width at half maximum of 110 cm^{-1} is observed at 95 °K for HCB polarized $\perp b$ in the bc^* section. This gives an exciton scatter time of 2.4×10^{-14} sec. Using the value of $D_{c^*c^*}$ obtained in this investigation (2.4×10^{-5} cm^2 sec^{-1}) and the crystal data of Tulinsky and White[34] we obtain $\beta' \simeq 1$ cm^{-1}. We note that $2|\beta'| \ll kT$ which is consistent with usage of the above model. This value of β' will represent the sum of electron exchange and coulombic terms for the interaction between the excited molecule and its nearest neighbour along the c^* direction.

No factor group splitting in $S_0 \rightarrow T_1$ of HCB has been observed.[10] It is expected[2] to be about $8\beta'$ i.e. 8 cm^{-1}. However, this technique has enabled the triplet interaction energy to be evaluated without knowledge of the factor group splitting. The calculated splitting will be spread over the total vibronic manifold. The breadth of the observed $S_0 \rightarrow T_1$ absorption in the ab and bc planes limits the observation of factor group splitting,[10] even at 4 °K and high resolution. If calculations were available for the electron exchange interactions the value of β' could be used to estimate the extent of the intramolecular spin orbit coupling between the triplet state and the perturbing singlet states.

Finally, we note that the triplet exciton scattering length ($\tau_s|\langle v_{c^*}^2\rangle|^{\frac{1}{2}}$) is 0.08 Å, a value significantly less than the lattice spacing. This is consistent with our usage of the hopping model.

Acknowledgements

We thank the Australian Research Grants Committee and the Department of Supply for financial support; Professor L. E. Lyons for fruitful discussions and Mr. J. Bonham for computer programming.

REFERENCES

1. Jortner, J., Rice, S. A., Katz, J. L. and Choi, Sang-Il, *J. Chem. Phys.* **42**, 309 (1965).
2. Avakian, P., Ern, V., Merrifield, R. E. and Suna, A., *Phys. Rev.* **165**, 974 (1968).
3. Avakian, P. and Merrifield, R. E., *Mol. Cryst.* **5**, 37 (1968).
4. Ern, V., Avakian, P. and Merrifield, R., *Phys. Rev.* **148**, 862 (1966).
5. Kepler, R. G. and Switendick, A. C., *Phys. Rev. Letters* **15**, 56 (1965).
6. Williams, D. F. and Adolph, J., *J. Chem. Phys.* **46**, 4252 (1967).
7. Smith, G. C., *Phys. Rev.* **166**, 839 (1968).
8. McClure, D. S., *J. Chem. Phys.* **17**, 905 (1949).
9. Castro, G. and Hochstrasser, R. M., *J. Chem. Phys.* **46**, 3617 (1967).
10. George, G. A. and Morris, G. C., to be published.
11. Slavin, W., Mooney, R. W. and Palumbo, D. T., *J. Opt. Soc. Am.* **51**, 93 (1961).
12. Lonsdale, K., *Proc. Roy. Soc. A* **133**, 536 (1931).
13. Marchetti, A. P. and Kearns, D. R., *J. Am. Chem. Soc.* **89**, 768 (1967).
14. Castro, G. and Robinson, G. W., *J. Chem. Phys.* **50**, 1159 (1969).
15. Parker, C. A. *Advances in Photochemistry* **2**, 305 (1964).
16. Pesteil, P., Shurvell, H. F. and Pesteil, L., *Can. J. Chem.* **43**, 3133 (1965).
17. Borisov, M. D. and Vishnevskii, V. N., *Ukr. Fiz. Zhur.* **1**, 371 (1956).
18. Eremenko, V. V. and Medvedev, V. S., *Soviet Physics-Solid State* **2**, 1426 (1960).
19. Mulder, B. J., Philips Res. Reports Suppl., **4** (1968).
20. Simpson, O., *Proc. Roy. Soc.* **238**A, 402 (1956).
21. Williams, D. F., Adolph, J. and Schneider, W. G., *J. Chem. Phys.* **45**, 575 (1966).
22. Gallus, G. and Wolf, H. C., *Phys. Stat. Sol.* **16**, 277 (1966).
23. Wolf, H. C., *Journal de Physique* **28**, C 3–127, (1967).
24. Levine, M., Jortner, J. and Szöke, A., *J. Chem. Phys.* **45**, 1591 (1966).
25. Rumyantsev, B. M. and Frankevich, E. L., *Opt. and Spect.* **25**, 518 (1968).
26. Kepler, R. G., *Phys. Rev.* **119**, 1226 (1960).
27. Johnston, G. R. and Lyons, L. E., *Chem. Phys. Letters* **2**, 489 (1968).
28. Gutmann, F. and Lyons, L. E., " Organic Semiconductors ", Wiley (1967).
29. Nakada, I., *J. Phys. Soc. Japan* **20**, 346 (1965).
30. Rice, S. A., Morris, G. C., and Greer, W. L., *J. Chem. Phys.* in press.
31. Ern, V., *Phys. Rev. Letters* **22**, 343 (1969).
32. Sternlicht, H., Nieman, G. C. and Robinson, G. W., *J. Chem. Phys.* **38**, 1326 (1963).
33. Durocher, G. and Williams, D. F., *J. Chem. Phys.* **51**, 1675 (1969).
34. Tulinsky, A. and White, J. G., *Acta Cryst.* **11**, 7 (1958).
35. Strel'tsova, I. N. and Struchkov, Yu. T., *J. Struct. Chem.* **2**, 296 (1961).
36. El-Sayed, M. A., *Acc. Chem. Res.* **1**, 8 (1968).