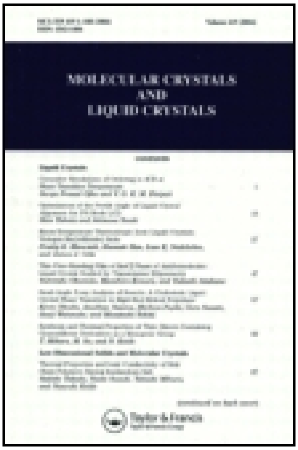

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Oscillator Strengths of Singlet Triplet Transitions of Molecular Crystals from Phosphorescence Excitation Spectra

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The measurement of spin-forbidden singlet-triplet absorption spectra of aromatic molecules and molecular crystals has been facilitated recently by the use of photoexcitation techniques. In direct absorption spectroscopy a long path length of sample is necessary to observe such weak ($f < 10^{-4}$) transitions. Such a problem is overcome by monitoring the concentration of triplet state molecules indirectly (via the phosphorescence(1,2) or delayed fluorescence(3) of the sample) as a function of excitation energy. The increased sensitivity of this technique over direct absorption spectroscopy has enabled high resolution $T_1 \leftarrow S_0$ absorption spectra to be obtained from pure(4) or doped crystals(2) of thickness less than 1 mm. Previously, transition energies and polarizations have been measured by this method. We wish, in this note, to indicate how the absorption coefficient as a function of energy (and hence the oscillator strength of the singlet-triplet transition) can be determined from the excitation spectrum of pure single crystal phosphorescence.

Aromatic molecular crystals exhibit a very low quantum yield ($\sim 10^{-4}$) of phosphorescence as a result of the high probability of triplet-triplet biexcitonic annihilation within the long triplet radiative lifetime (typically 30 secs). The haloaromatics show a substantial decrease in radiative lifetime, to the order of milliseconds as a result of the intramolecular spin-orbit coupling between the triplet state and the perturbing singlet states. Triplet exciton phosphorescence is then more readily obtained than in aromatic crystals and has been reported for the halogenated benzenes.(4,5)

In low resolution studies of phosphorescence excitation spectra of aromatic and carbonyl hydrocarbons, in frozen solution, Borkman and Kearns(6) reported a technique for measuring singlet-triplet extinction coefficients by a comparison with the extinction coefficient for the $S_1 \leftarrow S_0$ transition. The relation derived depends on the optical density being small for $S_1 \leftarrow S_0$ and $T_1 \leftarrow S_0$ absorption. However, in the crystal, this simple direct relationship does not exist throughout the first singlet exciton region. The high molar concentration of molecular crystals (~8 M) precludes obtaining excitation spectra symbatic with absorption spectra from crystals even with thickness as low as 2×10^{-4} cm.

In Fig. 1 is shown the excitation spectrum of phosphorescence for the *bc* face of a pure single crystal of *p*-dibromobenzene at 77 °K. For spectral regions corresponding to nontotal absorption of the exciting light (i.e. 27000 cm^{-1} to 35300 cm^{-1}) the phosphorescence intensity is directly related to the absorption coefficient. This region corresponds to $T_1 \leftarrow S_0$ absorption (27500 cm^{-1} to 32500 cm^{-1}), $T_2 \leftarrow S_0$ absorption (34000 cm^{-1} to 35000 cm^{-1}), and the tail of the singlet exciton band (35000 cm^{-1} to 35300 cm^{-1}). When the exciting light is strongly absorbed (the singlet exciton region, from 35300 cm^{-1} to higher energy) the excitation spectrum shows antibatic behaviour with respect to the absorption spectrum (i.e. maxima in the phosphorescence excitation spectrum correspond to minima in absorption). Similar behaviour in hexachlorobenzene single crystals has been interpreted to result from triplet exciton diffusion and subsequent surface quenching.(7) Thus, in Fig. 1, for higher energy than 35300 cm^{-1} the intensity of phosphorescence (I_p) is inversely related to the absorption coefficient α_s.

At the singlet exciton band edge (35000 cm^{-1} to 35300 cm^{-1}) I_p is directly related to α_s. The singlet exciton band edge of molecular crystals exhibit a tailing to lower energies that follows a simple relation (Urbach's Rule)

$$\alpha = \alpha_0 \exp\left[-\sigma(E_0 - E)/kT\right]$$

where: α = the absorption coefficient at photon energy E

α_0 = absorption coefficient at the extrapolated photon energy E_0 at zero degrees K

σ = a constant, $\simeq 1$.

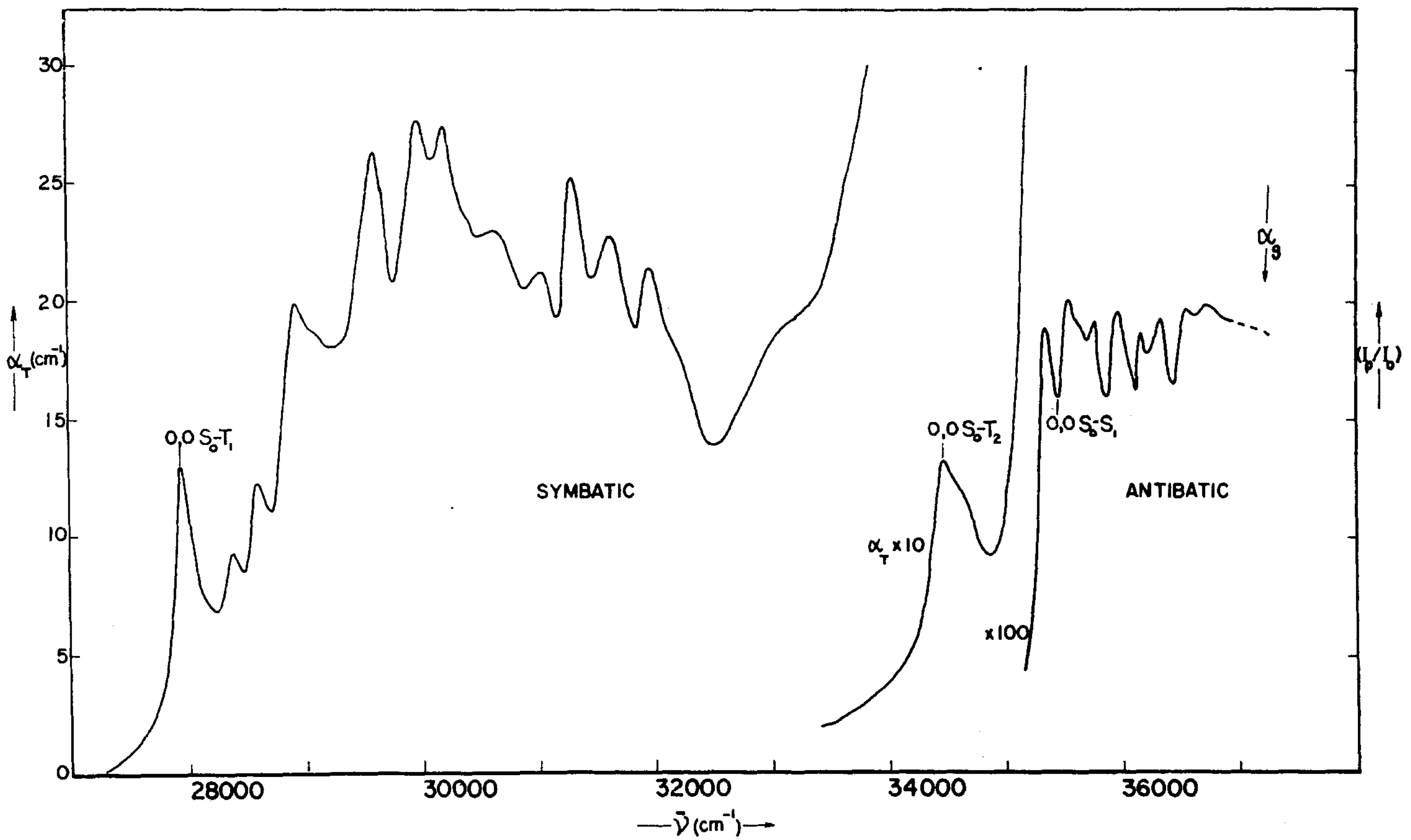

Figure 1. Excitation spectrum of triplet exciton phosphorescence of a 5×10^{-4} cm thick *p*-dibromobenzene crystal at 77 °K.

While the theoretical explanation of this relation over a large range of α and T is not clear(8) an explanation in terms of simultaneous absorption of a low energy photon and many phonons seems applicable over the range of α and T considered here.(9) The relation then implies that, at the band edge, an energy $E_{\text{incident}} - E_{\text{exciton}}$ must be supplied to create an exciton, i.e. within the singlet absorption edge singlet excitons are created by transitions from vibrational sublevels of the crystal lattice to the exciton band. These singlet excitons can undergo intersystem crossing to the triplet manifold (Fig. 2) and ultimately give rise to triplet exciton phosphorescence.

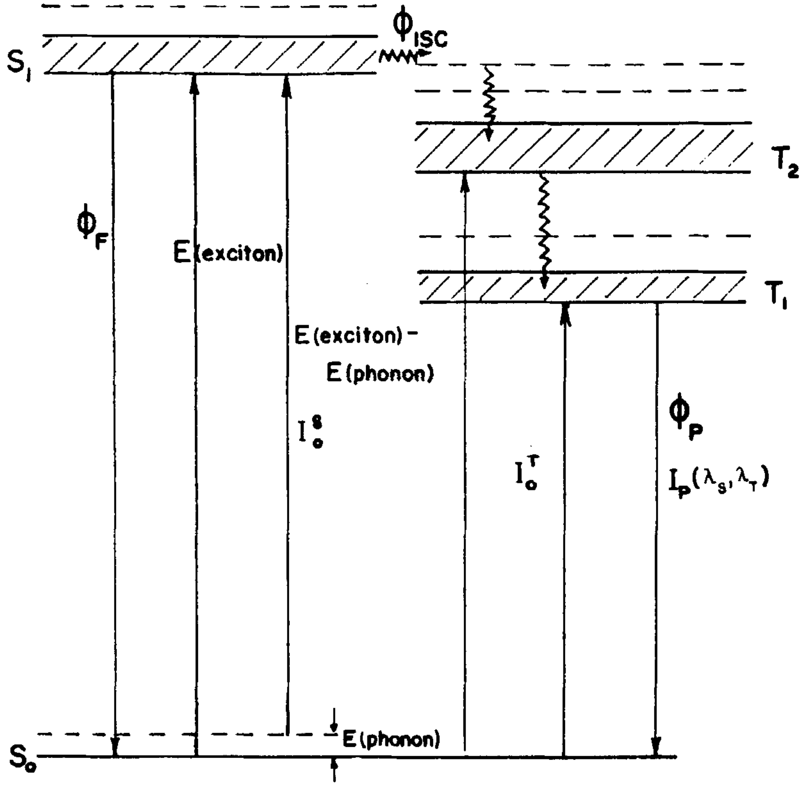

Figure 2. Typical manifold of low-lying electronic states in a molecular crystal. Excitation into the tail of the singlet exciton band is indicated as $(E_{\text{exciton}} - E_{\text{phonon}})$. Intersystem crossing and internal conversion processes leading to phosphorescence following singlet or triplet excitation are indicated.

By measuring α_s at the band edge it is possible to obtain α_T for the $T_1 \leftarrow S_0$ transition in the molecular crystal from a comparison of phosphorescence intensities from excitation into the triplet exciton band and the singlet exciton band edge.

Consider the typical manifold of low lying electronic states of a molecular crystal as shown in Fig. 2.

If α_s and α_T are the absorption coefficients (in cm^{-1}) for the transitions $S_1 \leftarrow S_0$ and $T_1 \leftarrow S_0$ respectively, and I_0^s and I_0^T the corresponding photon intensities incident in the crystal, then n_s, n_T the number of singlet and triplet excitons formed by direct absorption will be

$$\begin{aligned} n_s &= I_0^s\,(1 - \exp[-\alpha_s d]); \\ n_T &= I_0^T\,(1 - \exp[-\alpha_T d]) \end{aligned} \tag{1}$$

where d is the crystal thickness (cm).

The intensity of emitted phosphorescence following singlet absorption, $I_p(\lambda_s)$, and triplet absorption, $I_p(\lambda_T)$, will be

$$\begin{aligned} I_p(\lambda_s) &= (k/k')\,\chi_s\phi_{\text{isc}}\,n_s; \\ I_p(\lambda_T) &= (k/k')\,\chi_T n_T \end{aligned} \tag{2}$$

where ϕ_{isc} is the intersystem crossing quantum yield, χ_s and χ_T are the fractions of triplet excitons which give rise to phosphorescence and which are formed by the excitation processes $S_1 \leftarrow S_0$ and $T_1 \leftarrow S_0$ respectively, k' is the sum of radiative and non-radiative decay constants for triplet decay and k is a geometrical constant.

Since $\alpha_T d$ is small for a crystal or moderate thickness then

$$\begin{aligned} \alpha_T &= \frac{1}{d}\frac{I_p(\lambda_T)}{I_p(\lambda_s)}\,\phi_{\text{isc}}\,\frac{I_0^s}{I_0^T}\frac{\chi_s}{\chi_T}\,(1 - \exp[-\alpha_s d]) \\ &= K\,\frac{I_p(\lambda_T)}{I_0^T} \end{aligned} \tag{3}$$

The constant, K, may be readily evaluated if α_s is known at one wavelength in the singlet absorption edge. Hence, the absorption coefficient, α_T, for any energy in the region of the transition $T_1 \leftarrow S_0$ is directly related to the normalized phosphorescence intensity.

To obtain accurate absorption coefficients, certain experimental requirements should be fulfilled.

(a) The exciting light should be well collimated and uniformly illuminate the crystal so that d is well defined.

(b) A low incident photon flux should be maintained ($<10^{12}$ photons cm^{-2} sec^{-1}) to eliminate triplet-triplet annihilation. Under this condition $\chi_s \simeq \chi_T$.

(c) $\alpha_s < 1/d$ so that surface quenching of triplet excitons does not occur, and $\alpha_T \ll 1/d$ so that $\exp(-\alpha_T d) \simeq 0$.

The applicability of Eq. (3) to $T_1 \leftarrow S_0$ transitions may be tested by calculating the oscillator strength f_{ST} for the first singlet triplet transition of 1,4-dibromobenzene single crystal at 77 °K. This value may then be compared with existing experimental information for this transition.

The parameters required in Eq. (3) may be readily determined: α_s is obtained by conventional polarized absorption spectroscopy on bc oriented platelets ($\sim 1 \times 10^{-4}$ cm thickness determined from the measured retardation and known birefringence); I_0^s and I_0^T are obtained from the spectral distribution of the source and monochromator. With conditions (a) to (c) fulfilled and $\phi_{\mathrm{isc}} \simeq 1$ (since $\phi_F \simeq 0$) the measured " raw " excitation spectrum obtained as $I_p(\lambda_T)$ vs λ may be converted to a plot of α_T vs $\bar{\nu}$. The oscillator strength may be obtained from the usual formula

$$f_{ST} = 4.32 \times 10^{-9} \int \epsilon_{\bar{\nu}}\, d\bar{\nu} \quad \text{where} \quad \epsilon \simeq 0.08\alpha_T$$

for 1,4-dibromobenzene.

The corrected unpolarized $T_1 \leftarrow S_0$ absorption spectrum is shown in Fig. 1 and gives $f_{ST} = 1.8 \times 10^{-5}$. In order to compare the results obtained by phosphorescence excitation with direct absorption studies in the crystal$^{(5)}$ and in solution$^{(10)}$ polarized excitation spectra are required.† The measured values for the origin region f(0–0) only and for the whole spectrum are

$$f_{\perp b}\,(0\text{–}0) = 5.5 \times 10^{-7}; \quad f_{\parallel b}\,(0\text{–}0) = 2.7 \times 10^{-7}$$

$$f_{\perp b}\,(\text{total}) = 1.6 \times 10^{-5}; \quad f_{\parallel b}\,(\text{total}) = 8.7 \times 10^{-6}.$$

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† The polarized data reported here are somewhat less accurate than the unpolarized spectrum (Fig. 1) because of the rapid change in the transmission properties of the polarizer employed (Polaroid HNP'B) in the region of measurement of α_s.

The measured oscillator strength for the *origin region* only may be compared with the value from the direct absorption spectrum of a single crystal at 25 °K as reported by Castro and Hochstrasser.⁽⁵⁾ At 25 °K the oscillator strength for the electronic origin plus phonon structure built on this origin would be expected to be equivalent to the measured origin oscillator strength at 77 °K (at which temperature phonon structure is not resolved). From the reported direct absorption spectrum⁽⁵⁾ we have calculated $f(0\text{–}0) \simeq 3.3 \times 10^{-7}$. Such a value agrees very well with our values obtained through data from the excitation spectrum.†

The greatest source of error in the application of Eq. (3) is the determination of α_s in the singlet exciton band edge where α_s varies rapidly with energy. As only one value of each of α_s and I_0^s is required to determine α_T this error may be minimized by considering many values of α_s and I_0^s at the band edge (provided requirement (c) before is fulfilled).

It is concluded that the phosphorescence excitation technique which has already been successfully applied to molecular crystals to determine $T_1 \leftarrow S_0$ transition energies may, under certain circumstances, e.g. when the intersystem crossing quantum yield can be measured, be readily extended to determine absorption intensities and oscillator strengths.

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† The measured oscillator strength for *p*-dibromobenzene in solution is reported⁽¹⁰⁾ to be 3.5×10^{-6}. The estimated isotropic oscillator strength from this investigation is 1.2×10^{-5}.

REFERENCES

1. Marchetti, A. P. and Kearns, D. R., *J. Am. Chem. Soc.* **89**, 763 (1967).
2. Castro. G. and Robinson, G. W., *J. Chem. Phys*, **50**, 1159 (1969).
3. Avakian, P., Abramson, E., Kepler, R. G. and Caris, J. C., *J. Chem. Phys.* **39**, 1127 (1963).
4. George, G. A. and Morris, G. C., *Mol. Cryst. and Liq. Cryst.* **10**, 187 (1970).

5. Castro, G. and Hochstrasser, R. M., *J. Chem. Phys.* **46,** 3617 (1967).
6. Borkman, R. F. and Kearns, D. R., *Chem. Commun.* **14,** 446 (1966).
7. George, G. A. and Morris, G. C., *Mol. Cryst. and Liq. Cryst.* **10,** 115 (1970).
8. Hopfield, J. J., *Comments on Solid State Physics* **1,** 16 (1968).
9. Davydov, A. S., *Phys. Stat. Sol.* **27,** 51 (1968).
10. McClure, D. S., Blake, N. W. and Hanst, P. L., *J. Chem. Phys.* **22,** 255 (1954).