Photochemical and photophysical properties of various triaryl-2-pyrazolines

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PHOTOCHEMICAL AND PHOTOPHYSICAL PROPERTIES
OF VARIOUS TRIARYL-2-PYRAZOLINES

By

GRAEME PETER KELLY, B.Sc. G.R.S.C.

Supervisor: Professor F. Wilkinson

A doctoral thesis submitted in partial fulfilment of the requirements for the award of the Degree of Doctor of Philosophy of Loughborough University of Technology.

September 1987

Department of Chemistry

C G.P. Kelly, 1987
The work presented in this thesis has been carried out by the author, except where otherwise acknowledged, and has not previously been submitted to this University or any other institution for a higher degree.
To my late Grandmother who sadly passed away during the preparation of this thesis
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Lastly, but certainly not least, I would like to thank my Mother and Father for moral support and sacrifices they have had to make to allow me to reach this stage in my education, and my girlfriend Pam for support during the thesis.
4. A B S T R A C T

The main aim of the research was to obtain a detailed insight into the photochemical and photophysical properties of various triaryl-2-pyrazolines, with a view to understanding better their role in photoconductive materials. The technique of laser flash photolysis, in both transmission and diffuse reflectance mode, was employed to study the compounds as microcrystalline powders, within polymer films, on fabrics and in solution. In those media where the triplet state was not directly observed it was sensitized with a suitable triplet energy donor such as benzophenone. Microcrystalline powders of these samples yielded the first ever transient decay obtained using diffuse reflectance laser flash photolysis in the sub-nanosecond time domain and was assigned to the superimposed transient absorption decays of the $S_2$ and $S_1$ states.

The fluorescence of the pyrazolines, as microcrystalline solids, and in polymer films and solution, constituted another major research. Corrected fluorescence spectra and lifetime measurements were obtained for a number of these systems, together with fluorescence quantum yields in solution. In addition a quenching study analysing the effect of disulphone magenta (DSM) on the fluorescence of 1,5-diphenyl-3-styryl-2-pyrazoline, PYA, in dichloromethane yielded some interesting results. Namely the existence of both radiative and non-radiative transfer with the latter occurring at distances much greater than the encounter distance (i.e. long range transfer).

Polymer films containing PYA and the dye, DSM, were subjected to photoconduction and flash photolysis studies. In the latter a transient was observed and assigned to the anion radical of the dye, a precursor of this transient was quenched by the addition of PYA to yield the triplet of PYA. The photoconduction studies showed a linear increase of the charge generation quantum efficiency with increasing PYA content, together with a decrease in the field dependence of quantum efficiency, $\rho_e$. In addition a variation of
\( \rho_e \) with the wavelength of illumination leads to the conclusion that the charge generation occurs via the Onsager mechanism.
CHAPTER 1: INTRODUCTION

The primary aim of this project was to study the photochemical and photophysical properties of various 2-pyrazolines, in connection with their use as charge transport materials in electrophotography. Initially the salient points relating to the technique of electrophotography will be considered prior to any discussion of the pyrazolines or the new technique of diffuse reflectance laser flash photolysis.

1.1 Electrophotography and Photoconductivity

The development of the process of electrophotography (sometimes commercially called Xerography) by Carlson in 1937 [1] revolutionized the way in which information is processed by eliminating the need for carbon paper. The new technique provided a method of producing cheap, quick, simple and reliable, high quality copies of documents. The principle part of the process is the "photoreceptor" which collects optical images projected onto it using a combination of photoconductivity and electrostatic processes to develop the latent image. Photoconductivity is defined as the production of an electrical current following irradiation with electromagnetic radiation in the ultraviolet to infrared region. In other words photoconductors are materials, which under the influence of an electric field, are electrical insulators in the absence of illumination and conduct electrical charge when illuminated with the appropriate wavelength of radiation.

The photoreceptor has to be manufactured into the form of a drum, sheet or flexible belt to enable it to be conveniently incorporated in a typical commercial office copier. This means that good
photoconduction properties (i.e. negligible dark conduction and high conduction upon irradiation) is not the only property which must be present in a commercially viable photoreceptor. For instance, the photoreceptor must be inexpensive and easy to manufacture, flexible and mechanically strong, panchromatic, highly photosensitive and non-toxic. The main photoreceptors employed until fairly recently are inorganic materials such as vitreous selenium [2,3], arsenic triselenide [4], zinc oxide [5] and cadmium sulphide [6]. However, the performance of organic photoreceptors has recently improved significantly and consequently they are beginning to be used in preference to inorganic materials. Various aromatic and heterocyclic compounds both in binder dispersions and as homogeneous polymers provide excellent photoconduction properties and, although the inherent sensitivity normally lies in the ultraviolet, their response can be extended into the visible by the addition of sensitizing dyes [7].

The choice of organic material employed as the photoreceptor is important because a large number of organic compounds possess photoconduction properties, however, very low photosensitivity and limited spectral response make them commercially non-viable. The first commercial organic photoreceptor (produced by IBM) consisted of polyvinyl cabazol~(PVK) and trinitrofluorenone (TMF) charge transfer complex, however the photoconductivity of such a system was only about one-third that of the conventional amorphous selenium system [3]. This organic system was a so called "single layer" photoreceptor with the two components together in one homogeneous layer on a conductive base. However, it was found that the photoconductivity could be drastically improved by using a double-layer structure, in which a thin charge generation layer (GCL) and a much thicker charge transport layer (CTL) are placed in order on the
conductive base. Normally the various layers are incorporated in an electronically inert polymer matrix. Discussion of double-layer structures and some examples of commercial organic photoreceptors are given elsewhere [8,9,10].

An overview of the process steps in electrophotography has been clearly detailed in the literature [11], however a brief step by step description will be given here. Initially the photoreceptor coated on a conductive base is charged using a corona. In commercial copiers the photoreceptor is coated on a drum to allow the various processes to occur sequentially. The charged photoreceptor is then exposed to the reflected light from the document which is to be reproduced. In exposed regions of the photoreceptor the number of photocarriers created is proportional to the intensity of the incident light flux, and these carriers are subsequently transported across the film producing a reduction in the surface potential in these regions (these processes are detailed for the system under study in section 3.2 (d) (i)). As the consequence of the above a latent electrostatic image, representing the unexposed (dark) areas, is present on the photoreceptor. This latent image is then rendered visible using charged toner particles consisting of 10μm polymer particles containing carbon black, and charged with the opposite polarity to the photoreceptor. The charged areas of the exposed photoreceptor attract the toner and represent the dark areas of the original document. The final copy is then achieved by transferring the toner particles to an oppositely charged piece of paper and the copy is made permanent by thermal fixing.

The electrophotography process is represented in a step by step manner in schematic diagrams in Figure 1.1-vi. After a copy of the
FIGURE 1.1 Schematic illustration of the basic principles of electrophotography

1. **Composite Plate**
   - Charge Generation: Dye in Polymer
   - Charge Transport: Material in Polymer
   - Aluminum Film
   - Plastic Base

2. **Corona Discharge**
   - Area of the surface not illuminated is still charged.

3. **Illumination of Original**
   - Electrons produced in illuminated photoconductor travel to the surface and neutralize the charge.

4. **Development Stage**
   - Negatively charged toner
   - Using toner

5. **Fixing and Transfer of Image to Paper**
   - Paper
original document has been achieved, the final step is to prepare the photoreceptor for another cycle (i.e. another copy). This involves removing any excess charge and toner from the surface of the photoreceptor.

The above provides a very brief introduction to the complex subjects of organic photoconductors and electrophotography. The latter has been extensively reviewed elsewhere [11,12,13].

1.2 Di- and Triaryl-2-Pyrazolines

Pyrazolines were first reported by Knorr and Blank [14] in 1885 by reducing 1,3-diphenyl-5-methylpyrazole to the corresponding strongly fluorescent 2-pyrazoline. Another preparation which employs this rather crude reduction methodology is the reduction of 1-phenylpyrazole to the appropriate pyrazoline using a palladium catalyst at 20°C [15]. Obviously the reduction of pyrazoles is not the most convenient preparation procedure and in 1887 Fisher and Knoevenagel [16] prepared 1-phenyl-2-pyrazoline by reaction of acrolein and phenyl hydrazine.

\[
\begin{align*}
\text{CH}_2\text{=CH CHO} + \text{C}_6\text{H}_5\text{NHNH}_2 \\
\downarrow \\
\text{N} \quad \text{N} \\
\text{Ph}
\end{align*}
\]
In 1894 Curtius and Wirsing [17] carried out an analogous reaction with hydrazine to produce the parent heterocycle. Most of the preparations reported in the literature employ a variation of the above ring closure in which α,β-unsaturated aldehydes (or ketones) react with aliphatic derivatives of hydrazine. The above reaction has been reported in a variety of solvents, at different temperatures and for different times of reaction [18].

In addition to the above simple reaction, precursors of α,β-unsaturated compounds have been employed in reactions with the hydrazine and such a procedure has been widely applied to the preparation of fluorescent 1,3-diaryl-2-pyrazolines [19,20,21]. The variation can be illustrated by the reaction of hydrazine with Mannich bases of ketones, under both acidic and basic media.

\[
R'COCH_2CH_2NR''_2 + C_6H_5NHNH_2 \rightarrow R' + R''_2NH
\]

The above provides some brief descriptions relating to the preparation of various 2-pyrazolines, however, full details concerning such preparations can be found in the literature [18,22,23]; the latter reference is of particular relevance since the 2-pyrazolines used in this project were prepared during this work.
Pyrazolines have been employed in many commercial uses since their initial development. The most famous use is for the optical brightening of textiles, paper and plastics [24,25,26,27], also the compounds have been investigated as fluoros and wavelength shifters for improving the efficiency of scintillation counting [28]. In recent years interest has been shown in using pyrazolines in the charge transport layer in the photoreceptor for electrophotography [29]. Since a majority of the commercial applications to which 2-pyrazolines are applied involves the fluorescence of the compound, most of the literature concentrates on the spectral properties in solution in particular the fluorescence. However, some work has been reported relating to the photostability and dye sensitized photooxidation of various 2-pyrazolines.

One of the earliest studies of the spectral properties of 1,3,5-triaryl-2-pyrazolines by Sandler and Tsou [28] attempted to develop a new type of wavelength shifter for scintillation counting. The main conclusions arrived at in this and earlier work [30] were firstly that, a 3-aryl group is essential for fluorescence and secondly that the 5-aryl group has very little effect on the emission. The final point is that the 1-aryl group is essential to prevent air oxidation of 2-pyrazolines [31]. On the basis of the various correlations established in their work Shandler and Tsou suggested that the excited state of 1,3,5-triaryl-2-pyrazolines is of the form :-
The excited state has $\delta^+$ character on the 3-carbon and thus an electron withdrawing group at $R'$ in the 3 position will make it more stable.

At first sight the fact that triaryl-2-pyrazolines exhibit such large amounts of fluorescence seems surprising because the classical formulation of the molecule contains no continuous conjugation. However, Neunhoeffer and Rosahl [32] extended the ideas of Förster[33] that planarity of molecules is important for efficient fluorescence, and postulated the existence of mesomeric canonic forms via which the aromatic systems in positions 1 and 3 interact.

The fact that an aromatic substituent in the 5 position has no great influence on either the absorption or fluorescence maximum can be explained in terms of the mesomeric ground state because this can not be postulated for a system involving the substituent in the 5-position. The aromatic substituents in the 1 and 3 positions can also be replaced by heterocycles or styryl groups without the loss of the ability to exhibit strong fluorescence [34].

The most comprehensive study undertaken so far in relation to the spectral properties of substituted 1,3,5-triphenyl-2-pyrazolines was undertaken by Rivett et al [35]. The validity of this work is
enhanced by the fact that Strahle et al [36] produced virtually identical conclusions from a series of similar experiments. Prior to this work the only conclusions which had been drawn, relating to specific substitution, were firstly that there is normally considerable quenching of pyrazoline fluorescence by oxygen and secondly in general the fluorescence maxima is shifted to longer wavelengths in polar media [37,38].

Rivett et al [35] considered a large number of substituted 1,3,5-triphenyl-2-pyrazolines which were divided into three categories of substitution; namely halogen, electron donating (e.g. NH₂, NHAc, NH-Me, N-Me₂, OMe, SMe or OAc) and electron withdrawing (e.g. CO₂Me, CN, CS₂Me). The observations relating to the first two categories of substitution are generally fairly similar, namely a bathochromic shift in the absorption and fluorescence maxima accompanied by an increase in the absorption intensity and a dramatic decrease in the fluorescence quantum yield in changing from a non-polar solvent to a polar solvent. One possible explanation of this quenching phenomenon could involve the formation of non-fluorescent complexes through hydrogen bonding with the polar solvent, similar to those suggested by Van Douren [39].

In the latter of the above categories (i.e. electron withdrawing groups) the same basic trends observed (above) are still operational, however, a few very interesting anomalies occur which warrant some discussion. Firstly, it was found that para substitution of the 1-phenyl ring with a cyano or methylsulfonyl group yielded compounds which have fluorescence quantum yields of close to unity in both cyclohexane and methanolic (i.e. non polar and polar) media. A second anomaly relates to the fact that a cyano, methoxycarbonyl or methylsulfonyl group substituted in the para position of the 5 phenyl
ring causes a dramatic quenching of the fluorescence in all solvents, not just polar solvents. These compounds do absorb to a much smaller extent than a majority of other 1,3,5-triaryl-2-pyrazolines, but this is unlikely to cause such a dramatic change in steric crowding or planarity to quench the fluorescence completely. It is rather surprising that a substituent not directly involved with the fluorescing chromophore (i.e. not on the 1-phenyl or 3-phenyl ring) can cause such a profound effect on the fluorescence. One possible explanation of this very low level of fluorescence is the existence of a strongly competing internal radiationless transition, such a transition was discussed by Leaver and Rivett [38].

In the aforementioned work by Leaver and Rivett [38] they showed a decrease in the fluorescence of 1,3,5,5-tetraphenyl-2-pyrazoline compared with other 2-pyrazolines. However, the tetraphenyl derivative exhibited no major deviations in the intensities or positions of the absorption bands when compared with other 2-pyrazolines. As a result it was deduced that the weak fluorescence was unlikely to be due to steric crowding or distortion of the planar conjugated system. In addition a strong temperature dependence on the fluorescence quantum yield was found to exist in the tetraphenyl derivative which is strongly indicative of the existence of a temperature dependent radiationless deactivation process.

The above provides a fairly brief overview of the main trends that exist in the spectral characteristics of 1,3-diaryl-2-pyrazolines and 1,3,5-triaryl-2-pyrazolines in various solvents. Other examples of 2-pyrazoline preparation and subsequent characterisation of spectral properties can be found in the literature [23,40,41,42,43,44]. A table of absorption and fluorescence data which illustrates many of the
Table 1.1 Absorption and fluorescence data for substituted 1,3,5-triaryl-2-pyrazolines

<table>
<thead>
<tr>
<th>Substitution in Phenyl Rings</th>
<th>In Cyclohexane at 20°C</th>
<th>In Methanol at 20°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Absorption</td>
<td>Fluorescence</td>
</tr>
<tr>
<td></td>
<td>$\lambda_{\text{max}}$</td>
<td>$\epsilon_{\text{max}}$</td>
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<td>Cl&lt;sub&gt;2&lt;/sub&gt; CN H</td>
<td>396</td>
<td>2.90</td>
</tr>
<tr>
<td>H CN Br</td>
<td>394</td>
<td>2.50</td>
</tr>
</tbody>
</table>

Table 1.1 (continued)
Table 1.1 (continued)

<table>
<thead>
<tr>
<th>Substitution in Phenyl Rings</th>
<th>In Cyclohexane at 20°C</th>
<th>In Methanol at 20°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Absorption Fluorescence</td>
<td>Absorption Fluorescence</td>
</tr>
<tr>
<td></td>
<td>( \lambda_{\text{max}} )  ( 10^4 \epsilon_{\text{max}} ) ( \lambda_{\text{max}} ) ( \phi )</td>
<td>( \lambda_{\text{max}} )  ( 10^4 \epsilon_{\text{max}} ) ( \lambda_{\text{max}} ) ( \phi )</td>
</tr>
<tr>
<td>NH(_2) CN H</td>
<td>423 2.10 537 0.36</td>
<td>417 2.00 - 0.00</td>
</tr>
<tr>
<td>NH(_2) CN H</td>
<td>414 2.90 - -</td>
<td>408 2.80 456 0.03</td>
</tr>
<tr>
<td>SO(_2)CN H</td>
<td>385 A 423/453 B 1.00</td>
<td>385 3.30 470 0.78</td>
</tr>
<tr>
<td>CN(^\text{C}) CN Br</td>
<td>385 3.50 426/446 B 1.00</td>
<td>387 3.70 472 0.99</td>
</tr>
<tr>
<td>H Br Br CN</td>
<td>365 2.00 438 1.00</td>
<td>364 2.10 473 0.55</td>
</tr>
<tr>
<td>H Br CN</td>
<td>367 2.00 440 0.09</td>
<td>363 2.00 - 0.00</td>
</tr>
<tr>
<td>CN Br H</td>
<td>368 3.30 412/432 B 0.97</td>
<td>367 3.60 435 0.97</td>
</tr>
<tr>
<td>H Cl2 SO(_2)Me SO(_2)Me</td>
<td>A A A A</td>
<td>388 2.60 507 0.66</td>
</tr>
<tr>
<td>H Cl2 Cl2</td>
<td>363 2.10 437 1.05</td>
<td>362 2.30 475 0.51</td>
</tr>
<tr>
<td>H Cl Cl</td>
<td>367 2.30 437 1.03</td>
<td>365 2.30 473 0.51</td>
</tr>
<tr>
<td>H Cl Cl</td>
<td>355 2.00 429 1.08</td>
<td>354 2.20 467 0.54</td>
</tr>
<tr>
<td>Cl Cl Cl</td>
<td>366 2.40 438 1.02</td>
<td>364 2.40 470 0.60</td>
</tr>
<tr>
<td><strong>A.</strong> Extremely low solubility in solvent.</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>B.</strong> Double maxima in fluorescence spectrum.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
points previously discussed is presented in Table 1.1 [35,42]. In addition to the solution work, other media have been employed; for example absorption and fluorescence spectra of 1,3-diphenyl-2-pyrazoline and 3(p-cyanophenyl)-1-phenyl-2-pyrazoline have been measured in polar and non-polar solvents at 77°K [45] and also absorption and fluorescent spectra of polymers containing pendant 1,3,5-triphenyl-2-pyrazoline chromophores have been studied [46].

Numerous 1,3-diphenyl-2-pyrazoline derivatives have been patented for use as fluorescent whitening agents for wool, synthetic fibres and plastics [47,48]. However, some concern has been expressed as to the stability of such species [49]. In fact a report by Schröder [50] suggests that benzene solutions of various substituted 1,3-diphenyl-2-pyrazolines, in the presence of oxygen, undergo photohydrogenation to the appropriate, non-fluorescent, 1-3-diphenyl-pyrazole. The above work prompted Evans et al [51] to carry out a more systematic study in which a series of 1,3-diphenyl-2-pyrazoline derivatives were irradiated (wavelength > 290nm), in the presence of air, in both cyclohexane and methanol. This work confirmed that the major photochemical reaction pathway was dehydrogenation, with a small amount of photo-oxidation in cases where dehydrogenation is blocked by disubstitution in the 5-position (e.g. 1,3,5,5-tetraphenyl-2-pyrazoline). In addition it was demonstrated that the introduction of a phenyl group at the 4 or 5 position of the pyrazoline increases the photostability, the former to a greater extent. This fact is exemplified using trans-1,3,4,5-tetraphenyl-2-pyrazoline which showed a large amount of photostability in both cyclohexane and methanol, when compared to the other 2-pyrazolines studied.

Another area of research in which there is considerable interest...
involves the study of the dye-sensitized photo-oxidation of 1,3-diphenyl-2-pyrazoline [52] and various substituted derivatives [53,54]. The mechanistic details of the above process are unclear, and although singlet oxygen appears to be involved there are also other pathways occurring. Full details of the complex reaction is given in the literature [52,53,54], plus a detailed review of this and all the above literature is given elsewhere [55].

The final major area of 2-pyrazoline literature not yet reviewed involves their use as fluorescent brightening agents and in particular the photofading effect that they exert on dyes and vice versa. Yamoda et al [56] observed that pyrazoline type fluorescent brightening agents accelerated the rates of photofading of triphenylmethane dyes, via a mechanism involving the triplet sensitization of the dyes by the pyrazoline. In 1978 Evans and Waters [57] used a variety of 2-pyrazolines to study their spectral and dyeing properties (on wool and nylon). It was found that exhaustion and fastness to washing are better on a nylon matrix as opposed to wool. In addition it was found that the stability towards light was independent of the fabric but increased by substitution in the 4 and 5 position of the 2-pyrazoline ring, a fact which is in agreement with work carried out previously [51]. Shosenji et al [58] investigated the accelerated fading of methyl violet by the fluorescent brightening agent, 1,5-diphenyl-3-(p-chlorophenyl)-2-pyrazoline, in a film of polyacrylonitrile on irradiation at 366nm. Also studied was the effect of changing the substrate to commercially available acrylic fabric, cellulose acetate and gelatin.

The above survey of the literature of di-and triaryl-2-pyrazolines, although brief, is representative of the research that
has been undertaken on such compounds. Obviously as with any compounds of commercial interest some work may have been deemed not permissible for publication and is consequently lost from the "free" literature.

1.3 Diffuse Reflectance Laser Flash Photolysis

One of the most powerful techniques for investigation of primary photochemical processes is flash photolysis [59], which can be applied to any transparent sample. Numerous publications deal with the general methodology of flash photolysis [59,60,61,62], in which a pulse of exciting light is employed to generate transient species which are subsequently detected by absorption of light from an analysing source. Recently there has been considerable interest in the photochemical properties of heterogeneous systems, many of which are opaque and often highly scattering. Although conventional transmittance laser flash photolysis cannot be applied to such samples, the new technique of diffuse reflectance laser flash photolysis [63,64,65] provides a perfect tool to study opaque media. In this technique the transient species is detected by measuring the changes in the level of diffusely reflected light from the analysing source. In this section a brief discussion on the subject of reflectance, in particular diffuse reflectance, will be presented, followed by a review of some of the uses to which the technique of diffuse reflectance laser flash photolysis has been applied.

Reflection from any surface contains two components the first due to "specular" (or "regular") reflectance which is discussed fully elsewhere [65,66,67]. The other component is the diffuse reflectance, which is unpolarised and distributed symmetrically with respect to the surface normal irrespective of the angle of incidence or the state of
polarisation of the incident light [65, 67, 68]. The relative amounts of the specular and diffuse components of the reflection is dependent on the nature of the surface. For instance a mirror surface will yield virtually exclusively specular reflection, while a fine powder will possess mainly diffuse reflection. The diffusely reflecting light arises from incident light which has penetrated below the surface and into the interior of the individual particles making up the sample, returning to the surface as a result of multiple scattering at the individual particle interfaces and being attenuated by absorption within the particles.

The most simple and widely adopted approach for describing the interaction of light with diffusing media is the Kubelka-Munk theory [65,67,68,69]. This approach provides a good approximation for diffuse incident radiation and applies reasonable well for directed incident beams where the light flux penetrating into the sample rapidly becomes diffuse and where the regular reflection is negligible (e.g. weakly absorbing finely divided powders and dyes on fabrics). However, in cases where the specular component cannot be neglected (i.e. with very strongly absorbing materials) the Kubelka-Munk approach is not particularly applicable.

In the Kubelka-Munk treatment the medium is assumed to be comprised of randomly distributed, uniformly absorbing and scattering particles. The usual approach in dealing with the theory involves two differential equations which describe the light flux in a thin slice of thickness dx at a depth x beneath the irradiated surface [67].

i.e.

\[ dI(x) = -(K+S)I(x)dx + S J(x)dx \]  \hspace{1cm} (1.1)

\[ dJ(x) = (K+S)J(x)dx - S I(x)dx \]  \hspace{1cm} (1.2)
where $\mathcal{J}(x)$ and $\mathcal{I}(x)$ are the perpendicular light fluxes away from and towards the surface, respectively. $K$ and $S$ are the absorption and scattering coefficients, respectively, of the sample. The change of sign in equation 1.2 is due to the fact that the flux is now moving in the opposite (-x) direction. Most chemists are familiar with Lamberts law for transparent media which is obtained from equation 1.1 when $S = 0$,

i.e.

$$d\mathcal{I}(x) = -\mathcal{I}(x)Kdx \quad (1.3)$$

in which case $K = \alpha = \varepsilon C$, where $\varepsilon$ is the Napierian absorption coefficient and $C$ is the concentration. For an ideal diffuser, where the radiation has the same intensity in all directions, $K = 2\varepsilon C$. The factor of 2 accounts for the increased average distance travelled by the light in an ideal diffuser.

A given opaque sample has a certain reflectance $R^0_A$, at a wavelength $\lambda$. $R^0_A$ is defined as $J^0_A / I^0_A$, where $J^0_A$ and $I^0_A$ represent the levels of the reflected and incident light, respectively, at the sample surface. The transmittance, $T$, for a layer of thickness $d$ is defined as $I(d)/I^0_A$. Equations (1.1) and (1.2) can be solved [67,68,69] when $K$ and $S$ are independent of $x$ in which case for a layer of thickness $d$

$$R = \frac{\sinh (b S_d)}{a \sinh (b S_d) + b \cosh (b S_d)} \quad (1.4)$$
24.

and

$$T = \frac{b}{a \sinh (b S_d) + b \cosh (b S_d)}$$  \hspace{1cm} (1.5)$$

where

$$a = \frac{K + T}{S} \quad \text{and} \quad b = (a^2 - 1)^{\frac{1}{2}}$$  \hspace{1cm} (1.6)$$

If the layer is so thick that any further increase in thickness of the sample does not affect $R$ it follows that

$$R = -b \quad \text{and} \quad T = 0$$  \hspace{1cm} (1.7)$$

and also for such so called "optically thick" samples

$$I(x) = I_A^0 \exp (-b S x)$$  \hspace{1cm} (1.8)$$

and

$$J(x) = R I_A^0 \exp (-b S x)$$  \hspace{1cm} (1.9)$$

In addition

$$\frac{(1-R)^2}{2R} = \frac{K}{S} = F(R)$$  \hspace{1cm} (1.10)$$

The expression on the left hand side of equation 1.10, which can be written as $F(R)$, is known as the remission function and is a linear function of the concentration of homogeneous absorbers. If $S$ is assumed independent of wavelength, plots of the remission function versus wavelength for powdered samples and other diffuse reflectors is representative of the absorption spectra. Such absorption spectra
derived from the remission function have been shown to superimpose with spectra measured by transmission spectroscopy for cases where both can be obtained from the same material. For example a neodymium glass filter before and after grinding to a powder gave superimposable spectra [68]. The two spectra are of course displaced by log S and when S shows some dependence on wavelength superimposition is not possible at all wavelengths.

If we now consider the production of a transient T from a ground state species, A, in a diffuse media with a yield $\phi_T$

\[ A \xrightarrow{h\nu_e} T \quad \text{with yield } \phi_T \]

For irradiation of a diffuse medium absorbing at wavelength, $\lambda_e$, the equation developed above can be employed and initially it follows that:

\[ -\frac{d[A]}{dt} = \frac{d[T]}{dt} = K_e \phi_T (I(x) + J(x)) \tag{1.11} \]

For an optically thick sample equation 1.11 becomes

\[ -\frac{d[A]}{dt} = \frac{d[T]}{dt} = K_e \phi_T (1 + R_e) I_0 \exp(-b_e S_x) \tag{1.12} \]

The above predicts that the initial concentration profile decreases exponentially with increasing penetration depth into the sample.

In a flash photolysis experiment, absorption at the exciting wavelength is used to produce transients absorbing at another wavelength. Equation 1.12 clearly demonstrates that the concentration of transient
initially falls off exponentially as a function of penetration depth and thus for optically thick samples with very small percentage conversion of ground state molecules equation 1.10 cannot be used to predict the change in diffuse reflectivity expected. What is actually required is the solution of equations 1.1 and 1.2 at the analysing wavelength indicated by superscript "a" where, following laser excitation, \( K \) varies exponentially with \( x \). This solution has already been solved by Lin and Kan [70]. who gave

\[
R^a = R_B^a \left[ \frac{1 + \frac{\gamma u}{\delta} + \frac{\gamma (\gamma + 1)}{\delta(\delta + 1)} \frac{u^2}{2!} + \ldots}{1 + \frac{\gamma + 1}{\delta} u + \frac{(\gamma + 1)(\gamma + 2)}{\delta(\delta + 1)} \frac{u^2}{2!} + \ldots} \right]
\]

(1.13)

where \( R_B^a \) is the background reflectance at the analysing wavelength and \( \gamma = (b_e R_B^a)^{-1} \), \( \delta = (\gamma + 1 - R_B^a) / b_e \) and \( u = 2K^a(0) / b_e \).

The above series converges for all values of \( u \). In diffuse reflectance laser flash photolysis the measured quantity is the photoinduced change in reflectance, \( R \), as a function of time. The reflectance before and after excitation at the analysing wavelength may be represented by \( R_B^a \) and \( R^a(t) \), respectively and

\[
\frac{R_B^a - R^a(t)}{R_B^a} = 1 - R_T^a
\]

(1.14)

where \( R_T^a \) is the relative transient reflectance. Except where the laser causes changes in scattering as well as absorption coefficients,
(1-R_T^a) is the transient absorption. By substitution of typical values for S, K^A, K^a and K^A into equation 1.13 it shows that when 1-R_T^a < 0.1 ; (1-R_T^a) is itself a linear function of the amount of transient present [71].

The use of the technique of diffuse reflectance laser flash photolysis, using nanosecond laser excitation, first yielded results in 1984 for microcrystalline benzophenone [72] and benzil [73]. Both transient absorptions were positively identified as triplet-triplet absorptions. In the case of benzophenone an absorption, centred at 540nm, was observed which has, within experimental error, identical kinetics to the phosphorescence decay, which is predominantly second order. In the case of benzil a transient absorption of 60% at 510nm was observed after 354nm excitation. The assignment as a triplet-triplet absorption was made on the basis of the absorption and phosphorescence kinetics being virtually identical, namely a mixture of first and second order kinetics.

Studies have also been undertaken in dyed fabrics and polymers. For example polymeric benzophenone (benzoylated polystyrene beads) gave characteristic transient absorptions typical of the triplet benzophenone chromophore [74]. Non-fluorescent cotton fabric dyed with aluminium sulphonated phthalocyanine also yields a triplet-triplet absorption characteristic of the compound [75]. The photosensitizing dye rose bengal was studied in a variety of matrixes including chemically bound within cross-linked polymers (i.e. as the commercially available heterogeneous photosensitizers known as Sensitox I and II), adsorbed on polyacrylamide and polystyrene, and adsorbed on woven cotton and nylon fabric [76]. For each sample the kinetics of the transient absorption and emission decays, after 354nm excitation, are
virtually identical and thus the transient is assigned to triplet rose bengal.

The technique has also been applied to semiconductors [75,77] zinc sulphide phosphors [78] and zinc oxide powders [79], both doped and undoped. In the case of titanium dioxide the transient absorption detected was assigned as a photo-induced thermal phenomenon [65,77]. In the case of zinc oxide transient absorption spectra were observed when undoped and doped with copper, nickel, cobalt, iron and manganese, following 532nm excitation [79].

Another area in which this technique can be applied is in the study of adsorbed molecules on surfaces, which was the first area to be explored by this technique [80]. In a recent article by Thomas [81] the importance of understanding reactions on surfaces, with its industrial relevance in such fields as catalysis and corrosion chemistry, is emphasized. The properties of excited molecules included in zeolites [82] is also of considerable interest and several systems have been examined by our group [80,83,84,85] and others [86,87]. The example which will be cited here is the study of xanthone included within the manufactured "zeolite" Silicalite [85]. Silicalite is over 99% SiO₂ and consists of a system of near-circular zig-zag channels, cross-linked by elliptical straight channels. The transient has been assigned as the xanthone triplet, showing a characteristic maximum at 605nm. It is well known [88] that the position of the maximum of the xanthone triplet is sensitive to the polarity of the host environment. The value obtained for this system is indicative of a fairly polar medium despite the fact that this is a hydrophobic zeolite. A further rather interesting observation is that the decay process is very non exponential extending over several orders of magnitude with respect to
time, suggesting that triplet xanthone in different channels or surface environments decay at very different rates. The production of the xanthone triplet has been studied on the picosecond time domain [83]. Recently Turro et al [86,87] have applied the same technique to study energy transfer and photoreactions of organic substrates on several types of silica.

The above provides a broad overview of some of the areas of study to which the technique of diffuse reflectance laser flash photolysis has been applied. It is obviously impossible to give full details of all the published work, however a number of excellent reviews are available [63,64,65,89] which between them provide a complete picture of "the state of the art" of diffuse reflectance laser flash photolysis.
2.1 Diffuse Reflectance Laser Flash Photolysis

(a) Laser

Excitation in diffuse reflectance laser flash photolysis is usually achieved using one of the available harmonics of a pulsed Nd/YAG laser (supplied by J.K. Laser Ltd., now Luminonics Ltd.). However, it is possible to use it in conjunction with a dye laser to produce other exciting wavelengths. Most of the details relating to the laser system have been published previously [90,91], thus only the main points of interest will be presented.

The laser rod consists of a 10.2cm x 0.95cm anti-reflection coated rod of Yttrium aluminium garnet (YAG) doped with neodymium. This is optically pumped by two high voltage flash lamps to produce population inversion and ultimately a series of random laser spikes each lasting a fraction of a nanosecond. These spikes are brought under control by deliberately spoiling the quality of the laser cavity until maximum population inversion is achieved, using a Q switch. The effect of restoring the full oscillation capability of the cavity is to give a virtually single pulse of 1064nm radiation of short duration (typically 20ns). The Q switch in the laser system used is a crystal of potassium deuterium phosphate (KD\textsuperscript{+}P), which is known as Pockels cell. This acts as an electroptic shutter by the application and removal of a high voltage axially across the crystal.

The fundamental 1064nm pulse that emerges from the laser cavity is Gaussian in shape (with respect to time) with a half width of 20ns and a typical energy of approximately 550mJ per pulse. However,
infra-red excitation is generally not very useful and one of the harmonics of the fundamental is most commonly employed as the excitation source. These harmonics are generated by passing the fundamental through various crystals at slightly elevated temperatures. Details of these harmonic generation processes are presented in Table 2.1 (below).

Table 2.1: Details of the Various Harmonic Generation Processes using a 1064nm Fundamental

<table>
<thead>
<tr>
<th>HARMONIC</th>
<th>WAVELENGTH OF HARMONIC (nm)</th>
<th>DETAILS OF THE HARMONIC GENERATION CRYSTAL(S) USED (operating temp. given in parenthesis)</th>
<th>TYPICAL ENERGY OF PULSE (mJ/pulse)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SECOND</td>
<td>532nm</td>
<td>Caesium dihydrogen arsenate, CDA\textsubscript{6} crystal (47.5°C)</td>
<td>200</td>
</tr>
<tr>
<td>THIRD</td>
<td>354nm</td>
<td>Combination of a CDA crystal (see above) and a potassium deuterium phosphate, KD\textsuperscript{3}P, crystal (40.0°C).</td>
<td>65</td>
</tr>
<tr>
<td>FOURTH</td>
<td>266nm</td>
<td>Combination of a CDA crystal (see above) and a ammonium dihydrogen phosphate, ADP, crystal (49.5°C).</td>
<td>49</td>
</tr>
</tbody>
</table>

Harmonic generation is not a very efficient process and hence residual wavelengths are present in the pulses, which can subsequently be removed by passing through a separation box. This is basically a pair of dielectric coated mirrors which are set to preferentially reflect the particular harmonic and not the residuals, the latter being dumped in a stainless steel cone.
The energy of the harmonic used is determined using a photodiode in conjunction with a cathode ray oscilloscope and an energy monitor. The orientations of the harmonic generation crystals can then be altered to achieve maximum energy, of which typical values are quoted in Table 2.1 (above).

(b) Arc Lamp

The analysing light in the diffuse reflectance laser flash photolysis set-up is normally supplied by a 250W xenon arc lamp, positioned in such a way that the analysing light arrives normal to the sample. The arc lamp is connected to a pulsing unit which discharges up to 80J through the lamp to increase the brilliance by (typically) 200 times at 200nm, 150 times at 300nm, 120 times at 500nm and 100 times at 800nm. The actual xenon arc lamp is contained within a water-cooled housing, this has the advantage that there is an absence of mechanical vibration produced by conventional cooling fans.

The pulsed arc lamp has a profile with a duration of approximately 1.5ms and is designed to be flat to within 5% for 0.35-0.4ms and to within 1% over 100μs. The arc lamp is normally synchronised with other events to ensure that the transient absorption is recorded on the flat portion of the profile. However, obviously at time bases of 100μs/div and greater, the flat portion of the profile is too short. This problem is overcome by using an unpulsed arc lamp but this has the major disadvantage of decreased lamp brightness and consequently a less favourable signal to noise ratio. Figure 2.1 (a) and (b) gives an illustration of the arc lamp profile when pulsed, using two different time bases.
FIGURE 2.1 Profile of pulsed 250 W Xenon arc lamp within two different time domains

(a) Complete pulsed arc lamp profile

(b) Flat portion of pulsed arc lamp profile
(c) Sample

The sample type used in diffuse reflectance laser flash photolysis is a scattering, opaque material. The sample is usually contained in either a special brass, screw type, sample holder, which has a quartz cover as a window or in a U.V. spectroscopic cell.

(d) Monochromator and optical layout

The analysing light diffusely reflected from the sample contains the whole spectrum of wavelengths and a monochromator has to be placed before the photodetector in order that only one wavelength is analysed. The monochromator used is a Czerny-Turner grating instrument with a f3.4 relative aperture. It has a calibrated range with a digital display, from 200nm to 1000nm. At the front and back there are fully variable bilateral slits of 21mm height and of adjustable width (0 to 8mm). A collecting lens (focal length = 8cm) is placed before the entrance of the monochromator to increase efficiency of light collection.

The optical layout around the sample is unique to diffuse reflectance laser flash photolysis and is the major difference between this technique and the conventional transmission technique [59,60]. The analysing light is normal to the sample, and causes a majority of the specular reflection from the sample to be coincident with the incident beam. The exciting pulse (from the laser) is positioned at angle of just under 45° to the sample. It is also important to ensure that the analysing light is only reflected from the area of the sample which has been excited by the laser beam (typically an area of 1cm²), otherwise a proportion of the diffusely reflected analysing light will contain no information about the transient event [65,90].
The monochromator and associated collecting lens is placed at such an angle that the amount of diffuse reflectance being detected is optimised and so that the specular reflection from the laser can be seen visibly to miss the monochromator entrance. One problem not considered so far is that the diffusely reflected light from both the laser and arc lamp are being collected from the sample, this can be overcome by filtering out the former. The filters used for the second (532nm), third (354nm) and fourth (266nm) laser harmonics are aqueous cobalt sulphate solution, aqueous sodium nitrite solution and a 300nm non-fluorescent cut off filter, respectively. The geometry and optical layout around the sample are illustrated in figure 2.2 and the spectra for the laser filters are shown in figure 2.3 (a), (b) and (c).

(e) Photomultiplier

Usually a R928 photomultiplier tube (supplied by Hamamatsu Ltd.) is used as the photodetector, this is a general tube with a spectral response from 185nm to 930nm and a peak response at 400nm. The photomultiplier has a working voltage applied to it from a power supply unit. The signal obtained from the photomultiplier can therefore be increased, if the incident light is low, by changing this applied voltage.

(f) Shutters

In the experimental set-up, there are two electromechanical shutters, one situated in front of the arc lamp and the second between the laser and the sample. These shutters, manufactured by Uniblitz Ltd., can be operated manually or under computer control via a Uniblitz shutter control power supply.
FIGURE 2.2 Schematic illustration of the unique sample geometry used in diffuse reflectance laser flash photolysis.
FIGURE 2.3 Absorption spectra for various filters, namely (a) Aqueous cobalt sulphate, (b) Aqueous sodium nitrite and (c) 300 nm cut-off filter
(g) Computer control

In the Loughborough set-up a DEC MINC PDP-11 microcomputer is used to control laser firing, pulsing of the arc lamp, shutter operation, triggering and transfer of data from the digitizer (see later). A computer interface control box acts as an intermediate between the computer and the various components under its control. The device takes the 5V logic level signals from the computer (DIGITAL OUTPUT SOCKET) and converts them into an appropriate voltage to operate the various components. A complete description of the triggering of the apparatus has been given elsewhere [90].

There are two main FORTRAN programs used in the running of the apparatus, the first program (called SETUP) sets up the digitizer and then supplies regular laser pulses in order that adjustments can be made to optimise the signal. The second program (called OPTICS) is used to run the apparatus and transfer transient absorption data from the digitizer to the computer.

(h) Digitizer

The digitizer used is a TEKTRONIX 7912AD programmable device. This device is operated with a 7B90P Tektronix programmable time base and 7A16P Tektronix programmable amplifier plug-ins. The latter has recently been replaced with a newly purchased 7A13 Tektronix differential comparator plug-in which has the offset facility to enlarge small signals, however, this device has the disadvantage of not being programmable.

The digitizer is interfaced to the PDP-11 computer via a IEEE-488 bus, which transmits instructions from the computer and data from the digitizer. A full description of the digitizer can be found elsewhere [90,92].
FIGURE 2.4 Schematic diagram of the apparatus used in diffuse reflectance laser flash photolysis

MONOCHROMATOR

PHOTOMULTIPLIER

SAMPLE

PULSED ARC LAMP

PULSED DYE LASER

NEODYMIUM/Y.A.G. PULSED LASER

TEKTRONIX 7912AD Programmable Digitizer

MINC PDP 11/03 Computer

--- LIGHT PATH

--- ELECTRICAL SIGNAL

S = SHUTTER

L = LENS
A large number of FORTRAN programs exist on the PDP-11 computer to analyse data obtained from the previously described apparatus, however, the two main programs are called DECAY and SPECT. As the name suggests the latter extracts time resolved spectral data from a data file. The former is a full kinetic analysis program, which corrects the data for baseline fluctuations and emission, and then gives the option of various kinetic analysis procedures. The analysis program has been well documented [93] and the theory of the analysis is described briefly in section 3.2 (a) i. The program is used in conjunction with a (RS-232 interfaced) TEKTRONIX 4662 graphics plotter and a DEC line printer, in order to obtain hard copies of plots, results and data.

A diagramatic representation of the diffuse reflectance set up is given in figure 2.4.

### 2.2 Transmission Laser Flash Photolysis

The excitation used was obtained from a LASER ASSOCIATES MODEL 211A ruby laser, which is passively Q-switched. The output was passed through a Wratten 39 gelatine filter to remove scattered light from the flash lamps that pump the ruby laser rod; the pulse then entered an ammonium dihydrogen phosphate (ADP) crystal and, with about 5% conversion, yields a pulse of about 80mJ at 347nm with a half-peak width of approximately 20ns. A 15mm cell containing 0.05m aqueous copper sulphate solution, placed after the ADP crystal, removes a high percentage of the residual fundamental.

The monitoring beam is supplied using excess light from the comparatively long lived (approximately 2ms), high intensity discharge
lamp used to pump the ruby laser rod. This beam is collected through the side of the laser cavity by an optical fibre and is passed through the sample, which is contained in a 10mm fluorometer cell, at right angles to the laser pulse. A second optical fibre picked up the transmitted monitoring beam and conveyed it to the Bausch and Lomb high intensity grating monochromator. This had a RCA 931-A photomultiplier tube fitted on to the exit slit. The tube was normally working in the voltage range 440-550V, supplied by a Fluke 415B power supply unit. The overall spectral response of the above monitoring system (i.e. fibre optics, filters, monochromator and photomultiplier) was reasonable from 400 to 600nm, and maximum at 500nm.

The photomultiplier signal is sent to a Datalab DL 922 transient recorder which is triggered by a photodiode which detects a portion of the scattered laser light, the transient decay is subsequently displayed on a Hewlett-Packard 1340A display. The digitized data can then be transferred to a PET Commodore computer, by means of an 8 bit word parallel interface, under the control of a recording program written in BASIC. There are two reading programs; TREC, for single wavelengths and RECORD, for a series of wavelengths when recording transient spectra. In addition there are two analysis programs, one for each recording mode, namely KIN-FIT and SIMPLE-FIT respectively.

The above apparatus was modified and interfaced to the PET computer by C. Michael, who also wrote all of the recording and analysis programs mentioned above. A more full description of the laser and detection system is given by Adams [94], while the more recent modification and interfacing work is detailed by Michael [95]. A schematic diagram of the apparatus is given in Figure 2.5.
FIGURE 2.5 Schematic diagram of the ruby laser transmission flash photolysis apparatus
2.3 Picosecond Pump and Probe Set-up

This work was carried out at the Rutherford Appleton Laboratory (R.A.L.) at their Laser Support Facility (L.S.F.) and involves the application of the so called "pump and probe" method to diffuse reflectance flash photolysis in the picosecond time domain. The opaque sample is excited (pumped) at one wavelength and analysed (probed) with a wavelength of double the frequency, however, in some of the more recent work a continuum was produced from the probe beam by passing it through a cell of distilled water. This produces a range of probe wavelengths either side of the incident probe light [97]. The laser system used is based around a SPECTRA PHYSICS SERIES 3000 C.W. Nd/YAG laser, which when modelocked and frequency doubled (using a potassium titanyl phosphate, KTP, crystal), can produce 532nm with less than 85ps pulses.

These pulses are then used to synchronously pump a dye laser (SPECTRA PHYSICS 375B) which is tuneable in the range 560-680nm. The low energy pulses produced can then be amplified at 10Hz, with a typical energy gain of $5 \times 10^5$, using a pulsed dye amplifier. This consists of a frequency doubled Q-switched Nd/YAG laser (QUANTA RAY DCR-2) and a three stage travelling wave dye amplifier chain (QUANTA RAY PDA-1). The above system is capable of exhibiting energies of 500μJ at 590nm with a pulse width of approximately 6ps. Full details of the above laser system are published elsewhere [97], and a schematic diagram is given in Figure 2.6.

In the experiments at R.A.L. the 590nm output was frequency doubled (with an efficiency of 7-10%) to produce a laser beam of 295nm with residual 590nm, which is subsequently split into constituent
FIGURE 2.6 Schematic illustration of the picosecond laser system used at the Rutherford-Appleton laboratory.

- LIGHT PATH
- MIRROR

CW MODELOCKED Nd YAG

SYNCHRONOUSLY PUMPED DYE LASER

Q-SWITCHED Nd YAG

PULSED DYE AMPLIFIER

PULSE LENGTH = 5 ps
PULSE ENERGY = 0.5 mJ
wavelengths using a 90° quartz prism. The 590nm portion is used to
probe and the 295nm is employed as the pump. The latter is directed
through a system of mirrors, diaphragms and quartz lenses on to the
sample, and during its path it is passed through a ROFIN MODEL 7500
frequency programmable light chopper. This is chopping at 35Hz and is
synchronised with the 10Hz laser signal, giving an overall effect of
chopping out every other pump pulse. This facility enables results to
be interleaved. For example, with no probe light a series of 200
shots would consist of interleaved background (no pump or probe) and
emission (pump and no probe) data (see section 3.2 (b) (i) for full
details of data collection).

The probe beam is directed on to the sample via a delay line,
consisting of a corner cube mounted on a computer controlled slide
unit. The corner cube is able to move anywhere along the 76cm slide
and can consequently introduce a variable delay of up to about 5ns for
the probe beam. A schematic diagram of the pump and probe beams
optical paths', plus a representation of the detection system, is
given in Figure 2.7.

The detection system used in the set-up involves the measurement
of three different detector signals, namely incident pump, incident
probe and the diffusely reflected probe off the sample. Each signal
is measured on a difference detector, based on the design of Pollard
and Zenith [98], but only operated in single channel mode. This
detector employs 1cm x 1cm HAMAMATSU U.V. sensitive PIN diodes
(S1723-05). It has been found [99] that to preserve the linear
response of the detector the signal should be less than 250mV. This
limit is adhered to by inserting the appropriate neutral density
FIGURE 2.7 Schematic diagram of the optics and detection system employed in picosecond diffuse reflectance laser flash photolysis.

**LASER SYSTEM**
- OUTPUT 590 nm (PROBE) AND 295 nm (PUMP)
- 10 μJ/pulse. Width 6 ps

**Components:**
- MONOCHROMATOR
- SR 245 GATED INTEGRATOR AND BOXCAR AVERAGER
- I.B.M. COMPUTER
- SAMPLE DETECTOR
- PROBE REFERENCE DETECTOR
- PUMP REFERENCE DETECTOR
- CORNER CUBE
- OPTICAL FIBRE
- ELECTRICAL SIGNAL
- MIRROR
- SHUTTER
- LENS
- BEAM CHOPPER
- BEAM SPLITTER
filters in the beams, also some signal is removed by electrical
gateing. The detectors are positioned to collect the desired portion
of the filtered pump or probe beams. However, with the recent
introduction of continuum generation into the probe beam a more
practical method of probe detection was required. This was supplied by
collecting the reference and reflected probe light using fibre optics
and passing both beams through the same monochromator. It was found
that the appropriate photodiodes could be positioned intimately against
the exit slit of the monochromator and the two detector signals were
independent of each other (i.e., virtually zero "cross-talk" between
the two beams within the monochromator). This modification allowed
the analysis to occur with variable wavelength probe beam, rather than
the very restrictive single probe wavelength.

The electrical signals from the detectors are collected using model
SR250 (Stanford Research Ltd.) gated integrator and boxcar averager.
This device applies a suitable electrical gate to each signal, and
integrates the signal over this gate. In addition it samples the signal
from each detector when the device is triggered by the laser (i.e., each
time a laser pulse hits the sample). During a series of interleaved
shots (e.g. 200 interleaved baseline and emission shots) the SR250
stores the data in an internal buffer, and after the run it transfers
the data (under computer control) to the IBM XT microcomputer which is
used to operate the apparatus. The computer is also interfaced to the
delay line slide stepper motor and to an SR245 (Stanford Research Ltd.)
programmable computer interface. This acts as an analogue to digital,
digital to analogue interface and via this the computer can both control
devices such as electrical shutters and also sample averaged detector
outputs from the SR250 boxcar averager. The latter function is of great
use in setting-up the correct sensitivities, gate widths and positions and light intensities for each detector.

As illustrated in Figure 2.7 there are two computer controlled shutters in the set-up, one in the probe beam and the second in both beams before the separation prism. The collection (and subsequent analysis) of data is controlled using a BASIC program called SR which was written mainly by P.A. Leicester (Loughborough University). With the automated data collection option the program reads a series of slide delays from a file and collects data at each delay. In general two data sets are collected, firstly the probe shutter is shut (by the computer) and 200 shots are recorded, however, the chopper removes every other shot and consequently an interleaving of data is achieved. This consists of alternate background (no beams) and emission (pump only) shots, 100 of each. The program then allows for the collection of interleaved baseline (probe only) and transient (pump and probe) by opening the probe shutter. During the periods of data transfer and processing, when data is not being collected, the shutter that stops both beams is shut by the computer to prevent sample damage.

The automatic data collection is a very important part of the set-up which allows data to be collected in the most reproducible and efficient manner possible. This method of detection has provided some interesting results with reasonable levels of scatter, but there are still problems that need careful consideration in the future (e.g. hot spots in the laser which would afford fluctuations in the results).

2.4 Fluorescence Lifetime Measurements using Single Photon Counting

Many excellent articles describing the various theoretical and experimental aspects of the technique of single photon counting are
available in the literature [100,101]. The basic principle of operation is that a signal is sent simultaneously to trigger a light source and start a voltage ramp in a time to amplitude converter (TAC). A sample is excited by the light source and the resultant emission is detected on a photomultiplier, which in turn provides a stop signal for the TAC voltage ramp. The final value of this voltage is then presented to a Multichannel Analyser (MCA) as a representation of the delay time. The process is repeated many times in order to provide statistical significance (see later for details).

The light source is provided by the strong nitrogen line (at 358nm) from a Nitrogen/Hydrogen arc (350 millibars N\textsubscript{2}/250 millibars H\textsubscript{2}) which is capable of producing about 20000 photons per second, and has a pulse width (at half height) of 2-3ns. The excitation source is passed into a FLUOROLOG 222 SERIES SPECTROFLUOROMETER which contains a Jobin Yvon excitation double monochromator and Spex 1032 emission double monochromator fitted with an RCA (C31034) photomultiplier on the exit slit. The sample positioned after the excitation monochromator is excited and the resultant emission is detected on the photomultiplier. The complex timing electronics used in the set-up are provided by ORTEC and are described fully elsewhere [102], however, due to instrumental difficulties the normal ORTEC model 6200 MCA was replaced by a NORLAND INO TECH 530 MCA during this period of research at the University of Tübingen.

Accurate single photon data can only be obtained if no more than one emission photon is detected per excitation, otherwise distortions in the results occur due to pulse pile-up. The emission beam of photons from the sample must be attenuated in order to ensure that detecting more than one photon per excitation is a very rare statistical
event; Poisson's equation predicts that this can be achieved by recording 2% of the available photons (i.e. 400 photons per second) [101].

In any fluorescence decay recorded for a sample an overlapping light source decay will also be present. The light source decay must be recorded, by replacing the sample with non-fluorescent Barium sulphate, to allow a deconvolution procedure to be applied. However, it has been shown [101] that for the data to be statistically significant, with a low enough signal to noise ratio to enable accurate lifetime calculations, at least $10^4$ counts should be accumulated in the peak channel. The lifetime calculations are described fully elsewhere [103].

2.5 Photoconduction Studies using Electostatic Test Rig

This series of experiments were undertaken using equipment at 3M's Research Ltd., Harlow, Essex. The general aim of the experiments is to apply a surface charge to a polymer film containing photosensitive materials, and then to irradiate the sample and observe the change in surface potential as a function of time.

The photosensitive material within a polymer is coated on an aluminium base (see section 2.7 for details). A section of the coated aluminium, of approximate dimensions 6cm x 3cm, is then grounded on a turntable. This can be moved using a conventional stepper motor in order that the sample can be shifted to various operating positions. The sample is allowed to dark-adapt for a period of about five minutes and is then moved under a corona charging unit where it is charged to an initial surface potential $V_0$. The corona charging unit consists of fine wires which have a potential of 5-6kV applied between themselves.
and the conductive base of the sample. The magnitude and polarity of this potential is controlled by a MONROE CORONAPLY MODEL 151A voltage supply unit. Further details relating to corona discharge characteristics and their application in this field of study have been published elsewhere [104].

The sample is then moved to the analysis position, using the stepper motor, where the resultant surface potential is measured using a MONROE transparent electrostatic probe. Directly above the transparent probe sits a continuous tungsten lamp used to irradiate the sample. The wavelength of the light source can be modified using 10nm bandpass interference filters, while the intensity of the output can be altered by the insertion of a neutral density filter. The absolute intensity of the light source, when combined with different interference and neutral density filters, is determined using a MODEL 730A RADIOMETER (OPTRONIC LABORATORIES LTD.). A general description of the construction, operation and performance of transparent electrostatic probes has been published elsewhere [105].

The electrostatic probe output is connected to a MONROE MODEL 244 ISOPROBE electrostatic voltmeter which displays the magnitude of the surface potential. This output is subsequently sent to a chart recorder (BRYANS 26000 A3 XY RECORDER) to provide a graphical representation of the variation of surface potential with respect to time. Such a variation is analysed with and without illumination, i.e. light and dark decay, and the results from this give the rate of photoinduced discharge for the particular sample (see section 3.2 (d) (i)). A schematic diagram of the apparatus, in both the charging and analysis positions, is given in Figure 2.8.
FIGURE 2.8 Schematic illustration, in both charging and analysing positions, of the apparatus used in the photoconduction studies.
2.6 Other Apparatus

Ground state absorption spectra were recorded using a PYE UNICAM SP8-250 U.V./VIS. spectrophotometer. This instrument could also be converted to measure ground state reflectance spectra using a PYE UNICAM DIFFUSE REFLECTANCE ACCESSORY. During research at 3M's Research Ltd. absorption spectra were recorded on a PERKIN ELMER LAMBDA 5 U.V/VIS. SPECTROPHOTOMETER.

Fluorescence emission and excitation spectra were recorded using a PERKIN ELMER 3000 FLUORESCENCE SPECTROMETER. However, during a period of research at the University of Tubingen more accurate spectra were obtained using a FLUOROLOG 2 SERIES SPECTROFLUOROMETER with a DATAMATE data acquisition system. The DATAMATE not only controls the operation of the apparatus but also allows data at each wavelength to be collected and averaged over a set time period. In addition noise on spectra can be reduced by summation of a number of spectra, there is also the facility to correct the resultant spectra for variation in photomultiplier response as a function of wavelength.

As mentioned above, ground state diffuse reflectance spectra can be recorded using the PYE UNICAM attachment, however, this system only monochromates the excitation beam and can not be used to study fluorescent samples. In the case of fluorescent samples an 'in house' apparatus was set up by cannibalizing a redundant APPLIED PHOTOPHYSICS fluorescence spectrometer, and allowing the reflected beam to be monochromated and consequently remove the fluorescence component of the diffuse reflectance spectrum. Some spectra were also run at the University of Tubingen on a double monochromator 'in house' apparatus.
In addition to the apparatus discussed in section 2.2 a few transmission flash photolysis results were also obtained using a basic APPLIED PHOTOPHYSICS flash photolysis apparatus with flash lamp excitation. This apparatus, at 3M's Research Ltd., was interfaced to an APPLE computer which provided a data collection and analysis program.

2.7 Polymer Film Sample Preparation

A fairly large proportion of the samples studied consisted of material within polymer films, coated on various bases. Such samples are prepared by dissolving an appropriate mass of the material in an approximately 10% solution of the required polymer in chloroform. A portion of the resultant solution is then coated on to either an aluminium or transparent polyester base, using a number 8 K-bar (manufactured by R-K PRINT-COAT INSTRUMENTS LTD.). A K-bar consists of a stainless steel bar wound with wire of a selected diameter to give a predetermined thickness of wet film deposit, for example, the number 8 K-bar used gives a wet thickness of approximately 100μm which dries to approximately 10μm. The sample is then left to dry overnight in an oven at 60 - 70°C, allowing the solvent to evaporate and producing a hard, durable polymer coating. The characterisation of the above films, in terms of optical density and thickness, is detailed elsewhere [106] together with full preparation details.

2.8 Materials

(a) Reagents supplied by 3M's Research Limited

(i) Pyrazolines

\[
\begin{align*}
R-\text{CH}=\text{CH}-&-\text{C}^2\text{N}^3\text{N}^4\text{Ph}^5 \\
\text{H}-\text{C}^2\text{C}^5\text{H}^4&\text{H}^4R
\end{align*}
\]
**PYA** \( (R = Ph) \)

1,5-diphenyl-3-styryl-2-pyrazoline

**PYB**

\[
\begin{array}{c}
\text{R} \\
\text{S}
\end{array}
\]

1-phenyl-5 (thien-2'-yl) -3 [2''- (thien-2'-yl) vinyl] -2-pyrazoline

**PYC**

\[
\begin{array}{c}
\text{R} \\
\text{S}
\end{array}
\]

1-phenyl-5 (thien-3'-yl) -3 [2''- (thien-3'-yl) vinyl] -2-pyrazoline

**PYD**

\[
\begin{array}{c}
\text{R} = C_6H_4-\mu(CH_3)_2 \\
\text{phenyl} \quad \text{phenyl}
\end{array}
\]

1-phenyl-5 (dimethylamino) -3 [(dimethylamino) vinyl] -2-pyrazoline.

**PYE**

different structure to the general one described above (i.e. 'no substituent in position 3 or 5).

1-phenyl-2-pyrazoline

Purified by recrystallization from petroleum ether, using carbon black to decolorize the solution.
(ii) Dyes

Azo dyes used in the first year of the project will not have their structure disclosed due to 3M's Research confidentiality agreement. If any relevant results had been presented on these compounds the structures would have been presented, however, since only negative results were obtained and the use of the compounds were discontinued it was felt that there was no need to name the substances.

The 3M's dye Disulfone magenta (DSM) (Chemical Abstracts Registry Number 58559-02-7) is the subject of a number of patents all assigned to 3M's [107,108]. The structure of the dye DSM is:

\[
\begin{array}{c}
\text{Me} \\
\text{N} \\
\text{Me} \\
\end{array}
\begin{array}{c}
\text{SO}_2\text{CF}_3 \\
\text{SO}_2\text{CF}_3 \\
\end{array}
\]

Chemical abstracts name 4-[(4-bis [(trifluoromethyl) sulfonyl]-1,3-butadienyl]-N,N-dimethybenzenomine.

(iii) Polymers

Polycarbonate (PC) Panlite L1 250  Pc Low, NA = 30K
Polymethylmethacrylate (PMMA) Dupont  Mw = Med (Elvaite 2009)

(b) Solvents

Benzene (spectroscopic grade) Fisons
Acetonitrile (HPLC grade) Aldrich (water removed by distillation with calcium hydride (Fisons) and kept dry using molecular seives 4A Laporte)).
Tetrahydrofuran (HPLC grade) Aldrich
Cyclohexane (HPLC grade) Aldrich
Dichloromethane (spectroscopic grade) Fisons
Chloroform (spectroscopic grade) Fisons
Absolute Ethanol James Barrows Ltd.
Petroleum ether Careless Solvents Ltd. (40:60)

(c) Other Chemicals

Xanthone (Aldrich) purified by dissolving in Petroleum ether and passing through a column of grade 3 alumina (BDH) to remove impurities. The resultant material was then recrystallized three times from petroleum ether.

Benzophenone (Aldrich) purified by recrystallizing three times from absolute ethanol

Anthracene (scintillation grade, BDH)
Naphthalene (scintillation grade GOLD LABEL Aldrich)
1,4-di[2-(5-phenyloxazolyl)]-benzene (POPOP) (GOLD LABEL, Aldrich)
9,10-diphenyl anthracene (DPA) (Aldrich)
1,1,4,4-tetraphenyl-1,3-butadiene (TPB) (Aldrich)
Nitrosonium tetrafluoroborate NOBF$_3$ (Lancaster Synthesis Ltd.)
p-dinitrobenzene (Aldrich).
CHAPTER 3: RESULTS AND DISCUSSION

3.1 Solution Studies

(a) Ground State spectroscopic Studies

The ground state absorption spectra of the pyrazolines exhibited two main bands in general, one in the U.V. and the second in the near U.V./Visible. Work by Nurmukhameter [109,110] suggests that the longer wavelength absorption is due to a $\pi \rightarrow \pi^*$ transition, while the short wavelength absorption is associated with an $n \rightarrow \pi^*$ transition. One explanation of this reversal from the normal situation of $\pi \rightarrow \pi^*$ at shorter wavelength, is that upon absorption a major disturbance of the $\pi$ system could be occurring. The visible band of the spectra will be considered in more detail since this is the spectral region where flash photolysis excitation is normally achieved.

The absorption spectra of PYA in benzene, dichloromethane and tetrahydrofuran gave absorption maxima and extinction coefficients of 386nm ($\varepsilon = 3.3 \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$), 383nm ($\varepsilon = 3.6 \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$) and 381nm ($\varepsilon = 3.6 \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$), respectively. The above solutions obey Beer's law in the concentration range $8 \times 10^{-6}$ mol $\text{l}^{-1}$ to $3 \times 10^{-5}$ mol $\text{l}^{-1}$. The values quoted above for the extinction coefficients are averaged from three spectra with an error of $\pm 0.1 \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$. The observed solvent shifts suggest that the excited state has more polar nature than the ground state, which is in agreement with Sandler and Tsou [111]. In Table 3.1 spectroscopic data in benzene solution is presented for all the pyrazolines. The data is obtained over a range of concentrations ($8 \times 10^{-6}$ to $3 \times 10^{-5}$ mol $\text{l}^{-1}$) and all the pyrazolines obey Beer's law. The extinction coefficients are averaged and contain an error of approximately $\pm 0.1 \times 10^4$. The above does not apply to PYE which were obtained over a
concentration range of $5 \times 10^{-3}$ to $2 \times 10^{-2}$ mol l$^{-1}$ and the error on the extinction coefficient is $\pm 0.2 \times 10^1$.

### Table 3.1 Spectroscopic Data for Pyrazolines in Benzene

<table>
<thead>
<tr>
<th>PYRAZOLINE</th>
<th>$\lambda_{\text{max}}$/nm</th>
<th>$\varepsilon$/mol$^{-1}$ cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PYA</td>
<td>386</td>
<td>$3.3 \times 10^4$</td>
</tr>
<tr>
<td>PYB</td>
<td>395</td>
<td>$3.1 \times 10^4$</td>
</tr>
<tr>
<td>PYC</td>
<td>378</td>
<td>$3.2 \times 10^4$</td>
</tr>
<tr>
<td>PYD</td>
<td>400</td>
<td>$4.8 \times 10^4$</td>
</tr>
<tr>
<td>PYE</td>
<td>397</td>
<td>$6.1 \times 10^1$</td>
</tr>
</tbody>
</table>

#### (b) Flash Photolysis

When the various pyrazolines were subjected to flash photolysis, with 347 nm ruby laser excitation, in benzene solution no transient absorption was observed with or without oxygen. Various concentrations of PYA, PYB, PYC and PYD ranging from $1 \times 10^4$ to $1 \times 10^5$ mol l$^{-1}$ were investigated. The absence of a transient is not very surprising when the very high fluorescence quantum yield is considered (see section 3.1 (c)). However, in the absence of oxygen a transient could be sensitized using a suitable triplet energy donor. Benzophenone ($1 \times 10^{-2}$ mol l$^{-1}$) provides an excellent donor with a triplet quantum yield of essentially unity in a degassed benzene solution [112] and consequently produced substantial amounts of the sensitized pyrazoline transient in the case of PYA, PYB, PYC and PYD. All of the following systems were investigated using each of these pyrazolines unless otherwise stated.
The concentration of pyrazoline is very important in achieving optimum sensitization, because at low concentrations (1 x 10^-5 mol l^-1) the pyrazoline cannot intercept enough of the donor triplet's decay causing reduced sensitization. However, if the concentration is increased too high (1 x 10^-4 mol l^-1) the pyrazoline absorbs too much of the 347nm excitation source thus reducing the fraction absorbed by the donor and causing fewer donor triplets to be available for transfer. By varying the concentration of the various pyrazolines from 1 x 10^-5 to 1 x 10^-4 mol l^-1 an optimum concentration of 2 x 10^-4 mol l^-1 was found to give reasonable sensitization for all four pyrazolines studied.

The other two triplet energy donors investigated were xanthone (3 x 10^-4 mol l^-1) and anthracene (2 x 10^-4 mol l^-1). With these donors, although sensitization of the pyrazoline transient was achieved, for all four pyrazolines, the amount of transient absorption was found to be much less compared to using benzophenone as the triplet energy donor. Time resolved transient spectra for PYD with benzophenone and PYB with anthracene, both in benzene at the concentrations used above, are given in Figure 3.1 a and 3.1 b, respectively.

The rate constant, k_p, for the decay of the pyrazoline transient can be determined at the absorption maximum, λ_max, by applying the kinetic analysis at times where the transient decay is solely due to the pyrazoline species because all the donor has either transferred or decayed. Triplet benzophenone decays fully within 5μs of production, in the absence of oxygen, therefore with pyrazoline present after this time the decay is due to the pyrazoline transient, and can be fitted
FIGURE 3.1a Time resolved spectra for PYD species sensitized from Benzophenone in benzene solution

![Graph showing absorbance vs wavelength for PYD species sensitized from Benzophenone.]

FIGURE 3.1b Time resolved spectra for PYB species sensitized from Anthracene in benzene solution

![Graph showing absorbance vs wavelength for PYB species sensitized from Anthracene.]

WAVELENGTH / nm

TIME / μS.

1.5

5

10

2.5

4

6
with a first order kinetic expression. The spectra and decay's of the pyrazoline transient are identical within experimental error with different donors. The rate constants were calculated for each pyrazolines with each of the triplet energy donors and the values were averaged, see Table 3.2. In some cases (e.g. PYC and xanthone) it was difficult to analyse the decay because of the low absorption of the sensitized transient. The values of $k_p$ have an estimated error of $\pm 0.1 \times 10^5 \text{ s}^{-1}$.

Table 3.2 Rate Constant, $k_p$, for First Order Decay of Pyrazoline Transient

<table>
<thead>
<tr>
<th>PYRAZOLINE</th>
<th>$\lambda_{\text{max}}$/nm</th>
<th>$k_p$/s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PYA</td>
<td>460</td>
<td>$1.3 \times 10^5$</td>
</tr>
<tr>
<td>PYB</td>
<td>490</td>
<td>$1.8 \times 10^5$</td>
</tr>
<tr>
<td>PYC</td>
<td>490</td>
<td>$1.7 \times 10^5$</td>
</tr>
<tr>
<td>PYD</td>
<td>480</td>
<td>$1.4 \times 10^5$</td>
</tr>
</tbody>
</table>

To assist with the assignment of the pyrazoline transient it is important to investigate the possibilities of chemical reaction and complex formation. The absorption spectra of all pyrazolines were found to be additive for all the solutions which suggests the absence of any appreciable complex formation. Also the absorption spectra before and after each flash photolysis experiment (i.e. up to 50 laser shots) were recorded and found not to differ within experimental error for any of the solutions. This is indicative of the absence of any net chemical reaction between the pyrazoline and donor. In some of
the assignment experiments β-carotene was used (see later) and the absence of any net chemical reaction or complex formation was again inferred from absorption spectra recorded in the presence of β-carotene. However, β-carotene has a low light stability and the above results suggested that fresh solutions should be used after 20-30 laser shots to be sure of no degradation.

The pyrazoline transient could either be the triplet or the cation radical produced from the triplet, another possibility is a species resulting from donor hydrogen abstraction, however, unless the process is reversible the fact that the absorption spectra before and after flash photolysis are identical is evidence against the latter occurring. A good method of triplet assignment is to add a triplet energy acceptor, such as β-carotene, to the pyrazoline/donor system. β-carotene exhibits no direct triplet production with or without oxygen and its role as a triplet acceptor has been characterised elsewhere [113,114]. A range of β-carotene concentrations from 5 x 10^{-6} to 1 x 10^{-5} mol l^{-1} were examined with donor and/or pyrazolines. At low concentrations there was too little acceptor to intercept the pyrazoline triplet decay, while at high concentrations the β-carotene was absorbing too much of the analysing light, and thus masking the transient, and in addition intercepting any excess triplet donor decay rather than the pyrazolines triplet. It was found experimentally that an optimum β-carotene concentration of 2.5 x 10^{-5} mol l^{-1} avoided the problems encountered at the concentration extremes.

Qualitative work appeared to produce an increase in β-carotene triplet, at its absorption maximum (520nm), in the presence of pyrazoline and donor compared to just donor. This result was confirmed
for all pyrazolines in the presence of each donor, however, the pyrazoline triplet has a very low absorption in some cases and also several triplet species are decaying simultaneously at the β-carotene transient maxima. It was therefore felt that a more quantitative mathematical treatment was required.

The mechanism involved in the system containing donor (D), pyrazoline (P) and β-carotene (C) can be represented as follows :-

\[
D^* \xrightarrow{k_d} 2D^* \xrightarrow{k_{dc}[C]} 3C^* \xrightarrow{k_c} C
\]

The first approach to mathematical fitting was to attempt to fit the complete mechanism, including the mixed first and second order decay of the donor which is especially important when dealing with benzophenone. However, the very strong pyrazoline fluorescence completely masked the area relating to the build up of pyrazoline triplet and it proved impossible to gain any information about the rate constant, \( k_{dp} \).
A less sophisticated fitting methodology was therefore employed in which xanthone was used as the energy donor. The donor decays and transfers very rapidly therefore the data was only considered after the triplet xanthone processes were complete, this happened to occur in the region masked by the pyrazoline fluorescence. The fitting process uses a new relative value of time zero as a starting point with pyrazoline and β-carotene triplets as the initial species present. The mechanistic steps are:

\[ \begin{align*}
3_p^\ast & \xrightarrow{k_p} p \\
3_c^\ast & \xrightarrow{k_c} c \\
3_p^\ast + c & \xrightarrow{k_{pc}} p + 3_c^\ast 
\end{align*} \]

It follows from the mechanism that

\[ \frac{d[P^\ast]}{dt} = -k_p[P^\ast] - k_{pc}[P^\ast][C] \] (3.1)

i.e. \([P^\ast]_t = [P_0^\ast] \exp(-(k_p + k_{pc}[C])t) \] (3.2)

and \[ \frac{d[C^\ast]}{dt} = -k_c[C^\ast] + k_{pc}[P^\ast][C] \] (3.3)

It can also be shown, see Appendix A, that the solution to equation 3.3 is:

\[ [C^\ast]_t = \frac{[C_0^\ast]}{\exp(k_c t)} + \frac{k_{pc}[C][P_0^\ast]}{(k_c - k_p - k_{pc}[C])} \exp((k_c - k_{pc}[C] - k_p)t) \exp(k_c t) \] (3.4)

It is the absorbance which is being fitted therefore the total absorbance, \( A \), must be considered

\[ A = c_p[P^\ast]_t + c_c[C^\ast]_t \] (3.5)
With equations 3.2, 3.4 and 3.5 the above mechanism can be represented, these can be combined into a single equation suitable for computation, namely

\[ A = [P_o^*] \exp(-(k_p + k_{pc}[C])t) + [C_o^*]\exp(-k_c t) + \]

\[ \frac{c_c}{c_p} \frac{k_{pc}[C]}{(k_c - k_p - k_{pc}[C])} \] \[ \exp(-(k_{pc}[C] + k_p) t) - \exp(-k_c t) \] \]

(3.6)

Where \(c_c\) = Extinction coefficient of \(\beta\)-carotene triplet, \(c_p\) = Extinction coefficient of pyrazoline triplet, \(P_o^*\) = Initial absorption of pyrazoline triplet at the chosen \(t = 0\), \(C_o^*\) = Initial absorption of \(\beta\)-Carotene triplet \(k_p\) = Rate constant for decay of the Pyrazoline triplet and \(k_{pc}\) = Energy transfer rate constant from pyrazoline triplet to \(\beta\)-carotene triplet.

A FORTRAN program was written on the university mainframe to fit the above expression to a set of experimental data, by varying \(k_{pc}\) and \(c_c/c_p\) and keeping the other terms constant. The fitting was achieved using a modification of the Gauss-Newton method supplied in NAG FORTRAN Library routine E04FCF. The user sets the values of \(P_o^*\) and \(C_o^*\) (see later), while \(k_p\) is set at the appropriate value from Table 3.2 and \(k_c\) is set at the literature value of \(1.3 \times 10^5\) \(s^{-1}\) [113].

The value of the absorbance at the new zero time (at 520nm) for PYD and \(\beta\)-carotene each with only xanthone (in degassed benzene) were 0.069 and 0.074 (average of 3 transients). When PYD, \(\beta\)-carotene and xanthone are present in the system, the former two species compete to intercept the decay of xanthone triplet. The values of the rate
constants relating to the xanthone transfer to PYD and \( \beta \)-carotene (i.e. \( k_{dp} \) and \( k_{dc} \)) have not been determined for this system, as explained previously. However, if the values are assumed to be between \( 1 \times 10^{10} \) and \( 2 \times 10^{10} \) \( \text{s}^{-1} \) this will provide a reasonable approximation. The value of the transfer rate constant between PYD and \( \beta \)-carotene is approximately \( 1.5 \times 10^{10} \) \( \text{s}^{-1} \) (see fit later). This system (i.e. PYD, \( \beta \)-carotene and xanthone) can be treated mathematically to provide approximate values for \( P_0^* \) and \( C_0^* \):

\[
[P_0^*] = 0.069 \frac{k_{dp} [P]}{k_{dp} [P] + k_{dc} [C] + k_{pc} [C]} \quad (3.7)
\]

\[
[C_0^*] = 0.074 \frac{k_{dc} [C]}{k_{dc} [C] + k_{dp} [P] + k_{pc} [C]} \quad (3.8)
\]

When the fluctuations in laser energy output are considered, together with the approximate nature of the values of the constants in equation 3.7 and 3.8, it was felt that the range of \( P_0^* \) and \( C_0^* \) used in Table 3.3 provided a realistic model. In Table 3.3 the results obtained using the fitting program are illustrated for a series of different \( P_0^* \) and \( C_0^* \) values, the values obtained from it are \( \varepsilon_c/\varepsilon_p \) and \( k_{pc} \).

**Table 3.3** Results from fit of transient absorption data from PYD, \( \beta \)-Carotene and Xanthone System (Details given above)

<table>
<thead>
<tr>
<th>( P_0^* )</th>
<th>( C_0^* )</th>
<th>( \varepsilon_c/1 \text{ mol}^{-1} \text{cm}^{-1} )</th>
<th>( k_{pc}/\text{s}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.04</td>
<td>0.03</td>
<td>3.97</td>
<td>( 1.44 \times 10^{10} )</td>
</tr>
<tr>
<td>0.04</td>
<td>0.01</td>
<td>4.34</td>
<td>( 1.90 \times 10^{10} )</td>
</tr>
<tr>
<td>0.04</td>
<td>0.005</td>
<td>4.43</td>
<td>( 2.01 \times 10^{10} )</td>
</tr>
<tr>
<td>0.05</td>
<td>0.03</td>
<td>3.25</td>
<td>( 1.21 \times 10^{10} )</td>
</tr>
<tr>
<td>0.05</td>
<td>0.02</td>
<td>3.37</td>
<td>( 1.44 \times 10^{10} )</td>
</tr>
<tr>
<td>0.05</td>
<td>0.01</td>
<td>3.52</td>
<td>( 1.70 \times 10^{10} )</td>
</tr>
<tr>
<td>0.05</td>
<td>0.005</td>
<td>3.59</td>
<td>( 1.78 \times 10^{10} )</td>
</tr>
<tr>
<td>0.06</td>
<td>0.03</td>
<td>2.78</td>
<td>( 9.87 \times 10^{9} )</td>
</tr>
<tr>
<td>0.06</td>
<td>0.01</td>
<td>2.98</td>
<td>( 1.44 \times 10^{10} )</td>
</tr>
</tbody>
</table>
The basic conclusion that can be drawn from the fitting routine is that $\varepsilon_c/\varepsilon_p$ is $3.6 \pm 0.8$ and $k_{pc}$ is $1.5 \pm 0.5 \times 10^{10}$. A typical fit is illustrated in Figure 3.2. Land, Sykes and Truscott [115] quote the extinction coefficient of β-carotene triplet, $\varepsilon_c$, to be in excess of $10^5 \text{ mol}^{-1} \text{ cm}^{-1}$, therefore it can be deduced, using the value of $\varepsilon_c/\varepsilon_p$ derived from the above fit, that the extinction coefficient of PYD triplet, $\varepsilon_p$, is in excess of $2.8 \pm 0.5 \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$.

One slightly disappointing aspect of this work was that PYD was the only pyrazoline that gave a large enough signal to enable fitting to be achieved. However, in conjunction with the qualitative observations discussed previously, the above fit provides conclusive evidence for the validity of the proposed mechanism, and more importantly, the existence of the pyrazoline triplet.

One observation not yet commented upon is the low sensitization achieved using xanthone and anthracene as triplet energy donors, compared with benzophenone. As mentioned previously this can be explained in the case of xanthone by the very short triplet lifetime of xanthone (i.e. 0.092μs [113]) and consequently a lower level of pyrazoline interception of the donors triplet decay. In the case of anthracene, however, the triplet lifetime is of a similar magnitude to benzophenone and the triplet quantum yield is reasonably large (approximately 0.72 [116]). A plausible explanation of the low level of sensitization observed with anthracene as the donor, is that the triplet energies of donor and acceptor are comparable. The triplet energy of anthracene is 42 K cal mol$^{-1}$ [117] while the pyrazoline 1,3-diphenyl-2-pyrazoline is reported as having a triplet energy of 48 K cal mol$^{-1}$ [45]. The actual pyrazolines used in this work are of a
FIGURE 3.2 Illustration of a typical fit of transient absorption data for the sensitized PYD triplet, using data created from the proposed triplet energy transfer mechanism (see text for details).

VALUES OF FIXED CONSTANTS:
- RATE CONSTANT FOR DECAY OF PYRAZOLINE TRIPLET = 1.4x10^5
- INITIAL ABSORBANCE OF PYRAZOLINE TRIPLET = 0.04
- INITIAL ABSORBANCE OF β-CAROTENE = 0.03

VALUES OF CONSTANTS FROM THE FIT:
- RATE CONSTANT FOR ENERGY TRANSFER = 1.44x10^10 S^-1
- RATIO OF EXTINCTION COEFFICIENTS (\(\epsilon_p/\epsilon_r\)) = 3.97
different structure to the one cited in the literature and it is therefore conceivable that this explanation could be true.

This section of work was carried out partly in collaboration with C. Michael (University of Thessalonika) who developed the computer software for data collection and simple kinetic analysis. My responsibilities included actual experimentation and the development of the more complex fitting routines (described above) in order to carry out a full interpretation of the results. This work was jointly presented at XI IUPAC Symposium on Photochemistry [118].

(c) Fluorescence

The fluorescence properties of a large selection of 2-pyrazolines have been extensively reviewed in the literature [35,36,37] in connection with their use as optical brighteners [25]. In this section some background fluorescence data relating to the particular pyrazolines under study, will be presented in various solvents and then a quenching study using Disulphone magenta dye will be described.

Initially the PERKIN ELMER 3000 FLUORESCENCE SPECTROMETER had to be calibrated to account for the variation in instrumental response as a function of wavelength. This was achieved by comparing the experimental spectra, for a series of fluorescence standards, with reference spectra obtained from the literature [119]. The fluorescence standards used were Naphthalene \(\left(5 \times 10^{-2} \text{ mol l}^{-1}\right)\), POPOP \(\left(1,4\text{-di[2-(5-phenyloxazolyl)]-benzene}\right) \left(1.2 \times 10^{-3} \text{ mol l}^{-1}\right)\), DPA \(\left(9,10\text{-diphenyl anthracene}\right) \left(1 \times 10^{-2} \text{ mol l}^{-1}\right)\) and TPB \(\left(1,1,4,4\text{-tetraphenylbutadiene}\right) \left(2.9 \times 10^{-3} \text{ mol l}^{-1}\right)\), and resultant calibration curve is given in Figure 3.3. The FLUOROLOG spectrofluorometer used at the University of Tubingen provided a
FIGURE 3.3 Calibration curve for a Perkin Elmer 3000 fluorescence spectrometer, to allow corrected emission spectra to be obtained.
correction facility in good agreement with spectra obtained in Loughborough.

The corrected fluorescence spectra for PYA, PYB and PYC in dichloromethane (all solutions about $1.6 \times 10^{-3}$ mol l$^{-1}$) gave emission maxima at 480nm, 490nm and 470nm, respectively. The spectra were recorded over a range of concentrations and using different excitation wavelengths, and the resultant spectra possessed reproducible spectral shape. The corrected fluorescence maxima for PYB in toluene, ethanol and dichloromethane were 460nm, 493nm and 490nm, again over a range of concentrations.

The fluorescence lifetimes of PYB in ethanol and toluene were determined for solutions of approximate molarity $2 \times 10^{-5}$ mol l$^{-1}$ using the technique of single photon counting at the University of Tubingen, unfortunately due to the limit of time only these two samples were run allowing me to concentrate on solid samples (see section 3.2 (c)). The fluorescence decays were fitted mono-exponentially yielding lifetimes of 3.1 and 2.6ns in ethanol and toluene, respectively. The apparatus used in these experiments is detailed in section 2.4 and in reference 103, also contained in the reference are details of the deconvolution analysis of the fluorescence decays. The technique of single photon counting, including the analysis of the data, has been clearly described elsewhere [100,101,120].

The above work has produced solvent shifts in both fluorescence lifetimes and fluorescence wavelength maxima, namely longer lifetimes and a shift to long wavelengths for the fluorescence spectra in polar solvents. These general trends are in agreement with results already
reported in the literature [35,37].

During the course of the investigation of the electronic energy transfer from PYA to DSM (discussed below) the value of the radiative lifetime of PYA in an oxygenated solution of dichloromethane was required. The limit of time during the visit to the University of "Tubingen had prevented the measurement of this lifetime, however, the value was kindly measured by Prof. S.M.B. Costa (Universidade Tecnica de Lisboa, Lisbon, Portugal), to allow full quantification of the energy transfer problem (see later). The fluorescence lifetime at 480nm for a solution of PYA in dichloromethane (with oxygen) was 3.2nm ± 0.1ns at a concentration of 1 x 10^{-5} and 1.6 x 10^{-3} mol 1^{-1}, exciting at 337nm. The constant lifetime over the above concentration range confirms the absence of any concentration effects within the PYA solution. The lifetime for the more concentrated solution is for the major 93% contribution of a double-exponential fit, and the minor 7% fast component of lifetime 0.5ns would lead to an average lifetime of approximately 3.0ns ± 0.1ns [121].

The fluorescence quantum yields of PYA, PYB and PYC were determined by comparing absolute intensities (i.e. area under the fluorescence spectra) for the sample with a standard material of known quantum yield in solution using the corrected emission spectra [119]. The two reference solutions employed for this purpose were DPA (1 x 10^{-2} mol 1^{-1}) and naphthalene (5 x 10^{-2} mol 1^{-1}) both in cyclohexane. The latter has a quantum yield of 0.23 ± 0.02 without oxygen [119] while DPA has a value of 0.90 ± 0.02 [122] and a ratio of intensities without and with oxygen of 1.38 [119]. Using a value of 0.23 for the quantum yield of naphthalene the quantum yield of DPA in the absence of oxygen was
calculated as 0.86. While when DPA was employed as the standard, with a quantum yield of 0.90 without oxygen, the calculated value of the naphthalene without oxygen was 0.24. In addition the ratio of intensities in the absence and presence of oxygen for DPA was 1.37 from the experimental data, which is in excellent agreement with the literature value of 1.38 [119]. The above consistency between standards adds extra validity to the quantum yields calculated for the various pyrazolines.

The quantum yields of the pyrazolines PYA, PYB and PYC were determined using dichloromethane solution of molarity $1.6 \times 10^{-3}$ mol $1^{-1}$ (approximate) and were calculated with and without oxygen using DPA as the standard. The pyrazolines and standards were recorded using front face reflectance geometry and all spectra were corrected using the calibration mentioned previously, in addition each spectrum was recorded in triplicate to check for consistency. The resultant quantum yields are presented in Table 3.4

Table 3.4 Quantum Yields of Pyrazolines in Dichloromethane

<table>
<thead>
<tr>
<th>PYRAZOLINE</th>
<th>$\Phi$ with oxygen $\pm 0.02$</th>
<th>$\Phi$ without oxygen $\pm 0.02$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PYA</td>
<td>0.66</td>
<td>0.65</td>
</tr>
<tr>
<td>PYB</td>
<td>0.83</td>
<td>0.85</td>
</tr>
<tr>
<td>PYC</td>
<td>0.89</td>
<td>1.01</td>
</tr>
</tbody>
</table>

The next section of work involves a study of the pyrazoline, PYA, in the presence of disulphone magenta (DSM) in a dichloromethane solution. Addition of DSM caused a modification of the PYA fluorescence spectra and intensity. This effect is caused by a transfer of
electronic energy from the donor (PYA) to the acceptor (DSM) via a radiative (trivial) and/or non-radiative mechanism. The former consists of absorption by the acceptor of the emitted radiation from the donor, and it is essential to correct for this before any non-radiative processes can be analysed. The modification of the PYA \((1.6 \times 10^{-3} \text{ mol l}^{-1})\) fluorescence spectra, upon adding varying amounts of DSM \((0 \text{ to } 1.6 \times 10^{-3} \text{ mol l}^{-1})\), is illustrated in Figure 3.4.

This work was carried out in reflectance geometry for which Conte and Martinho [123] have proposed a mathematical correction to effectively "remove" the component due to the radiative process from the fluorescence intensity of the donor. The derivation of the expression is given fully in the reference, and the treatment has been successfully applied elsewhere [124,125]. The correction not only accounts for radiative transfer but also for direct absorption by the acceptor, however, the latter is negligible in this system. The simplified expression for this correction is given in equation 3.9, and a summary of the derivation provided in Appendix B.

\[
I_D^c = I_D^{\text{expt}} = \frac{\varepsilon_D^c C_D + \varepsilon_A^E C_A + \varepsilon_A^E C_A \sin \alpha}{\varepsilon_D^E C_D \sin \beta} \quad (3.9)
\]

In this expression the subscript D and A refer to donor and acceptor, respectively, while the superscript Ex and Em refer to the excitation and emission wavelengths. The terms \(\varepsilon, C, I_D^c, I_D^{\text{expt}}\) are the extinction coefficient, concentration of donor or acceptor (depending on subscript), the corrected donor emission intensity and the experimental (uncorrected) donor emission intensity, respectively.

The angles \(\alpha\) and \(\beta\) in equation 3.9 are related to the geometry of the excitation and emission beams. The exciting beam and the detected
FIGURE 3.4 Illustration of the modification of the PYA emission spectra [in dichloromethane] by the addition of varying amounts of DSM

<table>
<thead>
<tr>
<th>[DSM] / $10^{-4}$ mol l$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
</tr>
<tr>
<td>1.299</td>
</tr>
<tr>
<td>2.597</td>
</tr>
<tr>
<td>3.899</td>
</tr>
<tr>
<td>7.792</td>
</tr>
<tr>
<td>10.39</td>
</tr>
<tr>
<td>12.99</td>
</tr>
<tr>
<td>15.58</td>
</tr>
</tbody>
</table>
beam make the angles $\alpha'$ and $\beta'$ respectively with the front face of the cell, and these are related to $\alpha$ and $\beta$ by Snell's refraction law.

\[
\frac{\cos \alpha'}{\cos \alpha} = \frac{\cos \beta'}{\cos \beta} = n \tag{3.10}
\]

where $n$ is the refractive index of the solvent ($n= 1.42$ for the dichloromethane / air interface). The geometry around the cell is illustrated in Figure 3.5. The values of $\alpha'$ and $\beta'$ for the particular geometry used were 60° and 30°, respectively, leading to value of 69° and 53° for $\alpha$ and $\beta$, respectively.

For the system with PYA as the donor (1.68 x 10^{-3} mol 1^{-1}) and DSM as the acceptor (concentration range 1.3 x 10^{-4} to 1.6 x 10^{-3} mol 1^{-1}), the excitation and emission wavelengths are 380nm and 475nm, respectively. The experimentally derived values of the extinction coefficients required for the application of equation 3.9 are as follows: $\varepsilon_{A}^{380} = 70.4 \text{ l mol}^{-1} \text{ cm}^{-1}$, $\varepsilon_{D}^{380} = 3.58 \times 10^{4} \text{ l mol}^{-1} \text{ cm}^{-1}$, $\varepsilon_{A}^{475} = 5.15 \times 10^{3} \text{ l mol}^{-1} \text{ cm}^{-1}$ and $\varepsilon_{D}^{475} = 0.1 \text{ mol}^{-1} \text{ cm}^{-1}$. In Figure 3.6 the donor emission and acceptor absorption spectra are illustrated for this system. In Figure 3.7 a Stern-Volmer type plot is illustrated with both experimental and corrected donor fluorescence intensities. The fact that some quenching still exists after the removal of the radiative process is clear evidence for the existence of simultaneous non-radiative transfer. This procedure was repeated at a donor concentration of 3.2 x 10^{-4} mol 1^{-1} and yielded the same corrected plot after the removal of the radiative contribution.

The analysis is continued by obtaining a value for the transfer rate constant, $k_t$, from the Stern-Volmer plot for the experimental
FIGURE 3.5 Schematic illustration of the experimental arrangement about the sample when reflection geometry is employed to record emission spectra.
FIGURE 3.6 Emission and absorption spectra for the donor (PYA) and acceptor (DSM), respectively, in dichloromethane solution.
FIGURE 3.7 Stern–Volmer plots of the quenching of PYA emission by DSM in dichloromethane solution

\[ [\text{PYA}] = 1.68 \times 10^{-3} \text{ mol l}^{-1} \]

Uncorrected for radiative transfer

Corrected for radiative transfer
data corrected for radiative transfer. This value can then be compared with a calculated value of the constant accounting for a diffusion process at the encounter radius, $k_0$. In order to calculate the approximate value of $k_D$ the Smoluchowski equation [126,127,128] is employed, see equation 3.11 (below).

$$k_D \approx 4\pi N_A D_0 R_e \left(1 + \frac{R_e}{\sqrt{\tau_D D_0}}\right)$$  \hspace{1cm} (3.11)

The definitions of the terms within the equation are: $N_A = \text{Avogadro's constant}$, $D_0 = \text{the sum of the diffusion coefficients for donor and acceptor}$, $R_e = \text{the sum of molecular radii for donor and acceptor (i.e. the encounter radius)}$ [128,129] and $\tau_D = \text{the lifetime of the donor}$.

Obviously the values of $R_e$ and $D_0$ must be determined by calculation for this system of donor and acceptor. The value of $R_e$ can be obtained by summing the Van der Waals molecular radii for donor and acceptor. The molecular volumes of donor (PYA) and acceptor (DSM) (i.e. $V_D$ and $V_A$) can be estimated using data given by Edwards [129]. Then using the simple expression given in equation 3.12 the molecular radii can be calculated.

$$R_x = \frac{3 V_x}{4\pi} \quad \text{where } x = \text{D (donor) or A (acceptor)}$$  \hspace{1cm} (3.12)

For PYA and DSM the molecular volumes were calculated as $3.05 \times 10^{-28} \text{ m}^3$ and $3.20 \times 10^{-28} \text{ m}^3$, respectively which resulted in molecular radii of $4.18 \times 10^{-10} \text{ m}$ and $4.25 \times 10^{-10} \text{ m}$, respectively. The encounter radius, $R_e$, is thus $8.42 \times 10^{-10} \text{ m}$. The individual radii can then be used in equation 3.13 to determine the value of the diffusion coefficients for both species [128].
where $x = D$ (donor) or $A$ (acceptor) 

$$D_x = \frac{kT}{6\pi \eta R_x} \quad \text{where } x = D \text{ (donor)} \quad \text{or } A \text{ (acceptor)} \quad (3.13)$$

where $k$ = Boltzmann constant, $T$ = absolute temperature, $\eta$ = viscosity of solvent ($4.3 \times 10^{-4}$ kg m$^{-1}$ s$^{-1}$ in dichloromethane). The calculated diffusion coefficients are $1.20 \times 10^{-9}$ m$^2$ s$^{-1}$ and $1.17 \times 10^{-9}$ m$^2$ s$^{-1}$ for donor and acceptor, respectively, resulting in a combined value, $D_o$, of $2.37 \times 10^{-9}$ m$^2$ s$^{-1}$. (Note, the value of $T$ used is 293 K).

The values of $D_o$ and $R_e$ can now be placed into equation 3.11 to give $k_D$. The only constant missing is $\tau_D$ which was found to be 3.0ns [121] (see above for details). The calculated value of $k_D$ for PYA and DSM in dichloromethane is $1.99 \times 10^{10}$ 1 s$^{-1}$ mol$^{-1}$, which must be compared with $4.88 \times 10^{11}$ 1 s$^{-1}$ mol$^{-1}$ from the corrected experimental Stern-Volmer plot. The main conclusion which can be drawn from this comparison is that the non-radiative transfer is occurring more efficiently than the diffusion process therefore long range non-radiative energy transfer is occurring at distances much greater than the encounter radius.

The theory for long range energy transfer was developed by Förster [130] in which it was shown that the transition dipoles of donor and acceptor would couple with an inverse sixth power dependence on separation. The efficiency of this process depends on the spectral overlap between donor fluorescence and acceptor absorption, which is quantified by the spectral overlap integral, $J_{DA}$,

$$J_{DA} = \int I_D(\nu) \epsilon_A(\nu) (\nu)^{-4} d\nu \quad (3.14)$$

where $\int I_D(\nu) d\nu = 1$.
In equation 3.14 integration is carried out with respect to wavenumber, \( \tilde{v} \), \( \varepsilon_A \) is the molar decadic absorption coefficient of the acceptor and \( I_D' \) is the corrected fluorescence intensity of the donor. \( J_{DA} \) is normalized to the integrated area under the fluorescence spectrum of the donor with respect to wavenumber, \( \tilde{v} \). The actual value of \( J_{DA} \) is obtained graphically by determining the area under the plot of the function versus \( \tilde{v} \). For PYA and DSM the Förster overlap integral was calculated as 2.883 x 10^{-10} \, \text{cm}^6 \, \text{mol}^{-1}.

The Förster equation [130], referred to above is given in equation 3.15, where \( J_{DA} \) has units of \( \text{cm}^6 \, \text{mol}^{-1} \)

\[
\left( \frac{R_0}{(\text{cm})} \right)^6 = \frac{9 \, k^2 \, \ln 10}{128 \pi^5 \, N_A} \, \frac{\theta_D \, I_D'}{n^4 \, J_{DA}} (\text{cm}^6 \, \text{mol}^{-1})
\]

The quantum yield of the donor (PYA), \( \theta_D \), is 0.66 (see quantum yield determinations previously), the refractive index, \( n \), is 1.42 for dichloromethane and the orientation factor, \( k^2 \), takes the value 0.67 [131]. The resultant calculated value of the Förster radius, \( R_0 \), using the above constants is 5.47 x 10^{-9} \, \text{m}. This value is very much larger than the encounter radius (\( R_e = 8.42 \times 10^{-10} \, \text{m} \)) which adds further credence to the suggestion that long range non-radiative energy transfer is present in this PYA/DSM system.

The final stage in the analysis is to use a model that allows for both diffusion and long range energy transfer, rather than only the latter as in Förster theory (see above). Such a model was developed by Gosele [132,133], to give the effective Gosele radius, \( R_{\text{eff}} \). The first step in the calculation is to determine a value for the energy transfer...
constant, $\alpha$, using equation 3.16.

$$\alpha = \frac{R_o^6}{\tau_D} \quad (3.16)$$

where $R_o$ is the Förster radius and $\tau_D$ is the lifetime of the donor. In the system under study $\alpha$ was calculated as $8.93 \times 10^{-42} \text{ m}^6 \text{ s}^{-1}$. The theory [132] provides an expression for the term $Z_0$, which is a measure of the diffusion and long range transfer contributions. With $Z_0 \ll 1$ the diffusion process dominates and with $Z_0 \gg 1$ long range energy transfer is the dominant process. The value of $Z_0$ is given by equation 3.17 and is calculated to be 43.3 for this system, suggesting dominant long range energy transfer.

$$Z_0 = \frac{1}{2} \frac{1}{R_e^2} \left[ \frac{\alpha}{R_o^6} \right]^{\frac{1}{2}} \quad (3.17)$$

For such a large value of $Z_0$, equation 3.18 (below) provides an excellent approximation to the effective Gosele radius, $R_{\text{eff}}$, yielding a value of $5.30 \times 10^{-9} \text{ m}$.

$$R_{\text{eff}} = 0.676 \left[ \frac{\alpha}{R_o^6} \right]^{\frac{1}{4}} \quad (3.18)$$

The experimental interaction radius must be extracted from the experimental data, corrected for the radiative process, in order to compare with the Gosele radius. The extraction is achieved via a "manual" iterative method in which $(\Phi_o/\Phi)$ is calculated, at various acceptor concentrations $[A]$, and at a "guessed" interaction radius, $R_{\text{exp}}$. This value is then compared with the experimental value of $(\Phi_o/\Phi)$. The value of $R_{\text{exp}}$ is then varied until a good agreement between calculated and
experimental values of \((\varnothing_0/\varnothing)\) is achieved at all values of the acceptor concentration [134].

The calculation of \((\varnothing_0/\varnothing)\) is achieved using a modified form of the Stern-Volmer equation allowing for the time dependence of the energy transfer rate constant, \(k_t\). The expression used in this calculation is:

\[
\frac{\varnothing_0}{\varnothing} = \frac{1 + k_o \tau_D [A]}{I(\lambda)}
\]

(3.19)

where

\[
I(\lambda) = 1 - \frac{1}{2} \lambda (\pi)^{\frac{1}{4}} \exp \left(\frac{\lambda}{2}\right)^2 \text{erfc} \left(\frac{\lambda}{2}\right)
\]

(3.20)

and

\[
\lambda = \frac{2}{(\pi)^{\frac{1}{4}}} \cdot \frac{k_o \tau_D [A]}{(1 + k_o \tau_D [A])^{\frac{1}{2}}} \cdot \frac{R_{\exp}}{(\tau_D D_0)^{\frac{1}{2}}}
\]

(3.21)

The derivation of the above theory, involving some complicated mathematical concepts, has been given fully elsewhere [134,135] and the tabulated values of \(I(\lambda)\) at various \(\lambda\) values can be found in the literature [136]. The values of \(k_o\) at each \(R_{\exp}\) value and the value of \(D_0\) can be calculated from equation 3.11 (with \(R_e = R_{\exp}\)) and equation 3.13, respectively. The method discussed above is illustrated in Table 3.5 in which the calculated values of \((\varnothing_0/\varnothing)\) at various acceptor concentrations are presented at several \(R_{\exp}\) values. Also present in Table 3.5 is the corrected experimental \((\varnothing_0/\varnothing)\) data, and it can be
Table 3.5  Correlation between \( \frac{\theta_0}{\theta} \) derived from the experiment with calculated values assuming different interaction distances \( R_{\text{exp}} \) \( ([D] = 1.68 \times 10^{-3} \text{ mol l}^{-1}) \)

| \([A] \times 10^4\) | \( \frac{\theta_0}{\theta_{\text{exp}}} \) (corrected for radiative process) | \( \frac{\theta_0}{\theta_{\text{calc}}} \) calculated at \( R_{\text{exp}} \) values (shown below) |
|---------------------|-------------------------------------------------|
|                     | \(5.3 \times 10^{-9}_m\) | \(5.5 \times 10^{-9}_m\) | \(6.0 \times 10^{-9}_m\) | \(6.2 \times 10^{-9}_m\) | \(6.3 \times 10^{-9}_m\) | \(5.5 \times 10^{-9}_m\) | \(7.0 \times 10^{-9}_m\) |
| 0                   | 1.00               | 1.00               | 1.00               | 1.00               | 1.00               | 1.00               | 1.00               |
| 1.299               | 1.19               | 1.16               | 1.12               | 1.13               | 1.15               | 1.16               | 1.16               | 1.17               |
| 2.597               | 1.33               | 1.22               | 1.32               | 1.29               | 1.31               | 1.33               | 1.35               | 1.39               |
| 3.899               | 1.56               | 1.35               | 1.42               | 1.46               | 1.49               | 1.51               | 1.56               | 1.59               |
| 7.792               | 2.02               | 1.77               | 1.83               | 2.02               | 2.07               | 2.11               | 2.19               | 2.40               |
| 10.39               | 2.47               | 2.09               | 2.22               | 2.39               | 2.54               | 2.55               | 2.67               | 3.02               |
| 12.99               | 3.01               | 2.45               | 2.56               | 2.96               | 3.08               | 3.13               | 3.23               | 3.72               |
| 15.58               | 3.80               | 2.83               | 2.98               | 3.34               | 3.62               | 3.64               | 3.96               | 4.53               |
clearly seen that the best agreement between experimental and calculated values occurs at $R_{\text{exp}} = 6.2 \times 10^{-9}$ m. For the data in Table 3.5 the following constants were used: $[D] = 1.68 \times 10^{-3}$ mol $\cdot$ l$^{-1}$, $\tau_D = 3.0 \times 10^{-9}$ s, $R_e = 8.42 \times 10^{-10}$ m and $D_0 = 2.37 \times 10^{-9}$ m$^2$ s$^{-1}$.

In summary the values of $R_e$ (encounter radius), $R_o$ (Forster radius), $R_{\text{eff}}$ (Gösele radius) and $R_{\text{exp}}$ (experimental interaction radius) are $8.42 \times 10^{-10}$ m, $5.47 \times 10^{-9}$ m, $5.30 \times 10^{-9}$ m and $6.2 \times 10^{-9}$ m, respectively. It is clear that both radiative and non-radiative transfer are occurring between PYA and DSM, and when the radiative component is corrected for, the non-radiative transfer operates at distances much greater than the encounter distance. The large value of the long range Förster overlap integral between the donor fluorescence spectrum and the acceptor absorption spectrum, as well as the high fluorescence quantum yield of the donor are both contributing factors to an efficient long range energy transfer process. The excellent agreement between the interaction radii obtained from the Förster and Gösele models, is a clear indication that diffusion plays very little importance in this system and energy transfer between donor and acceptor occurs virtually exclusively by a long range mechanism before diffusion can influence the process. The experimental interaction radius, $R_{\text{exp}}$, is slightly larger than the Gösele radius, $R_{\text{eff}}$, which would suggest that an additional process, such as energy migration between donor molecules, is occurring. As mentioned previously the donor concentration was varied by a factor of 10 with the an identical corrected Stern-Volmer plot resulting. However, to observe such small amounts of donor-donor energy transfer a much larger range of donor concentrations would need to be investigated, which would prove difficult due to the large fluorescence intensities observed at large donor concentrations.
Another point worth considering is the effect of the diffusion coefficient on the values of $R_{\text{eff}}$ and $R_{\text{exp}}$. The calculation of the diffusion coefficient is achieved for donor and acceptor using equation 3.13, with the term $6\pi nR$ as the denominator in the expression, which is indicative of large solute molecules moving amongst small solvent molecules [128], which is believed to be realistic for this system. The value of the sum of the donor and acceptor diffusion coefficients, $D_o$, for this situation is $2.37 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. However, if the opposite case of small solute molecules and larger solvent molecules is applied, the denominator of equation 3.13 becomes $4\pi nR$, leading to a $D_o$ value of $3.55 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. When this less realistic value of $D_o$ is employed in the calculation of $R_{\text{eff}}$ and $R_{\text{exp}}$ the values become $4.79 \times 10^{-9} \text{ m}$ and $5.20 \times 10^{-2} \text{ m}$, respectively. Although the difference between $R_{\text{eff}}$ and $R_{\text{exp}}$ has reduced when the unrealistic $D_o$ value is used, the value of $R_{\text{exp}}$ is still in excess of $R_{\text{eff}}$.

In conclusion the PYA and DSM system has provided a very interesting long range energy transfer process to study, which appears not to be greatly altered by diffusion processes. The above work is in the process of being published elsewhere [137].

3.2 Solids and Polymer Films
(a) Flash Photolysis
(i) Data collection and analysis in diffuse reflectance laser flash photolysis

As mentioned briefly in section 2.1 the collection and on line analysis of the transient data in the new technique of diffuse reflectance laser flash photolysis is achieved using a PDP 11 MINC minicomputer. The intensity of the diffusely reflected analysing
FIGURE 3.8 Schematic illustration of the various analysis methods which can be applied to flash photolysis transients, namely:

(a) Beer–Lambert law  
\[
[T] \propto \log \left( \frac{I_o}{I} \right)
\]

(b) Kubelka Munk theory
\[
[T] \propto \left\{ \frac{(1-R)^2}{2R} - \frac{(1-R_{100})^2}{2R_{100}} \right\}
\]

(c) \[ \frac{\Delta I}{\Delta I_o} \]
light is recorded with and without laser excitation, providing an uncorrected transient absorption decay and a baseline, respectively. The former is manifested by a decrease in the intensity of diffusely reflected light off the sample. A third trace is then recorded with only laser excitation to give the sample luminescence decay. The uncorrected transient absorption is then corrected by the computer for the laser induced luminescence and for reproducible irregularities in the baseline.

In transmission mode laser flash photolysis the resultant transient absorption is analysed using the Beer-Lambert law (see Figure 3.8 a). This analysis procedure can not be applied in diffuse reflectance mode because the optically dense sample permits no transmission of the monitoring light. In this case laser excitation has been observed to induce two limiting types of initial excited state concentration profiles, namely homogeneous and exponential fall off. The former case is encountered with large exciting light penetration depths or with very low concentrations of ground state absorbers, and the Kubelka-Munk theory applies [67,69]. This theory relates the reflectance, \( R \), to the absorption coefficient, \( K \), and the scattering coefficient, \( S \), via equation 3.22 (see section 1.3 for details).

\[
F(R) = \frac{(1-R)^2}{2R} = \frac{K}{S} \quad (3.22)
\]

\( F(R) \) is known as the remission function and is a linear function of the concentration of homogeneous absorbers [65,71] (see Figure 3.8 b).

In the case of an exponential fall off in transient concentration the remission function (see equation 3.22) can not be used to predict the change in diffuse reflectivity. In fact the defining equations
have to be solved analytically using the method of Lin and Kan [70] for optically thick samples [65,67,71]. The reflectance before and after excitation at the analysing wavelength may be represented by $R_B^a$ and $R_a(t)$, respectively;

$$\frac{R_B^a - R_a(t)}{R_B^a} = 1 - R_T^a$$ (3.23)

where $R_T^a$ is the relative transient reflectance. It has been shown, for typical K and S values, that when $1 - R_T^a < 0.1$; $(1 - R_T^a)$ is a linear function of the amount of transient produced [71]. The basis of this analysis technique is illustrated in Figure 3.8c.

The principle aim of the above is to extract a term which is proportional to the concentration of transient which is realistic for the type of transient concentration depth profile. This would consequently allow kinetic analysis of the transient decay to be undertaken using concentration of transient at different times into the decay of the transient, in conjunction with the first and second order rate laws.

To obtain a transient absorption spectrum a transient decay (plus the associated emission and baseline traces) are recorded for the sample at a series of different monitoring wavelengths. The corrected transient absorption at each wavelength is used to obtain percentage transient absorption values at a fixed set of given times after the laser excitation pulse. The time resolved transient absorption spectra are then constructed by plotting percentage absorption against wavelength for a series of times after the laser excitation.
It was a policy to record all transient absorption spectra in randomized wavelength order, in addition a reference wavelength was recorded several times during the collection of the spectrum. The fact that several repeat points are obtained at the reference wavelength in the transient absorption spectrum, firstly allows some comment about experimental error to be made and secondly indicates the existence of any systematic changes that may have occurred during the duration of the collection of the spectrum (e.g. sample damage).

(ii) Microcrystalline solids

A great deal of my initial work using the technique involved an unsuccessful study of microcrystalline samples of various azo dyes (supplied by 3M's Research Ltd.). The main problem encountered was the high level of laser damage even when the laser was attenuated and a transient signal was essentially an optothermal effect due to the laser inducing very large temperature changes [90].

The results presented will apply to microcrystalline pyrazoline samples, however, prior to considering these results it is worth pausing to look at the ground state diffuse reflectance spectra of the various pyrazolines. As a consequence of the very strong pyrazoline fluorescence it was found that ground state diffuse reflectance spectra recorded on a spectrometer with a monochromator only in the incident beam, exhibited a reflectance signal in excess of that of the Barium sulphate white standard. A similar effect to this has been cited in the literature [25] for other pyrazolines, and the effect is illustrated for PYA in Figure 3.9. When a second monochromator is introduced into the reflected beam, the induced fluorescence is eliminated, leaving only the actual diffuse reflectance to be
FIGURE 3.9 Ground state diffuse reflectance spectrum of microcrystalline PYA (not corrected for induced fluorescence)
measured. The resultant spectra for PYA, PYB, PYC, PYD and PYE are illustrated in Figure 3.10. The main observation drawn from the corrected ground state diffuse reflectance spectra is that the pyrazoline microcrystals are virtually completely absorbing (i.e. approximately zero reflectance) at 354nm, the laser wavelength used to excite the sample in the flash photolysis studies.

A diffuse reflectance laser flash photolysis study of microcrystalline pyrazoline samples yielded a transient absorption with its maximum in the wavelength range 490nm - 540nm, depending on the sample, and a lifetime in the range 1.5 - 2.0μs. Excitation was achieved using the 354nm laser harmonic which was attenuated five fold by a suitable filter to produce a working energy of approximately 10mJ per pulse. When the full laser energy was employed to excite the sample a slight increase in the amount of transient was accompanied by a dramatic increase in laser damage. The percentage absorption, at the maximum, was found to be 15 - 20% for PYA, PYB, and PYC, while PYD and PYE exhibited much weaker transients. There was no significant changes in the transient decay with or without oxygen present, for any of the pyrazolines studied.

The time resolved transient absorption spectra for a microcrystalline sample of PYA and PYB are given in Figure 3.11 a and 3.11 b, respectively. The time resolved spectra show a fairly uniform decay of the transient absorption, at various times after laser excitation, across the measured wavelength range. This is indicative of the decay of only one transient species. The estimated error on these spectra was determined using the repeats recorded at the reference wavelength, at several times during the collection, and are in the order of ±5 %.
FIGURE 3.10 Ground state diffuse reflectance spectra of various microcrystalline Pyrazoline samples (corrected for fluorescence)
FIGURE 3.11 Time resolved transient absorption spectra from samples of microcrystalline (a) PYA and (b) PYB
Microcrystalline benzophenone has been fully characterized using diffuse reflectance laser flash photolysis [72], exciting at 354nm, and consequently provides an excellent standard to confirm that the apparatus is functioning correctly. Consequently, following any adjustment to the laser or collection geometry, the benzophenone sample was recorded to confirm that the observed triplet-triplet absorption was in good agreement with Wilkinson and Willsher [72].

The microcrystalline pyrazolines all have very strong fluorescence with a rapid decay, which was impossible to study using the time domain, available on our apparatus. At high photomultiplier voltages the fluorescence was so strong that an overloading of the photomultiplier occurred resulting in a false emission signal primarily due to photomultiplier recovery. Generally the maximum amount of distortion observed in the decay effects only the first 0.5μs.

The transient absorption decay shows a level of reflectance at the end of the decay (on the time base used) which is fractionally less than in the pre-pulse region prior to excitation. However, after a long period of recovery (i.e. the one second between laser pulses) the reflectance does eventually return to the value exhibited in the pre-pulse region. This now provides the problem of whether to analyse the kinetics with respect to the pre-pulse region or the end of the decay. When the analysis was carried out using both points of reference it was found that kinetic plots (i.e. 1st and 2nd order plots) exhibited some curvature in opposite directions at later times in the decay, however, at earlier times the kinetic plots were virtually identical. Since the relevant kinetic information was not being extracted from the later decay times it was decided to use the
pre-pulse region as the datum. This choice will enable the values of kinetic terms, from various pyrazolines, to be compared more reproducibly.

As mentioned previously (see 3.2(a)) there are two types of analysis used to extract a concentration of transient from the data, namely kinetic Kubelka-Munk and $\Delta I/\Delta I_0$, which apply to a homogeneous or exponentially decaying transient concentration profile, respectively. However, in the literature Oelkrug et al [138] have defined expressions to qualitatively predict which of these two limiting cases is occurring. In order to make such a prediction the following quantities are required: the laser intensity per unit area, $I$, the concentration of ground state absorbers at time zero, $C_A^0$, the scattering coefficient, $S$, and the quantity, $b_e$, which is given by:

$$5b_e = \left[ \left( K_e^2 + 2K_eS \right) \right]^{\frac{1}{2}}$$

(3.24)

where $K_e$ is the absorption coefficient at the exciting wavelength and $(b_eS)^{-1}$ is the penetration depth.

The prediction of the type of transient concentration profile uses the expression:

$$\frac{Ib_eS}{C_A^0} = x$$

(3.25)

and when $x < 0.1$ the concentration of transient decreases exponentially while when $x > 10$ a homogeneous layer of transient is predicted. The value of $K_e$ is defined by equation 3.26 (below) in terms of the
extinction coefficient at the exciting wavelength, $\varepsilon_e$, which is estimated from solution studies.

$$K_e = 2C_A^0 \varepsilon_e$$  (3.26)

The mass of pyrazoline required to pack a 1 cm$^3$ volume was measured in order to assess an approximate value of $C_A^0 = 1.96 \times 10^{-3}$ mol cm$^{-3}$, $K_e = 6.6 \times 10^4$ cm$^{-1}$ and $I = 2.96 \times 10^{-8}$ photons cm$^{-2}$. The value of $S$ is normally between 50 and 200 cm$^{-1}$ for most microcrystals and with a large value of $K_e$, the second term in equation 3.24 can be neglected and the equation re-written as :-

$$b_e S = K_e$$  (3.27)

When the approximate constants are placed into equation 3.25 the numerical value of $x$ is approximately unity, which is not conclusively indicative of either transient concentration profile. However, in the case of low percentage absorption transients the kinetic plots from either Kubelka-Munk or $\Delta I/I_0$ treatments provide essentially the same information, and since the prediction is nearer the value that indicates an exponential decay of the transient concentration, it was decided to use $\Delta I/I_0$ analysis.

As mentioned previously considerable laser damage was observed at the high laser energies a fact which obviously warrants some discussion of thermal effects within the sample. The problem of optothermal effects have been discussed by Wilkinson and Kelly [65] and such effects have been successfully predicted and observed for titanium dioxide powder [77]. The heat flow occurring at the surface of a sample is given by equation 3.28 [65,77,139].
\[ \Delta T(0) = \frac{f K F_o (1 + R)}{c \rho'} \]  

(3.28)

where \( F_o \) is the laser fluence per unit area (usual units J cm\(^{-2}\)), \( c \) is the specific heat capacity, \( f \) is the fraction of absorbed energy converted "instantaneously" to heat and \( \rho' \) is the apparent powder density (g cm\(^{-3}\)). The values of specific heat capacities are very scarce for organic solids and not available for microcrystalline pyrazolines. The value for TiO\(_2\) was 0.69 J K\(^{-1}\) g\(^{-1}\) [77] and in the absence of a better approximation this will be used. The value of \( \rho' \) for a packed sample as used in the experiment, was determined as 0.63 g cm\(^{-3}\) and the value of \( F_o \) was 0.01 J cm\(^{-2}\). Using a value of \( f = 1 \) the predicted temperature rise (from equation 3.28) is about 1500°C at the surface. However, in the case of pyrazolines a very strong fluorescence is observed which gives a clear indication that \( f \) is much less than unity, which would serve to substantially decrease the predicted temperature rise.

A measureable transient absorption of about 4% was detected at very small laser energies of 0.4 mJ/pulse (i.e. 0.0004 J/cm\(^{-2}\), assuming area of excitation is 1 cm\(^2\)), and within experimental error was kinetically identical to the transient absorptions at other laser energies. The low energy excitation only gives a predicted temperature rise of about 60°C, when \( f \) is set unrealistically to unity, and it seems very unlikely that a few degrees rise in temperature could be responsible for an opto-thermal transient.

The kinetic analysis of the pyrazoline transient, using \( \Delta I/I_o \), gave similar results for all the samples studied. The decay of the transient was predominantly second order, with only a slight deviation within the first 1-2 \( \mu \)s of the decay. The deviation from second order kinetics was
apparent for more of the initial decay as the laser excitation energy was increased. This fact is consistent with the deviation from second order decay in the initial portion of the decay, being due to a contribution from thermal processes. Typical first and second order kinetic plots for the transient decay of microcrystalline PYB (exciting at 10mJ) are illustrated in Figure 3.12 (a) and (b), respectively.

In Table 3.6 (below) the gradient of the second order plot is presented for a series of microcrystalline pyrazoline transient decays, between 1.9μs and 11.7μs after excitation. This gradient is proportional to $k_2C_0$, where $k_2$ is the second order decay rate constant and $C_0$ is the initial concentration of transient. Also presented in Table 3.6 is the wavelength maximum for the transient absorption spectra.

<table>
<thead>
<tr>
<th>Pyrazoline</th>
<th>Gradient of second order plot ($= k_2C_0$) / s$^{-1}$</th>
<th>Max.of transient spectrum / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>PYA</td>
<td>$4.5 \times 10^4$</td>
<td>490</td>
</tr>
<tr>
<td>PYB</td>
<td>$5.0 \times 10^5$</td>
<td>520</td>
</tr>
<tr>
<td>PYC</td>
<td>$1.0 \times 10^6$</td>
<td>540</td>
</tr>
<tr>
<td>PYD</td>
<td>$6.2 \times 10^5$</td>
<td>500</td>
</tr>
</tbody>
</table>

The transient absorption for microcrystalline pyrazolines are in a similar spectral position to the sensitized pyrazoline triplet detected in benzene solution (see section 3.1 (b)). In addition a analogous sensitization study in polymer films has provided fairly strong evidence for the above transient absorption, for microcrystalline pyrazolines, being due to the triplet (see section 3.2 (a) iii). However, the
FIGURE 3.12 (a) First and (b) Second order kinetic plots derived from the transient absorption decay from a sample of microcrystalline PYB ($\lambda_{ex} = 354$ nm and $\lambda_{an} = 520$ nm)
possibility of an opto-thermal effect can not be totally neglected and it is believed that the deviation from second order decay kinetics in the initial decay region may be due to a superimposed opto-thermal process occurring simultaneously with the decay of the electronically excited state.

(iii) Benzophenone and pyrazoline within a polymer film and absorbed on cotton fabric

The aim of this section of work was to extend the triplet energy transfer process between benzophenone and pyrazoline, which has been observed in solution (see section 3.1 (b)) using different media such as a polymer matrix and "dyed" cotton fabric. These studies were carried out using the diffuse reflectance laser flash photolysis geometry, even in the case of the transparent polymer films, where inert barium sulphate was placed behind the sample.

The polymer films were made, as discussed in section 2.7, by coating a polymer solution onto a transparent polyester base material. The main polymer studies were carried out using polycarbonate as the polymer, which does not absorb at the exciting wavelength of 354nm. A blank, consisting of just polymer on base, gave no transient signal when excited at 354nm, either with or without oxygen.

It was found that a Polycarbonate film, containing about 35 % benzophenone (by mass), gave a transient absorption signal which was in very good agreement with literature for benzophenone in various media [72,140]. The spectral details for this sample, namely the transient absorption maxima at 535nm and emission spectrum having three peaks in
the region between 420-480nm, is consistent with the transient being the benzophenone triplet. The time resolved absorption and emission spectra for benzophenone in polycarbonate are given in Figure 3.13 (a) and 3.13 (b), respectively. The kinetics of the transient absorption and phosphorescence decays, analysed using $\Delta I/\Delta I_0$, exhibit similar first order decays with a slightly quicker process occurring initially. In fact when the two first order plots are superimposed on the same scale, see Figure 3.14, there are no significant differences between the decays. The presence or absence of oxygen makes no measurable difference to the above results. The fact that the transient absorption and phosphorescence are decaying at the same rate provides a conclusive assignment of the benzophenone triplet.

A polycarbonate film containing just PYA (amount varied from 0-20%), and no benzophenone, yielded a weak transient which had a maximum absorption at about 490nm, the same as for microcrystalline PYA. The predominantly second order decay observed for microcrystalline PYA transient is also exhibited by the transient of PYA in polycarbonate. The gradients of the two second order kinetic plots were measured as $0.50 \times 10^6 \text{ s}^{-1}$ (see Table 3.6) and $0.44 \times 10^6 \text{ s}^{-1}$ for the microcrystals and polycarbonate film, respectively. The above is fairly strong evidence for the PYA transient observed in microcrystals and within a polycarbonate matrix being the same species. If the PYA transient at 490nm can be enhanced by adding benzophenone to the polycarbonate matrix, then we can assign the formentioned transient as a triplet.

The next consideration is a polycarbonate film containing both PYA and benzophenone ($\approx 35\%$). When the PYA content was low (e.g. 0.31%) the transient absorption spectrum showed virtually all benzophenone character,
FIGURE 3.13 Time resolved (a) Transient absorption and (b) Emission spectra from Benzophenone (35 %) within a polycarbonate matrix
FIGURE 3.14 Superimposed first order kinetic plots derived from the emission decay and transient absorption decay from a sample of benzophenone (35%) contained within a polycarbonate matrix.
however, with a higher PYA content (e.g. 5.31%) the transient absorption spectrum was broad and contained a large contribution from the PYA transient at 490nm. Finally when the PYA content was increased to 10.34% the transient species due to PYA, at 490nm, dominated over the benzophenone transient, at 535nm. However, the percentage absorption at both 490nm and 535nm had dropped when compared to the film containing only 5.31% PYA. The reason for this is that the PYA is absorbing a greater proportion of the exciting light as its concentration is increased, and a corresponding reduction in the amount of benzophenone triplet results. Therefore an analogous situation to the solution study (see section 3.1 (b)) exists with an optimum concentration of pyrazoline.

Time resolved spectra for PYA and benzophenone in polycarbonate at PYA contents of 5.31% and 10.34% are given in Figure 3.15 (a) and 3.15 (b), respectively.

If the benzophenone is undergoing triplet energy transfer to pyrazoline, one might expect to observe quenching of the benzophenone transient absorption and phosphorescence. The quenching of the transient absorption is not observed because pyrazoline transient is making a contribution to the decay of this species at 535nm. The lifetime of the benzophenone phosphorescence was not altered, within experimental error, as the PYA content was increased. However, the amount of benzophenone phosphorescence decreased as the PYA content increased. This reduction in the amount of benzophenone triplet could not only be explained by the reduced proportion of exciting light available to benzophenone, thus there was a definite quenching of the benzophenone triplet by PYA. This quenching does not alter the benzophenone triplet lifetime, thus it is likely to be a static process, rather than a dynamic quenching process.
FIGURE 3.15 Time resolved transient absorption spectra for samples of Benzophenone (Bp.) and PYA in Polycarbonate; namely (a) Bp. = 32.6 %, PYA = 5.3 % and (b) Bp. = 35.1 %, PYA = 10.4 %
The final test of the above work is to establish if the two component transient absorption spectra, for PYA in polycarbonate and benzophenone in polycarbonate, could realistically combine to produce the composite transient spectrum of PYA and benzophenone in polycarbonate. The spectrum of PYA in polycarbonate has very low spectral resolution and this prompted us to use PYA dyed on cotton fabric as the PYA component transient absorption spectra. It was found that 40% of the pyrazoline component and 60% of the benzophenone component, yielded a transient absorption spectrum which within experimental error "mimiced" the experimental spectrum of PYA (5.31%), benzophenone and polycarbonate. The combination was also successfully achieved when applied to the time resolved portion (after 5μs) of the component transient absorption spectra, and the resultant composite spectrum was within experimental error identical to the experimental spectrum of PYA (5.31%), benzophenone and polycarbonate in the same state of decay (i.e. after 5μs of decay).

In conclusion, it appears that a similar triplet energy transfer mechanism to that observed in solution, also occurs between benzophenone and PYA within a polycarbonate matrix. However, the evidence appears to suggest the existence of a static transfer process as opposed to a dynamic process. This study has also indirectly assigned the PYA transient at 490nm as the triplet, and therefore provides further evidence that the microcrystalline PYA transient is a triplet.

It was decided to study the above triplet energy transfer process on a cotton fabric medium to compare with the results from a polymer matrix. The samples were prepared by soaking a piece of pure cotton fabric (i.e. not impregnated with any other fluorescent materials) in a solution of the appropriate substances which you require to study. After
soaking overnight the piece of fabric is removed and allowed to dry in a flat position in an oven at 50°C.

When the cotton fabric was soaked in a solution of benzophenone in benzene and dried, very little transient signal was observed with or without oxygen, even with solution concentrations of 1 mol 1⁻¹. The loading of benzophenone on the fabric is very low and when combined with its relatively low extinction coefficient, only a small proportion of the exciting laser is absorbed. This causes a very large amount of scattering of the exciting light and consequently considerable overloading of the photomultiplier.

The only method by which a high enough load of benzophenone could be obtained, was by soaking the cotton fabric in molten benzophenone and then allowing the sample to cool and consequently solidify. The resultant sample exhibited a large amount of benzophenone triplet with its characteristic transient absorption and phosphorescence [72]. However, a long lived species (still present after 1ms) was observed initially, but disappeared after a number of laser shots. The above observations were not altered by the absence or presence of oxygen. One possible explanation of the long lived species is that it is due to the radical of benzophenone which is produced by an interaction with the fabric. This is pure speculation, but the existence of the triplet is of prime importance. The sample is in essence a "thin layer" of microcrystalline benzophenone and not a piece of fabric containing benzophenone which was initially the aim.

When just PYA was incorporated with a cotton fabric, by soaking in a 2 x 10⁻⁴ mol 1⁻¹ solution of PYA, it yielded a fairly weak 10%
FIGURE 3.16 Time resolved transient absorption spectra from a sample of PYA on cotton fabric
transient absorption at the maximum (490nm). As far as could be established from spectral evidence this was the same transient species which has been observed for PYA in the various environments (e.g. solution, polymer film and microcrystalline solid). The time resolved transient absorption spectrum of PYA on cotton fabric is given in Figure 3.16.

Some preliminary measurements were undertaken on a cotton fabric prepared from a melt of benzophenone and PYA. However, the fact that the sample is a "thin layer" of surface microcrystals rather than incorporated within the fabric, coupled with the doubt about the benzophenone transient, makes this system far from ideal. The limited measurements taken appeared to suggest that the expected enhancement of the 490nm transient was occurring at the expense of the benzophenone triplet (535nm).

These studies were not continued any further because of doubts about the nature of the sample.

(iv) Polymer films containing PYA and DSM

The system under study during the photoconduction experiments (see section 3.2 (d)) consists mainly of DSM and PYA in various polymer media. It was therefore decided to undertake a study, using flash photolysis, of any transient events which may occur in polymer films containing DSM and/or PYA. Polycarbonate films containing PYA have been discussed previously (see section 3.2 (a) iii) and a weak transient with a spectral maximum at 490nm has been assigned as the triplet of PYA.
A preliminary study of this system was undertaken in Loughborough using the diffuse reflectance laser flash photolysis geometry, by placing inert barium sulphate behind the transparent films. A series of polycarbonate films containing varying DSM contents (0.1 to 10%) were prepared and analysed. When excited at 354nm no transients were obtained either with or without oxygen. However, when excited using the 532nm laser harmonic a transient absorption was observed with a spectral maximum at about 600nm. The transient decay was fairly long lived and did not decay within lms (i.e. the longest time base available at present) and spectrally the transient absorption was very narrow (e.g. 20nm either side of the maximum).

A polycarbonate film containing PYA and DSM (0.15%) was now subjected to laser flash photolysis exciting at 532nm and the transient species due to DSM at 598nm was absent, while a transient absorption at 490nm appeared. However, a polycarbonate film containing only PYA (45%) yielded no transient absorption at any wavelength when excited at 532nm. This therefore leads to the very interesting conclusion that the DSM transient is disappearing and the pyrazoline triplet is being indirectly produced. At this stage attempts were made to vary the DSM and PYA contents within the polymer matrix. However, the weak PYA transient coupled with the long lived DSM transient made any interpretation virtually impossible using this apparatus.

The study of this system was continued using a transmission flash photolysis apparatus at 3M's Research Ltd. (described previously in section 2.6) which had been adapted for use with thin film and used a pair of Xenon flash lamps to provide the excitation source which were filtered (using a Number 16 Wratten filter) in order to cut off wavelengths lower than 520nm.
The decay of the DSM transient at 598nm was studied in three different polymer matrixes, namely polycarbonate (PC) poly(styrene-methylnmethacrylate) (PSM) and poly(methylnmethacrylate) (PMMA). A blank film containing just polymer, and no DSM, yielded no transient absorption at any wavelength for any of the three polymers, either with or without oxygen. The non-blank polymer films contained 2.16% DSM (by mass) and were all about 4µm thick. The transient absorption in the different polymer media had an initial half-life of 0.7ms, 0.4ms and 1.3ms for PC, PSM and PMMA, respectively. The kinetic analysis using Beers Law, showed that the transient decay was essentially second order for the PSM and PC matrixes. However, for PMMA the transient decay was only second order for the initial 1.0 - 1.5ms and then became first order. The decay of the DSM transient was not effected by the presence or absence of oxygen, in any of the polymer films.

All of the following investigations of the DSM transient were carried out in a polycarbonate matrix, since this is the polymer which has been most frequently used in other studies. The first problem was to establish how the DSM transient production varied with the excitation energy. The energy of the excitation flash can be varied to 15, 10 and 5 Joules. Three transients were recorded at each excitation energy using a film that contained 1.5% DSM and the average initial absorbance of the transient species with increasing excitation energy were 3.87 x 10^{-3}, 5.50 x 10^{-3} and 7.95 x 10^{-3}, respectively. The above results firstly illustrate the low levels of transient absorption being investigated and secondly the fact that the production of transient appears to increase in a reasonable linear fashion with increasing excitation energy.
The effect of adding different amounts of PYA on the production and decay of the DSM transient, within a polycarbonate matrix, is of crucial importance to understanding the sensitization of PYA. The absorbance at the beginning of the transient absorption decay trace, $A_{\text{max}}$, is presented with varying amounts of PYA in Table 3.7 (below). This table provides information relating to the effect of PYA on the production of DSM transient, however, the transient absorption is so weak in the presence of PYA that it is impossible to carry out a kinetic analysis to provide information about the decay of the transient. The transient decay appears "by eye" to be decaying over the same time domain with or without PYA.

Table 3.7 Variation of $A_{\text{max}}$ (see above) with PYA content of film

<table>
<thead>
<tr>
<th>PYA$^+$</th>
<th>$A_{\text{max}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$3.9 \times 10^{-3}$</td>
</tr>
<tr>
<td>0.0752</td>
<td>$3.2 \times 10^{-3}$</td>
</tr>
<tr>
<td>0.1541</td>
<td>$2.5 \times 10^{-3}$</td>
</tr>
<tr>
<td>0.3876</td>
<td>$1.8 \times 10^{-3}$</td>
</tr>
<tr>
<td>0.5520</td>
<td>$1.1 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

$^+$ PYA = grams in 6ml (polymer/chloroform/DSM) solution (i.e. 0.8537g polycarbonate : 6ml chloroform : 0.01333g DSM)

One point about the higher PYA content in films is that the DSM transient absorption is so weak that it can not be clearly distinguished from the background noise, this is especially true for the highest PYA content in Table 3.7 (i.e. 0.5520g). Even taking this into
account it is very clear that the maximum amount of DSM transient decreases with increasing concentration of PYA, indicating that PYA is reacting with a precursor of the DSM transient species. It would also seem likely that PYA is also not reacting simultaneously with the actual DSM transient species, because there appears to be no quenching of this species upon the addition of PYA. Similar observations to the above have been made for this system in poly methylmethacrylate [141], the only difference being that a greatly reduced PYA concentration was required to completely stop the production of the DSM transient, in fact PYA amounts could be reduced by a factor of four from those outlined in Table 3.7. This point serves to add another illustration of the differences that exist with DSM in polymethylmethacrylate.

One very interesting observation was noted when the excitation flash was not filtered, allowing both PYA and DSM to be excited. In this case the DSM transient had a similar absorption regardless of whether PYA is present or not, thus the precursor of the transient appears not be be consumed by the PYA. The transient absorption with only DSM present follows a similar second order decay as observed in the case of the flash excitation being filtered. However, with PYA present the decay of the DSM transient is no longer a perfect second order process, suggesting that the presence of electronically excited PYA is effecting the decay of the DSM transient.

The earlier investigation clearly indicates the sensitization of the DSM transient, therefore assuming triplet energy transfer the precursor of the DSM transient is likely to be the triplet. The use of DSM in the photoconduction studies (see section 3.2 (d)) is as a charge generation material, which operates by absorbing light and producing a hole together with the DSM radical anion, DSM⁻. It
would therefore seem likely that the DSM transient is due to the DSM⁻ species, further evidence for this is given later (see section 3.2 (d)) and also the second order decay process of the DSM transient is consistent with this assignment. Another piece of evidence in favour of this assignment is the different lifetimes of the transient in various polymer environments, because the recombination of the DSM radical anion and the hole will depend on the polymer matrix since this will influence the local polarisability at the site of recombination.

(v) Other experiments

One of the initial aims of the project was to study the transient absorption processes leading up to the field dependent photoconduction processes, within a polymer matrix. In the studies detailed above a great deal of information has been gathered relating to the transient processes that occur within a polymer film containing PYA and DSM. However, since the photoconduction processes occur under the influence of an applied electric field, it was decided to carry out a laser flash photolysis study under the same conditions. The polymer films containing various amounts of PYA and DSM were prepared on a transparent conductive base, and this was grounded onto an aluminium cylinder. The back of the conductive base was painted with barium sulphate paint to allow the normal diffuse reflectance geometry to be employed and also to prevent "mirror" reflection from the aluminium cylinder. The aluminium cylinder was mounted on a stepper motor and the sample could be moved under a charging corona wire (see section 2.5 for details) and then back into a suitable position to allow a flash photolysis study, in pseudo diffuse reflectance mode, to be undertaken.

The correct operation of the flash photolysis apparatus, using the abnormal geometry of a sample on a curved aluminium surface, was
fully investigated using a polymer film containing benzophenone. This sample was found to provide a signal characteristic in all respects to the literature observations on the benzophenone triplet [72], thus the correct operation of the apparatus was confirmed. When the standard benzophenone film was replaced by various films containing PYA and DSM both together and separately, the transient absorption signals observed with and without the application of an electric field were identical to those outlined in section 3.2 (a) (iii) and (iv) above. During the above experiments with the presence of the electric field the room lights were removed to ensure that no degradation of the applied field was occurring.

We believe that this experiment was the first time that laser flash photolysis has been attempted using polymer films under the influence of an electric field. The negative results obtained appear to indicate that the photochemistry of the DSM/PYA system is not modified by the application of an electric field to the polymer sample, however, as explained later (see chapter 4) this experiment may not have been totally representative.

Another series of experiments which cannot be grouped with any other experiments involve the chemical production of the pyrazoline cation radical, in solution, in order to compare with pyrazoline species detected in flash photolysis. The cation radical of pyrazoline is one of the species which is expected to be involved in the photoconduction process (see section 3.2 (d)). It was felt that an idea of this species spectral properties, even when chemical produced in solution, would be very useful background information in the assignment of the pyrazoline transient.
The chemical production of the cation radical of various pyrazolines was achieved by mixing together nitrosonium tetrafluoroborate, \( \text{NOBF}_4, \) \( (4 \times 10^{-3} \text{ mol l}^{-1}) \) and pyrazoline \( (1 \times 10^{-4} \text{ mol l}^{-1}) \) in dry acetonitrile, under nitrogen \([142, 143]\). Once the mixing had occurred a portion of the resultant solution was withdrawn and diluted with degassed dry acetonitrile, allowing the absorption spectrum of the cation radical to be recorded. The existence of the cation radical was confirmed by adding p-dinitrobenzene, as a radical scavenger, and observing a dramatic decrease in the absorption of the cation radical. The absorption spectra of chemically produced cation radicals of various pyrazolines are illustrated in Figure 3.17.

The decay of the cation radical of the pyrazolines studied was reasonable slow. The change of absorption at the spectral maximum was recorded as a function of time, if it is assumed that the absorbance is proportional to the concentration of the species, the half life for the cation radical of \( \text{PYA} \) is about 25 minutes, with the other pyrazolines being of a similar order of magnitude.

(b) Picosecond diffuse reflectance laser flash photolysis

(i) Data collection and manipulation

Using the picosecond laser system at the Rutherford Appleton Laboratories (RAL) the technique of diffuse reflectance laser flash photolysis in the sub-nanosecond time domain has been developed. The transient decays illustrated later for microcrystalline pyrazolines are the first ever observed for an opaque sample on the sub-nanosecond time domain, a clear illustration of the novel nature of these studies. As with any new technique the development of efficient data collection and manipulation procedures is of primary importance, thus a brief
FIGURE 3.17 Absorption spectra for chemically produced cation radicals of various Pyrazolines in acetronitrile

PYRAZOLINE

PYA  
PYB  
PYC  
PYD  

WAVELENGTH / nm

ABSORBANCE

0.0  
0.1  
0.2  
0.3  
0.4  
0.5  
500  
550  
600  
650  
700  
750  
800  
850  
900

0.0 - 0.5
discussion of such procedures will be undertaken prior to considering any results.

The basis of the technique is to electronically excite the opaque sample with a pump beam and subsequently interrogate the resultant transient absorption by measuring the decrease in diffusely reflected probe beam at various times during its decay, full experimental details are given in Section 2.3. The fluctuations in laser energy create a necessity to normalize the transient signal with respect to pump energy, thus a small portion of both the pump and probe beams have to be deflected on to a suitable photodiode in order to gain a measure of this energy.

The normal data acquisition procedure involves collecting detector signals from all three photodiodes over two sets of 200 laser shots, the first with only the pump beam and the second series with both beams. An additional consideration is the fact that alternate pump shots are being removed by a programmable light chopper (see section 2.3). Consequently the first series of 200 shots consists of alternately interleaved background (no beams) and emission (pump only) signals, while the second series consists of interleaved baseline (probe only) and transient (pump & probe) signals. The probe beam is subjected to a variable optical delay in order to interrogate different time portions of the transient decay, and the above data acquisition procedure has to be undertaken at each probe delay.

The main information yielded by the first series of interleaved data relates the variation of signal due to emission from the sample, E, as a function of pump reference signal, P. Normally these quantities have been observed to vary linearly, however for pyrazolines a non-
linear saturation is observed (see later). The two quantities (i.e. $E$ and $P$) are mathematically related by a least-squares polynomial curve fitting routine to enable a value for the emission intensity, $E$, to be interpolated for a known pump intensity, $P$.

i.e.

$$E(P) = \sum_{i=1}^{n+1} C_i P^i \quad (3.29)$$

where $C_i$ is the $i$th coefficient of the calculated polynomial of order $n$.

The second sequence of interleaved data provides information about the intensity of reflected probe, $D$, and the probe reference intensity, $N$, in the presence and absence of the pump beam. It is clear that in the absence of pump a linear relationship should exist between $N$ and $D_{off}$, which can be fitted according to equation 3.30, where $\alpha$ and $\beta$ are arbitrary constants.

$$D_{off} = \alpha N + \beta \quad (3.30)$$

The quality of the above linear fit is a good indication of the level of geometric and electrical stability within the experimental set-up. The actual quantity which needs to be extracted from the data is the relative change of sample detector signal, $D$, with and without pump. At a pump intensity, $P$, the above relationship can be represented by equation 3.31.

$$\frac{\Delta R}{R} = \frac{\Delta D}{D} = \frac{D_{off} - D_{on}}{D_{off}} \quad (3.31)$$
For a fluorescent sample the emission intensity, $E$, at pump intensity, $P$, must also be considered using equation 3.29 to provide $E(P)$ (the emission intensity at $P$). The numerically value of $D_{\text{off}}$ can be calculated using equation 3.30 by taking the value of $N$ corresponding to $D_{\text{on}}$. In all of these calculations the background signals from the pump reference detector, $P_b$, and sample detector, $D_b$, have to be accounted for. The final relationship, accounting for each of these effects, is given in equation 3.32:

$$\frac{\Delta R}{R} = \frac{\Delta D}{D} = \frac{\alpha N + B - (D_{\text{on}} - (E(P) - P_b))}{\alpha N + B - D_b}$$

(3.32)

When the relative change in reflectance is proportional to pump energy the value obtained using equation 3.32 is normalized to $P$ and all the values are averaged. However, a non-linear dependence between $\Delta R/R$ and $P$ has also been observed and in this case a polynomial fit is calculated for $\Delta R/R$ upon $P$ and a typical value of $P$ is chosen to yield the actual absorption change and the same value of $P$ is used for a set of probe delays. The above details relating to data collection and manipulation have also been published elsewhere [144,145].

(ii) Results and analysis

The pioneering work using this technique involved the study of the growth of a transient, namely the xanthone triplet produced from xanthone adsorbed on silica gel [83]. The decay of this triplet had been previously studied using nanosecond diffuse reflectance laser flash photolysis [85]. The growth of the triplet was studied using a simple manual pump and probe technique, with no real automation of the data collection procedure. However, once the feasibility of the
technique had been established a great deal of development work was undertaken to automate the data collection and manipulation procedures discussed above (see section 3.2 (b) i). All of the work described below for pyrazolines was collected using these automated procedures.

Microcrystalline samples of PYA, PYB, PYC and PYE were subjected to picosecond laser flash photolysis and in addition polymer films containing PYA, PYB and PYC were investigated by placing barium sulphate behind the transparent film in order that the same experimental geometry could be employed. In the former case of the microcrystalline samples, with the exception of PYE, a strong transient absorption was observed to decay over about 5ns. The decay of the transient absorption showed an initial fast component followed by a slower component. The decays of the transient absorptions, which we believe to be the first recorded for opaque samples on the sub nanosecond time domain, are illustrated for PYA and PYB in Figure 3.18 (a) and 3.18 (b), respectively:

In the case of PYE microcrystals there is at least a ten fold decrease in the amount of transient absorption observed, in addition the transient absorption decay only appears to exhibit the initial fast component. However, it is difficult to make very quantitative observations because the later regions of the decay are within the background noise. During a study of the emission of microcrystalline pyrazolines (see later in section 3.2 (c)) the excitation spectrum of solid PYE showed an edge at 355nm, below which no fluorescence was observed. As a consequence of this the fluorescence quantum yield showed a rather abnormal wavelength dependence, and at the pumping wavelength of 295nm the sample is absorbing virtually all the incident radiation (see ground state diffuse reflectance spectrum in Figure 3.10) but has a fluorescence quantum yield of zero. Another anomaly
FIGURE 3.18 Transient absorption decays from samples of microcrystalline (a) PYA and (b) PYB, with pump and probe wavelengths of 295 nm and 590 nm, respectively.
exhibited by PYE was that in solution ground state absorption studies the extinction coefficient is about 100 times less than any of the other studied pyrazolines (see Table 3.1). This anomalously low extinction coefficient is also present when the second lower wavelength absorption band is being considered (see later for a discussion of these facts).

Polycarbonate films containing PYA, PYB and PYC (~35-40% by mass of pyrazoline) yielded an apparently similar transient absorption decay as detected for the microcrystalline samples. A polycarbonate film containing PYA (35%) and DSM (0.1% by mass) was then investigated, prompted by the fact that previously in solution the pyrazoline fluorescence had been quenched by DSM via a radiative and non-radiative mechanism (see section 3.1 (c) for details). The amount of transient absorption was observed to decrease dramatically, when DSM is present in the polycarbonate film. However, as a consequence of the low levels of absorption, it is very difficult to establish whether the decay of transient has become faster or the amount of transient has just decrease uniformly across the decay. By eye, it appears that the initial amount of transient has decreased but the decay is still occurring at the same rate. The transient absorption decays are illustrated in Figure 3.19. This observation provides strong evidence for the transient absorption being due to the singlet state of pyrazoline (or a related species) which is being statically quenched by DSM. A film containing only polycarbonate and DSM (0.1%) was also investigated and no transient absorption was observed. The above work has prompted a brief preliminary investigation of the effect of the DSM on the PYA fluorescence intensity within a polycarbonate film. Although some radiative transfer was observed there was strong evidence for simultaneous non-radiative quenching of the PYA fluorescence. In order
FIGURE 3.19 Transient absorption decays from (a) PYA in polycarbonate and (b) PYA and DSM (0.1%) in Polycarbonate, both samples containing similar amounts of PYA (35%) [pump = 295 nm and probe = 590 nm]
to achieve quantification of this quenching process, the above work would have to be carried out over a range of DSM concentrations within a polymer film, and it is hoped that this work can be followed up on future visits to RAL.

One point worth consideration is the problem of laser induced thermal effects within the sample. A prediction of the temperature rise expected can be achieved using equation 3.28 (see 3.2 (a) ii). The pump laser energy at the sample was about 4µJ, and with a irradiation area of approximately 0.04 cm², this gives a laser fluence, $F_0$, of $1 \times 10^{-4}$ J cm⁻². The apparent powder density, $\rho'$, was determined experimentally as 0.63 g cm⁻³ which for PYA (formula mass = 324) leads to a ground state concentration of absorbers at time zero, $C_A^0$, of $1.96 \times 10^{-3}$ mol cm⁻³. The value of the absorption coefficient, $K_e$, at the exciting wavelength (i.e. 295nm) can be calculated using equation 3.26 (see section 3.2 (a) ii) using an estimate of the extinction coefficient at the exciting wavelength from solution studies. The estimated value of $K_e$ is $2.18 \times 10^4$ cm⁻¹ at 295nm. The specific heat capacity, $c$, of 0.69 J K⁻¹ g⁻¹ [45] for TiO₂ has to be used in the absence of a better approximation for microcrystalline organic solids, while the value of $f$ is set equal to unity which is unrealistic because some of the absorbed radiation is clearly responsible for fluorescence. This means that the predicted temperature rise of 5.3°C is an overestimate, therefore it is very unlikely that opto-thermal effects are a problem.

Before any kinetic analysis of the data can be undertaken an idea of the nature of the transient concentration profile must be gained (as discussed in section 3.2 (a) ii). The existence of an homogeneous or exponentially decaying transient concentration profile can be
assessed using equation 3.25 in conjunction with equation 3.27 (see section 3.2 (a) ii). When the various constants (i.e. \( I = 2.959 \times 10^{-10} \) photons cm\(^{-2}\), \( C_A^0 = 1.96 \times 10^{-3} \) mol cm\(^{-3}\) and \( K_e = 2.18 \times 10^4 \) cm\(^{-1}\)) are inserted into equation 3.25 and 3.27 the value of \( x \) is 0.003, which is clearly indicative of an exponentially decreasing concentration of transient. This profile is treated using \( \Delta I/\Delta I_0 \) analysis, and this method will now be used to analyse the kinetics of decay of the transient absorption.

Kinetic analysis of the data was achieved by writing a Fortran computer program, called PICOFIT, on the University mainframe computer. The program reads an experimental data file containing the corrected change in reflectance values at a series of probe delays, this was then treated to extract the decay portion of the data. This decay region can then be analysed according to both the first and second order rate laws, using either Kubelka-Munk or \( \Delta I/\Delta I_0 \) to extract the concentration (see section 3.2 (a) i). The kinetic plots (i.e. first and second order plots) exhibited the same trends for all pyrazolines (except PYE - see previous) in the form of microcrystals or within polycarbonate films, namely a complex mixed order kinetics as illustrated in Figure 3.20 (a) and 3.20 (b) for PYB microcrystals.

Interpretation of the kinetics is made difficult by the large amounts of scatter and the limited number of data points that exist in some regions of the decay. There are many ways in which the data can be viewed and straight line regions visualized in many different regions of the kinetic plots. For instance there could be an initial first order decay followed by a second order decay at longer times, while it is just as realistic to visualize a first order decay initially followed by a first order decay at longer times with the second order...
FIGURE 3.20 (a) First and (b) Second order kinetic plots for the decay of the transient absorption obtained from a sample of microcrystalline PYB \( \text{[pump = 295 nm , probe = 590 nm]} \).
plot being curved throughout. At this stage it was felt that the most constructive way to proceed was to create some theoretical decays from various model mechanisms and compare them with the actual experimental decays. The comparison was achieved using a Fortran subroutine which was written to find the minimum of the sum of the errors squared, where the error is the difference between theory and experimental data. The routine worked reasonably well, and was fully tested with created data, but involved a large amount of initial "trial and error" work by the user.

The first model tested was a double exponential decay, which in practical terms can be visualized as the superimposition of two different transient absorptions, each decaying by a first order kinetic process.

\[ \Delta I(t) = \Delta I_1^0 e^{-k_1 t} + \Delta I_2^0 e^{-k_2 t} \] (3.33)

where \( k_1 \) and \( k_2 \) are first order rate constants and \( \Delta I(t) \) is the change in reflectance at time \( t \). The terms \( \Delta I_1^0 \) and \( \Delta I_2^0 \) are constants that represent the initial contribution of each transient absorption at time zero. This model did not appear to represent the experimental data very well, some of the better fits are illustrated with the decay of transient absorption from microcrystalline PYB in Figure 3.21.

The next model tested was the conventional mixed kinetics approach assuming one transient species

\[ -\frac{d \Delta I(t)}{dt} = k_1 \Delta I(t) + k_2' \Delta I(t)^2 \] (3.34)

\( k_1 \) and \( k_2' \) are the first and second order rate constants, respectively. This can be solved using a standard integral to give the expression:
FIGURE 3.21 Experimental transient absorption decay from a sample of microcrystalline PYB, fitted with various data sets created from a double exponential mechanism (i.e. two superimposed transient species both decaying by first order processes)

\[ k_1(1), k_1(2), \Delta l_0^1 \]

- EXPERIMENTAL DATA
\[ \Delta I(t) = \frac{k_1 \Delta I_0}{(k_1 + k_2 \Delta I_0)e^{k_1 t} - k_2 \Delta I_0} \]  

(3.35)

When this expression was used to create a theoretical decay it was found that none of the created decays compared very well with the experimental data, at any realistic values of the constants, see Figure 3.22 for illustration of fit with microcrystalline PYB providing the decay.

More success was obtained when the experimental data was fitted with a superimposition of two transients one decaying by first order and the other by a second order process. The expression for the variation of \( \Delta I \) with respect to time is:

\[ \Delta I(t) = \Delta I_0^1 e^{-k_1 t} + \frac{\Delta I_0^2}{1 + k_2 C_0 t} \]  

(3.36)

where \( k_1 \) and \( k_2 \) are the first and second order rate constants, respectively. As illustrated in Figure 3.23 for the transient absorption decay for microcrystalline PYB the fit of theory with the actual data is reasonably good with the following fairly realistic constants, namely \( k_1 = 12 \text{ns}^{-1} \), \( k_2 C_0 = 2.2 \text{ns}^{-1} \text{mol}^{-1} \) and \( \Delta I_0^1 = 0.1 \). This fit is fairly encouraging but it should not be instantly assumed that this is the mechanism. It is clear that more experimental data need to be obtained to assign a mechanism, in particular a time resolved spectrum of the transient decay could easily illustrate the existence of two transient species. The development of the technique in order that time resolved spectra can be recorded is discussed later.

The previously observed fact that DSM quenches the PYA transient absorptions is strong evidence for the transient species being the singlet (or a related species) (see previous). Also the absence of fluorescence
FIGURE 3.22 Experimental transient absorption decay from a sample of microcrystalline PYB, fitted with various data sets created from a mechanism in which a single transient species is decaying by a mixed first and second order process.
FIGURE 3.23 Experimental transient absorption decay from a microcrystalline sample of PYB, fitted with various data sets created from a mechanism involving the superimposition of two transient species, one decaying by a first order process and the other by a second order process.
from PYE when excited at 295nm and the corresponding lack of slower species can be used as evidence to relate this species to the first singlet \( (S_1) \) (see previous). The fact that in the case of microcrystalline PYE the initial rapid species still remains could suggest that this is associated with the absorptions from a transient of a higher singlet such as \( S_2 \), since this is the state which is excited at 295nm. In the case of PYE it would appear that intersystem crossing from \( S_2 \) to \( S_1 \), is forbidden and \( S_2 \) decays non radiatively back to the ground state. For this postulation to be true the transfer from \( S_2 \) to \( S_1 \) would have to be fairly slow. The value of the rate constant for the decay of rapid species, for microcrystalline PYB, is \( 1.2 \times 10^{10} \text{ s}^{-1} \).

The above mechanism does not totally agree with the scheme of two transients, one decaying by first order and the other by a second order process, because the second transient would be produced by the decay of the first and also the produced species is unlikely to decay by a pure second order mechanism if fluorescence is occurring. It is felt at this stage that more experimental work needs to be carried out in particular the time resolved spectra of the transient absorption needs to be refined before the mathematics and the problems of fitting a data set created from a mechanism are tackled. Therefore in summary one possible mechanism that requires more investigation is:

\[
\begin{align*}
S_0 & \xrightarrow{h\nu} S_2 \\
S_2 & \xrightarrow{k_1} S_1 \\
S_1 & \xrightarrow{k_2} S_0 \quad \text{(radiative and non-radiative)} \\
S_1 + S_1 & \xrightarrow{k_3} S_0 + S_0
\end{align*}
\]
where a rapid first order process \( (k_1) \) of \( S_2 \) to produce \( S_1 \), which decays by a first and second order mechanism \( (k_2, k_3) \).

The above mechanism would require any model fitting to take into account the growth of the second transient species (i.e. \( S_1 \)) as the first species decays. Thus if, for the purpose of the argument, we consider that the two transients decay by first order processes, the model for the superimposition of two first order transients (discussed above, see equation 3.33) would in terms of fitting be identical to the situation of the loss of one transient by a first order process and the build up and decay of the other, again by a first order process. The only main difference between the two situations is the different values of the pre-exponential constants. In the case of the first order build up model the expression is:

\[
\Delta I = \frac{\alpha_1}{\alpha_2} \frac{k_1}{(k_2 - k_1)} \Delta I_0 (e^{-k_1 t} - e^{-k_2 t}) + \Delta I_0 e^{-k_1 t}
\]

(3.37)

where \( k_1 \) and \( k_2 \) are the first order rate constants for the decay of the first and second transients, respectively, and the ratio \( \alpha_1/\alpha_2 \) is a constant where \( \alpha \) relates \( \Delta I \) to concentration. The expression above can clearly be viewed as a double exponential with different pre-exponential constants to equation 3.33, but essentially the same equation in terms of fitting.

The same argument can thus be applied to the more realistic situation of the superimposition of two transient species, one decaying by a first order process and the other by a second order process, which is equivalent in terms of fitting to a first order decay of the first transient producing the second transient which in turn decays by a second order process. In fact it is still essentially the same fitting problem if the second transient species decays with an additional first order component, only a modification of the initial first order process is encountered. Obviously one future development of this fitting work, once more data has
been acquired, would be to develop the mathematical model for the above mechanism and attempt to fit it to the experimental data. However until this has been done the previous fit provides a suitable first approximation.

One other very interesting observation from the picosecond studies of various pyrazoline samples involves the fluorescence. As mentioned above in section 3.2 (b)(i) the fluorescence is corrected for by fitting a polynomial to the fluorescence intensity as a function of pump energy (see equation 3.29). The actual plots of fluorescence intensity, $E$, versus pump intensity, $P$, reveal a very interesting non-linear saturation effect. This effect is illustrated for PYA microcrystals in Figure 3.24. This observation is only of academic interest at the moment but as more effort is put into solving the details of the mechanism it may become important.

The final and perhaps most important consideration is the development of the facility to acquire time resolved diffuse reflectance laser flash photolysis spectra in the sub-nanosecond time domain. This work is still in its infancy but it is believed that the time resolved spectra presented here (see later) are the first of their type to ever be recorded. The procedure used involves producing a continuum by passing the probe beam through water. The major difference in the technique is the detection procedure, where the probe reference and the reflected probe beam off the sample have to be passed through a monochromator (as discussed in section 2.3). The major problem encountered thus far is the very weak intensities of continuum which reach the photodiode detectors after monochromation. However, it has proved possible to measure a spectrum at two different probe delays, as illustrated in Figure 3.25. The spectra are for microcrystalline PYA and are at the maximum and 0.6ns after the
FIGURE 3.24 Illustration of the variation of emission intensity as a function of pump energy from a microcrystalline sample of PYA

[ Pump = 295 nm, probe = 590 nm ]
FIGURE 3.25 Time resolved transient absorption spectra from a sample of microcrystalline PYA [pump = 295 nm, probe = 510 - 680 nm]
maximum absorption, and show two peaks at 500nm and 590nm. The spectrum after 0.6ns shows very much less of the 590nm component and only a slight decrease in the 500nm species. This spectral evidence is consistent with the transient absorption being due to two superimposed transient species. It is hoped that the technique can be improved dramatically during further periods of research at RAL by replacing the photodiodes with small photomultipliers, which would hopefully increase the sensitivity.

As mentioned previously this work was carried out at RAL laser support facility, for which the financial support of SERC is gratefully acknowledged. The initial development of the technique was carried out by M.J.C. Smith (RAL) and P.A. Leicester (Loughborough University), including the preliminary measurements on xanthone discussed above [83]. I joined the project shortly after this initial period and was responsible for collecting all the pyrazoline data presented above plus the subsequent analysis of the data. P.A. Leicester was responsible for the automation of the technique and for writing the data collection software. It is hoped to continue this fruitful collaboration in order to develop this exciting new technique to its full potential and hopefully gain many more interesting and scientifically useful results. The development of the technique and the results presented above will be published elsewhere [145].

(c) Fluorescence spectra and lifetimes

During a period of research at the University of Tubingen the fluorescence spectra (corrected) and lifetimes, of various pyrazolines within polycarbonate films and as microcrystalline solids, were measured. The fluorescence excitation spectra of all the samples, except PYE (see
later), showed a fairly broad structure, which was characteristic of the light source used. A microcrystalline sample of PYA had fluorescence emission spectra recorded using both 430nm and 330nm excitation, and the resultant spectra were superimposable with a maximum at 489nm. Microcrystalline samples of PYB, PYC and PYE yielded fluorescence emission spectra with maxima at 510nm, 522nm and 490nm, respectively, when excited at 430nm. The fluorescence emission spectra of all of the above microcrystalline solids are illustrated in Figure 3.26. All of the above spectra are not altered either in the presence or absence of oxygen. The fluorescence emission spectra of PYA, PYB and PYC within polycarbonate films (35-40% of pyrazoline by mass) were recorded exciting at 430nm, and had maxima at 480nm, 502nm and 481nm, respectively.

As briefly mentioned above (see section 3.2 (b) ii) the fluorescence quantum yield of microcrystalline PYE exhibits a wavelength dependence. The excitation spectra of other pyrazoline solids have a broad excitation spectra across a large wavelength range, while PYE suddenly stops emitting when the excitation wavelength drops below 350nm; this comparison is illustrated in Figure 3.27 where the excitation spectra of microcrystalline PYB and PYE are given. The ground state diffuse reflectance spectra corrected for fluorescence (see Figure 3.10 in section 3.2 (a) ii) shows that at 350nm PYE solid is virtually completely absorbing (i.e. very low reflectance). These facts can only be explained by the occurrence of a wavelength dependence on the value of the quantum yield. It is likely that at below wavelengths of 340nm the excitation is producing a higher singlet of pyrazoline (e.g. $S_2$), rather than the $S_1$ state. In solution studies two absorption bands occur and the higher energy band begins in this region, it is therefore fairly likely that the same occurs within the solid. In the cases of the other solid pyrazolines excitation into the higher singlet does not seem to effect the fluorescence, because a rapid internal conversion occurs to produce
FIGURE 3.26 Corrected emission spectra from various samples of microcrystalline pyrazolines (Excitation wavelength = 430 nm)
FIGURE 3.27 Excitation spectra from microcrystalline PYB and PYE samples (Emission wavelength = 500 nm)

FIGURE 3.28 Ground state diffuse reflectance spectra, corrected and uncorrected for induced emission, from microcrystalline PYE
the $S_1$ state. However, with microcrystalline PYE it appears that the $S_2$ to $S_1$ transition is forbidden, and the former (i.e. $S_2$) deactivates via a non-radiative mechanism. The above anomaly is clearly illustrated in Figure 3.28, in which the ground state diffuse reflectance spectra, both corrected and uncorrected for induced fluorescence, are presented for PYE. The dramatic drop in the level of fluorescence is exemplified in the uncorrected ground state diffuse reflectance spectrum, which abruptly becomes identical to the corrected spectrum in the spectral region below 340 nm.

The fluorescence lifetime measurements, which are discussed in greater detail in section 3.1(b), were performed on a variety of pyrazoline samples. Microcrystalline PYA had a fluorescence lifetime which is of the same order of magnitude as the $N_2/H_2$ arc excitation source. The decay of the PYA fluorescence can be fitted by equal contributions of a double exponential fit (i.e. $\tau_1 = 1.2$ ns, $A_1 = 0.024$ $\tau_1 = 2.6$ ns, $A_2 = 0.012$). This situation is indicative that the real lifetime is somewhere between the two, namely $\tau = 2.0$ ns. This lifetime uses an excitation and emission wavelength of 358 nm and 490 nm, respectively.

The slightly inaccurate lifetime obtained from PYA is compensated for by microcrystalline PYB and PYC in which both fluorescence decays were monoexponential. The lifetimes were determined from the fit as 3.59 ns ($A = 0.036$) and 5.54 ns ($A = 0.053$), respectively, emission maxima are 500 and 520 nm. The decay of PYC is illustrated with the excitation source in Figure 3.29. When PYB and PYC are incorporated within polycarbonate films the decay is essentially a double exponential with approximately equal contributions from each component exponential. For PYB the lifetimes
FIGURE 3.29 Emission decay profile from microcrystalline PYC and the excitation source profile, obtained using the technique of single photon counting ($\lambda_{em} = 520$ nm and $\lambda_{ex} = 358$ nm).

FLUORESCENCE DECAY OF PYC WHICH CAN BE FITTED WITH A SINGLE EXPONENTIAL ($\tau = 5.54$ nS. AND $A = 0.053$)

EXCITATION SOURCE PROFILE SUPPLIED BY A $N_2/H_2$ ARC
were 5.0ns (A = 0.014) and 2.2ns (A = 0.097) at the emission wavelength of 500nm, while PYC in polycarbonate yielded lifetimes of 2.7ns (A = 0.007) and 5.1ns (A = 0.007) at the emission wavelength of 520nm.

The final lifetime determined was for a sample of microcrystalline PYE at the emission wavelength of 490nm. The decay was fitted by a double exponential, which contained 90% of a component of lifetime 2.0ns (A = 0.066) and a 10% component of lifetime 4.0ns (A = 0.003). This study of fluorescence lifetimes can only really be viewed as an initial survey, rather than a detailed study. However, with the small amount of time available at the University of Tubingen it is felt that the fluorescence lifetime results obtained provide useful background information.

(d) Photoconduction Studies

(i) Data collection and analysis

The function of the equipment, at 3M's Research Limited, is to measure the decay of the surface potential for a photosensitive material, with and without illumination (i.e. light and dark decay). Experimental traces are recorded at a variety of applied corona potentials which produce a corresponding series of initial surface potentials, $V_s$. At each value of $V_s$ the initial slope of the light decay, $dV/dt$, is measured off the experimental trace subtracting any small amount of dark decay. The terms $V_s$ and $dV/dt$ can then be related using the analysis procedure outlined below.

Before the theory of analysis is considered it is worth pausing to review the salient points in the general dye sensitized charge transport mechanism. Initially a sample, consisting of a sensitizing dye and a charge transport material within a polymer matrix, is charged
with a positive corona resulting in the development of an electric field, \( E \), across the layer (see Figure 3.30 (a)). This is then illuminated with an appropriate wavelength of radiation to electronically excite the sensitizing dye (i.e. 550nm), and this in turn interacts with the charge transport molecule to produce the anion radical of the dye and the cation radical of the charge transport molecule. The positive charge carriers migrate to the cathode leaving a distribution of the immobile negative ions within the sample, (space charge distribution) see Figure 3.30 b.

The very low mobility of the negative charge carriers (i.e. dye species) arises because these species are sufficiently far apart as to make electron transfer between them a very low probability event. In the following analysis the effect of the positive charge in the bulk sample is neglected in the calculation of the surface potential. This assumption is only valid when the relative proportion of the positive carriers is very low and their time spent in the sample bulk is short (relative to the experimental time). These conditions are most likely to be fulfilled when the initial discharge is measured under very low intensity illumination.

In response to continued illumination, more charge carrier pairs are generated, which can either undergo geminate recombination or the mobile positive carriers can migrate away towards the cathode and recombine with a different anion radical. The overall effect of this process is to cause an "effective" movement of the negative charge carrier (i.e. anion radical of the dye) even though the hole (i.e. positive charge carrier) is actually migrating, this is illustrated in Figure 3.30 c. Eventually after a long period of illumination all the negative species will undergo "effective" movement to the positively charged surface and consequently completely discharge the sample.
FIGURE 3.30  Schematic illustration of the dye sensitized charge transport mechanism operational during the photoconducton studies

(a)  
+ + + + + + + + + + + + Initial charged condition, with initial surface potential, $V_s$, and electric field $E$.

(b)  
+ + + + + + + + + + + + Space charge distribution of negative dye molecules

(c)  
+ + + + + + + + + + + + "Effective" movement of negative ions causing eventual charge neutralization
Under conditions of low intensity illumination the shape of the photoinduced discharge curve is largely determined by the electric field dependence of the quantum efficiency, $\rho_e$, which is a constant relating the quantum efficiency, $\varnothing$, and the electric field.

\[ \varnothing_E = \varnothing_0 \left[ \frac{E}{E_0} \right]^\rho_e \]  

(3.38)

where $\varnothing_E$ and $\varnothing_0$ are the quantum efficiencies at a variable, $E$, and a reference, $E_0$, electric field, respectively. A linear form of the above can be established by taking logarithms of equation 3.38, the resultant expression being:

\[ \log \left[ \frac{\varnothing_E}{\varnothing_0} \right] = \rho_e \log \left[ \frac{E}{E_0} \right] \]  

(3.39)

The quantum efficiency, $\varnothing_E$, at a fixed initial electric field is defined for this system by equation 3.40.

\[ \varnothing_E = \frac{\text{Number of free charge carriers produced}}{\text{Number of photons absorbed}} \]  

(3.40)

The quantum efficiency can be calculated using equation (3.41), the full derivation of which is given in Appendix C.

\[ \varnothing_E = \frac{\varepsilon \varepsilon_0}{q I_0 L \alpha (\alpha L)} \frac{dV}{dt} \]  

(3.41)

where $\varepsilon =$ relative dielectric constant of photoconductor , $\varepsilon_0 =$ permittivity of free space, $q =$ electronic charge, $I_0 =$ Incident photon flux at the sample surface and $L =$ sample thickness. The term $\alpha (\alpha L)$ is an abbreviation for an absorption term, shown in equation 3.42, the full derivation of which is given in Appendix C.
\[
\alpha(aL) = 1 - \frac{1}{aL} \left[ 1 - \exp(-aL) \right] \tag{3.42}
\]

where \( aL \) = Absorbance / 0.4343

The terms \( \epsilon, \epsilon_0, q \) and \( I_0 \) are constant throughout, while \( L \) and \( \alpha(aL) \) vary from sample to sample, due to a variation in sample thickness and content of absorbing material. Equation 3.41 can be re-written by introducing the composite constant, \( B \), where \( B = \epsilon \epsilon_0 / q I_0 \).

\[
\varphi_E = B \frac{dV}{a(aL)} \frac{dV}{dt} \tag{3.43}
\]

or alternatively

\[
\varphi_E = A \frac{dV}{dt}
\]

\[
A = \frac{B}{L} \frac{dV}{a(aL)} \tag{3.44}
\]

The value of \( A \) will be constant for a particular sample. The next concern is to convert the numerical value of the initial surface potential, \( V_s \), to the electric field, \( E \). This conversion can easily be achieved by employing equation 3.45 which holds true when there is an absence of space charge (i.e. under the initial conditions)

\[
\text{i.e. } E = \frac{V_s}{L} \tag{3.45}
\]

From equation 3.39 it is clear that the slope of a plot of \( \log(\varphi_E) \) versus \( \log(L_s^2) \) will yield a value which is numerically equivalent to \( \rho_e \). This can then be used to calculate quantum efficiencies at a particular applied electric field for a given sample.
(ii) Results

The following results were collected over several periods of research totalling about 3 months, at 3M's Research Limited. The results are primarily concerned with a system of PYA and DSM within a polymer matrix. When polycarbonate is used as the polymer the effect of varying the amount of PYA within the film was investigated using a constant DSM content of about 0.1% by mass. The studies involved recording between 8 and 12 light decays over a range of surface potentials, this being controlled by the applied corona potential. Once one potential had been investigated, the sample is discharged by flooding it with a strong white light source, and it was allowed to dark adapt for a 5 minute period. Once a complete range of potentials had been studied, a series of initial surface potentials, $V_s'$, could be extracted together with the corresponding initial slope of the light decay, which could then be employed to give a numerical value of the field dependence of quantum efficiency, $\rho_e$ (as discussed above in section 3.2 (d) i).

An extensive study over a large range of PYA contents within a polycarbonate matrix, unfortunately did not yield very conclusive results, as illustrated in Table 3.8 (below). The values of $\rho_e$ are significantly higher at the two lower PYA concentrations (namely 20.02 and 14.35% PYA) but the values of $\rho_e$ between 45-25% PYA are fairly scattered and illustrate no obvious trends.
Table 3.8 Variation of $\rho_e$ as a Function of PYA Content (Measured as % by Mass of Film Containing 0.1% DSM in Polycarbonate).

<table>
<thead>
<tr>
<th>% (PYA) IN SAMPLE</th>
<th>$\rho_e$</th>
<th>% (PYA) IN SAMPLE</th>
<th>$\rho_e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>45.38</td>
<td>1.74</td>
<td>33.31</td>
<td>1.66</td>
</tr>
<tr>
<td>44.06</td>
<td>1.83</td>
<td>29.34</td>
<td>1.71</td>
</tr>
<tr>
<td>42.99</td>
<td>1.76</td>
<td>24.85</td>
<td>1.82</td>
</tr>
<tr>
<td>39.98</td>
<td>1.80</td>
<td>20.02</td>
<td>1.99</td>
</tr>
<tr>
<td>36.98</td>
<td>1.83</td>
<td>14.35</td>
<td>2.18</td>
</tr>
<tr>
<td>36.63</td>
<td>1.82</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

At this stage it is worth considering experimental errors which may have contributed to the anomalous results. There are four main sources of error which can be postulated, namely (i) insufficient white light exposure was used to fully discharge the layers, (ii) initial surface charge distribution was not totally uniform, (iii) insufficient time was allowed for dark adaption between measurements and (iv) regions of high impedance may be present in the earthed ground-plane.

During the next period of research, similar experiments to those outlined above, were undertaken in a variety of polymer environments (including repeating the polycarbonate system). The polymer systems used were polycarbonate (PC), poly(styrene-methylmethacrylate) (PSM), polymethylmethacrylate (PMMA) and polyester (PE). However, in the latter great problems were experienced in coating the films and as a consequence the resultant films were not of a suitable quality to be used. The values of $\rho_e$ as a function of PYA content (at a constant 0.1% content of DSM) showed no obvious trends in any of the polymer media, only a scatter of values as observed previously for polycarbonate.
One interesting observation that was made during these studies was that the PMMA films exhibited a much lower level of quantum efficiencies at each PYA concentration, than either of the other polymers, at a fixed electric field. In Figure 3.31 the quantum efficiency is plotted as a function of PYA content, at a fixed electric field of $3 \times 10^5$ V cm$^{-1}$, for each of the three polymer systems studied. The most likely explanation for the observed differences in a PMMA media is that this particular polymer environment causes a dramatic modification of the effective permittivity of the medium surrounding a localized charge. It should be emphasized that the important quantity is the effective permittivity in the vicinity of the localized pair as opposed to the macroscopic relative permittivity (dielectric constant).

The above anomaly observed with PMMA may be related to the difference in the decay of the DSM transient species in the PMMA film, observed previously (see section 3.2 (a) iv). The flash photolysis study of the DSM transient in PMMA exhibited decay kinetics which were essentially first order after the first 1.5mS, as compared with the predominantly second order decay process observed in the other polymers. In addition the lifetime of the observed DSM species was longer in a PMMA matrix.

Another investigation attempted was to vary the DSM content of the polymer films (polycarbonate) and keep the PYA content constant. The study showed that 0.1% of DSM was the optimum concentration. The results are illustrated in Figure 3.32, in which the variation of the quantum efficiency as a function of DSM concentration is represented at different values of the applied electric field.

At this stage it was decided to attempt to eliminate some of the experimental problems discussed previously, in particular the uniformity
FIGURE 3.31 Variation in quantum efficiency of charge generation ($\phi$) as a function of PYA content within different polymer media

$E = 3 \times 10^5 \text{ V cm}^{-1}$

DSM content = 0.1 % (approx.)

POLYMER
- PSM
- PMMA
- PC

TREND FOR PSM AND PC

TREND FOR PMMA

% PYA IN POLYMER FILM
Figure 3.32 Variation of charge generation quantum efficiency, $\phi$, as a function of DSM content within a polycarbonate matrix, at various applied electric fields ($E$).

PYA content = 42% (approx.)

- $E = 5 \times 10^5$ V cm$^{-1}$
- $E = 4 \times 10^5$ V cm$^{-1}$
- $E = 2 \times 10^5$ V cm$^{-1}$
of the corona charging. This improvement was achieved by inserting a high voltage grid under the corona wire, which should provide a more evenly distributed surface potential. The magnitude of the surface potential could then be altered by varying the applied grid potential and consequently allowing the corona potential to be kept constant at 6 kV. The results obtained using the modified charging system appeared to show much less scatter than previously, and there was a conclusive trend observed that $p_e$ increased as the PYA content was decreased. For example at PYA contents of 43, 33.5 and 27.1% the calculated values of $p_e$ were 2.14, 2.27 and 2.42, respectively.

In an attempt to make some mechanistic interpretation of the results it was very important to establish whether a polymer film (containing PYA and DSM) produce different values of $p_e$ when illuminated at different frequencies of radiation, or more precisely different energies of radiation. All of the previous results were obtained employing 550 nm excitation, supplied by the insertion of an appropriate interference filter into the path of the beam from the Tungsten excitation source. A sample containing 0.1% DSM and 42% PYA within a polycarbonate matrix was illuminated at 490nm, 522nm, 579.4nm and 610nm (by the insertion of different interference filters) and the value of $p_e$ were 1.77, 1.91, 2.12 and 2.30, respectively. In Figure 3.33 the plots of log ($\Omega_e$) versus log ($V_s/L$) are represented for all four excitation wavelengths.

The above results strongly suggest that charge carrier production is following the Onsager mechanism [146,147,148,149]. In this model the process of charge generation is considered to be the result of two distinct steps, firstly the bound electron-hole pair is formed by excitation of the dye and subsequent electron transfer from suitable ground state neighbouring species (i.e. PYA). The second step involves the dissipation of excess energy possessed by the bound electron
FIGURE 3.33 Graphical illustration of the effect of changing the wavelength of DSM excitation, on a plot of $\log (\phi)$ versus $\log (E)$, for a Polycarbonate sample containing PYA (40%) and DSM (0.1%).
hole pair, via migration of the hole away from the immobile electron until thermal equilibrium with the matrix is achieved. At this equilibrium distance, known as the thermalization distance, the hole then diffuses under the perturbation of the applied field and may escape to become a free carrier or alternatively drift closer to the bound electron and undergo geminate recombination.

The efficiency of production of the bound electron-hole pair is characterized by the primary probability, $\phi_0$, which is assumed to be independent of the applied field strength. The presence of competing deactivation pathways for the dye excited state generally means that the maximum value of the bound pair generation quantum efficiency is usually much less than unity.

The thermalization distance, $r_0$, temperature and electric field strength will each contribute directly to the probability of dissociation of the bound charge carrier pairs [146]. For a particular system and temperature the escape probability shows, for intermediate field strength ($10^4 - 10^6 \text{ V cm}^{-1}$), a power law dependence on the electric field. The index, $\rho_e$, can be related to the statistical distribution of initial separations around $r_0$ and their spatial orientation with respect to the applied electric field

\[
\phi_2 = \phi_1 \left[ \frac{E_2}{E_1} \right] ^{\rho_e}
\]

i.e. \( \phi_2 = \phi_1 \left[ \frac{E_2}{E_1} \right] ^{\rho_e} \) \hspace{1cm} (3.46)

The precise relationship between $\rho_e$ and $r_0$ has not been fully quantified but the existence of an inverse relationship between $\rho_e$ and $r_0$ has been established (e.g. in the limit $r_0 \rightarrow \infty$, $\rho_e \rightarrow 0$)
The value of $r_0$ will increase with the energy of the exciting photons (i.e. the "hotter" the charge carrier bound pair produced the greater the value of $r_0$). The magnitude of $\rho_e$ should therefore decrease as the photon energy increases, if the Onsager formalism is to be postulated. In the PYA/DSM system this variation of $\rho_e$ with respect to photon energy was observed, consequently the Onsager mechanism is proposed (see above). The observed fact that $\rho_e$ increases with decreasing pyrazoline content, and that the plot of $\log (\Omega_e)$ versus $\log (V_s/L)$ was linear are both consistent with the Onsager mechanism \[146,150\].

The alternative Poole-Frenkel mechanism for conduction \[151\] explains the electric field dependence of $\Omega$ in terms of a reduction in the energy barrier to electron transfer by the application of an electric field. The bound electron-hole pair resides on a molecular site in a potential energy well, and the application of an electric field reduces the energy gap between the bound electron-hole pair in the ground state and the conduction band \[150\]. The reduction in the potential energy well occurs in the direction of the applied field. The consequence of this mechanism is that diffusion apart of the charge carrier pair is not explicitly considered and therefore no variation of $\rho_e$ with photon energy is anticipated.

The above photoconduction study has yielded a great deal of preliminary information relating to the photoconduction properties of the PYA/DSM system in various polymers. However, it is clear that a far more extensive study of the system needs to be undertaken in order to extend the work presented above.
CHAPTER 4: CONCLUSIONS

The basic emphasis of the project has changed slightly during its duration, initially the mechanism by which 2-pyrazolines act as charge transport agents within an electrophotography system was of prime concern. However, in an attempt to elucidate this problem it was found necessary to undertake a detailed study of the photochemical and photophysical properties of various 1,3,5-aryl-2-pyrazolines. In an effort to draw all of the different areas of study together a summary of the "state of the art" of the photochemistry of 2-pyrazolines after this study, will be presented.

The various 2-pyrazolines were first subjected to a flash photolysis investigation in solution and although no direct triplet production was observed (after 347nm excitation) it was found that the pyrazoline triplet could be efficiently sensitized using a suitable triplet energy donor such as benzophenone. The assignment of the triplet was achieved using β-carotene as a triplet energy acceptor. The triplet energy of the pyrazolines were found to be approximately in the range 40-45 K cal mol⁻¹, by virtue of the fact that anthracene exhibits a relatively low level of sensitization when employed as the triplet energy donor. Upon changing the environment from solution to a polycarbonate film it was found that small amounts of direct triplet production were observed, after 354nm excitation. However, substantial amounts of pyrazoline triplet could only be produced by triplet energy transfer (i.e. by incorporating benzophenone into the polycarbonate matrix). The sensitized enhancement of the pyrazoline triplet on a cotton fabric substrate was also considered, but there were inherent problems associated with achieving a high enough loading of benzophenone on the cotton fabric.
Microcrystalline samples of several pyrazolines yielded a transient absorption signal, employing the new technique of diffuse reflectance laser flash photolysis, which was assigned as being due to the triplet. Although it was conclusively established that the transient absorption signal was not completely due to an opto-thermal effect, there is some evidence to suggest that temperature fluctuations within the sample could be contributing to the deviation from second order kinetics observed in the initial portion of the decay.

The charge generation dye DSM was also investigated using flash photolysis, and although no transients were observed in solution, studies in various polymer films yielded positive results. A transient absorption was observed with a narrow spectrum, maximum about 600nm, and with a lifetime in the order of 1ms. Three polymer environments were studied, PC and PSM exhibited similar behaviour with slightly different lifetimes, however some differences were observed in a PMMA matrix, namely the second order decay process which predominates in the other polymers was only present for the initial 1.0-1.5ms in PMMA and then a first order process was observed and a longer lifetime. This information is of interest since the photoconduction studies clearly demonstrate a lower level of quantum efficiency for the charge generation process in PMMA films, which is consistent with the conclusion that the DSM transient species is related to the photoconduction efficiency. The DSM transient species was eventually assigned as the anion radical of DSM. When pyrazoline PYA was incorporated into a PC matrix containing DSM, the amount of DSM transient decreased, however, the lifetime appeared not to be altered. Sensitized production of the PYA triplet was observed at 490nm using excitation conditions which were not capable of producing the triplet directly. The results suggest that the precursor of the DSM anion
radical is producing the PYA triplet. The precursor is likely to be the DSM triplet which undergoes triplet energy transfer to form the PYA triplet.

One very curious observation made during the above study was the fact that when the excitation conditions were altered and PYA was simultaneously excited with DSM there was no apparent quenching of the DSM radical anion transient. One plausible explanation of the above is that the singlet state of PYA is transferring its energy to form the DSM singlet, a process which has been shown to be very efficient in solution studies (see later). In fact some preliminary investigations in a polycarbonate matrix have proved conclusively that PYA does transfer its singlet energy to DSM. The consequence of this is that DSM is not only being excited directly but also indirectly via singlet energy transfer from PYA. There is also the possibility that once the PYA molecule has transferred energy to the nearest DSM "neighbour" it can be re-excited by energy migration between PYA molecules (and thus be available again for transfer). Eventually saturation of the amount of PYA triplet occurs and the DSM triplet can longer undergo triplet energy transfer and consequently forms the DSM anion radical. It should be stressed that the above is one possible explanation and there are other ideas that could be cited to explain some of these observations.

The DSM radical anion is produced in conjunction with a hole and it seems likely that the PYA donates an electron to DSM to produce PYA\(^+\) and DSM\(^-\), respectively. It is therefore consistent that the DSM radical anion (DSM\(^-\)) decays via a second order process because this occurs by recombination with the pyrazoline cation radical (PYA\(^+\)) which is present in identical amounts to DSM\(^-\) (i.e. \([\text{DSM}^-]=\text{[PYA}^+\text{]})\). The influence of the polymer matrix upon the decay of the DSM radical can
be explained, in the system with no PYA present, by the fact that different polymer environments possess different affinities to donate or receive electrons, thus altering the rates of formation and decay of the DSM anion radical. When PYA is present in the system this acts as the donor of electrons, but the different polymer environments can effect the local polarsability in the vicinity of the excited states, thus altering the rates of decay and formation of DSM radical anion.

The postulated sequence of events, outlined above for the DSM/PYA system in polycarbonate, is presented in a schematic form (below):

```
+----------------+          +----------------+          +----------------+
| DSM            |         | DSM* (S)       |         | DSM* (T)       |
| hv             |          | DSM* (T)       |          | DSM            |
|                |          | DSM*           |          |                |
|                |          | DSM + PYA⁺     |          |                |
|                |          | PYA            |          |                |
|                                        |          |                |
|                                        |          |                |
|                                        |          |                |
|                                        |          |                |
```

One of the most novel and scientifically exciting pieces of work presented here are the results obtained for various 2-pyrazolines (microcrystalline samples and within polymer films), using diffuse reflectance laser flash photolysis in the picosecond time domain. As mentioned previously these results were the first ever transient absorption decays observed for opaque samples in the sub-nanosecond time domain. The evidence strongly suggests that the resultant transient absorption decay consists of two superimposed transient events, namely the decay of the $S_2$ state to produce $S_1$, and the subsequent decay of $S_1$ by a mixed first and second order process. The time resolved spectrum recorded for PYA microcrystals supports the conclusion that two superimposed species are present. It appears from a study of the
kinetic processes occurring, that the $S_2$ to $S_1$ internal conversion has a rate constant of $12\text{ns}^{-1}$ (i.e. $1.2 \times 10^{10} \text{s}^{-1}$) which is a little slow for such a process, but certainly still reasonable.

Another very interesting, and somewhat surprising, result was the peculiar wavelength dependence of the fluorescence quantum yield for microcrystalline PYA. Namely, the fluorescence quantum yield suddenly dropped to zero, at around 355nm, even though the sample was absorbing virtually 100% of exciting radiation. The sudden drop in quantum yield occurs in a spectral region at the beginning of the $S_2$ band in solution studies. It is not possible to resolve the two bands in the diffuse reflectance ground state spectrum of microcrystalline PYA because as a consequence of the nature of the sample there is too high a "concentration" of absorbers, and the system is totally absorbing across the two bands. It would appear that this effect is explained by the $S_2$ to $S_1$ internal conversion being a very slow or perhaps totally forbidden process or the $S_2$ to $S_0$ internal conversion being particularly efficient in this material.

Another area of study involves fluorescence quenching of PYA in dichloromethane solution using DSM. It was found that both radiative and non-radiative energy transfer mechanisms were in operation between PYA (donor) and DSM (acceptor). After the data was corrected, to account for the radiative process, it was found that the non-radiative process was long range in nature, with the Förster radius ($5.47 \times 10^{-9}\text{m}$) being much larger than the encounter radius ($8.42 \times 10^{-10}\text{m}$). By application of the Gosele model, which accounts for both long range energy transfer and diffusion, a value of $5.30 \times 10^{-9}\text{m}$ was obtained, which consequently provides a clear illustration that diffusion does not play a major role in the non-radiative energy transfer process.
The experimental interaction radius, extracted from the corrected data, yielded a value of $6.2 \times 10^{-9}$ m which is indicative of the existence of an additional process other than long range donor-acceptor energy transfer. One possibility is that a small amount of energy migration between donor molecules is responsible for the "extra" contribution observed experimentally. The above energy transfer mechanism was also investigated, in a less quantitative fashion, within a polycarbonate matrix, and during a study on the picosecond time scale the disappearance of the PYA singlet was observed upon the addition of DSM to the polymer matrix. One other related piece of work carried out in this study was the determination of the fluorescence quantum yield for dichloromethane solutions of PYA, PYB and PYC, both in the presence and absence of oxygen. In fact for PYC without oxygen the quantum yield of fluorescence was found to be unity.

The final major area of study presented involved some preliminary investigations of the photoconduction properties of PYA/DSM system in polycarbonate, as opposed to the photochemistry. The main conclusion from this was that the Onsager mechanism is in operation which involves a two step ionization process. Namely, the bound electron-hole pair forms (i.e. DSM-PYA species) and then this species dissociates under the influence of Coulombic attraction and applied field. One other noteworthy point drawn from this study is that the PMMA matrix gives generally much lower quantum efficiencies for the photoconduction process, than either of the other polymers. As mentioned above the flash photolysis study reported a longer lifetime for the DSM anion radical in a PMMA environment. The above facts tend to suggest that the bound species postulated in the Onsager mechanism (i.e. DSM-PYA) is more stable in a PMMA matrix under the influence of an electric field, possibly due to some change in the local polarisability of the matrix in
the region of the bound pair which adds stability to the bound species. This is only a speculation, however, the polymer effect is certainly a real event and a fairly important observation.

One slightly disappointing result was that the cation radical of PYA was not observed during the flash photolysis experiment under charge. However, when the methodology employed is considered fully there are some possible reasons for the negative result. The most profound difference between the photoconduction studies and the laser flash photolysis experiment under the influence of an electric field, is the light source used. The tungsten lamp used in the former is much less intense than the laser, namely $1 \times 10^{13}$ photons s$^{-1}$ cm$^{-2}$ and $4 \times 10^{24}$ photons s$^{-1}$ cm$^{-2}$, respectively. This comparison is slightly unfair because the laser only delivers a 20ns pulse (i.e. $8 \times 10^{16}$ photons cm$^{-2}$), however, this is still more than the tungsten lamp delivers in about 2 hours of operation. Since the lamp only needs to operate for 2 or 3 minutes to fully discharge the film, it is clear that the laser was far too intense to allow the experiment to work. Attempts were made to attenuate the laser but the intensity become so low that the observed transients without an electric field disappeared. The overall conclusion from this rather unsuccessful experiment is that the intensities involved are so low that the only very small amounts of transient species are likely to be present.

The above summary has hopefully drawn together all the various areas of study and linked ideas and observations where appropriate. The project has also provided the relevant experience and ideas by which highly fluorescent materials can be investigated using diffuse reflectance laser flash photolysis. One slight disappointment is the lack of knowledge which has been yielded with respect to the charge
transport mechanism. However, this has been compensated for by the interesting "avenues" of study that the photochemistry of 2-pyrazolines has provided. Probably the most novel piece of work are the results obtained on the picosecond time domain, primarily because of the development this represents with respect to the technique of diffuse reflectance laser flash photolysis. In order to develop and generally improve any technique standards must be available on which ideas and modifications can be tested. The pyrazolines studied have provided ideal reagents for this purpose, and as a consequence have made a major contribution to the development this technique in the picosecond time domain.
REFERENCES

5. W. Eckenback, in reference no. 4 ,133.


121. This value was kindly measured by Prof. S.M.B. Costa (Universidade Técnica de Lisboa, Lisbon, Portugal), (1987).


APPENDIX A

Integration of equation 3.3 to give equation 3.4
(see section 3.1 (b) for details)

\[ \frac{d[C^*]}{dt} + k_c[C^*] = k_{pc}[P^*][C] \] (A1)

Multiply (A1) by \( \exp(k_c t) \) gives

\[ \frac{d[C^*]}{dt} \exp(k_c t) + k_c[C^*] \exp(k_c t) = k_{pc}[P^*][C] \exp(k_c t) \] (A2)

Using the general expression \( \frac{d(uv)}{dt} = \frac{du}{dt} \cdot v + \frac{dv}{dt} \cdot u \) and applying to the left hand side of equation (A2) gives:

\[ \frac{d}{dt}([C^*] \exp(k_c t)) = k_{pc}[P^*][C] \exp(k_c t) \] (A3)

Therefore:

\[ \int_0^t \frac{d([C^*] \exp(k_c t))}{dt} \, dt = \int_0^t k_{pc}[P^*][C] \exp(k_c t) \, dt \] (A4)

By substitution of equation 3.2 for \([P^*]\) into (A4) gives:

\[ \int_0^t [C^*] \exp(k_c t) \, dt = k_{pc}[C][P_o] \int_0^t \exp(k_c - k_p - k_{pc}[C]) \, dt \] (A5)

By integrating and dividing the resultant equation by \( \exp(k_c t) \) equation 3.4 is produced. i.e.:

\[ [C^*] = \frac{[C_o]}{\exp(k_c t)} + \left( k_p - k_{pc}[C] \right) \frac{\exp((k_c - k_p - k_{pc}[C]) - 1)}{\exp(k_c t)} \]
APPENDIX B

Derivation of the expression used to correct fluorescence data for radiative transfer and acceptor absorption when reflectance geometry is employed.

If the experimental arrangement in Figure B.1 is considered, with a cell containing a solution of D (donor) and A (acceptor). The exciting radiation enters the cell with an incident angle $\alpha$ and produces a penetration of depth $x$. The exciting source of wavenumber, $v_{ex}$, has an incident intensity of $I_0$. This exciting radiation is then converted into emitted radiation from D of wavenumber, $v_{em}^D$, although this is emitted in all directions it will be assumed that this is detected via a light ray leaving the cell at angle $\beta$ after following an optical path $y$. The values of $y$ and $\beta$ are average values and simplify the calculation.

It is also possible to define a coordinate $z$, using simple trigonometry, such that:

$$z = x \sin \alpha = y \sin \beta \quad (B1)$$

FIGURE B.1 Reflection geometry at sample

SIMPLIFIED DIAGRAM WITH $\alpha' = \alpha$ AND $\beta' = \beta$
The amount of radiation absorbed by D within the interval $x$ to $x + dx$, when D and A are present at concentrations $C_D$ and $C_A$, is given as:

$$d I_D(\tilde{\nu}_\text{ex}; x, x+dx) = \mu_D(\tilde{\nu}_\text{ex}) C_D I_0 \exp(-[\mu_D(\tilde{\nu}_\text{ex}) C_D + \mu_A(\tilde{\nu}_\text{ex}) C_A] x) dx$$

(B2)

where the Napierian absorption $\chi$ are employed to allow easier integration later. i.e.:

$$\mu_D(\tilde{\nu}_\text{ex}) = 2.303 \epsilon_D(\tilde{\nu}_\text{ex}) \quad \text{and} \quad \mu_A(\tilde{\nu}_\text{ex}) = 2.303 \epsilon_A(\tilde{\nu}_\text{ex})$$

In the absence of radiative transfer the radiation absorbed in the interval $(x, x+dx)$ causes a set level of emitted radiation from D to be detected at wavenumber $\tilde{\nu}_\text{em}^D$, this is given by:

$$d I_D(\tilde{\nu}_\text{ex}, \tilde{\nu}_\text{em}^D; x, x+dx) = S(\tilde{\nu}_\text{ex}, \tilde{\nu}_\text{em}^D) \phi_D d I_D(\tilde{\nu}_\text{ex}; x, x+dx)$$

(B3)

where $S(\tilde{\nu}_\text{ex}, \tilde{\nu}_\text{em}^D)$ is an instrumental factor accounting for the detection system sensitivity. It is assumed that for small penetration depths the dependence of $S$ on the coordinate $z$ can be neglected.

The radiation emitted by D follows a path of length $y$ before leaving the cell and consequent detection, when the re-absorption of this emitted radiation by A is accounted for the intensity becomes:

$$d I_D(\tilde{\nu}_\text{ex}, \tilde{\nu}_\text{em}^D; x, x+dx) = S(\tilde{\nu}_\text{ex}, \tilde{\nu}_\text{em}^D) \mu_D(\tilde{\nu}_\text{ex}) C_D I_0 \phi_D \exp$$

$$(-[\mu_D(\tilde{\nu}_\text{ex}) C_D + \mu_A(\tilde{\nu}_\text{ex}) C_A] x) \exp(-\mu_A(\tilde{\nu}_\text{em}^D) C_A y) dx$$

(B4)

To calculate the total amount of radiation emitted from D an integration over all values of $x$ and $y$ has to be carried out. As mentioned above $\beta$ is constant, which means that the assumption is being made that this mean value of $\beta$ represents the average value at different penetration depths. The integration is evaluated with respect to the variable $z$, which is defined by equation B1 (see above).
where $\delta$ is the optical path for the exciting radiation ($= \chi_{\text{max}}$). The integration takes the general form:

$$\int_0^\delta \sin \alpha \exp^{-az} \, dz$$

where $a = \left[ \frac{\mu_D(\tilde{\nu}_{ex}) C_D + \mu_A(\tilde{\nu}_{ex}) C_A}{\sin \alpha} + \frac{\mu_A(\tilde{\nu}_{em}) C_A}{\sin \beta} \right]$. 

After a slight rearrangement of the appropriate portion of equation B5. The integration of the standard equation B6 is:

$$\int_0^\delta \frac{\exp^{-az}}{-a} \, dz = \left[ \frac{\exp^{-az}}{-a} \right]_0 = (-1/a) [ \exp^{-a\delta \sin \alpha} - 1 ]$$

When the result of the integration, equation B7, is replaced into equation B5 and the term a is re-introduced the result is:

$$I_D(\tilde{\nu}_{ex}, \tilde{\nu}_{em}^D, \delta) = S(\tilde{\nu}_{ex}, \tilde{\nu}_{em}^D) I_D(\tilde{\nu}_{ex}, \tilde{\nu}_{em}^D) I_0 \phi_D \cdot \left[ \frac{1}{\sin \alpha} \cdot \frac{\mu_D(\tilde{\nu}_{ex}) C_D \sin \alpha \sin \beta}{\lambda} \right]$$

$$(-\exp[-\delta \sin \alpha \cdot (\mu_D(\tilde{\nu}_{ex}) C_D + \mu_A(\tilde{\nu}_{ex}) C_A) \sin \beta + \mu_A(\tilde{\nu}_{em}^D) C_A \sin \alpha / \lambda] - (-1))$$

where $\lambda = \mu_D(\tilde{\nu}_{ex}) C_D + \mu_A(\tilde{\nu}_{ex}) C_A \sin \beta + \mu_A(\tilde{\nu}_{em}^D) C_A \sin \alpha$

The corrected value of fluorescence intensity, $I_D$, can be related by:

$$I_D = S(\tilde{\nu}_{ex}, \tilde{\nu}_{em}^D) I_0 \phi_D$$
Therefore by rearrangement of B8 and substitution of B9 into the resultant expression, yields equation B10 (below).

\[ I_D^t = I_D \left[ \nu_D(\Omega_{ex}) C_D \sin \beta / \lambda \right] [1 - \exp(-\delta (\lambda / \sin \beta))] \quad (B10) \]

where \( \lambda \) is the same as in equation B8.

The equation B10 is normally approximated by assuming that the second part of the equation is \( \approx 1 \), which is true for strongly absorbing samples. The advantage of this approximation is that a value for \( \delta \) does not have to be known in order to apply the correction. i.e.:

\[ [1 - \exp(-\delta (\lambda / \sin \beta))] \approx 1 \quad , \text{for strongly absorbing solutions.} \]

The final result, using this approximation and equation B10, is identical to equation 3.9 (see section 3.1 (c)), only slightly rearranged and with Napierson absorption \( \text{\Lambda} \) converted back to extinction coefficients.
APPENDIX C

Calculation of quantum efficiencies in bulk sensitised photoconductors
(see section 3.2(d)i for details)

In this derivation the space charge distribution is modelled by the Poisson equation (see below). Two main assumptions are employed, firstly that the mobile carriers are holes and the negative charges on dye molecules are immobile. The second assumption is that the rate of charge carrier generation is slow compared with the rate of flow of mobile carriers (i.e. "in flight" mobile carriers can be neglected in terms of their contribution to the field). The Poisson equation states that the change in electric field with respect to distance is proportional to the concentration of negative charges at distance x, \( \rho_x \). i.e.:

\[
\frac{d^2V}{dx^2} = \frac{\rho_x}{\varepsilon \varepsilon_0} \quad \text{or} \quad \frac{d(E)}{dx} = \frac{\rho_x}{\varepsilon \varepsilon_0}, \quad \text{since} \ E = dV/dx
\]  

(C1)

where \( \rho_x \) = charge density at distance x; \( x \) = distance into the sample; \( V \) = surface potential; \( \varepsilon \) = dielectric constant and \( \varepsilon_0 \) = permittivity of free space.

Double integration of equation C1 with respect to x gives:

\[
V = \left[ \frac{1}{\varepsilon \varepsilon_0} \right] \int_0^L \int_0^x \rho_x \cdot dx + \text{constant}
\]

(C2)

where \( L \) = sample thickness. Then by differentiation of equation C2 with respect to time, t,:

\[
\frac{dV}{dt} = \left[ \frac{1}{\varepsilon \varepsilon_0} \right] \int_0^L \int_0^x \frac{d\rho_x}{dt} \cdot dx
\]

(C3)

\[
\frac{d\rho_x}{dt}
\]

where \( \frac{d\rho_x}{dt} \) = charge generation rate at position x within the sample.
Therefore it follows that:

\[ \frac{d\rho_x}{dt} = q \cdot g_x \]  \hspace{1cm} (C4)

where \( q \) = electronic charge and \( g_x \) = carrier generation rate at \( x \).

The carrier generation rate at distance \( x \), \( g_x \), is a product of the quantum efficiency and the rate of absorption at position \( x \) within the sample. i.e.:

\[ g_x = \phi \cdot I_0 \cdot \alpha \exp(-\alpha x) \] \hspace{1cm} (C5)

where \( \phi \) = quantum efficiency; \( I_0 \) = incident photon flux at the sample surface and \( \alpha \) = absorption of the layer.

By substitution of equation C5 into C4 results in:

\[ \frac{d\rho_x}{dt} = \left[ q \cdot \phi \cdot I_0 \cdot \alpha \right] \exp(-\alpha x) \] \hspace{1cm} (C6)

Substitution of equation C6 into C3 gives:

\[ \frac{dV}{dt} = \frac{q \cdot \phi \cdot I_0 \cdot \alpha}{\varepsilon \varepsilon_0} \int_0^x \exp(-\alpha x) \, dx \] \hspace{1cm} (C7)

since \( \int_0^x \exp(-\alpha x) \, dx = \left[ \frac{-1}{\alpha} \exp(-\alpha x) \right]_0^x \)

then it follows that:

\[ \int_0^x \exp(-\alpha x) \, dx = \frac{1}{\alpha} \left[ 1 - \exp(-\alpha x) \right] \] \hspace{1cm} (C8)

A further integration of equation C8 gives:
\[ \int_{0}^{L} \left[ \frac{1}{\alpha} - \left( \frac{1}{\alpha} \exp(-\alpha x) \right) \right] dx = \left[ \frac{x}{\alpha} \right]_{0}^{L} - \left[ \left( \frac{-1}{\alpha^2} \exp(-\alpha x) \right) \right]_{0}^{L} \]

\[ \int_{0}^{L} \left[ \frac{1}{\alpha} - \left( \frac{1}{\alpha} \exp(-\alpha x) \right) \right] dx = \left[ \frac{L}{\alpha} - \left( \frac{1}{\alpha^2} \right) \left[ 1 - \exp(-\alpha L) \right] \right] \] (C9)

By substitution of equation C9 into C7 gives:

\[ \frac{dV}{dt} = \frac{q \phi I_{0} \alpha \left[ \frac{L}{\alpha} - \left( \frac{1}{\alpha^2} \right) \left[ 1 - \exp(-\alpha L) \right] \right]}{\varepsilon \varepsilon_{0}} \] (C10)

taking \( \frac{L}{\alpha} \) outside the brackets results in equation C11:

\[ \frac{dV}{dt} = \frac{q \phi I_{0} \alpha \left[ 1 - \left( \frac{1}{\alpha L} \right) \left[ 1 - \exp(-\alpha L) \right] \right]}{\varepsilon \varepsilon_{0}} \] (C11)

where \( \alpha L = \text{Absorbance}/0.4343 \)

When the abbreviation \( \alpha(\alpha L) \equiv \left[ 1 - \left( \frac{1}{\alpha L} \right) \left[ 1 - \exp(-\alpha L) \right] \right] \) is introduced into equation C11 the final expression is:

\[ \frac{dV}{dt} = \frac{q \phi I_{0} \alpha(\alpha L)}{\varepsilon \varepsilon_{0}} \] (C12)

rearrangement of equation C12 gives equation C13 which is equivalent to equation 3.41 in section 3.2(d)i.

\[ \phi = \frac{\varepsilon \varepsilon_{0}}{q I_{0} \alpha(\alpha L)} \frac{dV}{dt} \] (C13)