Quenching of triplet states of organic compounds by tris([beta]-dionato)iron(III) chelates

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Quenching of triplet states of organic compounds
by tris(β-dionato)iron(III) chelates

by
Chrisostomos Michael

A Master's Thesis

Submitted in partial fulfilment of the requirements for the award of the degree of Master of Philosophy of the Loughborough University of Technology

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ABSTRACT

The rate constants of quenching of triplet states of 14 organic compounds by 3 tris(β-dionato)iron(III) coordination compounds were measured in benzene using the technique of laser flash photolysis. The coordination compounds, tris(4,4-dimethyl-1,3-propanedionato)iron(III), Fe(bpdo)$_3$, tris(1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedionato)iron(III), Fe(tert-Bu-tfa)$_3$, and tris(3-cyano-2,4-pentanedionato)iron(III), Fe(acac-CN)$_3$ are shown to be very efficient quenchers and triplets with energies much lower than the lowest excited states of the quenchers, give relatively high quenching constants, i.e., $\sim 3 \times 10^8$ dm$^3$ mol$^{-1}$ s$^{-1}$.

The results are interpreted in terms of quenching involving electronic energy transfer to Fe(bpdo)$_3$ and a combination of electronic energy and reversible electron transfer to Fe(tert-Bu-tfa)$_3$ and Fe(acac-CN)$_3$. The contribution of reversible electron transfer is important for quenching by Fe(tert-Bu-tfa)$_3$ and predominates in the case of Fe(acac-CN)$_3$.

The values obtained for the "intrinsic barriers" for both energy and electron transfer to these quenchers are similar to values reported for analogous systems. The values obtained for the transmission coefficients for energy transfer reflect the degree of the steric effect of the substituents of the ligands.

The sensitized production of the triplet states of 4 substituted-2-pyrazolines is also reported. Xanthone, benzophenone and anthracene were used as sensitizers. Assignments of the sensitized transients were made by studies involving β-carotene as a triplet energy acceptor, in the presence of the pyrazoline and the sensitizer.
I would like to thank Prof. Frank Wilkinson for the opportunity he gave me to work in his laboratory. His inspiring guidance and his unfailing interest made the work pleasant and fascinating.

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I warmly thank my parents for their financial support, without which this work would have been impossible.
Laser flash photolysis has been proved a very powerful means of study of excited states. Using this technique, Wilkinson studied the quenching of triplet states of organic compounds by coordination complexes. He achieved selective excitation of the complexes to spin forbidden excited states and established electronic energy and electron transfer as the major mechanisms of quenching. In the case of β-diketonato complexes the nature of the mechanism was found to depend on the redox properties of the complex, and the efficiency of quenching to be affected by the stereochemical influence of the substituents of the chelate ring.

The scope of this work is to study the mechanism of quenching of triplet states of organic molecules by three tris(β-dionato)iron(III) complexes using laser flash photolysis. The substituents of the chelate ring of these complexes are steric blocking and electron attracting groups. It is interesting to study how the mechanism of quenching is influenced by these effects separately or in combination.

The Thesis is divided into four Chapters. In Chapter 1 are presented the mechanisms of quenching with a short survey on quenching by coordination compounds. Chapter 2 contains the experimental details, the description of the apparatus and the mathematical methods which were used for the treatment of the experimental results. In Chapter 3 the results are presented in three tables. In the same chapter are also presented the results of sensitization of triplet pyrazolines. The discussion of the results and the determination of the mechanism of quenching follow in Chapter 4.
Quenching of an excited state may occur through dynamic processes (dynamic quenching) or through association of ground state reactants (static quenching):

\[
D + A \xrightarrow{h\nu} D^* + A \quad \text{dynamic quenching} \quad \text{(Eq. 1.1)}
\]

\[
D + A \xrightarrow{\text{eq}} DA \xrightarrow{h\nu}[DA]^* \quad \text{static quenching} \quad \text{(Eq. 1.2)}
\]

(Star indicates excited molecules)

Static quenching reduces the concentration of the excited molecules but does not affect their lifetime, in contrast with dynamic quenching which may be defined as any intermolecular process which shortens the lifetime of an excited state.

In this work, the term quenching will refer to dynamic quenching. There are several ways by which an excited state can be quenched in solution, the most established of which are mentioned below:

1.1 Chemical Reaction

Since electronically excited molecules can be highly reactive species, a chemical reaction leading to permanent or transient products, may decrease the lifetime of the excited state. For example singlet oxygen, the \( ^1\Delta_g \) state of molecular oxygen\(^1\) is known\(^2\) to give photooxidation reactions. The one shown below (Eq. 1.3)

\[
\begin{array}{c}
\text{Ph} & \text{Ph} & \text{Ph} \\
\text{Ph} & \text{Ph} & \text{Ph} \\
\end{array} \xrightarrow{1O_2^*} \begin{array}{c}
\text{Ph} & \text{Ph} & \text{Ph} \\
\text{Ph} & \text{Ph} & \text{Ph} \\
\end{array} + \begin{array}{c}
\text{Ph} & \text{Ph} & \text{Ph} \\
\text{Ph} & \text{Ph} & \text{Ph} \\
\end{array} \quad \text{(Eq. 1.3)}
\]

has successfully been used by Adams and Wilkinson\(^3\) in order to determine the decay rate of singlet oxygen by monitoring the concentration of 1,3-diphenylisobenzofuran as a function of time, following laser flash photolysis.

Triplet benzophenone is quenched by hydrogen donating solvents\(^4\) yielding ketyl radicals and finally pinacol.
1.2 Heavy Atom Quenching

It has been observed\(^{(5 - 7)}\) that the presence of heavy atoms like xenon or bromine and iodine in the quencher molecule, increases the triplet state absorption of aromatic hydrocarbons like naphthalene, following fluorescence quenching. This mechanism is specified as external heavy atom quenching and the increase of the triplet concentration has been attributed to an enhanced intersystem crossing. The presence of the heavy atom in the collision complex increases the mixing of the triplet and singlet states and thus the probability of intersystem crossing is increased.

1.3 Concentration Quenching

Quenching may also occur by interaction between the excited and the ground state molecules. The case of pyrene is characteristic example of excimer formation between a ground state and an excited molecule. In concentrated pyrene solutions, the fluorescence intensity of the monomers is decreased with increasing concentration\(^{(8)}\), while a new emission maximum appears at a longer wavelength. This behaviour was explained \(^{(9,10)}\) by assuming that the excimers i.e., excited dimers, which exist only in the excited state, have their own characteristic emission \((\text{Eq. 1.4})\).

\[
\text{Py} + \text{Py}^* \rightarrow \text{Py...Py}^* + 2\text{Py} + \text{hv}' \quad (\text{Eq. 1.4})
\]

1.4 Energy Transfer Quenching

A distinctive feature of the electronically excited state is its potential to transfer energy to another species:

\[
\text{*D} + \text{A} \rightarrow \text{D} + \text{A}^* \quad (\text{Eq. 1.5})
\]
The simultaneous deactivation of the originally excited molecule to its ground state and the promotion of the acceptor molecule to an excited state is called (11 - 13) energy transfer. Energy transfer can occur via radiative or nonradiative mechanisms (14).

Radiative energy transfer is a "trivial" mechanism and it consists of the emission of a quantum of light by the excited donor which is followed by the absorption of the emitted photon by the acceptor. In this mechanism the acceptor molecule has no way to influence the emission ability of the donor, but only intercepts the photon before it can be observed. The radiative energy transfer can be presented as in the (Eq. 1.6) and (Eq. 1.7):

\[ *D \rightarrow D + \hbar \nu \]  
\[ \hbar \nu + A \rightarrow *A \]  

Such an energy transfer can occur over any donor-acceptor distance and can be readily explained by the laws of optics, light absorption and emission; therefore the matter will not be discussed any further.

Nonradiative energy transfer occurs when there is interaction between the donor and the acceptor molecules. All the theories that have been put forward in order to explain this mechanism require close resonance between the initial and the final states of the donor and the acceptor. The interaction between the donor *D and the acceptor A can be described by a perturbation Hamiltonian \( H_{DA} \) (14, 15). If there is an isoenergetic system (D•••A), where the excitation lies on the acceptor, then the interaction \( H_{DA} \) can cause evolution from the (*D•••A) system to (D•••*A). The rate of energy transfer depends on the magnitude of the interaction \( H_{DA} \) (15). The rate constant of energy transfer may be related to the probability of the energy transfer from (*D•••A) to (D•••*A). This probability
which is given by the expression:

\[
\text{Probability}(*DA + D*A) = \frac{2\pi}{\hbar} (\rho) <\psi(*D)\psi(A)|H_{DA}|\psi(D)\psi(*A)>^2
\]  
(Eq. 1.8)

where \(\rho\) is the density of the initial and final states capable of interaction; \(\psi(D), \psi(D^*)\) are the wavefunctions of the donor in the ground and excited state, and \(\psi(A), \psi(A^*)\) those of the acceptor. The Hamiltonian \(H_{DA}\) can be broken into two parts\(^{15}\) which represent the Coulombic and the Exchange interaction. One may then write the following expression for the energy transfer rate constant, \(k_{ET}\) (Eq. 1.9):

\[
k_{ET} \text{ (total)} \propto \langle\psi(*D)\psi(A)|H_{C}|\psi(D)\psi(*A)>^2 + \langle\psi(*D)\psi(A)|H_{C}|\psi(D)\psi(*A)>^2 \]  
(Eq. 1.9)

The Coulombic and the electron exchange interactions can be visualised in the simplified molecular orbital diagram which is given below (Fig. 1.1).

**FIGURE 1.1** Simplified orbital analogy of the Coulombic and electron exchange interactions. The black circles symbolise electrons and the arrows their movements.
1.5 The Coulombic Interaction

The Coulombic interaction has been interpreted in terms of the classical interaction between charged particles. The excited electron on *D, by its oscillating motion along the molecular framework of *D, creates an electric field which behaves like the one generated by an oscillating dipole. The field created can cause the electrons of a nearby ground state molecule to oscillate, in much the same way as does the electric field of a light wave, and thus energy transfer is achieved. (See Fig. 1.1)

It must be pointed out that energy transfer by the Coulombic interaction requires no physical contact between the pair of *D and A. The energy transfer occurs via the electromagnetic field between the transition dipoles, while the oscillating electrons remain on the individual interacting particles. Therefore, energy transfer can occur even when the donor and acceptor molecules are separated by distances much greater than their collisional diameters.

Förster has treated the case quantum mechanically and proposed an expression for the energy transfer rate constant, $k_{DA}$, considering dipole-dipole interaction terms. (Eq. 1.10)

$$k_{DA} = \frac{9000(\ln10)\kappa^2 \Phi(D)}{128\pi^3 n^5 N\tau_D R^6} \int_0^\infty f_D(\tilde{\nu}) \varepsilon_A(\tilde{\nu}) \frac{d\tilde{\nu}}{\tilde{\nu}}$$

(Eq. 1.10)

In Förster's equation $\varepsilon_A(\tilde{\nu})$ is the molar extinction coefficient of the acceptor A at wavenumber $\tilde{\nu}$; $f_D(\tilde{\nu})$ is the emission of *D at wavenumber $\tilde{\nu}$; $\Phi_D$ is the emission quantum yield of *D, n is the refractive index of the solvent; $\tau_D$ is the mean lifetime of *D and $\kappa$ is an "orientational factor" with the value of $\sqrt{2/3}$ for a random distribution of *D and A. R is the distance that separates the *D and A molecules.
We note that when \( k_{DA} = 1/\tau_D \), that is when the decay of the excited state is 50% due to energy transfer, then:

\[
R_0 = \frac{9000(\ln 10)k^2\phi(D)}{128\pi^2 n^4 N} \int_0^\infty f_D(\nu) \varepsilon_A(\nu) \frac{d\nu}{\nu^2}
\]  

(Eq. 1.11)

\( R_0 \) denotes the donor-acceptor distance for which the rates of energy transfer and of the decay of the donor are equal. The most important term of the Coulombic interaction is the dipole-dipole term, which obeys the same selection rules as the corresponding electric dipole transitions.

From equation Eq. 1.10 it can be seen that the energy transfer rate constant \( k_{DA} \) depends on the magnitude of \( \varepsilon_A \) -the extinction coefficient of the acceptor for the \(^A+*A\) transition-, integrated over the absorption band- and on the magnitude of the spectral overlap between the donor's emission and the acceptor's absorption.

It is thus expected that energy transfer by the Coulombic mechanism will be favoured when both the transitions \(^*D\rightarrow D\) and \(^*A\rightarrow A\) are fully allowed and where there is good spectral overlap between donor's emission and acceptor's absorption. In such cases the energy transfer rate constant can have much greater values than those for the diffusion controlled reactions. When the transitions of either the donor or the acceptor are forbidden, energy transfer by the Coulombic mechanism is forbidden. It has been reported \((18,19)\) that triplet to singlet energy transfer can occur by the Coulombic mechanism, since the long lifetime of the spin-forbidden transition in the donor compensates for the weak interaction \((15)\).

When the acceptor is a coordination compound, the dipole-dipole mechanism is very unlikely in fluid solution \((12)\); the efficiency of the energy transfer, being directly proportional to the transition probabilities of acceptor levels is very low because the acceptor transitions often are Laporte and/or spin-forbidden.
1.6 The Electron Exchange Interaction

In contrast with the Coulombic mechanism, the electron exchange interaction requires collision between donor and acceptor, because overlap of the electronic clouds is involved. Electron exchange can take place only when there is overlap of the appropriate orbitals of the donor and the acceptor. The situation is depicted in the simplified Figure 1.1.

The electron exchange case has been treated quantum mechanically by Dexter\(^{(20)}\) who proposed the equation Eq 1.12 for the energy transfer rate constant \(k_{DA}\):

\[
k_{DA} = \frac{\hbar^2}{\pi} \exp\left(-\frac{2R}{Q}\right) \int f_D(\tilde{\nu}) f_A(\tilde{\nu}) d\tilde{\nu} \quad \text{(Eq. 1.12)}
\]

where \(f_D(\tilde{\nu})\) is the donor's emission and \(f_A(\tilde{\nu})\) is the acceptor's absorption. \(\hbar\) and \(Q\) cannot be easily related to any experimentally determinable quantities. Although the rate constant cannot be readily calculated, the equation Eq.1.12 shows an exponential dependence of the rate constant on the distance between the donor and acceptor. From the same equation is also evident that spectral overlap between the donor's emission and the acceptor's absorption is required.

It has been shown\(^{(21)}\) that the spin selection rules arising from the orbital overlap requirement can be summarised in the Wigner's Spin Rule\(^{(22)}\), which states that, during the whole process of energy transfer by the exchange mechanism, there must be an overall conservation of spin.

We can describe the energy transfer process by the following reaction (Eq. 1.13):

\[
* D + A \rightarrow (*D\cdots A) \underset{+}{\xrightarrow{\cdot}} (D\cdots*A) \rightarrow D + *A \quad \text{(Eq. 1.13)}
\]

Encounters between the \(*D\) and \(A\) lead to the formation of a "collision complex", (*D\cdots A), which can often be energetically more stable than the free molecules. Within this collision complex the electron exchange takes place, and the
(D⋯*A) complex -where the excitation lies on the acceptor-is formed, which dissociates in the next step in the D and *A molecules.

If $S_D$ and $S_A$ are the initial spin quantum numbers of *D and A respectively, then the spin quantum number of the "collision complex" (*D⋯A) must have one of the following values (1.14)

$$S_D + S_A, S_D + S_A^{-1}, S_D + S_A^{-2}, \ldots, |S_D - S_A|$$ (1.14)

The same holds for the spin quantum number of the (D⋯*A) complex. If $S_D$ and $S_A^*$ are the spin quantum numbers of D and *A, then one of the numbers (1.15) must also appear in the above series (1.14)

$$S_D + S_A^*, S_D + S_A^{*-1}, S_D + S_A^{*-2}, \ldots, |S_D - S_A^*|$$ (1.15)

As an example of the application of the Wigner's spin rule we can mention the triplet-triplet energy transfer. By triplet-triplet energy transfer we mean that an electronically excited donor in its triplet state produces an electronically excited acceptor in its triplet state (Eq. 1.16):

$$^*D(T_1) + A(S_0) \rightarrow D(S_0) + ^*A(T_1)$$ (Eq. 1.16)

This process is allowed by the exchange mechanism, since it confirms with the Wigner's spin rule requirements, but it is spin forbidden by the Coulombic interaction mechanism because it involves two spin forbidden transitions. Therefore triplet-triplet energy transfer is expected to proceed, generally, only via the exchange mechanism (23). The above have been confirmed experimentally in rigid solution (24,25) and in fluid solution work (26). It was found that the $R_o$ distances predicted by the Förster's theory were much less than the sum of the collisional diameters of the donor-acceptor pair that was used. Therefore the long range dipole-dipole mechanism is unlikely to be involved.
In general for quenching of triplet states by a quencher Q with multiplicity \( m \), via exchange interaction and in accordance with the Wigner's spin rule, we have for all values of \( m \): \[
g_{k_d} \frac{k_{en}}{k_d} \rightarrow \frac{m+2(D^*\cdots Q)}{m+2(D^*\cdots Q)} \rightarrow 1D + m+2Q^* \quad \text{(Eq. 1.17)}
\]

For \( m \geq 2 \):
\[
3D^* + mQ \leftrightarrow m(D^*\cdots A) \rightarrow \frac{m(D^*\cdots Q^*)}{m(D^*\cdots Q)} \rightarrow 1D + mQ^* \quad \text{(Eq. 1.18)}
\]

And for \( m \geq 3 \):
\[
3D^* + mQ \leftrightarrow m-2(D^*\cdots Q) \rightarrow \frac{m-2(D^*\cdots Q)}{m-2(D^*\cdots Q)} \rightarrow 1D + m-2Q^* \quad \text{(Eq. 1.19)}
\]

Equation 1.19 was proposed by Porter and Wright\(^{(27)}\) as the mechanism of naphthalene quenching by transition metal ions and is known as Catalysed spin conversion or the Porter mechanism. However, if low lying states of the quencher are available (eq. 1.19, 1.20), then internal conversion within the collision complex is expected to be more efficient than the direct internal conversion of the complex \( m(D^*\cdots Q) \) to the ground state. Indeed today this mechanism is thought to be a rare event in quenching with paramagnetic species.\(^{(12)}\)

The influence of the spin on the maximum rate of quenching of excited aromatic molecules by paramagnetic species is described by Porter and Wright\(^{(27)}\) in terms of a "spin statistical factor", \( g \). In reaction 1.17 the spin statistical factor \( g = \frac{m+2}{3m} \) and in 1.18 \( g = \frac{m}{3m} = \frac{1}{3} \). In general, \( g = \frac{(2S+1)}{L(2S+1)} \) which means that the \( g \) factor is equal to the multiplicity of the common (reactive) spin component divided by the sum of the multiplicities of the spin components of the collision complex. The effects of the spin statistical factor on the efficiency of quenching are extensively discussed by Wilkinson and Tsiamis for the case of \( \text{Cr}^{3+} \) and \( \text{Fe}^{3+} \) \( \beta \)-diketonato complexes which were used as quenchers.\(^{(33,34,87,88)}\)
Let us consider the energy transfer as described by the following equation:

$$3D^* + n_A \xrightarrow{\text{kd}} n(D^* \cdots A) \xrightarrow{\text{kin}} n(D \cdots A^*) \xrightarrow{\text{kd}} 1D + n_A^*$$  \hspace{1cm} (Eq. 1.21)

where $k_d$ and $k_d$ are the rate constants for the formation and the dissociation of the encounter, which are taken equal for the reactants and products in the limit of purely physical encounter. $k_{en}$ and $k_{en}$ are the unimolecular rate constants for forward and back energy transfer within the encounter.

By applying the steady state approximation to the complexes $(D^* \cdots A)$ and $(D \cdots A^*)$ we can write the quenching constant $k_q$ in terms of the diffusional and unimolecular steps:

$$k_q = q = \frac{g k_d}{1 + \frac{k_{en}}{k_{en}} + \frac{k_d}{k_{en}}}$$  \hspace{1cm} (Eq. 1.22)

where $g$ is the spin statistical factor.

Assuming that $k_{en} \gg k_{en}$ and $k_{en} \gg k_{en}$, the equation can be written as:

$$k_q = g k_d$$  \hspace{1cm} (Eq. 1.23)

One can observe that when the reaction is exothermic and when the energy transfer within the complex is very fast, the quenching constant can have its maximum value of $g k_d$. In this case it is usually said that the reaction is “diffusion controlled”. $k_d$ depends on the individual diffusion properties of the participating reactants $D^*$ and $A$. Various relationships have been proposed for the $k_d$. The following one was proposed by Smoluchowski:

$$k_d = 4\pi N r_{AD^*} D_{AD^*} (1 + r_{AD^*} \sqrt{\frac{\pi D_{AD^*} t}{}})$$  \hspace{1cm} (Eq. 1.24)

where $N$ is the Avogadro's constant, $D_{AD^*}$ is the sum of the individual diffusion coefficients for $A$ and $D^*$ and $r_{AD^*}$ is the effective interaction distance between $A$ and $D^*$. The equation 1.24.
was modified by Yguerabide\(^{30}\) in the following form (Eq. 1.25):

\[
kd = 4\pi N r_{AD^*} D_{AD^*} (1 + r_{AD^*} (2 D_{AD^*} \tau_0)^{-\frac{1}{2}})
\]

where \(\tau_0\) is the excited state lifetime in the absence of any bimolecular quenching process. The term involving \(\tau_0\) becomes negligible for excited states with \(\tau_0 > 10^{-7}\) s.

Since it is difficult to have accurate estimates of \(r_{AD^*}\) and \(D_{AD^*}\) some approximations have to be used. \(D_{AD^*}\) is written as the sum of \(D_A\) and \(D_*\) using the Einstein-Stokes relationship:

\[
D = \frac{kT}{6\pi \eta}
\]

and \(r_{AD^*}\) is approximated as \(r_{AD^*} = 2r\).

We can then write:

\[
D_{AD^*} = \frac{2kT}{6\pi \eta}
\]

Substituting in (Eq. 1.25) we have:

\[
k_d = \frac{8RT}{3\eta}
\]

(Eq. 1.27)

The above equation (Eq. 1.27) assumes that there is a large coefficient of friction between solvent and solute. For the opposite case the modified Debye equation (Eq. 1.28) is used:

\[
k_d = \frac{4RT}{\eta}
\]

(Eq. 1.28)
1.7 **Quenching by Electron Transfer**

Quenching by electron transfer is a mechanism of equal importance to that of energy transfer quenching. Although for many years the interest of the photochemists was centered on energy transfer, today, electron transfer is well established as a major quenching pathway. (31–34) (35)

In quenching by electron transfer the excited molecule either donates one electron to (oxidative quenching) or accepts one from the quencher (reductive quenching). In either case quenching by electron transfer leads to the formation of a radical ion pair or a charge transfer complex which may dissociate into products or it may reform the initial ground state reactants:

\[
\begin{align*}
\text{D}^* + Q & \underset{k_d}{\overset{k_{-d}}{\rightleftharpoons}} (\text{D}^* \cdots Q) \quad \overset{k_{el}}{\underset{k_{-el}}{\rightleftharpoons}} (\text{D}^+ \cdots Q^-) \\
& \overset{k_{bt}}{\rightarrow} \quad \overset{k_p}{\rightarrow} \\
\text{D} + Q & \quad \text{products}
\end{align*}
\]

Scheme 1.1

Scheme 1.1 represents the various steps of (oxidative) electron transfer quenching. D and Q are the donor and the quencher molecules, \(k_{el}\) and \(k_{-el}\) are the rate constants for the electron transfer within the encounter complex, \(k_p\) is the rate constant for the formation of products other than the ground state reactants and \(k_{bt}\) is the rate constant for the "back reaction" (the formation of the ground state products by reverse electron transfer). \(k_d\) and \(k_{-d}\) are the diffusion and the back diffusion rate constants respectively.
Both electron transfer quenching and energy transfer quenching by electron exchange — where two independent electron transfers take place — require close approach of the reactants for sufficient orbital overlap. Both mechanisms are inefficient when the donor-quencher distance is greater than 10 Å and both obey the same spin restrictions as they are dictated by the Wigner's Spin Rule.

By applying the steady state approximation to the intermediates of the reaction (Scheme 1.1), we can derive, in much the same way as it has been done for energy transfer quenching (Eq. 1.22), the following expression for the electron transfer quenching rate constant (36,37), $k_q$.

$$k_q = \frac{k_d}{1 + \frac{k_d}{k_{el}} + \frac{k_{-d} k_{el}}{(k_p + k_b) k_{el}}} \quad \text{(Eq. 1.29)}$$

If we assume that the electron transfer is energetically favoured towards one direction then $k_{el} \gg k_{-el}$ and equation 1.29 becomes:

$$k_q = \frac{k_{el} k_d}{k_{el} + k_{-d}} \quad \text{(Eq. 1.30)}$$

or:

$$\frac{1}{k_q} = \frac{1}{k_d} + \frac{1}{k_{el}} \quad \text{(Eq. 1.31)}$$

If we also assume that $k_d \approx k_{-d}$ then equation 1.31 becomes:

$$\frac{1}{k_q} = \frac{1}{k_d} + \frac{1}{k_{el}} \quad \text{(Eq. 1.32)}$$
One can observe that when the electron transfer is slow, \( k_d \gg k_{el} \) then the quenching rate constant, \( k_q \), is equal to the electron transfer rate constant. When the electron transfer is very fast, \( k_{el} \gg k_d \), then the quenching rate constant is given by the diffusion rate constant; in this case it is said that the reaction is diffusion controlled (see page 11).

Let us examine the electron transfer step in Scheme 1.1.

If \( \psi_i \) is the wavefunction which describes the initial state of the system \((D^* \cdots Q)\) and \( \psi_f \) the one which describes the final state \((D^+ \cdots Q^-)\) then the "zero order" energy (32) of \((D^* \cdots Q)\) will be \( H_{ii} = \langle \psi_i | H | \psi_i \rangle \) and that of \((D^+ \cdots Q^-)\) will be \( H_{ff} = \langle \psi_f | H | \psi_f \rangle \). If the system is to pass from the initial to the final state, that is if there is to be electron transfer from \( D^* \) to \( Q \), there must be electronic interaction between the reactant and product states. \( H_{if} = \langle \psi_i | H | \psi_f \rangle \) is the electronic coupling element. The electronic coupling (31, 32) removes the degeneracy of the two states and it creates two new states the energies of which are given by the roots of the following equation:

\[
\begin{vmatrix}
    H_{ii} - E & H_{if} \\
    H_{if} & H_{ff} - E
\end{vmatrix} = 0
\]  
(Eq. 1.33)

The two roots are:

\[
E_\pm = \frac{(H_{ii} + H_{ff})}{2} \pm \frac{(H_{ii} - H_{ff})^2 + 4H_{if}^2}{2}^{\frac{1}{2}}
\]  
(Eq. 1.34)

where \( E_\pm \) is the lower energy state and \( E_\mp \) the higher energy state. The separation of the states at the intersection point \((H_{ii} = H_{ff})\) is \( 2H_{if} \).

In the electron transfer literature (31, 32, 38-40) it is usual to present the potential energy changes during a reaction, by energy profiles or energy surfaces. Let us consider the potential energy surfaces of the initial \((D^* \cdots Q)\) and the final \((D^+ \cdots Q^-)\) states of the electron transfer as a function of the nuclear geometry which may be bond length, bond angle or positional changes (Fig. 1.2).
FIGURE 1.2 Plot of the potential energy of the reactants \((D^*\cdots A)\), and the products, \((D^+\cdots A^-)\), for an electron transfer reaction.

The initial and the final state potential energy surfaces will have, in general, different minimum energies and different equilibrium nuclear configuration. The states which are produced by the interaction between the initial and the final state are called adiabatic \(^{32}\) and they are drawn with intense lines in Figure 1.2. The electron can move along the lower adiabatic surface from the initial to the final state of the system by crossing the intersection region.

The electron transfer must obey the Frank-Condon principle\(^ {32,33,42}\) since the frequency of the electron motion is in the range \(10^{15} - 10^{16}\) s\(^{-1}\) while the nuclear vibrational frequency is in the range \(10^{12} - 10^{14}\) s\(^{-1}\)\(^ {31}\). Therefore the initial system \((D^*\cdots Q)\) must adjust its nuclear coordinates to the distorted (nonequilibrium) configuration of the intersection point prior to the electron transfer. (See Figure 1.2)
The energy which is needed to achieve this reorganization corresponds to the free energy of activation $\Delta G^+$ of the electron transfer step.

The probability of the electron transfer is related to the magnitude of the electronic interaction $H_{if}$. If the splitting at the intersection point, $2H_{if}$, is small then there is the probability that the system will pass to the upper surface through the intersection region. If the splitting is large then the system will follow the lower potential energy surface throughout the course of the reaction. In this case the electron transfer is called adiabatic while in the former case it is called nonadiabatic.

According to the absolute rate theory \(^{(43)}\) the rate of the electron transfer (See Scheme 1.1) is given by the expression:

$$k_{el} = k^0_{el} \exp(-\Delta G^+ / RT) \quad \text{(Eq. 1.35)}$$

and

$$\ln\left(\frac{k_{el}}{k_{-el}}\right) = -\Delta G / RT \quad \text{(Eq. 1.36)}$$

$\Delta G^+$ and $\Delta G$ are the standard free activation energy and the standard free energy change for the forward electron transfer step respectively. The preexponential factor $k^0_{el}$ is equal to $k(\frac{kT}{h})$ where $\frac{kT}{h}$ is a universal frequency and $k$ is the so called transmission coefficient. The transmission coefficient can be considered as the product of a nuclear and an electronic factor \(^{(32,43,44)}\). The nuclear factor accounts for the possibility of nuclear tunneling \(^{(43)}\) leading to products without activation. The electronic factor is related to the magnitude of the electronic interaction, $H_{if}$, which, as mentioned earlier, is the measure of the adiabaticity of the electron transfer.
According to the equations 1.29, 1.35, 1.36, the general expression for the electron transfer quenching constant can be written:

\[
\frac{k_d}{1 + \frac{k_d}{(k_p+k_b)} \exp(\Delta G/RT) + \frac{k_d}{k_{el}} \exp(\Delta G^+/RT)}
\]  

(Eq. 1.37)

Various relationships according to which the standard free energy of activation \(\Delta G^+\) is related to the free energy change \(\Delta G\) of the electron transfer process have been proposed. One of them, Eq. 1.38, is the Marcus equation \((45, 46)\) where \(\Delta G^+(0)\) is the free energy of activation when \(\Delta G=0\).

\[
\Delta G^+ = \Delta G^+(0) (1 + (\Delta G/4\Delta G^+(0)))^2
\]  

(Eq. 1.38)

Another one, Eq. 1.39, was proposed by Rehm and Weller \((36, 47)\)

\[
\Delta G^+ = \frac{\Delta G}{2} + (\frac{\Delta G}{2})^2 + (\Delta G^+(0))^2)^{1/2}
\]  

(Eq. 1.39)

A third one, Eq. 1.40, was obtained by Agmon and Levine \((48)\) on the basis of an equation derived by Marcus \((49)\) for atom and proton transfer:

\[
\Delta G^+ = \Delta G + \frac{\Delta G^+(0)}{\ln 2} \ln (1 + \exp(-\frac{\Delta G \ln 2}{\Delta G^+(0)}))
\]  

(Eq. 1.40)
The last two equations (Eq. 1.39, 1.40) are empirical ones\cite{36,47,50} and they have been introduced in order to give a satisfactory explanation to experimental results\cite{51,52} for which the Marcus equation (Eq. 1.38) was inadequate.

The above free energy relationships, their origins, applications and disadvantages have been discussed by several authors\cite{51,52,34}. Balzani et al\cite{51} recognising that Eq. 1.39 and Eq. 1.40 are practically equivalent, advise that the Agmon-Levine equation "should be preferred, owing to its more general character". Substituting Eq. 1.40 in Eq. 1.37 one gets a general expression for the electron transfer quenching rate constant, which has been successfully used for fitting of experimental results\cite{33,34}.

Quenching by energy transfer has been treated by Balzani\cite{43} in a way parallel to that already used for electron transfer quenching. Using the absolute reaction rate theory, the following expressions, Eq. 1.41, 1.42, have been obtained for the energy transfer process (See Eq. 1.21)

\begin{align*}
  k_{en} &= k_{en}^0 \exp(-\Delta G_{en}^+/RT) \quad (\text{Eq. 1.41})
  \\
  \ln\left(\frac{k_{en}}{k_{en}^0}\right) &= -\Delta G_{en}/RT \quad (\text{Eq. 1.42})
\end{align*}

where $\Delta G_{en}^+$ and $\Delta G_{en}$ refer to the energy transfer step of Eq. 1.21. $k_{en}^0 = k_{en}^0 kT/\hbar$, where $k_{en}$ is the "transmission coefficient".

One can observe that Eq. 1.41 and 1.42 are analogous to Eq. 1.35 and 1.36. Using the Agmon-Levine equation in conjunction with Eq. 1.41 and 1.42 and substituting in Eq. 1.22, one may also obtain a general expression for the energy transfer quenching rate constant:

\begin{align*}
  k_q &= \frac{g k_d}{1 + \exp(\Delta G_{en}/RT) + \left(k_{en}^0 - k_d\right) \exp\left(\Delta G_{en}^+/RT\right)} \quad (\text{Eq. 1.43})
\end{align*}
1.8 Quenching of Triplet States by Coordination Complexes

The case of quenching by energy transfer has been thoroughly investigated for the interaction between organic compounds. The coordination compounds offer a variety of energy levels, centered on the same molecule, all of which can become accessible by energy transfer from suitable organic triplet states. By energy transfer one can excite the complex selectively to a specific energy level and thus probe electronically forbidden excited states \(^{(12)}\). These considerations and the desire to further understand the factors that influence the energy transfer have created an interest in using coordination compounds as quenchers.

Quenching of the triplet states of organic molecules by coordination compounds was observed as early as 1958 by Porter and Wright\(^{(27,56)}\). These investigations led to the conclusion that paramagnetic molecules can quench the triplet states by spin allowed catalysed intersystem crossing, known as the "Porter mechanism" (page 10). Later results failed to show correlation of the quenching rate constants with the magnetic susceptibility of the quencher. Instead it was found that the availability of low-lying excited states in transition metal complexes was a prerequisite for efficient quenching. Radiationless energy transfer was the proposed mechanism of quenching. Radiationless energy transfer by the coulombic interaction is very unlikely\(^{(12)}\) in quenching by coordination compounds since the efficiency of this mechanism is directly proportional to the transition probability of the acceptor levels which is generally low, since Laporte-forbidden and spin-forbidden transitions are often involved. Thus in fluid solution, quenching of a triplet donor by coordination compounds is likely to result from energy transfer by electron exchange interaction. From now on, when referring to quenching by coordination compounds, by energy transfer we shall mean the energy transfer by electron exchange interaction.
Sensitized luminescence of the quencher constitutes irrefutable evidence of energy transfer. For instance, sensitized luminescence was observed in the case of phosphorescence quenching of benzil (53) by [Cr(CN)₆]³⁻ and [Cr(NCS)₆]³⁻. Unfortunately, very few coordination compounds luminesce either in fluid solution or at room temperature in rigid solution. Consequently, other, less direct proofs had to be found in favour of the energy transfer mechanism.

The photochemistry of coordination complexes (54, 55) continues even when all the incident light is absorbed by another molecule which acts as a triplet sensitizer. Much of this sensitized photochemistry has been reviewed by Balzani (13).

Another indication very strongly in favour of the energy transfer mechanism is the sharp decrease of the values of the quenching rate constants when the lower excited state of the metal ion in the complex lies above the donor triplet level (endoothermic energy transfer). Indeed, a large number of examples from the literature (11, 84, 57) support this interpretation. Energy transfer continued to be regarded as the most important mechanism of quenching by coordination compounds, although in many cases (58, 59) the authors were unable to present positive proofs.

Adamczyk and Wilkinson (60) were the first to undertake a systematic study of the variation of the quenching constants with the energy of the triplet state being quenched. By observing the plots of $k_q$ versus triplet energy of the donor, they concluded, although they did not observe lack of quenching, that the quenching efficiency was critically dependent on orbital overlap, since the use of sterically blocked quenchers resulted in reduced quenching efficiency, although energy transfer was energetically possible and spin allowed.

In another study (61) Allsopp and Wilkinson observed lack of quenching when the triplet energy of the donor was below the lowest lying ligand field state of the quencher. Studies involving the variation of the triplet energy donor were undertaken by Farmilo and Wilkinson (62) for the case of ferrocene. From the fall of the quenching constants for all the
donors with triplet energy below 1.47 μm⁻¹ (triplet anthracene) the authors concluded that the lowest triplet state of ferrocene lies around 1.4 μm⁻¹, in agreement with spectroscopic observations (63, 64) and other studies (65).

In another systematic study (66), Wilkinson and Farmillo showed beyond doubt that in the case of quenching of aromatic triplets by Fe(acac)₃ and Fe(dpm)₃, the mechanism of quenching is that of energy transfer. They plotted the rate of quenching against donor triplet energy. (Fig. 1.3)

FIGURE 1.3  Plot of the quenching constants, kq, versus triplet energy. Triangles refer to quenching by Fe(acac)₃ and squares to Fe(dpm)₃. Arrows indicate the electronic transitions of the quenchers.

By the good correlation of the discontinuities of the curves with the spectroscopically determined energy levels of the complexes it becomes apparent that the quenching rate increases as complex excited states become available.
Exchange energy transfer, in the general sense, was treated from the classical point of view by Balzani and coworkers in a parallel way with electron transfer. The expression for the quenching rate constant (Eq. 1.43) includes the Agmon-Levine free energy relationship and accounts well for energy transfer processes involving excited states for which the Sandros equation proved to be inadequate.

The applicability of the proposed equation (Eq. 1.43) to quenching in which more than one excited state of the coordination compounds are involved, was elegantly shown by Wilkinson. In a series of papers on quenching of aromatic triplets by β-diketonato complexes, Wilkinson and Tsiamis discussed the role of the spin statistical factors in the modification of the maximum quenching efficiency and commented on the parameters which were used to obtain the best fit of the experimental results. The transmission coefficient was found to depend on the substituents of the chelate ring increasing as the nephelauxetic effect was enhanced. In the case of Cr(dpm)₃ (dpmH = dipivaloylmethane) the low value of the transmission coefficient reflected the poor overlap between the donor and acceptor orbitals due to steric blocking by the bulky t-Butyl substituents. The free energy of activation for the production of the doublet non-distorted excited states of Cr³⁺ was found to be five times less than the free energy of activation for the production of the distorted quartet excited states.

The role of the transmission coefficient as the rate determining factor in exchange energy transfer was discussed by Maestri and Sandrini in quenching of Ru(phen)₂CN₂ by a family of Cr(en)₂XY⁺ complexes. The authors attributed the low quenching rates not to activation energy terms but to the low value of the transmission coefficient which indicated poor electronic interaction between the donor and acceptor. In support to these arguments, correlations between the "preexponential factor" (kₜₕ) with the nephelauxetic effect were presented. Similarly Endicott et al argued in favour of the preexponential factor as the rate determining parameter in
energy transfer quenching of $\text{Cr(bpy)}_3^{3+}$ by various cobalt(III) complexes ($\text{CoL}_6^{3+}$).

Energy transfer is by no means the only mechanism of quenching by coordination compounds as was pointed out by Wilkinson$^{12}$. It is well known$^{35,31,13,70}$ that the excited states of the coordination compounds are both better oxidants and better reductants than the ground state because of their higher energy content. Therefore electron transfer to and from an excited complex can easily occur. A classical example is $\text{Ru(bpy)}_3^{2+}$ ($^{70,71}$) the lowest charge transfer state of which is quenched by $\text{Ru(NH)}_3^{2+}$ ($^72$) and $\text{Fe(CN)}_6^{3-}$ ($^{73}$) by reversible electron transfer, the products of quenching being the ground state reactants. Acting as a quencher, $\text{Ru(bpy)}_3^{2+}$ quenches the $^2E$ excited state of $\text{Cr(bpy)}_3^{3+}$ by the electron transfer mechanism ($^{31}$).

A combination of energy transfer and electron transfer was observed by Wilkinson and Tsiamis$^{34}$ in the case of quenching of aromatic triplets by $\text{Cr(hfac)}_3$ ($\text{hfacH} = 1,1,1,5,5,5$-hexafluoro-2,4-pentanedione) in benzene. The authors based the interpretation of their results on the assumption that energy transfer occurred to the quartet and doublet excited states, while electron transfer proceeded via sextet and quartet exciplexes. The theoretical quenching rate constants were calculated according to the above scheme, taking into account the spin statistical factors and the Agmon-Levine free energy relationship. The very satisfactory agreement between of the experimental and the calculated values, the authors proposed that the dependence of the rate constants on the free energy for electron transfer $\Delta G_{el}$ can be used as an alternative method to obtain a good estimate of the oxidation potentials of the donors. Accordingly the one electron oxidation potential of $\beta,\beta$-carotene, which the authors could not determine directly, was estimated to be $E^{Ox} = 0.35 \pm 0.03$ V.

Competitive energy and reversible electron transfer$^{33}$ quenching was also the mechanism of quenching of aromatic triplets by $\text{Fe(hfac)}_3$ and $\text{Fe(tfac)}_3$ ($\text{tfacH} = 1,1,1$-trifluoro-2,4-pentanedione). The experimentally determined quenching
rate constants in benzene were in very good agreement with the calculated ones, thus confirming the proposed kinetic scheme according to which electron transfer occurred via octet and sextet exciplexes, while energy transfer occurred to quartet ligand field states and to sextet and possible quartet charge transfer states. It is worth mentioning that the reduction potentials of the complexes with fluorinated diketonato ligands are very high, \( E_{\text{red}} \text{Cr(hfac)}_3 = -0.40 \text{ V vs. SCE}, \ E_{\text{red}} \text{Fe(hfac)}_3 = 0.73 \text{ V vs. SCE} \) \( \text{(77)} \), \( E_{\text{red}} \text{Fe(tfac)}_3 = -0.02 \text{ V vs. SCE} \) \( \text{(77)} \), compared to those of the other \( \text{Cr}^{3+} \) and \( \text{Fe}^{3+} \) tris \( \beta \)-diketonates, thus making electron transfer more probable. (N.B. S.C.E. = Standard Calomel Electrode)

Evidence for competitive energy and electron transfer quenching was also presented by McMillan et al \( \text{(74)} \) for the quenching of *Cu(dpp)$_2$ (dpp = 2,9-diphenyl-1,10-phenanthroline) by \( \text{Cr}^{3+} \) \( \beta \)-diketonates. The electron transfer process was discussed according to a variation of the Marcus \( \text{(75)} \) theory. In the endergonic region \( \text{(37)} \) the electron transfer rates were decreased and the dominating mechanism became energy transfer. It was assumed that energy transfer occurred to the doublet states of the \( \text{Cr}^{3+} \) quenchers and the rate constants for energy transfer quenching were found almost constant for all the quenchers.

From this brief survey of the literature of quenching by coordination complexes, the following remarks can be made: Two major mechanisms dominate in quenching by coordination complexes; electronic energy transfer and electron transfer which can operate either separately or simultaneously. There are strong indications that the electron transfer mechanism is favoured by quenchers with high reduction potential, while the availability of low lying excited states of the quencher is a prerequisite for the electronic energy transfer mechanism.

Electronic energy transfer to different ligand field states within the quencher proceeds with different rates. The spin selection rules apply in the case of energy transfer and the maximum rate of quenching is influenced by the spin statistical factors. In most of the cases of either electron or
energy transfer quenching, the rate determining factor is the magnitude of the electronic interaction between donor and quencher, expressed by the transmission coefficient.

Valuable information concerning the spectroscopic transitions and the excited states of the quencher can be gained from the quenching plots. The position of a spectroscopic transition should correspond to the increase of the rate of energy transfer to the relative excited state, while the distortion of the excited state, expressed by the value of the intrinsic barrier $\Delta G^+(0)$, is indicated by the slow rise of the rate of energy transfer to this state. Large transmission coefficient is indicated by large "plateau" rate constants.
CHAPTER 2: EXPERIMENTAL

2.1 The Laser Flash Photolysis Apparatus

The Laser Flash Photolysis Apparatus which was used in this work has been described in detail by previous workers\(^3\),\(^{80-82}\). Through the years of its service it has been subjected to a number of changes, mainly in the monitoring and data processing system, but otherwise it retains its initial features and efficiency. The experimental arrangement is shown schematically in Figure 2.1. The excitation pulse was produced by a Laser Associates 211A ruby laser, passively Q-switched, with an energy output of about 2 J at 694.3 nm. The ruby rod was pumped by a Xenon flash tube which was powered by a capacitor with a discharge potential of about 2 kV. A crystal of Ammonium dihydrogen phosphate, (ADP), suitably placed on the path of the laser pulse, generated the second harmonic of the fundamental frequency. As a result the laser pulse was converted into a mixture of 694.3 nm (95%) and 347 nm (5%) radiation. Most of the 694.3 nm light was removed by a copper sulphate solution filter with less than 2% transmittance at 694.3 nm and about 80% transmittance at 347 nm. Finally the pulse that reached the sample consisted mainly of 347 nm radiation with a small remaining portion of the red light. The energy of the pulse was estimated to be about 80 mJ and its half peak width was 20 ns. The removal of the red light was necessary since with its high intensity it could cause a "thermal shock" to the sample.

A part of the light from the Xenon flash lamp - which gives a flash with a duration of about 2 ms - was carried by fibre optics and was passed through the sample perpendicular to the path of the laser pulse. The sample holder provided housing for the sample cell and the fibre optics which were placed as close as possible to the front window of the cell. Part of the monitoring light was absorbed by the excited sample and the remainder was picked up by the opposite fibre optic and was carried to a Bausch & Lomb UV-Vis monochromator. An RCA931A photomultiplier tube, attached to the monochroma-
tor's exit slit, responded to the incoming light yielding an electric signal which was captured by a DL-922 Transient Recorder. The Transient Recorder was triggered by a signal which was produced by a photodiode which received (through a fibre optic, one end of which was placed close to the copper sul filter) part of the scattered light of the laser's pulse. The photomultiplier's signal corresponded to the changes of the intensity of the monitoring light at the maximum triplet-triplet absorbance wavelength. After being digitised and stored in the Transient Recorder's memory, the signal was displayed on an oscilloscope.

Alternatively the signal was immediately transferred to a DL-417 microprocessor unit which provided storage, display and signal processing facilities. The microprocessor was programmable and the instructions were typed in from a special keyboard with a VDU in a special code. Thus after a limited number of signals (usually 5) were stored and displayed, one could perform a series of calculations before the memory was again available for further data storage. The results were obtained on a teletype. The use of the DL417 offered great speed of data processing, but it introduced a number of inconveniences. For example, the experimental work had to be interrupted after a limited number of traces had been stored, the programming flexibility was restricted and it was not possible to obtain permanent records of the signals.

The need for permanent copies and more powerful programming urged us to employ the facilities which were offered by personal computers. A PET Commodore computer was connected, by means of an interface cable, with the DL417 and, under a special program (Appendix I), the signals were transferred as digital numbers to the PET's memory. Unfortunately the data transfer rate proved to be rather slow and it was realised that this modification introduced undesirable delays.

Finally a serious technical failure of the microprocessor was the reason for a further modification of the data recording and processing system. The major part of this work was car-
ried out using the modified system which is described below. A new interface cable was constructed and this time it connected the DL 922 Transient Recorder to the PET's User's Port. The speed of the data transfer was very satisfactory. Under a suitable program (Appendix II), the digitised signal was transferred to the PET's memory as a sequence of digital numbers ranging from 0 to 255 (one byte). Subsequently the data were stored on flexible diskettes while the experimental work was allowed to continue without interruption. In this manner we obtained a very convenient form of permanent signal record since it was possible to retrieve and analyse the data whenever it was desired, by using the more powerful—compared to those of the DL417—programming abilities of the PET.

FIGURE 2.1  Schematic representation of the Laser Flash Photolysis apparatus. F=copper sulfate solution filter, FO=Fiber optics, SH=sample holder, MC=monochromator, PM=photomultiplier, PD=photodiode, TT=teletype, OSC=osilloscope, DD=disk drive
2.2 Experimental Procedure

Most of the experimental work carried out in this project involved the determination of the rate constants for quenching of triplet states of organic molecules by tris(β-dionato)iron$^{3+}$ complexes.

The rate constants were determined by observing the change of the triplet-triplet absorption of the organic molecules with time, in the presence and in the absence of quencher. The usual procedure involved subjecting deoxygenated solutions of the organic donor and variable amounts of the β-dionato complex to laser flash photolysis at 347 nm.

The solutions were contained in a modified 10 mm square spectrosil fluorescence cell which had a long neck fitted with a rubber Suba seal. Through the Suba seal two hyperdermic needles were fitted; one of them was submerged to the bottom of the cell, while the other was above the solution surface. White Spot (Oxygen free) Nitrogen, which was saturated with solvent (benzene) vapour, was passed through the solution via the submerged needle and was carried away by the other. We verified that no significant solvent losses occurred during the five minutes degassing time; meanwhile we were able to carry out the laser flash photolysis with degassing in progress by simply lifting the needle so that it did not interfere with the part of the solution which accepted the laser pulse, while still being submerged.

The concentration of the organic compounds was chosen such that the ground state absorbance in benzene solution was in the range .9 to 1.2, through a pathlength of 10 mm, at 347 nm. This concentration usually gave large enough triplet-triplet absorbance near the front window of the photolysis cell.

In certain cases it was not possible to observe satisfactory amount of transient triplet-triplet absorbance. Although β,β-carotene absorbs strongly at 347 nm, no transient absorption of triplet β,β-carotene was observed upon direct laser flash photolysis. Its triplet production had therefore to be sensitized with anthracene. Sensitization techniques had to be employed in the case of Perylene and 2,3-Benzanthracene as well.
Perylene has a very low extinction coefficient at 347 nm and low quantum yield of triplet production in benzene. As a result direct observation of triplet perylene is very difficult. Therefore sensitization was essential and benzophenone was used as sensitizer.

2,3-benzanthracene was sensitized with benzophenone as well. Pentacene is only sparingly soluble in benzene and we had to use the largest possible concentration we could achieve. The maximum ground state absorbance we managed thus to obtain was 0.3 through a 10 mm pathlength. In addition pentacene is very easily photooxidised and special care had to be taken during the preparation of the solutions. The pentacene solutions were prepared in the dark using benzene which had been degassed by passing oxygen free nitrogen through it overnight. The solutions were kept in light protected flasks. 2,3-benzanthracene and \( \beta,\beta \)-carotene are equally sensitive to photooxidation and the same sample preparation procedures were followed. The triplet-triplet absorption was monitored at wavelengths corresponding to the maximum wavelength, taken from the literature. The organic compounds which were used as donors are listed in Table 2.2.

The sample preparation involved the mixing of appropriate volumes of quencher and donor solutions taken from individual stock solutions which were prepared previously. Before any experimental work we examined the ground state absorption spectra of the mixture and we compared them with the individual ones. Thus if any chemical reaction or complex formation had taken place after the mixing, we would be able to observe changes in the height and the shape of characteristic absorption bands of the donor or the quencher spectrum. Such changes were observed in the case of acridine and \( \text{Fe(tert-Bu-tfa)}_3 \) in solution and therefore no further work was undertaken for this pair. The absorption spectra of the sample were also examined after it had been subjected to more than 15 laser flashes. In the case of \( \beta,\beta \)-carotene we observed slight changes in the spectrum; therefore the \( \beta,\beta \)-carotene solutions were not exposed more than three times to the laser.
flash, after which no change was noticed. All the solutions were used within 24 hours of preparation.
The tris(β-dionato)iron(III) complexes, which were used as quenchers, absorb considerably at the laser's excitation wavelength (347 nm). They also absorb substantially at many of the monitoring wavelengths. (Figure 4.1). This fact limited the number and the range of quencher concentrations we could use. In every case 3 or more different quencher concentrations were used. Another factor which limited the range of the quencher concentrations we could use, was the need to keep the photomultiplier's voltage in the range of 440-550 V, in order to remain within its linear response. Whenever the signals were "noisy", we recorded more than 5 traces of the same quencher concentration and we averaged them before analysing. In this way a good deal of randomly occurring points on the trace were cancelled, but the regularly appearing points remained thus providing a much clearer picture of the trace.

2.3 Materials

a. Donors
All the organic compounds which were used as triplet energy donors were obtained commercially and were of high purity. Benzophenone, 2-acetylnaphthalene and pyrene were recrystallised three times from ethanol. All the rest were the best available commercially and they were used without further purification. The donors are listed in Table 2.2

b. Quenchers
The compounds which were used as quenchers were tris(β-dionato)iron(III) chelates of the general Formula 2.1
The chelates were prepared and purified by methods taken from the literature (77, 78, 79). The quenchers are listed in Table 2.1

c. Solvents
Fisons Spectroscopic grade benzene was used without any purification.
General Formula 2.1

**TABLE 2.1** Quenchers, names and abbreviations

<table>
<thead>
<tr>
<th>Compound</th>
<th>Abbreviation</th>
<th>( R_1 )</th>
<th>( R_2 )</th>
<th>( R_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. tris(4,4-dimethyl-2,4-propanedionato)Iron(III)</td>
<td>Fe(bpdo) (_3)</td>
<td>( \text{C(CH}_3\text{)}_3 )</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>2. tris(1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedionato)Iron(III)</td>
<td>Fe(tert-Bu-tfa) (_3)</td>
<td>( \text{C(CH}_3\text{)}_3 )</td>
<td>H</td>
<td>CF (_3)</td>
</tr>
<tr>
<td>3. tris(3-cyano-2,4-pentanedionato)Iron(III)</td>
<td>Fe(acac-CN) (_3)</td>
<td>CH (_3)</td>
<td>CN</td>
<td>CH (_3)</td>
</tr>
</tbody>
</table>

**TABLE 2.2** Wavenumbers of the triplet state, \( \nu_{00}(T) \), triplet-triplet analysing wavelength, \( \lambda_{TT} \) and concentration of the donors, [D], used in Laser Flash Photolysis experiments.

<table>
<thead>
<tr>
<th>Donors</th>
<th>( \nu_{00}(T) ) (^{a})</th>
<th>( \lambda_{TT} ) (^{a})</th>
<th>[D] (^{a})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \mu \text{m}^{-1} )</td>
<td>nm</td>
<td>mmol dm(^{-3})</td>
</tr>
<tr>
<td>1. benzophenone</td>
<td>2.43</td>
<td>535</td>
<td>10.0</td>
</tr>
<tr>
<td>2. phenanthrene</td>
<td>2.16</td>
<td>481</td>
<td>4.0</td>
</tr>
<tr>
<td>3. 2-acetylnaphthalene</td>
<td>2.06</td>
<td>425</td>
<td>1.0</td>
</tr>
<tr>
<td>4. chrysene</td>
<td>1.98</td>
<td>570</td>
<td>2.0</td>
</tr>
<tr>
<td>5. coronene</td>
<td>1.94</td>
<td>465</td>
<td>0.08</td>
</tr>
<tr>
<td>6. 1,2,5,6-DBA (^{b})</td>
<td>1.83</td>
<td>532</td>
<td>1.0</td>
</tr>
<tr>
<td>7. 1,2,3,4-DBA</td>
<td>1.78</td>
<td>454</td>
<td>1.0</td>
</tr>
<tr>
<td>8. pyrene</td>
<td>1.68</td>
<td>416</td>
<td>0.5</td>
</tr>
<tr>
<td>9. acridine</td>
<td>1.58</td>
<td>438</td>
<td>0.15</td>
</tr>
<tr>
<td>10. anthracene</td>
<td>1.47</td>
<td>425</td>
<td>0.33</td>
</tr>
<tr>
<td>11. perylene</td>
<td>1.24</td>
<td>488</td>
<td>0.8</td>
</tr>
<tr>
<td>12. 2,3-benzanthracene</td>
<td>1.03</td>
<td>459</td>
<td>0.1</td>
</tr>
<tr>
<td>13. pentacene</td>
<td>0.80</td>
<td>498</td>
<td>0.01</td>
</tr>
<tr>
<td>14. ( \beta,\beta)-carotene</td>
<td>0.63</td>
<td>520</td>
<td>0.03</td>
</tr>
</tbody>
</table>

\(^{a}\) Taken from ref. 33

\(^{b}\) DBA=dibenzanthracene
2.4 Signal Recording and Calculation of Triplet-Triplet Absorption

The changes of triplet-triplet absorbance with respect to time were recorded as follows:
Over a period of .1 ms after the laser flash, which also initiated the recording, we monitored the signal of the photomultiplier and displayed it on an oscilloscope. The signal was then transferred to the computer's memory and was recorded on a diskette. The signal corresponded to the changes of the intensity of the analysing light which had passed through the sample cell. It was mentioned earlier that as analysing light we used part of the light of the Xenon flash lamp which had a flash duration of about 2 ms. We assumed therefore, that over the .1 ms long monitoring period, the intensity of the analysing light, before it reached the sample was practically constant. (This assumption was verified by observing the intensity "profile" of the flash on the oscilloscope).

Three such oscilloscope traces were required for the calculation of the triplet-triplet absorbance. For the first trace we made sure that the laser pulse did not reach the sample cell in order to exclude the presence of any triplets, generated by the laser flash, in the sample. This trace was a horizontal line near the bottom of the oscilloscope screen. (Fig. 2.2a)
The second trace showed transient absorption (Fig. 2.2b). In this case we permitted the laser pulse to excite the sample. The loss of the light's intensity was obviously due to the absorption by the triplet state molecules whose concentration varied with time.

For the third trace we made sure that no analysing light reached the sample (by simply removing the carrier fibre optic) and we monitored only the emitted light by the sample after the laser pulse excitation. The picture of this trace was of scatter and a horizontal line on the top of the oscilloscope screen (Fig. 2.2c). The triplet-triplet absorbance was calculated, for every point of the trace, as $\log_{10}(I_o/I_t)$ using the values of $I_o$ and $I_t$ from the recorded trace. (See Fig. 2.3)
FIGURE 2.2 Picture of the oscilloscope with the three traces required for the calculation of the transient absorbance:

a. Base line
b. Transient
c. Scatter
FIGURE 2,3 Plot of triplet-triplet absorbance against time. The curve was calculated as $\text{Abs} = \log_{10}(I_0/I_t)$. The $I_0$, $I_t$ were taken from Fig. 2.2.
Subsequently the calculated values of the absorbance \( \log_{10}(I_o/I_t) \) were plotted against time (See Fig. 2.3) and they were subjected to kinetic analysis.

### 2.5 Kinetic Analysis of the Experimental Data

The rate with which an excited molecule returns to the ground state depends on the concentration of the ground state, the concentration of oxygen and on the quencher concentration.

If:

- \([T]\) = triplet state concentration
- \([S]\) = ground state concentration
- \([O_2]\) = oxygen concentration
- \([Q]\) = quencher concentration

we can describe the change in \([T]\) with respect to time as:

\[
- \frac{d[T]}{dt} = k_1^o[T] + k_2[T]^2 + k_g[S][T] + k_{O_2}[O_2][T] + k_q[Q][T]
\]

(Eq. 2.1)

where \(k_1^o\) and \(k_2\) are the first and the second order rate constants of the triplet decay, \(k_g\), \(k_{O_2}\) and \(k_q\) are the ground state the oxygen and the quenching rate constants respectively.

The ground state quenching is normally very small and most of the systems we studied showed good first order behaviour in the presence of quencher. Therefore: \(k_2[T]^2 + k_g[S][T] \ll k_q[Q][T]\) and equation 2.1 can be written as:

\[
- \frac{d[T]}{dt} = k_1[T] + k_{O_2}[O_2][T] + k_q[Q][T]
\]

(Eq. 2.2)

or:

\[
- \frac{d[T]}{dt} = k_1[T]
\]

(Eq. 2.3)

where \(k_1 = k_1^o + k_{O_2}[O_2] + k_q[Q]\)

(Eq. 2.4)
If care has been taken for the exclusion of oxygen from the sample, (e.g. with degassing, as in our case), then the term \( k_{O_2}[O_2] \) is negligible and we can write the Eq. 2.4 as:

\[
k_1 = k_1^o + k_q[Q]
\]  
(Eq. 2.5)

We can see that \( k_q \) can also be calculated by using Eq. 2.4 if we regard the concentration of the oxygen constant in our samples (e.g. inefficient but of equal duration degassing per sample). In this case though, it is not possible to determine the value of \( k_1^o \).

Integrating Equation 2.3 we obtain:

\[
- \ln([T]) = k_1 t + \text{constant}
\]  
(Eq. 2.6)

Although it was not possible to directly determine the concentration of the triplet state molecules, we could observe the allowed triplet-triplet absorption spectroscopically. The triplet concentration can be written, according to the Beer-Lambert law, as \([T] = A_T / \varepsilon l\), where \( \varepsilon \) is the molar extinction coefficient and \( l \) the pathlength of the analyzing light. Substituting in Equation 2.6 we have:

\[
- \ln(A_T) = k_1 t + \text{constant'}
\]  
(Eq. 2.7)

where \( A_T \) is the triplet-triplet absorbance.

From Equation 2.7 it is evident that a plot of \( \ln(A_T) \) versus \( t \) will be linear with a slope of \(-k_1\). From Equation 2.5 one can see that a plot of \( k_1 \) vs. \( [Q] \) should also be linear with a slope of \( k_q \) and intercept of \( k_1^o \). Typical plots of \( \ln(A_T) \) versus \( t \) and \( k_1 \) against the quencher concentration \([Q]\) are shown in Figures 2.4 and 2.5 respectively. The above relationships (Eq. 2.5) and (Eq. 2.7), also suggested the procedure we followed in order to obtain the quenching constants \( k_q \) which was the main objective of our experiments.
For every donor-quencher pair, a series of solutions was prepared where the concentration of the donor was constant and the concentration of the quencher varied. According to Equation 2.7 the natural logarithm of the triplet-triplet absorbance was plotted against time for each one of the solutions. The $k_1$ values were determined as the slopes of the best lines drawn through these points by using a least squares method. In Figures 2.6, 2.7, 2.8 we present typical samples of this procedure for one donor and three different quenchers.

According to Equation 2.5 we plotted the $k_1$ values, which were obtained in the manner described above, against the corresponding quencher concentration and the $k_q$ was obtained as the slope of the best line drawn through the points of the plot. Figure 2.9 is the plot of the $k_1$ values against the various quencher concentrations for one donor and three different quenchers.
FIGURE 2.6  

a. Decay of the triplet-triplet absorbance of phenanthrene monitored at $\lambda = 481$ nm, in the presence of $1 \times 10^{-4}$ M Fe(bpdo)$_3$.

b. Residuals plotted against time.

c. Plot of $\ln$(Absorbance) vs. time from which the slope ($= -k_1$) and the intercept ($T_0$) are used for the calculation of the curve passing through the points in a as $T_0 \exp(-k_1 t)$. 
FIGURE 2.7  a. Decay of the triplet-triplet absorbance of phenanthrene monitored at $\lambda = 481$ nm, in the presence of $1 \times 10^{-4}$ M Fe(tert-Bu-tfa)$_3$.

b. Residuals plotted against time.

c. Plot of $\ln$(Absorbance) against time, from which the slope ($-k_1$) and the intercept ($T_0$) are used for the calculation of the curve passing through the points in a as $T_0 \exp(-k_1t)$. 
FIGURE 2.8  

a. Decay of the triplet-triplet absorbance of phenanthrene monitored at $\lambda=481$ nm, in the presence of $1 \times 10^{-4}$ M Fe(acac-CN)$_3$.

b. Residuals plotted against time.

c. Plot of $\ln(\text{Absorbance})$ against time, from which the slope ($=-k_1$) and the intercept ($=T_0$) are used for the calculation of the curve passing through the points in a as $T_0 \exp(-k_1t)$.
FIGURE 2.9  Plot of the $k_1$ values against quencher concentration, |Q|, for triplet phenanthrene quenching by:

- Fe(acac-CN)$_3$
- Fe(tert-Bu-tfa)$_3$
- Fe(bpdo)$_3$
2.6 Deviations from First Order Kinetics

In certain cases it was noticed that the plot of \( \ln(A_T) \) against time was not linear but curved. This implied that the triplet-triplet absorbance decay did not follow first order kinetics (See Eq. 2.3). The deviation from first order kinetics was attributed to either a contribution of a second order term (Eq. 2.8) or to a more complex mechanism, as in the case of sensitization.

2.7 Mixed Kinetics

For most of the organic donors the decay of their triplet-triplet absorbance followed first order kinetics in the absence of quencher. Acridine, phenanthrene, chrysene, benzophenone and 2-acytlnaphthalene, showed mixed (first and second order kinetics) (Figs. 2.10, 2.11) which was evident even in the presence of small amounts of quencher. To overcome the problem, the obvious solution was to increase the concentration of the quencher (See Eq. 2.1). This however, was not always possible because on increasing the concentration, the absorbance of the quencher at 347 nm and at the monitoring wavelength was also increased; this resulted in low triplet production and it introduced difficulties in monitoring the triplet decay (high photomultiplier voltage).

If we consider the total rate for the radiationless decay of a triplet state in the absence of oxygen and ground state quenching, and if we allow for the second order term, we shall have for the presence of quencher:

\[
- \frac{d[T]}{dt} = k_1 [T] + k_2 [T]^2 + k_q [Q][T] \quad \text{(Eq. 2.8)}
\]

By integrating between \([T_1]\) and \([T]\) for time limits \(t_1\) and \(t\) the equation 2.8 gives:
FIGURE 2.10  a. Decay of the triplet-triplet absorbance of 2-acetylnaphthalene, monitored at λ = 425nm in deaerated benzene solution.

b. Plot of ln(absorbance) vs. time
FIGURE 2.11  
a. Decay of the triplet-triplet absorbance of phenanthrene, monitored at $\lambda = 481$ nm in deaerated benzene solution.

b. Plot of $\ln(\text{absorbance})$ vs. time
\[
\frac{[T]}{[T_1]} \cdot \frac{dT}{[T_1]} = -\int_{t_1}^{t} dt \quad \text{(Eq. 2.9)}
\]

which results to:

\[
[T] = \frac{(k_2[T] + k_1^o + k_q[Q])}{(k_2[T_1] + k_1^o + k_q[Q])} [T_1] \exp\{-\left(t-t_1\right)(k_1^o + k_q[Q])\}
\]

\[
\text{(Eq. 2.10)}
\]

We observe that when \(t_1\) is large enough, that is when the decay is close to the end, then \([T_1]\) and \([T]\) are small.

If we also allow for considerable amount of quencher \([Q]\), then the terms \(k_2[T_1]\) and \(k_2[T]\) are negligible compared with the term \(k_1^o + k_q[Q]\) and can be omitted. The equation is then written as:

\[
[T] = [T_1] \exp\{-\left(t-t_1\right)(k_1^o + k_q[Q])\}
\]

\[
\text{(Eq. 2.11)}
\]

It follows therefore that when the triplet state decay is close to the end it follows first order kinetics by a good approximation. This however depends on the efficiency \((k_q)\) and the concentration of the quencher \([Q]\).

According to the above approximation \(k_q\) can be calculated by using the "tail points" of the curve triplet-triplet absorption - time (See Figure 2.12). The last points of the decay curve have very low values, usually within the order of magnitude of the "noise" of the signal, a fact that can make the calculation of \(k_q\) difficult and the value obtained sometimes dubious. In addition to this method, which has been used by previous workers, we tried to fit the experimental data by using the Equation 2.10 written in the following form:

\[
T = \frac{T_1(k_1^o + k_q[Q])}{(k_1^o + k_q[Q] + k_2[T_1]) \exp\{(k_1^o + k_q[Q])(t-t_1)\} - k_2[T_1]}
\]

\[
\text{(Eq. 2.12)}
\]
where $T$ and $T_1$ represent the triplet-triplet absorbance at times $t$ and $t_1$ respectively. The term $k_2[T_1]$ still involves the indeterminable concentration of the triplet state at time $t_1$. Unfortunately there is lack of information about the triplet-triplet extinction coefficients; therefore converting the concentration $[T_1]$, in the term $k_2[T_1]$, into the directly observable absorbance $T_1$ would have been of little help since we would then introduce the extinction coefficient ($\varepsilon_T$) and the uncertain path length ($l$), ($T_1 = \frac{[T_1]}{\varepsilon_T}$).

Consequently in our fitting program, we used the term $k_2[T_1]$ as a variable. The other variable was the sum ($k_1^o + k_q[Q]$).

The term $T_1$ was regarded as a constant and it represented the triplet-triplet absorbance at time $t_1=0$. (Just after the laser flash). In most of the cases the agreement between the values of $k_1^o$ obtained by this method (Eq 2.12) and those obtained by the single exponential method (Eq 2.11) was very good.

In the following pages we give an example of the two methods we used for the pair 2-Acetylnaphthalene- Fe(tert-bu-tfa)$_3$. In Figure 2.12 the experimental curve of the triplet-triplet absorbance is fitted with the single exponential $T_1 \cdot \exp(-k_1 t)$. The value of $k_1$ was obtained from the last points of the curve by the method described earlier.

It can be seen that the fit is poor and that only the last points obey first order kinetics. The value of $k_1$ was $2.1 \times 10^5 \pm 0.2 \times 10^5$ s$^{-1}$.

In Figure 2.13 the same experimental curve is fitted with the Equation 2.12. It is obvious that the fit is good over all the range of the triplet-triplet absorbance. The values of $k_2[T_1]$ and $k_1 = k_1^o + k_q[Q]$ were continuously changed until the sum of the squares of the differences between the calculated and the experimental points was minimised.

The values determined by this method were $k_2[T_1] = 2.6 \times 10^5$ s$^{-1}$ and $k_1 = (k_1^o + k_q[Q]) = 2.25 \times 10^5$ s$^{-1}$.
FIGURE 2.12  a. Decay of the triplet-triplet absorbance of 2-acetylnaphthalene in the presence of $0.5 \times 10^{-4}$ M Fe(tert-Bu-tfa)$_3$.

The calculation of the solid curve is based on least squares analysis of the late points ($t \geq 7.5 \mu s$ after the laser flash).

b. Residuals
c. Plot of ln(absorbance) vs. time
FIGURE 2.13 Decay of the triplet-triplet absorbance of 2-acetylnaphthalene monitored at $\lambda = 425$ nm in the presence of $0.5 \times 10^{-4}$ M Fe(tert-Bu-tfa)$_2$. The curve drawn through the points was calculated using Eq. 2.12
2.8 Sensitization

Profound deviation from first order kinetics decay was observed in the cases where the triplet state had to be produced by sensitization.

In almost all the experiments where the production of the monitored triplet was sensitized, the oscilloscope trace, as well as the plot of triplet-triplet absorbance against time, showed a curve with characteristic shape. (Figure 2.14 a)

The curve consists of a fast rising component, a maximum and a slow decaying component for the major part of the decay. The fast rise of the absorbance indicates that there is a fast increase in the concentration of the triplet state molecules which reaches a maximum in a relatively short time after the laser flash. In longer times the absorbance decays exponentially as it is suggested by the plot of the logarithm of the absorbance against time, which is linear. (Fig. 2.14 b)

Therefore the calculation of the decay rate constant can be based on the "tail points" of the curve. In order to avoid the earlier mentioned disadvantages of such a treatment, we tried to fit the experimental data with a suitable equation which describes the whole process.

As an example, we shall mention the case of the pair β,β-carotene-Fe(tert-bu-tfa)₃ where the production of the triplet β,β-carotene was sensitized with anthracene.

The first step of the process involves the production of the triplet β,β-carotene by energy transfer from triplet anthracene (85,86). The production of the triplet anthracene is considered, regarding our equipment, simultaneous with the laser flash. If A= anthracene and C= β,β-carotene then the process:

\[ \text{A}^* + \text{C} \xrightarrow{k_{AC}} \text{A} + \text{C}^* \]  

(Eq. 2.13)

describes the production of triplet β,β-carotene. The energy transfer rate constant \( k_{AC} \) has been determined by previous workers (82,86) and the values reported range from 1.1×10^{10} M^{-1} s^{-1} to 1.3×10^{10} M^{-1} s^{-1}. 

FIGURE 2.14 a. Transient triplet-triplet absorbance of β,β-carotene monitored at λ = 520 nm. Benzophenone was used as sensitizer.

b. Plot of ln(absorbance) vs. time
Simultaneously the concentration of triplet anthracene is reduced due to quenching by Fe(tert-bu-tfa)$_3$, according to the equation:

\[ \text{A}^* + \text{Q} \xrightarrow{k_{AQ}} \text{A} + \text{Q}^* \]  \hspace{1cm} (Eq. 2.14)

where Q= Fe(tert-bu-tfa)$_3$. The quenching constant $k_{AQ}$ has been determined in this work to be: $k_{AQ} = 3.2\pm0.3\times10^9 \text{ dm}^3\text{mol}^{-1}\text{s}^{-1}$.

Finally the triplet $\beta,\beta$-carotene is quenched by Fe(tert-bu-tfa)$_3$ as in equation

\[ \text{C}^* + \text{Q} \xrightarrow{k_Q} \text{C} + \text{Q}^* \]  \hspace{1cm} (Eq. 2.15)

According to the equations 2.13 and 2.14 the loss of triplet anthracene concentration $[\text{A}^*]$ is:

\[ -\frac{d[\text{A}^*]}{dt} = k_{AC} [\text{A}^*][\text{C}] + k_{AQ}[\text{A}^*][\text{Q}] + k_1[\text{A}^*] \]  \hspace{1cm} (Eq. 2.16)

where $k_1$ is the pseudo-unimolecular decay rate constant for triplet anthracene which has a very low value (82), $k_1 < 10^4 \text{ s}^{-1}$ as determined in this work.

Triplet $\beta,\beta$-carotene is produced in step (2.13) and decays in step (2.15). The change in the concentration of $\beta,\beta$-carotene $[\text{C}^*]$ is described by the Equation:

\[ \frac{d[\text{C}^*]}{dt} = k_{AC} [\text{C}][\text{A}^*] - k_Q[\text{C}^*][\text{Q}] - k_{C}[\text{C}^*] \]  \hspace{1cm} (Eq. 2.17)

where $k_{C}$ is the pseudo-unimolecular decay rate constant for triplet $\beta,\beta$-carotene and it's value (85), determined in this work, is $1.4(\pm0.1)\times10^5 \text{ s}^{-1}$.

Integrating Eq. 2.16 one gets the triplet anthracene concentration:

\[ [\text{A}^*] = [\text{A}^*_0] \exp\{-(k_1 + k_{AQ}[\text{Q}] + k_{AC}[\text{C}])t\} \]  \hspace{1cm} (Eq. 2.18)

where $[\text{A}^*_0]$ is the concentration of triplet anthracene at time $t=0$ (Immediately after the laser flash).
Similarly the concentration of triplet β, β-carotene will be:

\[ [C^*] = \frac{k_{AC}[C][A_0^*]}{(k_C + k_Q[Q] - k_1 - k_{AC}[C] - k_{AQ}[Q])} \cdot \left( \exp\left[-(k_1 + k_{AC}[C] + k_{AQ}[Q])t\right] - \exp\left[-(k_C + k_Q[Q])t\right] \right) \]  

(Eq. 2.19)

In all the above integrations the assumption has been made that the concentration of ground state carotene [C] does not change significantly during the whole process. Since the absorbance of the quencher does not change with time, the change of the absorbance we observe is the change of the sum of the absorbances of triplet anthracene and triplet β, β-carotene.

If, according to the Beer-Lambert law, we substitute the concentrations [C*], [A*], [A_0*] in the equations 2.18 2.19 with the absorbances C*, A* and A_0* and then take the sum of the equations, we shall have the total absorbance:

\[ C^* + A^* = \left( \frac{\varepsilon_C}{\varepsilon_A} \right) \frac{k_{AC}[C][A_0^*]}{(k_C + k_Q[Q] - k_1 - k_{AC}[C] - k_{AQ}[Q])} \cdot \left( \exp\left[-(k_1 + k_{AC}[C] + k_{AQ}[Q])t\right] - \exp\left[-(k_C + k_Q[Q])t\right] \right) + A_0 \exp\left[-(k_1 + k_{AQ}[Q])t\right] \]  

(Eq. 2.20)

\( \varepsilon_C \) and \( \varepsilon_A \) are the extinction coefficients for triplet β, β-carotene and triplet anthracene respectively, at \( \lambda = 520 \) nm which is the monitoring wavelength for the triplet β, β-carotene absorbance.

The Equation (2.20) describes the change of the total absorbance during the process specified by the mechanism which is shown in Scheme 2.1:
We tried to fit the experimental data with the Equation 2.20 by using an iterative method in which we changed the values of the extinction coefficient's ratio $\frac{\varepsilon_C}{\varepsilon_A}$ and the quenching constant $k_Q$ until a satisfactory fit was obtained. In Figure 2.15 we present a characteristic sample of the results of the method for the system: triplet $\beta, \beta$-carotene, (produced by sensitization with anthracene), quenched by Fe(tert-bu-tfa)$_3$.

For the particular trace we used the values:

\[ [C] = (\text{ground state carotene conc.}) = 3 \times 10^{-5} \text{ M} \]
\[ [Q] = (\text{Fe(tert-bu-tfa)$_3$ conc.}) = 3 \times 10^{-4} \text{ M} \]
\[ k_1 = 8 \times 10^3 \text{ s}^{-1} \]
\[ k_C = 1.45 \times 10^5 \text{ s}^{-1} \]
\[ k_{AC} = 1.1 \times 10^{10} \text{ d}m^3 \text{ mol}^{-1} \text{ s}^{-1} \]
\[ k_{AQ} = 3 \times 10^9 \text{ d}m^3 \text{ mol}^{-1} \text{ s}^{-1} \]
\[ A_0^* = 0.05 \]
\[ \frac{\varepsilon_C}{\varepsilon_A} = 32.5 \]
\[ k_Q = 3 \times 10^8 \text{ d}m^3 \text{ mol}^{-1} \text{ s}^{-1} \]
FIGURE 2.15 Transient triplet-triplet absorbance of $\beta,\beta$-carotene monitored at $\lambda = 520$ nm, in the presence of $3 \times 10^{-4}$ M Fe(tert-Bu-tfa)$_2$. Anthracene was used as sensitizer. The curve was fitted to the experimental points was calculated using Eq. 2.20
3.1 The quenching results

The quenching results are presented in three Tables. In Table 3.1 are listed the results for Fe(bpdo)$_3$, in Table 3.2 the results for Fe(tert-Bu-tfa)$_3$ and in Table 3.3 the results for Fe(acac-CN)$_3$. The Tables contain the donors, the wavenumbers of their maximum 0-0 phosphorescence transition, $\tilde{\nu}_0(T)$, the number and the range of the quencher concentration used for each donor, and the $k_q$ values with the estimated error.

3.1.2 Determination and accuracy of the $k_q$ values

The pseudo-first order decay rate constants $k_1 (= k_q^0+k_q[Q])$ and the quenching rate constants $k_q$ were determined by methods described in Chapter 2.

For the determination of each quenching constant $k_q$, more than three pseudo-first order decay rate constants, $k_1$, corresponding to different quencher concentrations, were required. The calculation of each $k_1$ was based on the analysis of three decay traces. From the plot of ln(Absorbance) against time, the straightest and "noiseless" part was chosen and $k_1$ was determined as the slope of the line which resulted from least squares analysis on the points of the selected part. The extracted value was then used for the calculation of an exponential curve, $A=A_0 \cdot \exp(-k_1t)$, where $A_0$ is the expected absorbance at time $t=0$. The $A_0$ was determined from the intercept, which resulted from the least squares analysis, as $A_0=\exp(\text{Intercept})$. This curve was then superimposed on the observed Absorbance vs time curve and the values $A_{\text{obs}}-A_{\text{calc}}$ (the so called Residuals) were calculated and plotted against time in order to obtain a general picture of the fit over all the decay (Figures 2.6, 2.7, 2.8). If the residuals showed a good fit for the major part of the decay, the $k_1$ value was accepted. The same procedure was repeated for the other traces which corresponded to
the same quencher concentration. The mean of the accepted $k_1$ values was kept as the final $k_1$. The accuracy of the $k_1$ value was determined as the deviation of the maximum and the minimum $k_1$ from the mean.

For the calculation of $k_q$ the graphical method was used in conjunction with the least squares method, bearing in mind that the accuracy of the method is limited when applied to less than 10 data points. The accuracy of the $k_q$ values was determined from the plots of $k_1$ versus $[Q]$. As $k_q$ we selected the slope of the best line ($k_b$) plus the deviation of the maximum ($k_{\text{max}}-k_b$) and the minimum ($k_{\text{min}}-k_b$) of the slopes of the other lines, which could be drawn through the data points passing through the mean $\bar{x}, \bar{y}$ point.\(^{(83)}\)
TABLE 3.1 Rate constants in benzene solution at room temperature for quenching by tris(4,4-dimethyl-1,3-propanedionato) iron(III) of the triplet states of organic compounds ($k_q$), with the wavenumbers of the maximum 0-0 phosphorescence transition ($\tilde{\nu}_{00}(T)$), the number and the range of the quencher concentrations $[Q]$.  

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$\tilde{\nu}_{00}(T)/\mu m^{-1}$</th>
<th>$[Q]$ / $10^{-4}$ mol dm$^{-3}$</th>
<th>$k_q$ / $10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>number of $[Q]$</td>
<td>range of $[Q]$</td>
</tr>
<tr>
<td>Benzophenone</td>
<td>2.43</td>
<td>5</td>
<td>0.5 - 4</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>2.16</td>
<td>5</td>
<td>0.1 - 2</td>
</tr>
<tr>
<td>2-Acetylnaphthalene</td>
<td>2.06</td>
<td>6</td>
<td>0.5 - 3</td>
</tr>
<tr>
<td>Chrysene</td>
<td>1.98</td>
<td>5</td>
<td>0.5 - 4</td>
</tr>
<tr>
<td>Coronene</td>
<td>1.94</td>
<td>3</td>
<td>0.1 - 1</td>
</tr>
<tr>
<td>1,2,5,6 - DBA*</td>
<td>1.83</td>
<td>4</td>
<td>0.5 - 3</td>
</tr>
<tr>
<td>1,2,3,4 - DBA*</td>
<td>1.78</td>
<td>4</td>
<td>0.5 - 2.5</td>
</tr>
<tr>
<td>Pyrene</td>
<td>1.68</td>
<td>4</td>
<td>0.1 - 1</td>
</tr>
<tr>
<td>Acridine</td>
<td>1.58</td>
<td>4</td>
<td>0.5 - 3</td>
</tr>
<tr>
<td>Anthracene</td>
<td>1.47</td>
<td>5</td>
<td>0.5 - 2.5</td>
</tr>
<tr>
<td>Perylene $^\alpha$</td>
<td>1.24</td>
<td>5</td>
<td>0.5 - 4</td>
</tr>
<tr>
<td>2,3-Benzanthracene $^\alpha$</td>
<td>1.03</td>
<td>4</td>
<td>0.5 - 3</td>
</tr>
<tr>
<td>Pentacene</td>
<td>0.80</td>
<td>3</td>
<td>1 - 3</td>
</tr>
<tr>
<td>$\beta,\beta$- Carotene $^\beta$</td>
<td>0.63</td>
<td>5</td>
<td>0.5 - 4</td>
</tr>
</tbody>
</table>

$^*$ DBA = Dibenzanthracene
$^\alpha$ Sensitized with benzophenone
$^\beta$ Sensitized with anthracene
TABLE 3.2  Rate constants in benzene solution at room temperature for quenching by tris(1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedionato)iron(III) of the triplet states of organic compounds ($k_q$) with the wavenumbers of the maximum 0-0 phosphorescence transition ($\tilde{\nu}_{00}(T)$), the number and the range of the quencher concentrations $[Q]$.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$\tilde{\nu}_{00}(T)/\mu$m$^{-1}$</th>
<th>$[Q]$ / $10^{-4}$ mol dm$^{-3}$</th>
<th>$k_q$ / $10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>number</td>
<td>range of $[Q]$</td>
</tr>
<tr>
<td>Benzophenone</td>
<td>2.43</td>
<td>4</td>
<td>1 - 4</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>2.16</td>
<td>5</td>
<td>0.5 - 2.5</td>
</tr>
<tr>
<td>2-Acetylnaphthalene</td>
<td>2.06</td>
<td>5</td>
<td>0.5 - 3</td>
</tr>
<tr>
<td>Chrysene</td>
<td>1.98</td>
<td>5</td>
<td>0.5 - 4</td>
</tr>
<tr>
<td>Coronene</td>
<td>1.94</td>
<td>3</td>
<td>0.5 - 1</td>
</tr>
<tr>
<td>1,2,5,6-DBA*</td>
<td>1.83</td>
<td>4</td>
<td>0.5 - 2</td>
</tr>
<tr>
<td>1,2,3,4-DBA*</td>
<td>1.78</td>
<td>4</td>
<td>0.5 - 4</td>
</tr>
<tr>
<td>Pyrene</td>
<td>1.68</td>
<td>5</td>
<td>0.1 - 1</td>
</tr>
<tr>
<td>Acridine</td>
<td>1.58</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Anthracene</td>
<td>1.47</td>
<td>5</td>
<td>0.5 - 4</td>
</tr>
<tr>
<td>Perylene$^\alpha$</td>
<td>1.24</td>
<td>4</td>
<td>0.5 - 2</td>
</tr>
<tr>
<td>2,3-Benzanthracene$^\alpha$</td>
<td>1.03</td>
<td>5</td>
<td>0.5 - 3</td>
</tr>
<tr>
<td>Pentacene</td>
<td>0.80</td>
<td>3</td>
<td>1 - 3</td>
</tr>
<tr>
<td>$\beta,\beta$-Carotene$^\beta$</td>
<td>0.63</td>
<td>5</td>
<td>0.5 - 4</td>
</tr>
</tbody>
</table>

* DBA = Dibenzanthracene
$\alpha$ Sensitized with benzophenone
$\beta$ Sensitized with anthracene
TABLE 3.3 Rate constants in benzene solution at room temperature for quenching by tris(3-cyano-2,4-pentanedionato)iron(III) of the triplet states of organic compounds \( k_q \) with the wave-numbers of the maximum 0-0 phosphorescence transition \( \nu_{00}(T) \), the number and the range of the quencher concentrations \([Q]\).

<table>
<thead>
<tr>
<th>Compounds</th>
<th>( \nu_{00}(T)/\mu m^{-1} )</th>
<th>([Q]) / (10^{-4}) mol dm(^{-3})</th>
<th>( k_q ) / (10^9) dm(^3) mol(^{-1}) s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>number</td>
<td>range of ([Q])</td>
<td>range of ([Q])</td>
</tr>
<tr>
<td>Benzophenone</td>
<td>2.43</td>
<td>5</td>
<td>0.5 - 4</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>2.16</td>
<td>5</td>
<td>0.5 - 1</td>
</tr>
<tr>
<td>2-Acetylnaphthalene</td>
<td>2.06</td>
<td>5</td>
<td>0.5 - 3</td>
</tr>
<tr>
<td>Chrysene</td>
<td>1.98</td>
<td>5</td>
<td>0.5 - 2</td>
</tr>
<tr>
<td>Coronene</td>
<td>1.94</td>
<td>3</td>
<td>0.05- 0.5</td>
</tr>
<tr>
<td>1,2,5,6 - DBA*</td>
<td>1.83</td>
<td>4</td>
<td>0.5 - 2</td>
</tr>
<tr>
<td>1,2,3,4 - DBA*</td>
<td>1.78</td>
<td>4</td>
<td>0.5 - 2</td>
</tr>
<tr>
<td>Pyrene</td>
<td>1.68</td>
<td>3</td>
<td>0.02- 0.5</td>
</tr>
<tr>
<td>Acridine</td>
<td>1.58</td>
<td>4</td>
<td>0.1 - 2.5</td>
</tr>
<tr>
<td>Anthracene</td>
<td>1.47</td>
<td>4</td>
<td>0.01- 1</td>
</tr>
<tr>
<td>Perylene (\alpha)</td>
<td>1.24</td>
<td>5</td>
<td>0.1 - 1</td>
</tr>
<tr>
<td>2,3-Benzanthracene (\alpha)</td>
<td>1.03</td>
<td>5</td>
<td>0.5 - 2.5</td>
</tr>
<tr>
<td>Pentacene</td>
<td>0.80</td>
<td>2</td>
<td>0.5 - 1</td>
</tr>
<tr>
<td>(\beta,\beta) - Carotene (\beta)</td>
<td>0.63</td>
<td>5</td>
<td>0.5 - 3</td>
</tr>
</tbody>
</table>

* DBA = Dibenzanthracene
\(\alpha\) Sensitized with benzophenone
\(\beta\) Sensitized with anthracene
3.2 Further Results

Here we present the results of work\(^{100}\) on triplet substituted 2-pyrazolines, which was carried out in collaboration with Graeme P. Kelly.

In order to study the excited state properties of substituted 2-pyrazolines, four compounds of the general formula 3.1, listed below, were subjected to laser flash photolysis in deaerated benzene solution. However, no transients were observed upon direct photolysis. Upon addition of benzophenone, new absorption bands, in addition to the characteristic ones of triplet-triplet benzophenone absorption, appeared in the time resolved transient absorption spectrum.\(^{3.1}\) Comparison between the ground state spectra of the mixed benzophenone and pyrazoline solutions, showed that no changes took place before and after repeated photolysis, thus excluding chemical reaction or complex formation. Therefore, the observed transient absorption should be attributed to excited pyrazoline produced by sensitization from triplet benzophenone.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(R)</th>
<th>(R')</th>
</tr>
</thead>
<tbody>
<tr>
<td>Py(I)</td>
<td>Ph</td>
<td>Ph</td>
</tr>
<tr>
<td>Py(II)</td>
<td>p-Et(_2)NC(_6)H(_4)</td>
<td>p-Et(_2)NC(_6)H(_4)</td>
</tr>
<tr>
<td>Py(III)</td>
<td>2-Thienyl</td>
<td>2-Thienyl</td>
</tr>
<tr>
<td>Py(IV)</td>
<td>H</td>
<td>O</td>
</tr>
</tbody>
</table>

General Formula 3.1
FIGURE 3.1  Time resolved absorption spectrum of *Py(I) sensitized with benzophenone. The spectrum was recorded at 1.5 µs (Δ), 5.0 µs (X) and 10.0 µs (□) after the laser flash.
Xanthone and anthracene were also successfully used as sensitizers. However, the amount of transient absorption produced was significantly smaller than in sensitization by benzophenone. This behaviour may be explained if one considers the short lifetime of xanthone's triplet, $\tau = 0.092 \, \mu s$ (89) which reduces the amount of triplet energy transferred to pyrazoline (Scheme 3.1) with the result of limited excited pyrazoline production. In the case of anthracene, one may interpret the small transient production as an indication of energetically unfavourable energy transfer i.e., the triplet energy of anthracene being lower than the energy of the excited pyrazoline.

Sensitization may be represented by the following Scheme:

\[
\begin{align*}
\text{S}^* & \xrightarrow{k_1} \text{Py}^* \\
& \xrightarrow{k_2} \text{Py} \\
& \xrightarrow{k_3} \text{Py}
\end{align*}
\]

Scheme 3.1

where S=sensitizer and Py=pyrazoline.

According to Scheme 3.1 the transient absorption as a function of time will be given by the following expression:

\[
\begin{align*}
\text{Abs} &= \frac{\epsilon_{\text{Py}} k_2[\text{Py}] S_0^*}{\epsilon_{\text{S}} (k_3-k_1-k_2[\text{Py}])} \left[ \exp(-k_1 + k_2[\text{Py}] )t\right] \\
& \quad - \exp(-k_3 t) + S_0^* \exp(-(k_1 + k_2[\text{Py}] )t) \\
& \quad \text{(Eq. 3.1)}
\end{align*}
\]

where $\epsilon_{\text{Py}}$ and $\epsilon_{\text{S}}$ are the triplet-triplet extinction coefficients -at the monitoring wavelength- of the pyrazoline and sensitizer respectively. Usually, $k_3 < k_1 + k_2[\text{Py}]$; in long times after the laser flash, Eq. 3.1 becomes:

\[
\begin{align*}
\text{Abs} &= \frac{\epsilon_{\text{Py}} k_2[\text{Py}] S_0^*}{\epsilon_{\text{S}} (k_1+k_2[\text{Py}]-k_3)} \exp(-k_3 t) \\
& \quad \text{(Eq. 3.2)}
\end{align*}
\]
The decay rate constants $k_3$ were determined by performing first order kinetics analysis on the "tail points" of the decay trace (Fig. 3.2) of each pyrazoline. The decay was monitored at wavelengths corresponding to the maximum absorbance as indicated by the transient absorption spectra of the compounds. The $k_3$ values and the monitoring wavelengths are given below:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Monitoring wavelength/ nm</th>
<th>$k_3/s^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Py(I)</td>
<td>490</td>
<td>$1.4 \times 10^5$</td>
</tr>
<tr>
<td>Py(II)</td>
<td>460</td>
<td>$1.3 \times 10^5$</td>
</tr>
<tr>
<td>Py(III)</td>
<td>480</td>
<td>$1.8 \times 10^5$</td>
</tr>
<tr>
<td>Py(IV)</td>
<td>530</td>
<td>$1.9 \times 10^5$</td>
</tr>
</tbody>
</table>

In order to assign the sensitized transients, β-carotene was used as triplet energy acceptor. According to Scheme 3.2 triplet β-carotene is produced by energy transfer from the sensitizer, S, and the excited pyrazoline, Py:

\[
\begin{align*}
1_S & \xrightarrow{k_1} 3_S^* \\
3_S^* & \xrightarrow{k_{SP}[Py]} 3_Py^* \\
3_Py^* & \xrightarrow{k_{PC}[C]} 3_C^* \\
3_C^* & \xrightarrow{k_{SC}[C]} 3_C \\
1_C & \xrightarrow{k_3} 1_{Py}
\end{align*}
\]

Scheme 3.2

By adjusting the concentration of β-carotene and pyrazoline in such a way that $k_{SP}[Py] \gg k_{SC}[C]$, sequential energy transfer to β-carotene via the pyrazoline triplet becomes the predominant pathway of the reaction. In order to verify that Scheme 3.2 complies with the experimental data, the transient triplet-triplet absorbance, monitored at $\lambda=520$nm was fitted with that
FIGURE 3.2 Typical plot of triplet-triplet absorbance vs. time. Triplet Py(II) was produced by sensitization with benzophenone. Monitoring wavelength $\lambda = 460$ nm.
expected from Scheme 3.2. The expression which describes triplet-triplet absorbance as a function of time, is rather complicated and in the case of benzophenone as sensitizer, it becomes difficult to handle. However, with xanthone as sensitizer, it is considerably simplified due to the fast decay ($k_1$) of the sensitizer and the negligible triplet-triplet absorbance of xanthone ($\lambda_{\text{max}}=610\text{nm}$) at the monitoring wavelength ($\lambda=520\text{nm}$).

Figure 3.3 shows a typical plot of the experimental and calculated data according to Scheme 3.2.

From the particular trace, it was found that the rate constant $k_{pc}$ (See Scheme 3.2), for the production of triplet $\beta,\beta$-carotene by energy transfer from $^3\text{Py}(I)$ is $k_{pc} = 1.1 \pm 0.1 \times 10^{10}\text{ dm}^3\text{mol}^{-1}\text{s}^{-1}$.

The mechanism of the sensitization of $\beta,\beta$-carotene with benzophenone was also investigated. In this case it was found that the rate constant for the production of triplet $\beta,\beta$-carotene by energy transfer from benzophenone is $k = 1.5 \pm 0.1 \times 10^{10}\text{ dm}^3\text{mol}^{-1}\text{s}^{-1}$.

Further work on energy transfer to $\beta,\beta$-carotene from the 4 pyrazolines, with benzophenone as sensitizer, is in progress.

* Due to its fast decay ($k_1 = 10.8 \pm 0.5 \times 10^6 \text{s}^{-1}$) triplet xanthone is, virtually, nonexistent in the solution $1\mu\text{s}$ after the laser flash. Therefore, its contribution is limited to the "rise time" part of the absorbance vs. time curve of Fig. 3.3. This part of the curve is obscured by a strong emission, and the rest of it is the sum of the triplet-triplet absorbance of carotene and pyrazoline. In this case, if xanthone is ignored, the kinetics of Scheme 3.2 are simplified and the triplet-triplet absorbance is given by the expression:

$$\text{Abs.} = \text{Py}^\# \exp\left(-\left(k_3+k_{pc}[C]\right) t\right) \left(1+ \frac{\varepsilon_c k_{pc} [C]}{\varepsilon_p \left(k_c-k_3 k_{pc}[C]\right)}\right) +$$

$$\frac{C^\# \left(k_c-k_3-k_{pc}[C]\right) - \left(\varepsilon_c/\varepsilon_p\right) k_{pc}[C] \text{Py}^\# \exp(-k_c t)}{k_c - \left(k_3+k_{pc}[C]\right)}$$

where $\varepsilon_c$ and $\varepsilon_p$ are the extinction coefficients of triplet carotene and triplet pyrazoline, $[C]$ the ground state carotene concentration and $C^\#$, $\text{Py}^\#$ the initial absorbance of triplet carotene and triplet pyrazoline respectively.
FIGURE 3.3  

a. Transient absorbance of benzene solution of $2.5 \times 10^{-5}$ M $\beta, \beta$-carotene, $2 \times 10^{-4}$ M Py(I) and $2 \times 10^{-4}$ xanthone. The curve drawn through the points is the expected absorbance according to Scheme

b. Residuals
CHAPTER 4: DISCUSSION

Energy transfer is associated with excited states while electron transfer depends on redox potentials. Both processes are related to the frontier orbitals for which information may be obtained from spectral investigations.

The iron(III) ion has a $d^5$ configuration. The arrangement of the $\beta$-dionato ligands about the iron(III) ion conforms with $D_3$ symmetry rather than $O_h$. However, the distortion is insigificant since no splitting in the spectral bands is evident and one may use labels appropriate to $O_h$ symmetry to describe the orbitals and the states of the tris($\beta$-dionato)iron(III) complexes.

The magnetic susceptibility of these iron(III) compounds is quite high ($\mu_{\text{eff}} \approx 5.9$ B.M) indicating high spin complexes. This $t_{2g}^3 e_g^2$ configuration with all five electrons unpaired gives rise to a $^6A_{1g}$ ground state.

In the electronic absorption spectra of the tris($\beta$-dionato) iron(III) chelates four bands usually appear in the region (330-1400 nm). (Figure 4.1) The broad band occurring in the near infrared and the band often appearing as a shoulder on the tail of the intense band in the visible are due to ligand field (LF), transitions. In these high spin complexes LF transitions, in addition to being Laporte forbidden, are also spin forbidden. This results in very low extinction coefficients of the observed bands which correspond to ligand field transitions. In addition, there is a good deal of uncertainty in establishing the exact position of the maximum absorbance due to the broadness of the band. The low energy LF band has been assigned (78, 90) to the $^4T_{2g} \leftarrow ^6A_{1g}$ transition and the high energy one to the $^4T_{1g} \leftarrow ^6A_{1g}$ transition. The remaining two bands have been assigned to charge transfer transitions $e_g \leftarrow \pi$ and $\pi^* \leftarrow t_{2g}$ in view of their extinction coefficients.

The assignments and the band maxima ($\nu_{\text{max}}$) of the observed transitions are given in Table 4.1 in which also appear the reduction potentials of the quenchers. The compounds Fe(acac)$_3$ and Fe(dpm)$_3$ have been included for comparison purposes. There have been many discussions concerning the assignment of the transitions shown in Table 4.1. The successful outcome...
FIGURE 4.1 Absorption spectrum of Fe(acac-CN)$_3$ in benzene (---) and chloroform (---)
TABLE 4.1

Spectral transitions, Band maxima ($\tilde{\nu}_{\text{max}}$), Wavenumbers at 5% of band maximum absorbance ($\tilde{\nu}_{0.05}$), and Reduction potentials ($E_{1/2}$) for the tris($\beta$-dionato)iron(III) complexes

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>$4T_{1g} \leftrightarrow 6A_{1g}$</th>
<th>$4T_{2g} \leftrightarrow 6A_{1g}$</th>
<th>$6CT \leftrightarrow 6A_{1g}(e_g \leftrightarrow \pi)$</th>
<th>$6CT \leftrightarrow 6A_{1g}(\pi^* \leftrightarrow t_{2g})$</th>
<th>$E_{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\tilde{\nu}_{\text{max}}$ $\mu$m$^{-1}$</td>
<td>$\tilde{\nu}_{\text{max}}$ $\mu$m$^{-1}$</td>
<td>$\tilde{\nu}_{\text{0.05}}$ $\mu$m$^{-1}$</td>
<td>$\tilde{\nu}_{\text{max}}$ $\mu$m$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>Fe(bpdo)$_3$</td>
<td>0.975</td>
<td>1.299</td>
<td>2.270</td>
<td>1.750</td>
<td>2.730</td>
</tr>
<tr>
<td>Fe(acac-CN)$_3$</td>
<td>0.980</td>
<td>1.320</td>
<td>2.232</td>
<td>1.724</td>
<td>2.940</td>
</tr>
<tr>
<td>Fe(tert-Bu-tfa)$_3$</td>
<td>0.990</td>
<td>1.316</td>
<td>2.293</td>
<td>1.818</td>
<td>2.700</td>
</tr>
<tr>
<td>Fe(acac)$_3$</td>
<td>0.979$^a$</td>
<td>1.333$^a$</td>
<td>2.30$^a$</td>
<td>1.81$^a$</td>
<td>2.83$^a$</td>
</tr>
<tr>
<td>Fe(dpm)$_3$</td>
<td>0.980$^b$</td>
<td>1.370$^b$</td>
<td>2.32$^b$</td>
<td>1.75</td>
<td>2.80$^b$</td>
</tr>
</tbody>
</table>

$^a$ Values taken from reference 33.

$^b$ Band maxima taken from reference 66.

$^c$ Reduction potentials taken from reference 77.
of many investigations \((66, 33)\) gives support to the assignments favoured by Lintvedt \((78, 91)\) and Barnum \((90)\). The band corresponding to the \(e_g \leftrightarrow \pi\) transition is a broad one and the observed maximum absorbance may not \((33)\) correspond to \(\nu_0\). For this reason the \(\nu_{\text{e,0.05}}\) values are also given in Table 4.1. The \(\nu_{\text{e,0.05}}\) is the wavenumber, to the red of the absorption maximum, at which the absorbance equals the 5% of the maximum absorbance. (See Figure 4.1). This notation was first used by Adamson \((92)\) who associated the true energy of spin allowed thermally equilibrated excited states \(\text{thexi}\) with the \(\nu_{\text{e,0.05}}\) value.

There should be two more LF transitions, \(4E_g \leftrightarrow 6\Lambda_1g\) and \(4\Lambda_1g \leftrightarrow 6\Lambda_1g\) and two more charge transfer, CT, transitions, the \(t_2g \leftrightarrow \pi\) and \(\pi \leftrightarrow e_g\). The CT transitions have not been observed and neither have the LF ones. However, the approximate energy of the LF transitions may be calculated using the appropriate Tanabe-Sugano \((93)\) matrices as performed by Wilkinson and Tsiamis \((33)\). Their results indicate that both LF states should lie about 1.2 \(\mu\text{m}^{-1}\) higher than the \(4T_1g\) state.

In contrast with the spectra where the changes in transition energy are insignificant, the variation in the reduction potentials is quite appreciable (Table 4.1). The reduction potentials have been obtained from a polarographic and cyclic voltammetric study \((77)\) of a series of tris(\(\beta\)-dionato) iron(III) chelates on acetonitrile and propylene carbonate. The cyclic voltamograms of the quenchers, obtained at potential scan rates of 0.05 to 100 \(Vs^{-1}\) indicate that in these solvents, the electron transfer process is thermodynamically reversible. Solvents other than acetonitrile and propylene carbonate may influence the mechanism of electron transfer \((94)\); nevertheless, the \(E_{1/2}\) values obtained in the aforementioned study \((77)\) compare favourably with other literature values \((95)\).
It has been established\(^{12,33,34,88}\) that the major mechanisms of quenching of organic triplets by tris(\(\beta\)-dionato)Iron(III) complexes are electronic energy transfer and electron transfer operating either separately or in conjunction. However, before one interpretes the quenching results of this work in terms of the above mechanisms, one should examine the posibility of quenching by the mechanisms mentioned in Chapter 1.

Chemical reaction should be excluded since it has been confirmed that the donors and the quenchers do not react in the ground state and no product formation was observed after repeated laser flash photolysis. Moreover, no additional transient species were observed during the photolysis. Concentration quenching was avoided by adjusting the amount of the donors as suggested\(^{80-82}\) and as described in Chapter 2. Finally, energy transfer by the Coulombic interaction is very unlikely\(^{12}\) in quenching by coordination complexes in solution and no hint of such an event was encountered. In view of the above considerations, the mechanism of quenching by Fe(bpdo)\(_3\), Fe(acac-CN)\(_3\) and Fe(tert-Bu-tfa)\(_3\) is restricted to energy transfer or electron transfer.

The behaviour of each quencher will be discussed separately.

1. Quenching by Fe(bpdo)\(_3\)

In Table 4.2 are listed the triplet energies and the logarithms of the quenching constant, \(k_q\). Since the mechanism of quenching of the above triplets by Fe(acac)\(_3\) was found\(^{68}\) to be electronic energy transfer it is worth comparing the reduction potentials of Fe(acac)\(_3\) and Fe(bpdo)\(_3\) to see whether there is a possibility for simultaneous electron transfer. The reduction potential of Fe(bpdo)\(_3\) (\(E_{1/2}=-0.61\) V, Table 4.1) equals within experimental error that of Fe(acac)\(_3\) (\(E_{1/2}=-0.62\) V, Table 4.1). Therefore, electron transfer seems very unlikely to occur. Moreover, a plot of log(\(k_q\)) versus the free
energy for electron transfer, $\Delta G_{el}$, shows no dependence of the quenching rate on $\Delta G_{el}$. (Figure 4.2)

Quenching by electronic energy transfer implies dependence on the energy levels of the acceptor. In a plot of $\log(k_q)$ versus the triplet energy of the donors, $E_T$, there will be a stepwise increase of $\log(k_q)$ as the triplet energy increases. In Figure 4.3 one can see that the correlation of the quenching rate, $k_q$, and $E_T$ is very similar to that of Fe(dpm)$_3$ and Fe(acac)$_3$.

Scheme 4.1 represents energy transfer quenching by Fe(bpdo)$_3$:

According to Wigner's Spin Rule, the multiplicities of the encounter complexes $(D*\cdots Q)$ will be 4, 6 and 8. However, no octet excited states are predicted for tris($\beta$-dionato)Iron(III) complexes, and therefore, quenching will occur via quartet and sextet exciplexes. The excited states of Fe(bpdo)$_3$ (Table 4.1) to which energy transfer is feasible are the two low-lying
FIGURE 4.2 Dependence of the bimolecular quenching rate constant \( k_q \) on \( \Delta G_{el} \), the free energy change for electron transfer to Fe(bpdo)\(_3\).
FIGURE 4.3  Dependence of the bimolecular quenching rate constant $k_q$ on donor triplet energies. Arrows marked with diamonds (↑) and circles (○) indicate electronic transitions of Fe(bpdo)$_3$ and Fe(dpm)$_3$ respectively.
quartet ligand field states ($^4T_{1g}$ and $^4T_{2g}$) and the first sextet charge transfer state ($^6CT$, $e_g \leftrightarrow \pi$). Energy transfer to $^6CT$ ($\pi^* \leftrightarrow t_{2g}$) is energetically unfavourable since the energy of this state (2.73 μm$^{-1}$) is higher than the triplet energy of benzophenone ($E_T=2.43$ μm$^{-1}$), the highest energy donor in this work.

According to Scheme 4.1 the quenching constant will be:

$$k_q = 6k_q + 4k_q$$  
(Eq. 4.1)

Applying the steady state approximation to the intermediates of Scheme 4.1 we have for quenching by the $^6CT$:

$$6k_q = \frac{1}{3} k_d / (1 + \frac{6k_{en} + k_d}{6k_{en}})$$  
(Eq. 4.2)

And for quenching by the quartet ligand field states:

$$4k_q = \frac{2}{9} k_d / (1 + (\frac{4k_{en}}{4k_{en}^1 + k_d} + \frac{4k_{en}^2}{4k_{en}^2 + k_d}))$$  
(Eq. 4.3)

According to Balzani (43), energy transfer can be treated classically with the same formalism as the case of electron transfer. The equations which correspond to energy transfer are:

$$\ln(\frac{k_{en}}{k_{-en}}) = -\Delta G_{en} / RT$$  
(Eq. 4.4)

(where $\Delta G_{en}$ is the standard free energy change for the energy transfer process)
Following Wilkinson (87, 88) the donors were regarded as a homogeneous series with constant intrinsic barrier $\Delta G_D^\dagger(0) = 0.06 \text{ eV}$. The value of $\Delta G_D^\dagger(0)$ is equal (88) to that of $\frac{1}{2} \left( \Delta G_D^\dagger(0) + \Delta G_Q(0) \right)$, where $\Delta G_Q(0)$ is very small or zero when the accepting state is non-distorted or slightly distorted. When distorted excited states are involved, $\Delta G_Q^\dagger(0) \neq 0$.

In the case of energy transfer quenching by Fe(bpdo)$_3$ according to Scheme 4.1, the best fit of the experimental results (Figure 4.3) required the following values:

For the quencher's transitions:

- $\tilde{\nu}_{00} (Q^*)$ (Corresponding to $4 T_{1g} \leftarrow 6 A_{1g}$) \pm 0.84 \text{ \AA}^{-1}
- $\tilde{\nu}_{00} (Q^*)$ (Corresponding to $4 T_{2g} \leftarrow 6 A_{1g}$) = 1.33 \text{ \AA}^{-1}
- $\tilde{\nu}_{00} (Q^*)$ (Corresponding to $6 \text{CT} + 6 A_{1g}, e_g + \pi$) = 1.69±0.01 \text{ \AA}^{-1}

For the intrinsic barriers:

- $4 \Delta G^\dagger(0)$ (Corresponding to $4 T_{1g}$ state) = 0.03 \text{ eV}
- $4 \Delta G^\dagger(0)$ (Corresponding to $4 T_{2g}$ state) = 0.03 \text{ eV}
- $6 \Delta G^\dagger(0)$ (Corresponding to $6 \text{CT}$ state) = 0.078±0.006 \text{ eV}

For the transmission coefficients:

- $4 \kappa_{en}$ (Corresponding to $4 T_{1g}$ state) = $1 \times 10^{-3}$
- $4 \kappa_{en}$ (Corresponding to $4 T_{2g}$ state) = $2.3 \times 10^{-4}$
- $6 \kappa_{en}$ (Corresponding to $6 \text{CT}$ state) = $9 \times 10^{-3}$

For comparison purposes, the experimental results for Fe(dpm)$_3$ (66) were also fitted for energy transfer quenching according to Scheme 4.1. The best fit, shown by the dotted curve in Figure 4.3 was achieved for the following values:
Quencher's transitions:

\[ \tilde{\nu}_{00}(Q^*) \] (Corresponding to \( ^4T_{1g} \rightarrow ^6A_{1g} \)) \leq 0.9 \ \mu m^{-1}

\[ \tilde{\nu}_{00}(Q^*) \] (Corresponding to \( ^4T_{2g} \rightarrow ^6A_{1g} \)) = 1.37 \ \mu m^{-1}

\[ \tilde{\nu}_{00}(Q^*) \] (Corresponding to \( ^6CT, e_g + \pi \)) = 1.72\pm0.02 \ \mu m^{-1}

Intrinsic barriers:

\[ ^4\Delta G^+(0) \] (Corresponding to \( ^4T_{1g} \)) = 0.03 \ eV

\[ ^4\Delta G^+(0) \] (Corresponding to \( ^4T_{2g} \)) = 0.03 \ eV

\[ ^6\Delta G^+(0) \] (Corresponding to \( ^6CT \)) = 0.065\pm0.005 \ eV

Transmission coefficients:

\[ ^4\kappa_{en} \] (Corresponding to \( ^4T_{1g} \)) = 8.2\times10^{-5}

\[ ^4\kappa_{en} \] (Corresponding to \( ^4T_{2g} \)) = 6.5\times10^{-5}

\[ ^6\kappa_{en} \] (Corresponding to \( ^6CT \)) = 7.7\times10^{-4}
<table>
<thead>
<tr>
<th>DONORS</th>
<th>$E_T$/eV</th>
<th>$E_{D}^{\text{ox}}$/V($\alpha$)</th>
<th>$\log(k_q/dm^3mol^{-1}s^{-1})$</th>
<th>$\Delta G_{el}/eV(\beta)$</th>
<th>$\log(k_q/dm^3mol^{-1}s^{-1})$</th>
<th>$\Delta G_{el}/eV(\beta)$</th>
<th>$\log(k_q/dm^3mol^{-1}s^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzophenone</td>
<td>3.01</td>
<td>2.46</td>
<td>9.53</td>
<td>-0.64</td>
<td>9.60</td>
<td>-0.45</td>
<td>9.38</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>2.68</td>
<td>1.50</td>
<td>9.68</td>
<td>-1.27</td>
<td>9.98</td>
<td>-1.08</td>
<td>9.81</td>
</tr>
<tr>
<td>3,2-Acetylnaphthalene</td>
<td>2.55</td>
<td>1.69</td>
<td>9.51</td>
<td>-0.96</td>
<td>9.72</td>
<td>-0.76</td>
<td>9.62</td>
</tr>
<tr>
<td>Chrysene</td>
<td>2.47</td>
<td>1.35</td>
<td>9.59</td>
<td>-1.20</td>
<td>9.98</td>
<td>-1.01</td>
<td>9.75</td>
</tr>
<tr>
<td>Coronene</td>
<td>2.40</td>
<td>1.23</td>
<td>9.47</td>
<td>-1.26</td>
<td>9.92</td>
<td>-1.07</td>
<td>9.83</td>
</tr>
<tr>
<td>6,1,2,5,6-DBA</td>
<td>2.27</td>
<td>1.19</td>
<td>9.43</td>
<td>-1.17</td>
<td>9.88</td>
<td>-0.98</td>
<td>9.67</td>
</tr>
<tr>
<td>7,1,2,3,4-DBA</td>
<td>2.21</td>
<td>1.25</td>
<td>9.34</td>
<td>-1.05</td>
<td>9.88</td>
<td>-0.86</td>
<td>9.61</td>
</tr>
<tr>
<td>Pyrene</td>
<td>2.08</td>
<td>1.16</td>
<td>9.29</td>
<td>-1.01</td>
<td>9.92</td>
<td>-0.82</td>
<td>9.78</td>
</tr>
<tr>
<td>Acridine</td>
<td>1.96</td>
<td>1.58</td>
<td>8.91</td>
<td>-0.47</td>
<td>9.39</td>
<td>-0.28</td>
<td></td>
</tr>
<tr>
<td>Anthracene</td>
<td>1.82</td>
<td>1.09</td>
<td>8.93</td>
<td>-0.82</td>
<td>9.81</td>
<td>-0.63</td>
<td>9.50</td>
</tr>
<tr>
<td>Perylene</td>
<td>1.54</td>
<td>0.85</td>
<td>8.87</td>
<td>-0.78</td>
<td>9.75</td>
<td>-0.59</td>
<td>9.50</td>
</tr>
<tr>
<td>2,3-Benzanthracene</td>
<td>1.28</td>
<td>0.77</td>
<td>8.94</td>
<td>-0.59</td>
<td>9.58</td>
<td>-0.41</td>
<td>9.0</td>
</tr>
<tr>
<td>Pentacene</td>
<td>0.99</td>
<td>0.54</td>
<td>8.0</td>
<td>-0.54</td>
<td>9.15</td>
<td>-0.35</td>
<td>8.20</td>
</tr>
<tr>
<td>$\beta$, $\beta$-Carotene</td>
<td>0.78</td>
<td>0.35</td>
<td>8.48</td>
<td>-0.52</td>
<td>9.07</td>
<td>-0.33</td>
<td>8.44</td>
</tr>
</tbody>
</table>

$\alpha$ Values taken from ref. 33  
$\beta$ Calculated using Equation 4.9
2. Quenching by Fe(acac-CN)$_3$

In Table 4.2 are given the oxidation potentials of the donors, $E_D^{ox}$, the $\Delta G_{el}$ values and the logarithms of the quenching constants, $k_q$.

Due to the presence of the strong electron attracting -CN group in the acetylacetonate ring which shifts the reduction potential from $E_{1/2} = -0.62V$ (Fe(acac)$_3$) to $E_{1/2} = 0.09V$ (Fe(acac-CN)$_3$), the quencher Fe(acac-CN)$_3$ might be susceptible to electron transfer. It is therefore reasonable to consider reversible electron transfer quenching which may be represented by Scheme 4.2:

\[
3D^* + 6Q \xrightarrow{k_d} 4,6,8(D^*\cdots Q) \xrightarrow{k_{el}} 4,6,8(D^+\cdots Q^-) \xrightarrow{k_{bt}} D + 6Q
\]

Scheme 4.2

The free energy change, $\Delta G_{el}$ for the formation of $(D^+\cdots Q^-)$ is given\(^{34}\) by Equation 4.8

\[
\Delta G_{el} = F(E_D^{ox} - E_Q^{red}) - E_T + \Delta \omega \quad \text{(Eq. 4.8)}
\]

where $E_D^{ox}$, $E_Q^{red}$ are the oxidation potential of the donor and the reduction potential of the quencher respectively, and $F$ is the Faraday constant. $\Delta \omega$ is a work term which accounts\(^{34}\) for Coulombic interaction energy and changes in solvation free energies of separate ions $D^+$ and $Q^-$ and the exciplex $(D^+\cdots Q^-)$. Typical value\(^{96}\), for electron transfer in benzene, is $\Delta \omega = 0.1 \pm 0.1$ eV, and therefore, $\Delta \omega$ can be omitted. Thus:

\[
\Delta G_{el} = F(E_D^{ox} - E_Q^{red}) - E_T \quad \text{(Eq. 4.9)}
\]

As one can see in Figure 4.5 the correlation of $\log(k_q)$ and $\Delta G_{el}$ is quite good indicating that electron transfer predominates in quenching by Fe(acac-CN)$_3$. In view of Wilkinson's finding\(^{33,34}\) that energy transfer competes with reversible
electron transfer in quenching by fluorinated β-dionato complexes of Cr(III) and Fe(III), it is worth while to examine this possibility. A plot of log(kq) versus ET in Figure 4.4 shows that there is no apparent correlation of the quenching rate with ET. Clearly energy transfer alone cannot account for the quenching rates for phenanthrene and chrysene which equal within experimental error the diffusion controlled quenching rate $k_d = 1 \times 10^{10} d_m \text{mol}^{-1} \text{s}^{-1}$ in benzene. According to Scheme 4.1 the maximum quenching rate expected is $(\frac{1}{3} + \frac{2}{9}) k_d$ or $5.6 \times 10^9 d_m \text{mol}^{-1} \text{s}^{-1}$. However, one can observe (Figure 4.4) that the increase in log(kq), as the triplet energy of the donors increases from $0.8 \mu m^{-1}$ (triplet pentacene) to $1.03 \mu m^{-1}$ (triplet 2,3 benzanthracene) correlates well with the energy of the $^{4}T_{2g}$ state ($0.98 \mu m^{-1}$) of Fe(acac-CN)$_3$. A hint of energy transfer is also given by the quenching rate of the high energy donor acridine, which is higher than that of the low energy donors pentacene and β,β-carotene, although the $\Delta G_{el}$ values $-0.47$ eV, $-0.54$ eV and $-0.52$ eV respectively, suggest the opposite. (See Figure 4.5)

In competitive energy transfer and reversible electron transfer quenching, both processes are subjected to Wigner's Spin Rule. Energy transfer follows Scheme 4.1, as in quenching by Fe(bpdo)$_3$. The multiplicities of the exciplexes, via which electron transfer occurs, depend on the orbitals which accommodate the acquired electron. Thus if the electron is placed on the metal centered $t_{2g}$ or $e_g$ orbitals the multiplicities of $(D^+\cdots Q^-)$ will be 6 $(2(2+1/2)+1)$ and 4 $(2(2-1/2)+1)$, while if it enters the π* ligand centered orbital the multiplicities will be 8 $(2(3+1/2)+1)$ and 6 $(2(3-1/2)+1)$. Since the reduction potentials of the tris(β-dionato)iron(III) complexes depend on the $\sigma$ Hammett parameters of the substituents in the ligands, it is reasonable to assume that the electron enters an orbital of appreciable ligand character. Therefore, electron transfer will occur via sextet and octet exciplexes. The process of competitive energy and reversible electron transfer quenching may be represented by the following Scheme:
According to Scheme 4.3

\[ k_q = 4k_q + 6k_q + 8k_q \]

Applying the steady state approximation

\[ 4k_q = \frac{2}{9} k_d / \left[ 1 + 1/\left( \frac{4k_{en}^2}{4k_{en}^2 + k_d} + \frac{4k_{en}^1}{4k_{en}^1 + k_d} \right) \right] \]  \hspace{1cm} \text{(Eq. 4.10)}

\[ 6k_q = \frac{1}{3} k_d / \left[ 1 + 1/\left( \frac{6k_{en}}{6k_{en} + k_d} + \frac{6k_{el}k_{bt}}{k_d(k_{bt} + 6k_{el})} \right) \right] \]  \hspace{1cm} \text{(Eq. 4.11)}

\[ 8k_q = \frac{4}{9} k_d / \left[ 1 + \frac{k_d}{8k_{el}} \left( 1 + \frac{8k_{el}}{k_{bt}} \right) \right] \]  \hspace{1cm} \text{(Eq. 4.12)}
FIGURE 4.4 Dependence of the bimolecular quenching rate constant $k_q$ on donor triplet energies. Arrows marked with triangles ($\uparrow$) and circles ($\phi$) indicate electronic transitions of Fe(acac-CN)$_3$ and Fe(acac)$_3$ respectively.
FIGURE 4.5 Dependence of the bimolecular quenching rate constant $k_q$ on the free energy change $\Delta G_{el}$ for electron transfer to Fe(acac-CN)$_3$. 
For electron transfer the following equations apply:

\[
\ln \left( \frac{k_{el}}{k_{-el}} \right) = -\Delta G_{el}/RT \quad \text{(Eq. 4.13)}
\]

and

\[
k_{el} = k_{el} \frac{kT}{h} \exp(-\Delta G_{el}^*/RT) \quad \text{(Eq. 4.14)}
\]

Combining equations 4.13, 4.14 and 4.9 with the Agmon-Levine free energy relationship (Eq. 4.7) and taking into account the relevant equations for energy transfer (Eq. 4.4, 4.5, 4.6) one may calculate the \( k_q \) values from equations 4.10, 4.11, 4.12.

To fit the experimental results we used the energy transfer parameters obtained\(^{33} \) for Fe(acac)\(_3\). The values of \( \Delta G_{el}^0(0) \) and \( k_{el} \) were varied until the differences of the experimental and calculated \( k_q \) were minimised. The best fit was achieved for the following values:

**Quencher's transitions:**

\begin{align*}
\kappa_{00}(Q^*) & \quad \text{(Corresponding to } 4T_1g \leftrightarrow 6A_{1g}^g \text{)} & \leq 0.980 \text{ m}^{-1} \\
\kappa_{00}(Q^*) & \quad \text{(Corresponding to } 4T_2g \leftrightarrow 6A_{1g}^g \text{)} & = 1.33 \text{ m}^{-1} \\
\kappa_{00}(Q^*) & \quad \text{(Corresponding to } 6CT, e_g \leftrightarrow \pi \text{)} & = 1.68 \text{ m}^{-1}
\end{align*}

**Intrinsic barriers:**

\begin{align*}
\Delta G_{en}^\pm(0) & \quad \text{(Corresponding to } 4T_1g \text{)} & = 0.03 \text{ eV} \\
\Delta G_{en}^\pm(0) & \quad \text{(Corresponding to } 4T_2g \text{)} & = 0.03 \text{ eV} \\
\Delta G_{en}^\pm(0) & \quad \text{(Corresponding to } 6CT \text{)} & = 0.04 \text{ eV} \\
\Delta G_{el}^\pm(0) & = 8\Delta G_{el}^\pm(0) & = 0.29 \pm 0.01 \text{ eV}
\end{align*}

**Transmission coefficients:**

\begin{align*}
\kappa_{en} & \quad \text{(Corresponding to } 4T_1g \text{)} & = 9.8 \times 10^{-4}
\end{align*}
The experimental and the calculated quenching constants are listed in Table 4.3 below:

**TABLE 4.3** Experimental and calculated quenching constants for competitive energy and reversible electron transfer quenching by Fe(acac-CN)₃

<table>
<thead>
<tr>
<th>DONOR</th>
<th>Experimental</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Benzophenone</td>
<td>4.0±0.3</td>
<td>6.07±0.8</td>
</tr>
<tr>
<td>2 Phenanthrene</td>
<td>9.7±0.4</td>
<td>8.24±0.1</td>
</tr>
<tr>
<td>3 2-Acetylnaphthalene</td>
<td>5.3±0.3</td>
<td>7.65±0.3</td>
</tr>
<tr>
<td>4 Chrysene</td>
<td>9.6±0.3</td>
<td>8.19±0.1</td>
</tr>
<tr>
<td>5 Coronene</td>
<td>8.4±0.4</td>
<td>8.23±0.1</td>
</tr>
<tr>
<td>6 1,2,5,6 DBA</td>
<td>7.7±0.4</td>
<td>7.80±0.2</td>
</tr>
<tr>
<td>7 1,2,3,4-DBA</td>
<td>7.7±1.1</td>
<td>7.89±0.2</td>
</tr>
<tr>
<td>8 Pyrene</td>
<td>8.3±0.7</td>
<td>7.70±0.4</td>
</tr>
<tr>
<td>9 Acridine</td>
<td>2.5±0.4</td>
<td>2.31±1.2</td>
</tr>
<tr>
<td>10 Anthracene</td>
<td>6.4±0.2</td>
<td>6.55±0.7</td>
</tr>
<tr>
<td>11 Perylene</td>
<td>5.6±0.4</td>
<td>5.84±0.8</td>
</tr>
<tr>
<td>12 2,3-Benzanthracene</td>
<td>3.8±0.3</td>
<td>3.56±1.4</td>
</tr>
<tr>
<td>13 Pentacene</td>
<td>1.4±0.5</td>
<td>2.13±1.4</td>
</tr>
<tr>
<td>14 8β-Carotene</td>
<td>1.2±0.2</td>
<td>1.32±1.3</td>
</tr>
</tbody>
</table>

The range of the calculated values was estimated assuming an uncertainty of 0.1 eV in ΔGₑₑ (See Eq. 4.8, 4.9)
The experimental data have also been fitted assuming reversible electron transfer only, without spin restrictions, according to Scheme 4.2. The curve drawn through the points in Fig. 4.5 was calculated using the following equation:

\[ k_{qel} = \frac{k_d}{1 + \frac{k_{el}}{k_{bt} + \frac{k_{el}}{k_{bt}}}} \]  

(Eq. 4.15)

In this case the best fit was achieved for \( \Delta G_{el} = 0.29 \text{ eV} \) and \( k_{el} = 0.036 \). However, the fit based on Scheme 4.3 is better.
3. Quenching by Fe(tert-Bu-tfa)$_3$

The reduction potential of Fe(tert-Bu-tfa)$_3$ ($E_{1/2} = -0.1$V, Table 4.1), is high enough to suggest the possibility of electron transfer. From Figure 4.6 it becomes evident that the quenching rate constant, $k_q$, depends on $\Delta G_{el}$, as might be expected for electron transfer quenching. However, a plot of $\log(k_q)$ vs. $E_T$ (Fig 4.7) gives indications of energy transfer quenching. One can observe that the quenching rate increases when the $^4T_{1g}$ state becomes available and increases further, although slightly, when $\tilde{\nu}_{oo}(T) \approx 1.7$ $\mu m^{-1}$ which is close to $\tilde{\nu}_{o,e5}(1.8$ $\mu m^{-1})$ of the $e_g \rightarrow \pi$ transition (Table 4.1). The quenching rate for donors with $\tilde{\nu}_{oo}(T) \approx 1.83$ $\mu m^{-1}$ agrees well with the maximum quenching rate $5.6 \times 10^9$ $dm^3mol^{-1}s^{-1}$ predicted according to Scheme 4.1. However, in the case of Fe(tert-Bu-tfa)$_3$, one should expect an appreciably lower quenching rate since the steric blocking induced by the bulky -C(CH$_3$)$_3$ and -CF$_3$ groups will result in reduced transmission coefficients. Therefore, energy transfer alone is not sufficient to explain quenching by Fe(tert-Bu-tfa)$_3$. Competitive energy transfer and reversible electron transfer quenching, as described by Scheme 4.3, is more likely. Scheme 4.3 and the relevant equations derived for quenching by Fe(acac-CN)$_3$ apply as well in the present case.

Using the energy transfer parameters obtained for Fe(dpm)$_3$ the best fit of the experimental results requires the following values:

Quencher's transitions:

$\tilde{\nu}_{oo}$ (Q*) (Corresponding to $^4T_{1g} + ^6A_{1g}$) $= 0.84$ $\mu m^{-1}$
$\tilde{\nu}_{oo}$ (Q*) (Corresponding to $^4T_{2g} + ^6A_{1g}$) $= 1.33$ $\mu m^{-1}$
$\tilde{\nu}_{oo}$ (Q*) (Corresponding to $^6CT$ $e_g \rightarrow \pi$) $= 1.7$ $\mu m^{-1}$

Intrinsic barriers:

$^4\Delta G^\ddagger(0)$ (Corresponding to $^4T_{1g}$) $= 0.03$ eV
$^4\Delta G^\ddagger(0)$ (Corresponding to $^4T_{2g}$) $= 0.03$ eV
$^6\Delta G^\ddagger(0)$ (Corresponding to $^6CT$) $= 0.055$ eV
$^6\Delta G^\ddagger_{el}(0) = 8\Delta G^\ddagger_{el}(0)$ $= 0.24$ eV
Transmission coefficients:

\[
\begin{align*}
&{^4\kappa}_{en} \quad \text{(Corresponding to } {^4T_{1g}}) \quad = \ 3.3 \times 10^{-4} \\
&{^4\kappa}_{en} \quad \text{(Corresponding to } {^4T_{2g}}) \quad = \ 1.8 \times 10^{-4} \\
&{^6\kappa}_{en} \quad \text{(Corresponding to } {^6CT}) \quad = \ 3.1 \times 10^{-3} \\
&{^6\kappa}_{el} = {^6\kappa}_{el} \quad = \ 0.0082 
\end{align*}
\]

The experimental and the calculated quenching constants are listed in Table 4.4 below:

<table>
<thead>
<tr>
<th>DONOR</th>
<th>Experimental</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Benzophenone</td>
<td>2.4±0.3</td>
<td>3.29±0.5</td>
</tr>
<tr>
<td>2 Phenanthrene</td>
<td>6.6±0.2</td>
<td>6.17±0.21</td>
</tr>
<tr>
<td>3 2-Acetylnaphthalene</td>
<td>4.2±0.2</td>
<td>5.02±0.55</td>
</tr>
<tr>
<td>4 Chrysene</td>
<td>5.6±0.4</td>
<td>5.98±0.27</td>
</tr>
<tr>
<td>5 Coronene</td>
<td>6.8±0.2</td>
<td>6.15±0.23</td>
</tr>
<tr>
<td>6 1,2,5,6-DBA</td>
<td>4.7±0.5</td>
<td>5.20±0.32</td>
</tr>
<tr>
<td>7 1,2,3,4-DBA</td>
<td>4.0±0.4</td>
<td>5.23±0.47</td>
</tr>
<tr>
<td>8 Pyrene</td>
<td>6.0±0.4</td>
<td>4.74±0.60</td>
</tr>
<tr>
<td>9 Acridine</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>10 Anthracene</td>
<td>3.2±0.3</td>
<td>3.09±0.92</td>
</tr>
<tr>
<td>11 Perylene</td>
<td>3.2±0.3</td>
<td>2.52±0.94</td>
</tr>
<tr>
<td>12 2,3-Benzanthracene</td>
<td>1.0±0.09</td>
<td>1.01±0.75</td>
</tr>
<tr>
<td>13 Pentacene</td>
<td>0.16±0.05</td>
<td>0.45±0.57</td>
</tr>
<tr>
<td>14 Β,Β-Carotene</td>
<td>0.28±0.03</td>
<td>0.21±0.40</td>
</tr>
</tbody>
</table>

The range of the calculated values was estimated assuming an uncertainty of 0.1 eV in \( \Delta G_{el} \)
FIGURE 4.6 Dependence of the bimolecular quenching rate constant $k_q$ on the free energy change $\Delta G_{el}$ for electron transfer to Fe(tert-Bu-tfa)$_3$. The curve was calculated according to Scheme 4.2.
FIGURE 4.7 Dependence of the bimolecular quenching rate constant $k_q$ on donor triplet energies. Arrows marked with filled squares (■) and circles (●) indicate electronic transitions of $\text{Fe(tert-Bu-tfa)}_3$ and $\text{Fe(dpm)}_3$ respectively.
The parameters which were used to fit the results are associated with properties of the excited states of the quenchers. In order to explain energy transfer quenching of triplet pentacene by Fe(bpdo)$_3$, it is necessary to use a $\tilde{v}_{00}(4T_{1g})$ value of less than 0.84 $\mu$m$^{-1}$. Considering the uncertainty of 1 $\mu$m$^{-1}$ in $\tilde{v}_{00}(^3D^*)$ for triplet pentacene, the value used agrees with $\tilde{v}_{00}(4T_{1g})$ within experimental error as it has been pointed out\(^{33}\) in the case of Fe(acac)$_3$. The quenching constant of $\beta,\beta$-carotene is considerably high ($k_q=0.3\times10^9$dm$^3$mol$^{-1}$s$^{-1}$) and this was not possible to explain even allowing for electron transfer quenching. The values of $\tilde{v}_{00}(4T_{2g})$ are in agreement with those listed in Table 4.1. The $\pi^g \rightarrow \pi$ transition however, is 0.05 - 0.1 $\mu$m$^{-1}$ lower than the corresponding $\tilde{v}_{00}$ value.

The $^{\Delta G_{en}}(0)$ values for the $4T_{1g}$ and $4T_{2g}$ states are those (0.03 eV) proposed\(^{33}\) for Fe(acac)$_3$, Fe(tfac)$_3$ and Fe(hfac)$_3$. A larger value of $^{6}\Delta G_{en}(0)$ in the range 0.06-0.084 eV is necessary to fit the results of Fe(dpm)$_3$ and Fe(bpdo)$_3$. However, one may obtain satisfactory fits for Fe(acac)$_3$ quenching using $^{6}\Delta G_{en}(0)$ values in the range 0.04-0.07 eV.

In Table 4.5 are given the transmission coefficients and intrinsic barrier values for energy and reversible electron transfer quenching by tris($\beta$-dionato)iron(III) compounds determined in this work, or taken from the literature.

The transmission coefficients for energy transfer to $4T_{1g}$ and $4T_{2g}$ states of Fe(bpdo)$_3$ and Fe(dpm)$_3$ reflect the degree of the steric effect of the bulky tert-butyl groups on these low lying ligand field states. Replacement of one tert-butyl substituent with hydrogen apparently reduces the steric hindrance and allows more effective overlap between the donor and acceptor orbitals. Thus for Fe(bpdo)$_3$ $\kappa(4T_{1g}) = 1\times10^{-3}$ is 12 times the corresponding value of Fe(dpm)$_3$ ($\kappa(4T_{1g}) = 8.2\times10^{-5}$, Table 4.5). The Dexter equation (Eq. 1.12) can provide the means for quantitative predictions of the effect of the steric blocking if the values of the parameters involved were known. However, some approximations can be made. Since the absorption spectra of
TABLE 4.5 Transmission coefficients, κ, and intrinsic barriers, ΔG£(0), for energy and electron transfer to tris(β-dionato)iron(III) chelates, as determined from the best fits of experimental results, with $k_d=1.0\times10^{10}$ dm$^3$ mol$^{-1}$ s$^{-1}$ and $k_d=1.2\times10^{10}$ s$^{-1}$.

<table>
<thead>
<tr>
<th>Quencher</th>
<th>$\kappa_{\text{en}}(^4T_{1g})$</th>
<th>$\kappa_{\text{en}}(^4T_{2g})$</th>
<th>$\kappa_{\text{en}}(^6\text{CT})$</th>
<th>$\kappa_{\text{el}}=\kappa_{\text{el}}$</th>
<th>$\Delta G_{\text{en}}(0)$</th>
<th>$\Delta G_{\text{el}}(0)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(dpm)$_3$</td>
<td>$8.2\times10^{-5}$</td>
<td>$6.5\times10^{-5}$</td>
<td>$7.7\times10^{-4}$</td>
<td>-</td>
<td>0.065</td>
<td>-</td>
</tr>
<tr>
<td>Fe(acac)$_3$</td>
<td>$5.9\times10^{-4}$</td>
<td>$2.9\times10^{-4}$</td>
<td>$5.4\times10^{-3}$</td>
<td>-</td>
<td>0.04</td>
<td>-</td>
</tr>
<tr>
<td>Fe(tfac)$_3$</td>
<td>$5.9\times10^{-4}$</td>
<td>$2.9\times10^{-4}$</td>
<td>$5.4\times10^{-3}$</td>
<td>7.2$\times10^{-3}$</td>
<td>0.04</td>
<td>0.26±0.02</td>
</tr>
<tr>
<td>Fe(hfac)$_3$</td>
<td>$5.9\times10^{-4}$</td>
<td>$2.9\times10^{-4}$</td>
<td>$5.4\times10^{-3}$</td>
<td>16$\times10^{-3}$</td>
<td>0.04</td>
<td>0.26±0.02</td>
</tr>
<tr>
<td>Fe(tert-Bu-tfa)$_3$</td>
<td>$3.3\times10^{-4}$</td>
<td>$1.8\times10^{-4}$</td>
<td>$3.1\times10^{-3}$</td>
<td>8.2$\times10^{-3}$</td>
<td>0.055</td>
<td>0.24</td>
</tr>
<tr>
<td>Fe(acac-CN)$_3$</td>
<td>$9.8\times10^{-4}$</td>
<td>$8.2\times10^{-4}$</td>
<td>$8.2\times10^{-3}$</td>
<td>0.049</td>
<td>0.04</td>
<td>0.29±0.01</td>
</tr>
<tr>
<td>Fe(bpdo)$_3$</td>
<td>$1\times10^{-3}$</td>
<td>$2.3\times10^{-4}$</td>
<td>$9\times10^{-3}$</td>
<td>-</td>
<td>0.078±0.006</td>
<td>-</td>
</tr>
</tbody>
</table>

a. Experimental results taken from ref. 66 (See also pages 79, 80)
b. Values taken from ref. 33
Fe(bpdo)$_3$ and Fe(dpm)$_3$ do not differ, it can be assumed that for the same donor, the spectral overlap integral and the other parameters will have constant values for both quenchers. For the effective range for electron exchange, Q, a value of 0.1 nm may be accepted. It is reasonable to suggest that the distance between donor and acceptor, R, is determined by the Van der Waals radii of the substituents of the chelate ring. For Fe(dpm)$_3$ R=0.325 nm, which is the Van der Waals radius of the C(CH$_3$)$_3$ group. The ratio of the transmission coefficients $\kappa_{en}(4^T_{1g})$ of Fe(bpdo)$_3$ and Fe(dpm)$_3$ equals to the ratio of the corresponding $\kappa_{et}$, since $\gamma_{0,4^T_{1g}}$ is practically the same and the distortion of this state does not differ for both complexes. Agreement with the experimental data requires for Fe(bpdo)$_3$ a value of R=0.20 nm, which is close to the average, 0.22 nm, of the radius of C(CH$_3$)$_3$ and the C-H distance (0.11 nm). The ratio of the $\kappa_{en}(4^T_{1g})$ values of Fe(acac)$_3$ and Fe(dpm)$_3$ however, does not agree with that predicted by the Dexter equation. According to the same equation the transmission coefficients $\kappa_{en}(4^T_{1g})$ of Fe(bpdo)$_3$ and Fe(acac)$_3$ should be equal. However, $\kappa_{en}$ of Fe(bpdo)$_3$ is 1.7 times that of Fe(acac)$_3$.

In the case of Fe(acac-CN)$_3$ reversible electron transfer predominates. The contribution of energy transfer was determined by the quenching constant of acridine, which is quenched mainly by energy transfer to $4^T_{2g}$ and $4^T_{1g}$ states. The energy transfer parameters of Fe(acac)$_3$ with increased transmission coefficients were suitable for this purpose.

The average of the transmission coefficients for energy transfer to Fe(acac)$_3$ and Fe(dpm)$_3$ were used for Fe(tert-Bu-tfa)$_3$. The $\Delta G_{el}^+(0)$ values are 0.29±0.1 eV for Fe(acac-CN)$_3$ and 0.24eV for Fe(tert-Bu-tfa)$_3$ (Table 4.5). These values are in agreement with those proposed for Fe(tfac)$_3$ and Fe(hfac)$_3$ (Table 4.5). The transmission coefficients $\kappa_{el}$ for electron transfer are 0.049 for Fe(acac-CN)$_3$ and 0.008 for Fe(tert-Bu-tfa)$_3$. Comparison of these values with those proposed for Fe(tfac)$_3$ and Fe(hfac)$_3$ shows the influence of the substituents of the chelate ring on the efficiency of electron transfer.
Thus the transmission coefficient $\kappa_{el}$ of Fe(tert-Bu-tfa)$_3$ is 0.0082, while that of Fe(tfac)$_3$ is 0.007. This might seem contrary to the expected. However, one should consider that for Fe(ter-Bu-tfa)$_3$ the average of the transmission coefficients for energy transfer to Fe(acac)$_3$ and Fe(dpm)$_3$ were used, while the fit of the quenching results of Fe(tfac)$_3$ was based on the energy transfer parameters of Fe(acac)$_3$. Therefore, in the case of Fe(tert-Bu-tfa)$_3$, energy transfer is limited and electron transfer is increased.

The transmission coefficient of Fe(acac-CN)$_3$ (0.049) is three times that of Fe(hfac)$_3$ (0.016). $\kappa_{el}$ is related to the magnitude of the electronic interaction between the excited donor and acceptor. In the case of Fe(acac-CN)$_3$ the $\pi$-system of the ligand is extended over the -CN group, thus offering better donor-acceptor orbital overlap as compared with Fe(hfac)$_3$. In addition, if one considers the ability of the empty $p_{\pi}$ orbitals of the -CN group to accommodate an electron, then a higher $\kappa_{el}$ value for Fe(acac-CN)$_3$ than that of Fe(hfac)$_3$ might be expected.
CONCLUSIONS

From the quenching results, their treatment and the discussion, the following conclusions may be drawn:

1. All three coordination complexes examined in this work are very efficient quenchers of triplet states of organic compounds in benzene solution.

2. The mechanism of quenching is electronic energy transfer in one, and electronic energy transfer together with competitive reversible electron transfer in two of the three cases.

3. Reversible electron transfer quenching becomes more important as the reduction potential of the quencher increases.

4. The spectroscopically determined energies of the quencher transitions are in good agreement with those required to fit the quenching results.

5. The steric effect of the substituents of the chelate ring of the ligands affects the efficiency of quenching by energy transfer to the low lying excited states of the quencher. Bulky substituents e.g. -C(CH₃)₃ reduce the quenching efficiency. In an attempt to rationalize this effect by using the Dexter equation, it was found that it may be related to the Van der Waals radii of the substituents. This treatment, however, did not give satisfactory results in all cases.

6. The transmission coefficients for electron transfer, $\kappa_{el}$ were increased, compared with literature values. No obvious correlation between the reduction potential of the quencher and $\kappa_{el}$ was found. However, electron attracting groups e.g. -CF₃, and groups that extend the $\pi$-system of the chelate ring e.g. -CN, favour high values of $\kappa_{el}$.

7. The $\Delta G_{en}^{\dagger}(0)$ and $\Delta G_{el}^{\dagger}(0)$ values derived in this work are in agreement with literature values proposed for tris(β-dionato)iron(III) chelates.
REFERENCES

23. V.L. Ermolaev, Sov. Physics, Doklady, 6, 600 (1967)
43. V. Balzani, F. Boletta, F. Scandola, J. Amer. Chem. Soc.,102, 2152(1980), and references therein
82. A. Farmillo, Ph.D. Thesis, University of East Anglia, 1974
APPENDIX I
Program used to transfer data from DL417 to PET Commodore

PRINT"-------------------------------" "
PRINT" PROGRAM FOR DL417 DATA RECORDING " "
PRINT"-------------------------------" "
PRINT" THE DATA DISKETTE SHOULD BE IN DRIVE 1 " "
PRINT" IS IT IN DRIVE 1? (Y/N)" PRINT... AND PRESS RETURN" INPUT$:INPUT$="Y" THEN 100: IFN$="Y" THEN 50 PRINT"2": PRINT" SET THE DL417 IN DATA OUTPUT MODE " "
PRINT" TYPE THE NUMBER OF CHANNELS " "
INPUT$:DIM$(3+4095+NC+2):K=1:M=1:PRINT"0" "
PRINT" TYPE THE SAMPLE DETAILS " "
INPUT"DOOR":DO$ "
INPUT"QUENCHER":OU$ "
INPUT"QUENCHER CONCENTRATION":OC$ "
INPUT"SOLVENT":SO$ "
INPUT"RECORDING WAVELENGTH":WL$ "
INPUT"DATE":DA$ "
PRINT"3" PRINT"IF YOU ARE RECORDING... " "
PRINT"1. BASE LINE,TYPE " +OU$+"BL" "
PRINT"2. TRANSIENTS,TYPE " +OU$+"TP1< OR TP2,TP3...ACCORDINGLY>" "
PRINT"3. SCATTER,TYPE " +OU$+"SC" "
PRINT"...AND PRESS RETURN" INPUT$:PRINT"3" "
00SUB400 "
00SUB500 "
00SUB620 "
00TO1000 "
PRINT"... READING " ;OU$; " ;DO$; " ;" DATA" "
POKE59469,0 "
POKE59469,255 "
FORI=1TO21 "
POKE59468,253 "
IFPEEK(59469)AND2=0THEN450 "
X=PEEK(59457) "
POKE59468,221 "
NEXT "
FORI=0TO(3+4095+NC+2):POKE59468,253 "
IFPEEK(59469)AND2=0THEN500 "
D(I)=PEEK(59457) "
PRINTD(I) "
POKE59468,221 "
NEXT:PETUPN "
K=K+1:OPEN$2,8,15 "
INPUT$:A$;B$;C$;D$ "
IFVAL(A$)<1 THENPRINTA$;B$;C$;D$ "
OPEN$2,8,K,"1:"+S$+",SEQ.W" "
INPUT$:A$;B$;C$;D$ "
IFVAL(A$)<1 THENPRINTA$;B$;C$;D$ "
PRINT$1,DO$;CHR$(13) ;" "
PRINT$1,OU$;CHR$(13) ;" "
PRINT$1,OC$;CHR$(13) ;" "
PRINT$1,SO$;CHR$(13) ;" "
PRINT$1,NC$;CHR$(13) ;" "
PRINT$1,DA$;CHR$(13) ;" "
FORI=0TO(3+4095+NC+2) "
PRINT$1,D(I);CHR$(13) ;" "
INPUT$:A$;B$;C$;D$ "
IFVAL(A$)<1 THENPRINTA$;B$;C$;D$
0 NEXTI
0 CLOSE1:CLOSE2
0 RETURN
0 OPEN2,1,15
0 INPUT#2,A$,B$,C$,D$
0 IF VAL(A$)<>0 THEN PRINT#A$,B$,C$,D$
0 OPEN1,8,K,”11″+S$,”,SEO,R”
0 INPUT#2,A$,B$,C$,D$
0 IF VAL(A$)<>0 THEN PRINT#A$,B$,C$,D$
0 INPUT#1,DO$
0 INPUT#1,OU$
0 INPUT#1,OC$
0 INPUT#1,SO$
0 INPUT#1,WL$
0 INPUT#1,DA$
0 FORI=0TO34096/NC+2
0 INPUT#1,D$
0 D(I)=0:NEXT
0 PRINT”DONOP:“:DO$
0 PRINT”QUENCHER:“:OU$
0 PRINT”QUENCHER CONCENTRATION:“:OC$
0 PRINT”SOLVENT:“:SO$
0 PRINT”RECORDING WAVELENGTH:“:WL$
0 PRINT”DATE:“:DA$
0 FORI=0TO34096/NC+2:PRINT D(I);” “;:NEXT
0 CLOSE1:CLOSE2
0 PETUP
00 PRINT” PUT IT IN DRIVE 1....” ”;GOTO1100
00 STOP
APPENDIX II

Program used to transfer data from DL922 Transient Recorder to PET Commodore

```
PRINT"\nPRINT"PROGRAM FOR DL922 DATA RECORDING"\nPRINT"\nPRINT"THE DATA DISKETTE SHOULD BE IN DRIVE 1."
PRINT"IS IT IN DRIVE 1? (Y."'")":PRINT"... AND PRESS RETURN"
INPUT$:IF IN$=""THEN1000:IF IN$=""THEN60
DIM(2548):K=1:M=1
PRINT"TYPE THE DETAILS"
INPUT"DONOR":DO$" INPUT"QUENCHER":QU$ INPUT"QUENCHER CONCENTRATION":QC$ INPUT"SOLVENT":SO$ INPUT"RECORDING WAVELENGTH":WL$ INPUT"DATE":DA$ PRINT"PREVIOUS FILE NAME...";S$ PRINT"INPUT NEW FILE NAME..." INPUT$:=PRINT"\nGOSUB480
GOSUB600
PRINT"ANOTHER FUN... ":IN$" INPUT$:=""THEN1000
GOTO100
PPRINT... READING ";OU$": "DO$": "DATA" POKES59459,0:IF PEK(59459)=F0PI=TO511 POKES59459,221 IFPEK(59459)AND2=0THEN510 D(I)=PEK(59457):POKE59468,253 PRINT,D,I" NEXT:RETURN
K=K+1:OPEN2,.B.15
INPUT2,A$,B$,C$,D$ IF VAL(A$)<0 THEN PRINTA$,B$,C$,D$ OPEN1,.K,"1:"+S$","SEQ.W" INPUT2,A$,B$,C$,D$ IF VAL(A$)<0 THEN PRINTA$,B$,C$,D$ PRINT1,DO$;CHR$(13)$; PRINT1,OU$;CHR$(13)$; PRINT1,OC$;CHR$(13)$; PRINT1,SO$;CHR$(13)$; PRINT1,WL$;CHR$(13)$; PRINT1,DA$;CHR$(13)$; FORI=0TO511 PRINT1,D(I);CHR$(13)$; INPUT2,A$,B$,C$,D$ IF VAL(A$)<0 THEN PRINTA$,B$,C$,D$ NEXTI
CLOSE1+CLOSE2
PETURN
PRINT"DONOR---------------------":DO$
PRINT"QUENCHER-----------------":OU$
PRINT"QUENCHER CONCENTRATION":QC$
PRINT"SOLVENT-------------------":SO$
PRINT"RECORDING WAVELENGTH---":WL$
PRINT"DATE---------------------":DA$
RETURN
0 PRINT"PUT IT IN DRIVE 1....":GOT01100
0 STOP
```