

Photophysical Pathways in Metal Complexes

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The photochemistry and photophysics of inorganic complexes are extremely active areas of research (1-4). This is because of the intrinsic interest of these complex systems and because of their potential applications in such areas as solar energy conversion (4), synthesis, lasers, and light intensity measurements (5). Crucial to the understanding of the spectroscopy and photochemistry of inorganic complexes as well as to the rational design of useful systems is a knowledge of the paths of energy degradation in these systems. This knowledge requires understanding the dynamics, the pathways, and the efficiencies of interconversion between different excited states and between excited states and the ground state. Also, the efficiencies and rates of energy transfer between different molecules can have a decisive effect on the successful utilization of new chemical systems.

In this article we will focus on the photophysical relaxation pathways for decay of excited states. We will base our analysis on the Jablonski diagram for describing such processes in organic molecules (6-9). We will point out several important differences between inorganic and organic systems; in particular we will focus on the experimental methods used to determine the important properties of the systems. Finally, applications of these principles to several important platinum metal complex systems will be described.

Excited State Model

Figure 1 shows a Jablonski diagram. We have indicated a singlet ground state and singlet and triplet excited states. The organization and symbolism is similar to that given by Kasha and by Whan and Crosby (8, 9). Such a state diagram is common for a variety of luminescent inorganic complexes with metal ions having d^6 or d^8 electronic configurations (1, 2). However, as pointed out in earlier papers in this volume, the variety of electronic configurations of transition metal ions provides an abundance of states other than singlets and triplets. For example, Cr(III) with a d^3 configuration possesses a quartet ground state and quartet and doublet excited states. The important feature of all systems is that the excited states can have multiplicities that are the same as or different from the ground state.

The ground state is denoted by S_0 and excited states by S_1 ,

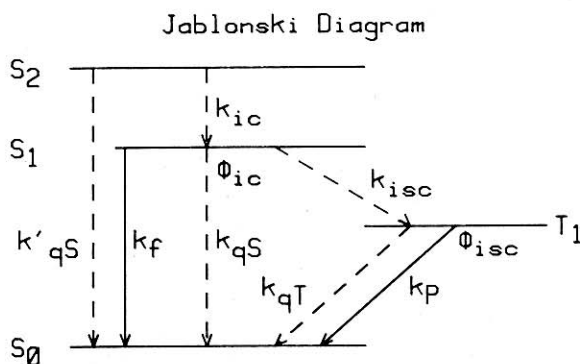


Figure 1. Schematic energy level diagram of a molecule showing the possible paths of energy degradation. Solid lines (—) represent radiative processes which occur with the emission of a photon, while dashed lines (---) represent nonradiative processes. Singlet states are denoted by S 's and triplet states by T 's.

S_2 , and T_1 , although there are higher singlet and triplet states. Emissive pathways are indicated by solid arrows while non-radiative pathways use broken arrows. Rate constants for each pathway are indicated by k 's. A nonradiative relaxation between two states of the same multiplicity (e.g., $S_2 \rightarrow S_1$) is called an interconversion while a relaxation between states of different multiplicity (e.g., $S_1 \rightarrow T_1$) is an intersystem crossing. A radiative or emissive transition between states of the same multiplicities (e.g., $S_1 \rightarrow S_0$) is referred to as a fluorescence. If an emissive transition involves a change of multiplicity (e.g., $T_1 \rightarrow S_0$), it is referred to as a phosphorescence.

In the spectroscopy of organic systems the distinction between a fluorescence and a phosphorescence can frequently be made phenomenologically on the basis of lifetime. If the emission lifetime is milliseconds or longer, the emission is a phosphorescence. If the lifetime is a few nanoseconds, the emission is a fluorescence. In inorganic systems, the distinctions are much more blurred.

Nonradiative transitions terminating on the ground state are quenching pathways. Efficiencies of relaxation between different levels are denoted by ϕ 's. The efficiency of relaxation from S_2 to S_1 is denoted by ϕ_{ic} , and ϕ_{isc} is the efficiency of intersystem crossing from S_1 to T_1 .

We have included an internal conversion quenching pathway from S_2 to S_0 which bypasses S_1 . Although we label this an internal conversion, a radiative coupling to the ground state is also possible. Emissions from other than the lowest excited state of a given multiplicity are rare in organic and inorganic systems, and we consider predominantly radiationless deactivation.

As shown in other papers in this volume, this model is rather simplistic. Population of higher triplet states can occur. Thermal equilibration of multiple levels of the same or of different multiplicities is possible. Further, we have considered all nonemissive deactivational pathways as photophysical, but in fact many photochemical pathways are so fast that they can compete successfully with radiative and photophysical deactivation. The inclusion of photochemical pathways in Figure 1 is, however, straightforward.

We comment briefly on the magnitude of the different rate constants for organic and inorganic systems. Where the transitions do not involve a change in multiplicity, inorganic and organic systems tend to be similar. For example both have k_{ic} 's typically on the order of $\geq 10^{12} \text{ s}^{-1}$. Also, k_f 's are on the order of 10^8 s^{-1} .

Where changes in multiplicity are involved, the differences can be substantial. These differences arise in part due to the larger spin orbit coupling constants associated with the high atomic number metal ions relative to C, H, and N. The increased spin orbit coupling causes mixing of singlet and triplet states which results in a breakdown of the selection rules prohibiting changes of multiplicity. For organic molecules containing low atomic number atoms, intersystem crossing processes are formally forbidden and therefore very slow or hindered. The k_{isc} 's for organic systems are typically $1-1000 \times 10^6 \text{ s}^{-1}$. In inorganic systems where spin orbit coupling is greater, k_{isc} 's of $10^9-10^{12} \text{ s}^{-1}$ are the rule rather than the exception. Indeed, the k_{isc} 's of inorganic systems are frequently so fast as to be indistinguishable from internal conversions which have no forbiddenness.

Even greater discrepancies occur in k_p . In organic systems, values larger than 100 s^{-1} are rare and k_p 's can easily fall to 0.02 s^{-1} . In inorganic systems k_p 's as slow as 10 s^{-1} are sometimes observed, but these typically would be for emissions which are almost exclusively localized in the organic portions of a metal complex and thus more closely resemble organic systems (10). More commonly, k_p 's for inorganic complexes might vary from 10^2 – 10^5 s^{-1} with most systems falling in the upper two decades of that range.

Experimental Methods

Luminescence Lifetimes and Yields

We now describe briefly the measurement of excited state lifetimes. We also show how this information can be related to the fundamental parameters in Figure 1.

If the molecules fluoresce or phosphoresce with any appreciable efficiency, the excited state lifetimes of S_1 or T_1 are, generally, easily measured by pulse techniques (11, 12). A short pulsed optical flash is used to excite the sample, and the luminescence decay following termination of the flash is monitored and analyzed. If the flash is much faster than the lifetime to be measured and the rate constants for feeding the emitting level, then the observed decay will be an exponential. The decay can then be analyzed by the normal methods (e.g., a semilogarithmic plot of intensity versus time for a first-order decay). The observed lifetimes for the fluorescence, τ_f , and for the phosphorescence, τ_p , are given by

$$\tau_f = 1/(k_f + k_{qS} + k_{isc}) \quad (1)$$

$$\tau_p = 1/(k_p + k_{qT}) \quad (2)$$

If, however, the emission decay times are short with respect to the excitation pulse, the normal semilogarithmic plot of intensity versus time fails to yield accurate lifetimes. There is no region of the decay which is free from continued pumping by the flash. Indeed, one is likely to measure the lifetime of the decaying edge of the lamp rather than the desired sample parameter. Under these conditions a process of deconvolution must be used to extract τ from both the observed flash and the decay (11, 12).

Even if the sample does not emit, it is possible to measure the decay of the excited state by flash photolysis methods where one excites the sample with an intense source and then follows the decay by means of absorption spectroscopy (13). We mention only in passing the fascinating subject of picosecond excited state lifetime measurements; the interested reader is referred to the proceedings of a Division of a Chemical Education Symposium, "Lasers From The Ground Up," for details (14). Experimental and mathematical procedures used in lifetime measurements are given elsewhere (11, 12).

The photon or luminescence yield is the number of photons that would be emitted per photon absorbed by the system. This quantity is so important that an enormous amount of work has gone into its determination. The interested reader is referred to a number of review articles (7, 15–17).

One of the reasons for interest in yields is that they can be used to extract the fundamentally interesting rate constants of the Jablonski diagram. The luminescence efficiencies for fluorescence, ϕ_f , and phosphorescence, ϕ_p , are given by

$$\phi_f(S_1) = k_f/(k_f + k_{qS} + k_{isc}) = k_f\tau_f \quad (3)$$

$$\phi_p(S_1) = \phi_{isc}k_p/(k_p + k_{qT}) = \phi_{isc}k_p\tau_p \quad (4)$$

$$\phi_p(T_1) = k_p/(k_p + k_{qT}) = k_p\tau_p \quad (5)$$

$$\phi_{isc} = k_{isc}/(k_f + k_{qS} + k_{isc}) \quad (6)$$

where ϕ_{isc} is the efficiency of intersystem crossing between S_1 and T_1 . The parenthetical S_1 or T_1 denote the state into which the photons are absorbed.

Note that from eqns. (3)–(6), the τ 's, and the ϕ 's, it is possible to obtain fundamentally important rate constants. From τ_f and $\phi_f(S_1)$ one can calculate the radiative rate constant for fluorescence k_f . Then $1/k_f$ is the lifetime of S_1 if there were no quenching of the excited state to the ground state or intersystem crossing to the triplet manifold. Frequently, $1/k_f$ is referred to as the radiative or natural lifetime. Because the term "natural lifetime" seems to some to imply a directly measureable quantity, the author prefers the use of "radiative lifetime." Similarly, k_p can also be obtained if ϕ_{isc} is known or if $\phi_p(T_1)$ is measureable. We will return to methods of measuring ϕ_{isc} later. The nonradiative rate constants can also be obtained. Once k_p or k_f is known, k_{qT} and $(k_{qS} + k_{isc})$ can be calculated from eqns. (3)–(6).

Measurement of ϕ_{isc}

For luminescent materials ϕ_{isc} is readily measured. One merely measures the photon yield with excitation into S_1 and into S_2 . Both $\phi_p(S_1)$ and $\phi_f(S_1)$ are given by eqns. (3)–(6) while for excitation into S_2 we have

$$\phi_p(S_2) = \phi_{isc}\phi_{isc}\phi_p(T_1) \quad (7)$$

$$\phi_f(S_2) = \phi_{isc}\phi_f(S_1) \quad (8)$$

$$\phi_{isc} = \phi(S_2)/\phi(S_1) \quad (9)$$

where ϕ can be for a fluorescence or phosphorescence emission. Clearly, this approach can be extended to any additional upper states.

While the measurement of absolute photon yields is difficult, only relative yields are required in eqns. (7)–(9) since the proportionality constant necessary for the absolute yields will divide out. Relative yields are readily measured using a spectrofluorimeter where the excitation light output is calibrated versus wavelength (7, 15–17). One then measures the relative emission intensity versus excitation wavelength for excitation in the different levels and corrects for the amount of excitation light absorbed. The resulting plot is a relative ϕ_{isc} versus wavelength plot. This can be corrected to true ϕ_{isc} 's versus wavelength by dividing each point by the relative yield on excitation into S_1 . Generally, in the absence of upper excited state chemistry, $\phi_{isc} = 1$. We will give examples of this approach later.

Measurement of ϕ_{isc}

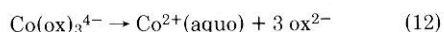
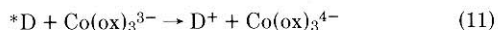
The ϕ_{isc} is frequently more difficult to measure. If the $S_0 \rightarrow T_1$ spin-forbidden transition is allowed enough to absorb appreciably, then an approach analogous to that for measuring ϕ_{isc} is suitable. One measures the relative photon yield for excitation into S_1 and T_1 . From eqns. (3)–(6)

$$\phi_{isc} = \phi_p(S_1)/\phi_p(T_1) \quad (10)$$

As for ϕ_{isc} , only relative rather than absolute yields are required. The problem here centers on being able to make the $\phi_p(T_1)$ determination. If the $S_0 \rightarrow T_1$ absorption is too weak or not well resolved from the $S_0 \rightarrow S_1$ absorption, $\phi(T_1)$ cannot be determined by this approach.

An attractive approach for setting lower limits on ϕ_{isc} uses photochemical or photophysical scavenging of the T_1 state to count the number of triplets formed per photon absorbed into S_1 . Suitable counting reactions include irreversible chemical reactions, fully reversible reactions, energy transfer followed by excited state reactions of the acceptor, or energy transfer followed by monitoring the luminescence of the acceptor.

We now describe several systems which have proved useful for platinum metal complexes with α -diimine ligands. Cobalt(III) complexes undergo irreversible photochemistry with $^*Ru(II)$ excited states. For example, $Co(ox)_3^{3-}$ ($ox^{2-} = C_2O_4^{2-}$) with $[Ru(bpy)_3]^{2+}$ ($bpy = 2,2'$ -bipyridine) as the donor yields (18)



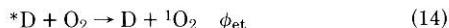
where $D = [\text{Ru}(\text{bpy})_3]^{2+}$ and $D^+ = [\text{Ru}(\text{bpy})_3]^{3+}$. The back reaction of the aquo Co^{2+} species with Ru(III) is thermodynamically not allowed so that Ru(III) formed will persist in solution and the amount formed can be measured spectrophotometrically. The limiting yield of Ru(III) formation corrected to total excited-state quenching is

$$\phi_{\text{lim}}(\text{Ru(III)}) = \phi_{\text{isc}}\phi_{\text{ET}} \quad (13)$$

where ϕ_{ET} is the probability that quenching of the sensitizer will yield separated Ru(III) . Since ϕ_{ET} may not exceed unity, $\phi_{\text{isc}} \geq \phi_{\text{lim}}(\text{Ru(III)})$.

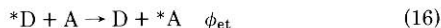
Peroxydisulfate has also proven quite suitable, although two molecules of Ru(III) are formed per quenching event due to the action of the powerfully oxidizing $\cdot\text{SO}_4^-$ radical formed (19). The peroxydisulfate system appears to have many merits, and at least at this time appears to be the most promising simple chemical method. It is colorless which avoids inner filter effects. The oxidation of the sensitizer, while thermodynamically allowed in the ground state, is slow enough to permit carrying out the reaction more or less at one's leisure. The only reservations are that the system has not been examined mechanistically and it has not been tried on more systems to prove its freedom from interferences.

Oxygen has proved a valuable counter (20). Singlet oxygen is formed by quenching of the excited state to yield reactive singlet oxygen which is scavenged by a suitable trap



where ϕ_{et} represents the efficiency of energy transfer to form free singlet oxygen. Tetramethylethylene is an excellent $^1\text{O}_2$ trap. The amount of singlet oxygen formed can be determined by monitoring the oxygen consumption volumetrically or by colorimetric analysis of the hydroperoxide formed. This reaction has been suggested as a chemical actinometer for measuring the intensities of high power lasers (21).

Spectroscopic methods directly count the number of acceptor excited states formed by their luminescence rather than by chemistry.

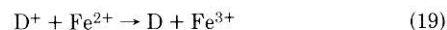
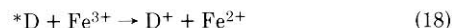


Acceptors have included Cr(III) complexes (22) and more recently laser dyes (23, 24). The laser dyes can have advantages over the Cr(III) complexes. The excited state interaction with the donor and Cr(III) acceptor is so weak that contact energy transfer is required. The contact pair can, however, form a weak complex or so perturb the excited states that quenching of the pair can compete with energy transfer and reduce ϕ_{et} to well below unity. This can result in a weak test because of the resultant large limits on ϕ_{isc} . With suitable organic dyes, however, energy transfer is exclusively by a long range (30–40 Å) resonance transfer (vide infra). Since the donor and acceptor never touch, every quenching event must yield a successful transfer and $\phi_{\text{et}} = 1.00$. All of the counting methods must make corrections for the degree of quenching of *D . In all cases these approaches set lower limits on ϕ_{isc} since ϕ_{ET} or ϕ_{et} may be subunity.

Systems exhibiting fully reversible photochemistry present special problems. The rapidity of the back reaction precludes the standard techniques used for stable systems where one photolyzes the sample and carries out the analysis at one's leisure.

To overcome these problems, pulsed techniques with flash lamps or lasers are used, and one then monitors the transient absorption on a microsecond or nanosecond time scale (25).

Extrapolation back to zero time may be required if the back reaction is too fast with respect to the excitation pulse. A suitable system is Fe^{3+}



where $D = [\text{Ru}(\text{bpy})_3]^{2+}$. Conventional flash photolysis methods are somewhat more difficult to use because of the broad spectral bandpass of the flashlamps. A flash actinometer having absorption characteristics as close as possible to the unknown system is necessary (26). Because of their high monochromaticity, use of pulsed laser sources avoids problems with trying to calculate the amount of light absorbed by the sample. The $[\text{Ru}(\text{bpy})_3]^{2+}/\text{Fe}^{3+}$ system has been suggested as a flash actinometer (26, 27).

We have described a step-excitation method which avoids using expensive, high-power pulsed lasers (27, 28). A more readily available CW laser (as in Raman instruments) is used. The laser is turned on abruptly with a mechanical, electro-optical, or acousto-optical shutter, and the consumption of D is monitored by the loss of emission intensity. From the kinetics of the transient, one can obtain not only ϕ_{ET} but also the rate constant for the back reaction.

Measurement of k_{isc} or k_{ic}

Direct measurement of rates of interconversion or inter-system crossing are possible in principle. One merely excites the upper excited state and watches the buildup of the fluorescence or phosphorescence. In practice such measurements are not easily done because of the enormously high relaxation rates. Indeed the measurement of these luminescence risetimes is fraught with insidious errors. If one uses too long an RC time constant on the measurement system, one sees a risetime which behaves correctly mathematically, but which is nothing more than the RC time constant of the measurement system. Such erroneous results have been reported for Cr(III) and Rh(III) phosphorescence where risetimes of microsecond were reported. It is now known that these values are in the low picosecond domain (29–31).

Risetime measurements have proven useful, however, for setting limits. Before picosecond measurements were made, Stuart and Kirk (32), using a simple single photon counting instrument, showed that k_{isc} for Cr(III) complexes was $\geq 10^8 \text{ s}^{-1}$. Peterson et al. (31), using a 10 nsec N_2 laser pulse and a deconvolution method, were able to show that the intersystem crossing rates in Rh(III) complexes are $\geq 10^{10} \text{ s}^{-1}$. Thus, in favorable systems picosecond resolution is possible using conventional nanosecond instrumentation.

Intermolecular Energy Transfer

Energy transfer between an excited donor and an acceptor can occur by two basic mechanisms (6, 33): 1) a contact exchange interaction; and 2) a long range resonance interaction. In general, both mechanisms require the acceptor level to be below the donor level.

Contact transfer requires an encounter of the donor and acceptor with overlap of their wavefunctions. For energy transfer to be facile, the Wigner spin conservation rule must be satisfied (34). Thus, for the energy transfer reaction to occur in the encounter



The spin states produced by coupling of the spins of *D and A in $^*D/A$ must yield at least one spin state which is in common with the spin states produced by coupling of the spins of D and *A in the final complex $D/^*A$. If S_D and S_A are the spins of *D and A , respectively, then the possible spin states of $^*D/A$ are

$$S_D + S_A, S_D + S_A - 1 \dots |S_D - S_A|$$

Similarly for D/*A we have

$$S_D + S_{*A}, S_D + S_{*A} - 1 \dots |S_D - S_{*A}|$$

Considering a donor and an acceptor with singlet ground states and singlet and triplet excited states, we can derive the spin selection rules for this system. For singlet to singlet energy transfer, the possible spin states of *D/A and S/*A are both 0. Since this state is common to both the precursor and the final energy-transferred complex, energy transfer is allowed. Similarly, triplet-triplet energy transfer is allowed. Triplet to singlet energy transfer is, however, forbidden as the precursor complex has only a state of 1 and the terminal complex has only a state of 0.

A more interesting example is for energy transfer from a normal organic sensitizer with a singlet ground state and singlet and triplet excited states to Cr(III) which has a quartet ground state and doublet and quartet excited states. For triplet energy transfer, *D/A has states of $5/2$, $3/2$, and $1/2$ while D/*A has states of $3/2$ (quartet acceptor) and $1/2$ (doublet acceptor). Since both acceptor complexes have states which match a donor state, singlet energy transfer to doublets and quartets is allowed. A similar analysis shows that for singlet energy transfer, only energy transfer to a quartet excited state is possible.

Contact transfer is diffusion-limited and obeys Stern-Volmer quenching kinetics.

$$\phi_0/\phi - 1 = K_{sv}[Q] \quad (20)$$

$$\tau_0/\tau - 1 = K_{sv}[Q] \quad (21)$$

$$1/\tau = 1/\tau_0 + k_2[Q] \quad (22)$$

$$K_{sv} = k_2\tau_0 \quad (23)$$

k_2 is the bimolecular quenching constant. The Stern-Volmer quenching constant, K_{sv} , equals the reciprocal of the quencher concentration required to shorten the lifetime by a factor of 2 or to decrease the emission intensity by a factor of 2. The emission intensities and lifetimes are ϕ and τ , respectively. The subscript "0" denotes the value in the absence of quencher. In principle, both intensity and lifetime data can yield the same results.

Resonance or Förster transfer involves a coupling of the electronic motions of the excited donor with the acceptor (33). This coupling can occur at distances of >40 Å. It requires a strongly allowed absorption of the acceptor level and good overlap of the donor emission with the acceptor state's absorption. There are, however, no spin restrictions. Thus, triplet to singlet energy transfer can be very facile in Förster transfer.

Contact energy transfer is highly allowed for Ru(II), Os(II), and Ir(III) photosensitizers to a variety of acceptors (3, 4). For example, efficiencies for energy transfer to oxygen to form singlet oxygen approach unity (20, 21).

Resonance energy transfer can also be very efficient. Figure 2 shows the efficiency of energy transfer, ϕ_{et} , from $[\text{Ru}(\text{bpy})_3]^{2+}$ to the laser dye Nile blue A as a function of the dye concentration. The limiting efficiency of energy transfer extrapolated to infinite dye concentration for several different laser dyes is within experimental error of unity (23, 24).

Examples

Bimolecular Quenching and a Physical Chemistry Experiment

Although most measurements reported in the literature are made on expensive, laser-based decay time instruments or expensive spectrofluorimeters, the efficient luminescence of Ru(II) photosensitizers and their relatively long lifetimes make them particularly convenient to use with much less expensive equipment. We have described two physical chemistry experiments using excited state quenching of

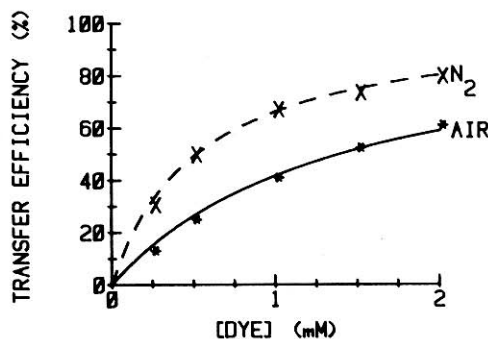


Figure 2. Energy-transfer efficiencies for the energy transfer from $[\text{Ru}(\text{bpy})_3]^{2+}$ to the laser dye Nile blue A. (X) deoxygenated methanol. (*) aerated methanol. The lines are the calculated least-squares best fit. Copyright 1983, The American Chemical Society. Adapted with permission from Reference (24).

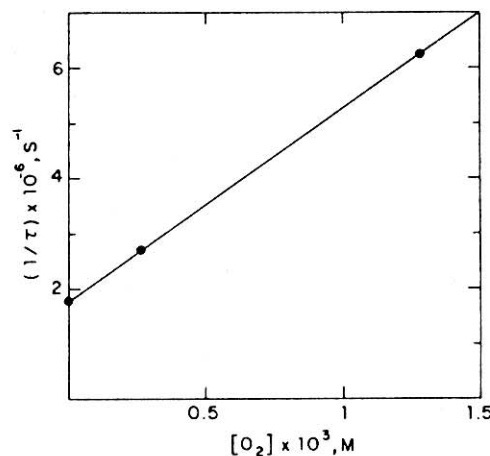


Figure 3. Lifetime intensity quenching plot for deactivation of $\text{Ru}(\text{bpy})_3^{2+}$ by oxygen. Copyright 1976, by the Division of Chemical Education, American Chemical Society. Adapted with permission from Reference (36).

$[\text{Ru}(\text{bpy})_3]^{2+}$ by $[\text{Fe}(\text{CN})_6]^{4-}$ (35) and by O_2 (36). In the first case, intensity quenching data are used while, in the second, lifetime measurements are employed. Although the least expensive spectrofluorimeter was used for this experiment, a filter fluorometer would also work. For the oxygen quenching experiment we used lifetime measurements. An inexpensive (several hundred dollar) lifetime instrument was developed which is capable of resolving, with deconvolution techniques, τ 's below 100 ns. Figure 3 shows a typical lifetime quenching plot taken on this instrument. τ 's range from ~ 160 ns to 600 ns.

Intersystem Crossing and Internal Conversion

We first consider an example of the $d-d$ phosphorescence of $\text{trans-}[\text{Rh}(\text{py})_4\text{Cl}_2]^+$ (37). This system exhibits a classic broad band $d-d$ emission which is greatly Stokes-shifted from the lowest energy absorption. At 77° K the lifetime is 500 μsec . There is no evidence of a fluorescence. Therefore, $k_{qs} + k_{isc} \gg k_f$. We will now show that the intersystem crossing yield approaches unity which implies that $k_{isc} \gg k_{qs}$.

Figure 4 shows the low temperature absorption spectrum, the corrected excitation spectrum, and the relative photon yield as a function of excitation wavelength of $\text{trans-}[\text{Rh}(\text{py})_4\text{Br}_2]^+$. The relatively intense bands at 25 kK and 26 kK ($1 \text{ K} = 1 \text{ cm}^{-1}$) correspond to $S_0 \rightarrow {}^1(d-d)$ transitions. The much weaker band at 20 kK is a spin-forbidden $S_0 \rightarrow {}^3(d-d)$ transition and is the inverse of the emission which peaks at ~ 15 kK.

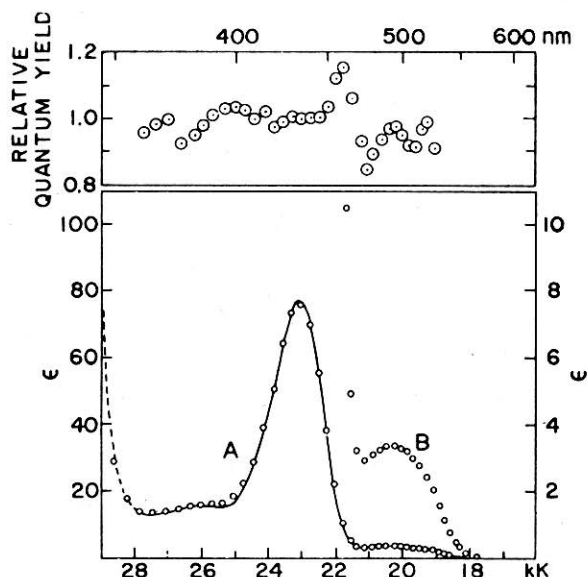


Figure 4. Excitation spectrum of *trans*-dibromotetra(pyridine)rhodium(III) bromide in an ethanol-methanol glass at 77°K. The circles (O) are the corrected excitation spectrum; the smooth curve is the low temperature absorption spectrum. Curve A refers to the scale on the left; curve B refers to the scale on the right. The excitation spectrum has been normalized to the absorption spectrum at 23 kK. Copyright 1970, by The American Chemical Society. Adapted with permission from Reference (37).

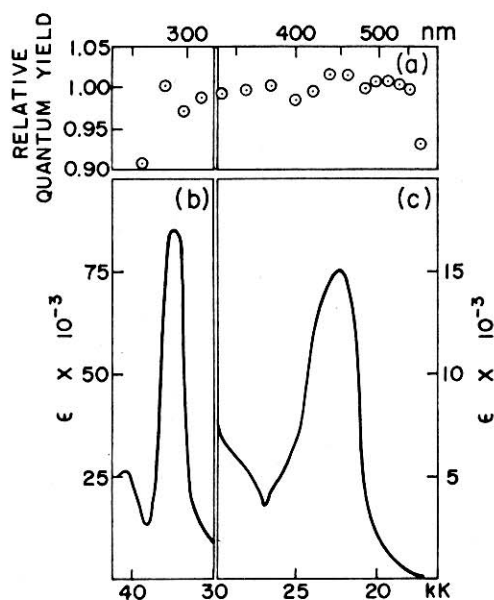


Figure 5. (a) Relative quantum yield and (b,c) absorption spectrum of tris (2,2'-bipyridine)ruthenium(II) chloride in methanol at room temperature. (a) 0.2 g in 5 ml using a 1 cm cell. (b) $6.7 \times 10^{-5} M$ using a 1 cm cell. (c) $6.7 \times 10^{-5} M$ using a 1 cm cell. Copyright 1971 by The American Chemical Society. Adapted with permission from Reference (38).

The corrected excitation spectrum should match the absorption spectrum if ϕ_{ic} and ϕ_{isc} are unity. The invariance of the photon yield on excitation into the different excited singlet states and into the emitting triplet level establishes that $\phi_{ic} = 1.0$ and $\phi_{isc} = 1.0$ within experimental error.

We next consider $[Ru(bpy)_3]^{2+}$ at both room temperature and at 77° K (38). Figure 5 shows the room temperature absorption and relative emission quantum yield as a function of wavelength. The bands below ~ 350 nm are ligand-localized transitions to $^1(\pi-\pi^*)$ states while the less intense bands at

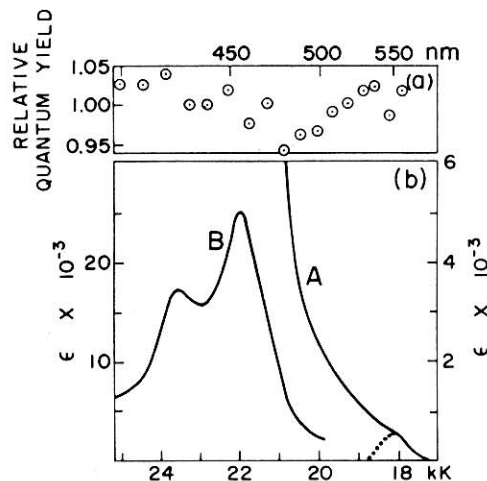


Figure 6. (a) Relative quantum yield and (b) absorption spectrum of tris(2,2'-bipyridine)ruthenium(II) chloride in an ethanol-methanol glass at 77°K (a) $3.4 \times 10^{-7} M$ in a 1.76 cm cell. (b) Curve A refers to the scale on the right: $1.32 \times 10^{-4} M$ in a 1.76 cm cell. Curve B refers to the left hand scale: $2.65 \times 10^{-5} M$ in a 1.76 cm cell. The dashed curve is the estimated position of the singlet triplet absorption. Copyright 1971 by The American Chemical Society. Adapted with permission from Reference (38).

longer wavelength are MLCT transitions. Again the invariance of the yield on excitation into the $\pi-\pi^*$ and CT states shows that $\phi_{ic} = 1.0$. It is noteworthy that the efficiencies of populating the emitting level is independent of the orbital parentage of the state initially excited. This wavelength independence of the emission yield is one of the many attractive features of Ru(II) photosensitizers.

Figure 6 is the low temperature emission spectrum of $[Ru(bpy)_3]^{2+}$ with emphasis on the CT region only. At lower energy than the intense CT transition is a weak absorption feature (~ 18 kK). This weak band has good mirror image symmetry with the CT emission. The intense absorption has been attributed to a ground state to 1CT transition while the weak absorption has been assigned to a transition from the ground state to the emitting 3CT state. The dotted line represents the estimated absorbance of the 3CT transition. We will return to the use of a 3CT label later. The invariance of the photon yield on excitation into the 1CT and 3CT states establishes $\phi_{isc} = 1.0$. Similar results have been obtained at room temperature for a variety of Ru(II) photosensitizers in both water and methanol (39).

The table shows some representative ϕ_{isc} for Ru(II) sensitizers measured by different approaches. It is clear that for

"Intersystem Crossing" Efficiencies for Ruthenium(II) Photosensitizers

Donor	Acceptor	ϕ_{isc}
$[Ru(bpy)_3]^{2+}$	$Co(C_2O_4)_3^{3-}$	$\geq 0.85 \pm 0.05^a$
	Fe^{3+}	$\geq 0.94 \pm 0.02^b$
	$S_2O_8^{2-}$	1.0 ± 0.1^c
	O_2	$\geq 0.85 \pm 0.05^d$
	Dyes	1.00 ± 0.05^e
	Flash Photolysis	1.0 ± 0.1^f
	Spectroscopic	1.00 ± 0.05^g
$[Ru(phen)_3]^{2+}$	Fe^{3+}	$\geq 0.69 \pm 0.02^h$
	$S_2O_8^{2-}$	1.0 ± 0.1^c
	O_2	$\geq 0.75 \pm 0.05^d$
	$Cr(en)_2(CNS)_2^+$	$\geq 0.65^i$
	Spectroscopic	1.00 ± 0.05^g

^a Ref. (18).

^b Ref. (27).

^c Ref. (19).

^d Ref. (20).

^e Ref. (24).

^f Ref. (41).

^g Ref. (39).

^h Ref. (42).

ⁱ Ref. (22).

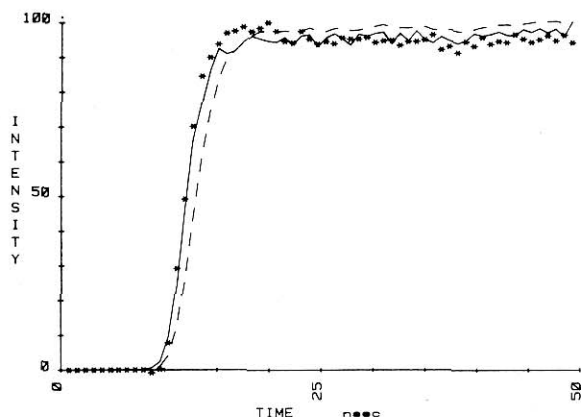


Figure 7. Corrected observed and calculated rise time curves for $[\text{Rh}(\text{bpy})_2\text{Br}_2]^+$ at 77° K: (*) blank corrected results; (—) calculated rise time curve for $\tau_R = 0.0$ ns; (---) calculated rise time curve for $\tau_R = 1.0$ ns where τ_R is the luminescence risetime. See the original paper for details of the calculation and presentation. Copyright 1979 by The American Chemical Society. Adapted with permission from Reference (37).

Ru(II)-bipyridine photosensitizers, ϕ_{isc} is very high. Indeed the available evidence points to it being unity in all cases. Again this is another very attractive feature of Ru(II) and Os(II) photosensitizers.

Rates of Internal Conversion and Intersystem Crossing

Figure 7 shows the observed rise times of the phosphorescence of $\text{cis-}[\text{Rh}(\text{bpy})_2\text{Br}_2]^+$ as measured with a 10 ns laser (31). The slow risetime is due to the continued pumping of the flash and not to intrinsic molecular processes. The dotted line is a calculated curve and corresponds to the case where the rate of relaxation from the upper excited state was 10^9 s^{-1} . The solid line was for an infinitely fast relaxation rate and yields a better fit to the data than if a value of 10^{10} s^{-1} was assumed. It was concluded that the effective internal conversion and intersystem crossing rate exceeded 10^{10} s^{-1} . More recently, using picosecond techniques, Kobayashi and Ohashi showed the actual risetime to be 1.3 psec (30).

Multiplicity of the CT Excited States

We return to the question of the multiplicity of the emitting CT state of $[\text{Ru}(\text{bpy})_3]^{2+}$ and related complexes. Hipps and Crosby (40) have called into question the use of spin labels on these states. They conclude that spin orbit coupling is so great that the CT states are strong admixtures of singlet and triplet character; this mixing means that singlet and triplet labels make no sense. In the absence of spin labels, the terms phosphorescence and fluorescence have no meaning. The states must be classified as spin-orbit states and the emissions as luminescences.

This result has important implications. If there is a break down of the traditional Russell-Saunders coupling scheme, then the Wigner spin selection rules are no longer operative. For example, the prohibition of triplet to singlet energy

transfer breaks down and singlet energy transfer from the so-called ^3CT state of $[\text{Ru}(\text{bpy})_3]^{2+}$ is allowed. We have confirmed this prediction experimentally using singlet energy transfer to laser dyes (23, 24). We find that collisional singlet energy transfer from the emitting CT state of $[\text{Ru}(\text{bpy})_3]^{2+}$ to Rhodamine 101 occurs with 100% efficiency. The quenching rate constant approaches the diffusion-controlled limit. This violation of the Wigner spin conservation rule shows that the sensitizing CT state has a very large component of singlet character and that the triplet label is inappropriate. Thus, the terms intersystem crossing and intersystem crossing efficiency have little meaning. Indeed, in our other papers we assiduously avoid use of the $^3(\text{CT})$ label and replace ϕ_{isc} with ϕ' to avoid any undesired implications.

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