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Review

Intersystem crossing in transition metal complexes

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Contents

Abstract

Intersystem crossing between zeroth-order states of different spin quantum numbers can be characterized as fast ($\geq 10^{12}$ s^{-1}) or slow. The bulk of the extant results on the fast unquenchable processes has been limited to the evaluation of efficiencies, the fraction of the initially excited molecules that undergo intersystem crossing. Cr(III) complexes have been the main systems studied. The increasing availability of sub-picosecond lasers has led to the determination of rates. Both prompt intersystem crossing which precedes thermalization and intersystem crossing from thermalized states contribute to the total efficiency, but the relative contributions of the two processes have not been determined. The magnitude of the efficiency reflects the relative rates of vibrational relaxation and prompt intersystem crossing in the Franck–Condon level, but both efficiencies and rates are available for few metal complexes.

The published efficiency results are examined with a kinetic model. The relationship between the several different measures of intersystem crossing is considered. Identification of reactive states cannot be made from kinetic measurements alone. The reliability of the results is evaluated and the possible dependence on excitation wave length is judged.

Keywords: Intersystem crossing; Transition metal complexes; Ultrafast processes; Excited state relaxation; Spin-forbidden processes

Abbreviations: acac, acetylacetonate; bpy, 2,2′-bipyridine; cyclam, 1,4,8,11-tetraazacyclotetradecane; en, ethylenediamine; phen, 1,10-phenanthroline; sen, 4,4′,4″-ethylidynetris[3-azabutan-1-amine]; tn, 1,3-propylenediamine; tpen, tetrakis[2-pyridylmethyl]ethylenediamine; tren, 2-aminoethylanone; $trenpy_3$, tris(2-pyridylmethylimimoethyl)amine

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1. Introduction

There are many steps between the absorption of a photon and the conversion to another species or the return unchanged to the ground state. To a first approximation, excited states are characterized by the spin quantum number, S. The validity of designating states by S has been questioned in transition metal complexes due to mixing under spin–orbit coupling [1]. However, the weak absorptions that are associated with nominally spin-forbidden transitions indicates utility to the classification of states in terms of S. The use of spin as a label is so pervasive that S will continue to play a role in describing electronic changes.

A quarter of a century has passed since it was proposed that photoprocesses could be characterized in terms of two limiting mechanisms [2]. In one limit, the process was slow enough to permit equilibration among the thermally accessible vibrational states. In the fast limit such thermalization was absent. The emphasis at the time was on photochemistry, but the application of the distinction to photophysics was recognized. Intersystem crossing is a photophysical process between zeroth-order states of "different" S and it is these transitions that are the focus of this review. These intersystem crossings can also be classified as fast, with rates of $10^{12}\ s^{-1}$ or larger, or slow ($\leq 10^{9}\ s^{-1}$). Emissions from transition metal complexes which come from states that, in the absence of spin–orbit coupling, have a different S than the ground state, are relatively long-lived. Such transitions have been described as spin-forbidden, e.g., $^2E \Rightarrow {}^4A_2$ in Cr(III) complexes (Fig. 1). Although the fast intersystem crossing processes, e.g., prompt $^4T_2 \Rightarrow {}^2E$, also involve a change in spin, their rates are not markedly reduced by a spin selection rule.

An operational definition, which is consistent with a kinetic treatment, is adopted here. The fast processes are defined as those that are unquenched when the long-lived states are quenched. By this definition, the slow ones are quenchable and have the same lifetimes as the ^2E (d^3) or ^{3}MLCT (d^6) states. The state designations in Figs. 1 and 2 refer to Cr(III) complexes. Appropriate changes in labels can be made for other systems. In this

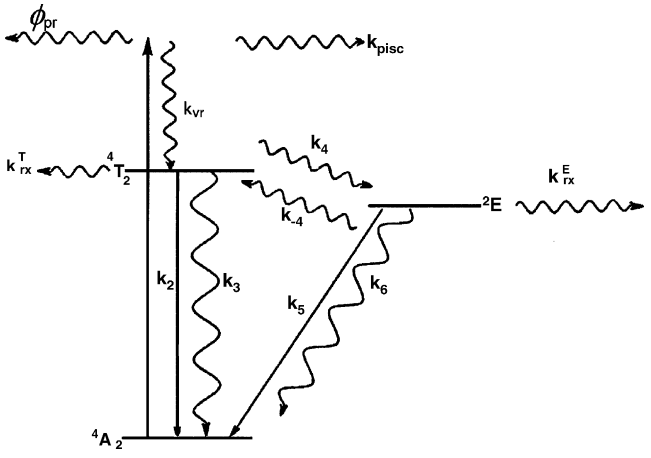

Fig. 1. Jablonski diagram for Cr(III)complexes. To change state labels for d^6 metal complexes, substitute $^1A_1$ for $^4A_2$, ^{1}MLCT or $^1T_1$ and ^{3}MLCT or $^3T_1$ for $^4T_2$ and ^2E.

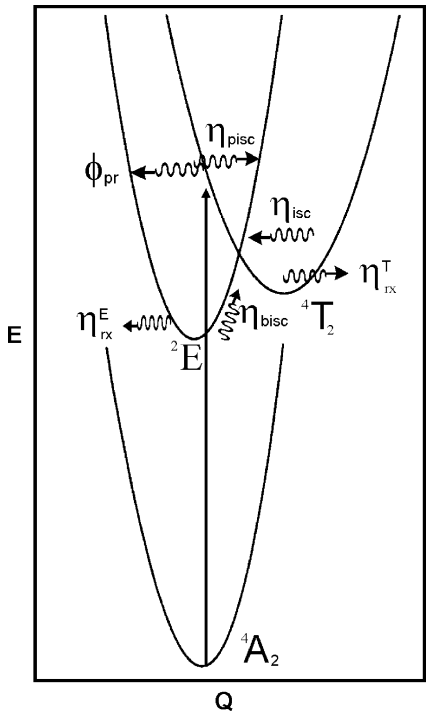

Fig. 2. Potential energy diagram for Cr(III) complexes.

model, excitation can lead to prompt reaction with a quantum yield ϕ_{pr}. Reactions in thermalized $^4T_2$ that take place prior to the first pass through ^2E, are unquenchable. All intersystem crossings that occur prior to thermalization are designated by η_{pisc}. The total intersystem crossing efficiency is $\eta_D = \eta_{pisc} + (1 - \eta_{pisc} - \phi_{pr})\eta_{isc}$ where all efficiencies other than η_{pisc} and ϕ_{pr} involve thermalized states and depend on ordinary kinetic constants [3]. For example, $\eta_{isc} = k_4/(k_2 + k_3 + k_4 + k^T_{rx})$. The ratio of the photochemical quantum yields for the slow and total reactions, f_D, has been used as a measure of intersystem crossing as has η_{isc}, but neither of these parameters necessarily describes intersystem crossing on a time scale that is short compared to the lifetime of the long-lived state.

There were a few efforts in the 1970s and 1980s to determine the rates of fast intersystem crossing in Cr(III) complexes [4–7]. In most cases only lower limits could be determined. More extensive determinations of fast intersystem crossing efficiencies, the fraction of initially excited states undergoing spin change, were made. This work has been reviewed by Kirk [3]. The availability of sub-picosecond lasers has led to a renewed interest in ultrafast intersystem crossing rates [8,9].

Quantum yields of reaction and emission, excited state lifetimes, and the risetimes of emission or transient absorption are the directly measurable photophysical and photochemical quantities. The desired molecular parameters are the rates and efficiencies of all the steps in the relaxation of the initially excited Franck–Condon state, vibrational relaxation, chemical reaction, and nonradiative transitions to other electronic states. There are usually too many constants in the relaxation pathway to infer the values of all these parameters from the few measured quantities. Instead, limits can be placed on η^T_{rx}, η^E_{rx}, η_{pisv}, η_{isc}, and ϕ_{pr} that are consistent with the measured quantum yields of reaction and

emission, given the experimental errors. These parameters, in turn, are model dependent.

Studies of the fast rates have mainly involved transitions following excitation of a charge transfer state and these have been reviewed [8]. In contrast, the bulk of the work on intersystem crossing efficiencies has been directed toward complexes in which excitation was into a ligand field state, principally $^4T_2$ in Cr(III).

A review of the extant work will point out the systems where more ultrafast rate measurements are likely to be important. In particular, the relative rates of vibrational relaxation (k_{vr}) and intersystem crossing in the initially populated Franck-Condon states (k_{pisc}) should depend upon η_D and the interpretation of the sub-picosecond kinetics can be related to the intersystem crossing efficiency.

2. Intersystem crossing efficiencies

2.1. Kinetic analysis

In most Cr(III) complexes the $^2T_1$ energy is approximately 500 cm^{-1} above ^2E and at room temperature it is common to treat both states kinetically as a single level designated as ^2E. Slow processes, either luminescence or reaction, con take place in ^2E or pass through it. If repopulation of $^4T_2$. occurs, recycling between $^4T_2$ and ^2E must be included [10].

The quantum yield for the $^2E \Rightarrow {}^4A_2$ emission after $^4T_2$ excitation is

$$\Phi_P^T = \frac{\eta_D \eta_{em}}{1 - \eta_{isc}\eta_{bisc}} \tag{1}$$

where $\eta_{em} = k_5/(k_5 + k_6 + k_{-4} + k_{TX}^E)$, $\eta_{bisc} = k_{-4}/(k_5 + k_6 + k_{-4} + k_{rx}^E)$, and $\eta_{isc} = k_4/(k_2 + k_3 + k_4 + k_{rx}^T)$ [11]. At higher temperatures k_3 increases [12] and η_{isc} can be reduced. The corresponding emission yield for direct ^2E excitation is

$$\Phi_P^E = \frac{\eta_{em}}{1 - \eta_{isc}\eta_{bisc}} \tag{2}$$

The denominators in Eqs. (1) and (2) are needed if recycling through $^4T_2$ is significant. The total reaction yields for $^4T_2$ excitation is $\Phi^T = \Phi_{fast}^T + \Phi_{slow}^T$ with

$$\Phi_{fast}^T = (1 - \eta_{pisc} - \phi_{pr})\eta_{rx}^T + \phi_{pr} \tag{3}$$

and

$$\Phi_{slow}^T = \frac{\eta_D(\eta_{rx}^E + \eta_{bisc}\eta_{rx}^T)}{1 - \eta_{isc}\eta_{bisc}} \tag{4}$$

For excitation in ^2E only slow processes are detected and the total reaction yield is

$$\Phi^E = \frac{\eta_{rx}^E + \eta_{bisc}\eta_{rx}^T}{1 - \eta_{isc}\eta_{bisc}} \tag{5}$$

and

$$\eta_D = \frac{\Phi_{slow}^T}{\Phi^E} \tag{6}$$

η_{pisc} and ϕ_{pr} are the essentially bookkeeping devices and are not necessarily simply related to rate constants. Rather they represent averages of processes that involve non-thermally equilibrated states. Only if vibrational relaxation is much slower than prompt reaction or prompt intersystem crossing can distinct rate constants be identified.The relation between $f_D = \Phi_{slow}^T/\Phi^T$ and η_D is

$$f_D = \frac{\eta_D(\eta_{rx}^T + \eta_{bisc}\eta_{rx}^T)}{(1 - \eta_{isc}\eta_{bisc})((1 - \eta_{pisc} - \phi_{pr})\eta_{rx}^T + \phi_{pr}) + \eta_D(\eta_{rx}^T + \eta_{bisc}\eta_{rx}^T)} \tag{7}$$

and

$$\eta_D = \frac{f_D\Phi^T}{\Phi^E} = \frac{\Phi_P^T}{\Phi_P^E} \tag{8}$$

Thus, the equality of Φ^T and Φ^E insures equality of η_D and f_D.

There are at most four relevant empirical quantities, Φ^T, Φ^E, Φ_{fast}^T, and Φ_P^T/Φ_P^E. No unique fit to these parameters is possible to obtain any of the remaining parameters. In particular, the fits are consistent with any value of η_{bisc} if both $^4T_2$ and ^2E are reactive, and limiting the reaction to $^4T_2$ does not require η_{bisc} to be close to unity. The reactive level cannot be inferred from a kinetic analysis alone. Other evidence is required.

The effect of environment and temperature on η_D can be evaluated from

$$\frac{\Phi_P^T}{\tau} = \eta_D k_5 \tag{9}$$

where τ is the lifetime of the emitting state [12].

Fig. 2 is a simplified potential energy diagram in which only one generalized configuration coordinate, Q, is used. Kane–Maguire has proposed a modification in which the $^4T_2$ and ^2E curves interact and produce an avoided crossing due to spin–orbit coupling (Fig. 3) [13]. Such mixing should be large only when the difference in the energies of the two states is small [14]. In the non-adiabatic model intersystem crossings from thermalized states involve tunnelling at all temperatures. If there is an avoided crossing (Fig. 3) tunnelling at low temperatures is joined by an activated process at higher temperatures. Langford has pointed out the inadequacies of the single coordinate model [15], but it is sufficient to interpret the photoprocesses in most Cr(III) complexes.

The effect of processes that precede thermalization in $^4T_2$ has often been ignored and the intersystem crossing yield identified with η_{isc}. Kirk has emphasized the importance of η_{pisc} [3,16]. Although the parameters extracted from fits with $\eta_{pisc} > 0$ will be different the mechanistic conclusions based upon assuming that the intersystem crossing is η_{isc} rather than η_D may be the same [17], but not necessarily so.

2.2. Experimental methods

The main experimental methods for evaluating η_D from Eq. (8) depend upon comparing emission or reaction yields following $^4T_2$ excitation with those induced by excitation of ^2E, either directly [18] or via sensitization [19,20]. Alternatively, several

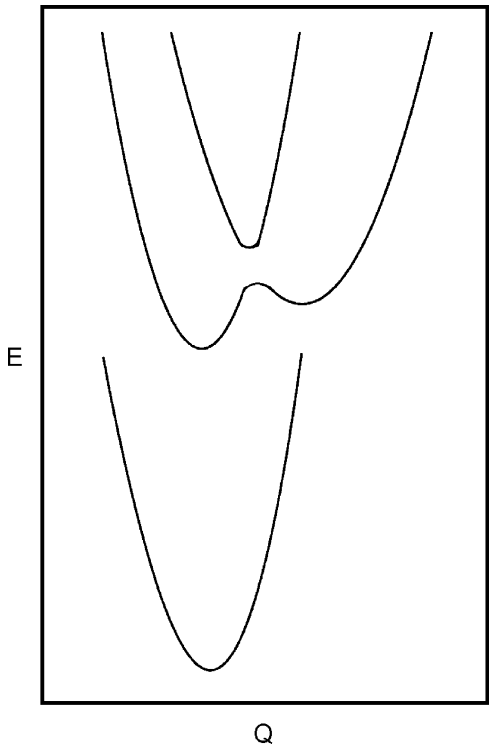

Fig. 3. Potential energy diagram for avoided crossing.

determinations of η_D have been made by transient absorption [21,22]. In favorable cases, where the complex is photoinert, a calorimetric approach with photoacoustic detection has been used In the photoacoustic technique the heat deposited during the fast relaxation processes is measured and, after quantum corrections, η_D can be computed [23,24].

In the sensitization technique the ratio between the phosphorescence yields of directly excited $^4T_2$ and ^2E populated by energy transfer from the triplet state of an excited donor is determined [19,20]. However, in contrast to the excitation of ^2E by direct light absorption, a number of assumptions are required. These include knowledge of the intersystem crossing efficiency in the sensitizer (η^s_{isc}) and the efficiency of energy transfer (η_{et}). Both of these quantities were assumed to be unity. Absence of specific interaction between donor and acceptor species was also assumed.

Measurements that involve excitation at a single wave length are used to determine f_D. These include comparison of the unquenchable yields with the total yield, both after $^4T_2$ excitation [25,26]. f_D represents the fraction of the reaction that is quenchable. f_D is affected by recycling between ^2E and $^4T_2$ and may differ from η_D. In pulsed conductivity measurements the ratio of the slow and total conductivity changes has been used to calculate f_D [26].

2.3. Specific complexes

2.3.1. $Cr(en)_3^{3+}$

This complex has been the subject of extensive study and provides a basis for assessing the reliability of the empirical results. Two methods were used to follow the aquation reaction, $Cr(en)_3^{3+} + 2H_2O \Rightarrow cis\text{-}Cr(en)_2(enH)(H_2O)^{4+} + OH^-$, spectral and polarimetric. The quantum yields were the same in both methods. Φ^T was quite reproducible and varied from 0.37 to 0.42 [18,27–29]. Estimates of f_D were based on data from more than one study. The f_D values ranged from 0.58 to 0.67 [25,26,28,30].

Several determinations of η_D have been made. In one case the emission intensities following absorption into $^4T_2$ and ^2E were converted into relative quantum yields and the ratio $\eta_D = \Phi_P^{514.5}/\Phi_P^{669} = 0.68$ [18]. In the same paper, the $Cr(en)_3^{3+}$ photochemical yields excited by 514.5, 0.42, and 668.9 nm radiation, 0.45, were determined. f_D was chosen as 0.68. This led to $\eta_D = 0.42 \times 0.68/0.45 = 0.64$, in good agreement with the value obtained from the phosphorescence yields. The near equality of η_D and f_D when the photolyses yields excited in $^4T_2$ and ^2E are the same is as expected. A sensitized emission study yielded $\eta_D = 0.71$ [19]. One estimate, 0.3, has been challenged [18]. The original data [21] were reanalyzed and the low estimate was due to an unreliable measure of light absorption in the spin-forbidden region. Another low value is based on $\Phi^E = 0.59$ and $f_D \leq 0.7$ [27]. It is difficult to resolve this discrepancy, but it is probably due to the uncertainty in measuring absorption in the weak $^2E \Leftarrow {}^4A_2$ transition. In spite of some scatter in the data, there is no doubt that η_D and f_D are substantially less than unity.

The invariance of the product distribution to excitation in $^4T_2$ and ^2E is strong evidence that only one state is reactive [31]. $^4T_2$ is the reactive state and back-transfer is implicated. Moreover, the product ratio constancy is evidence against a ϕ_{pr} contribution since prompt and thermalized reactions would follow a different mechanism [2].

The foregoing values of η_D were obtained with solutions. A determination of the intersystem crossing for $Cr(en)_3^{3+}$ in crystalline $[Cr(en)_3Cr(CN)_6]\cdot 2H_2O$ led to $0.8 \leq \eta_D \leq 1.0$ [32]. This estimate was based upon the absolute emission yield of $Cr(CN)_6^{3-}$ diluted in $K_3Co(CN)_6$. Absolute quantum yield determinations in powders depend on a number of assumptions. Consequently, it is not certain that η_D is really larger in the crystal.

Φ_P/τ is constant in alcohol/water solution over a temperature range that includes the rigid-fluid transition [33]. This points to the temperature invariance of η_D (Eq. (9)).

In $Cr(sen)^{3+}$, a distorted $Cr(en)_3^{3+}$ moiety is created by a macrocyclic framework [34]. $\Phi^T = 0.098$ and $\Phi^E = 0.077$. This complex is unusual since $\Phi^T > \Phi^E$. In the absence of information on f_D, η_D cannot be evaluated but from Eq. (8) $f_D < \eta_D$. Kirk fitted the two reaction yields by assuming $\phi_{pr} = \eta_{pisc} = \eta^E_{rx} = 0$, but recognized that other fits were possible. In fact, as in the case of $Cr(en)_3^{3+}$, an equally good fit is obtained with a prompt intersystem crossing contribution as well as one with both doublet and quartet state reactivity.

$f_D = 1.0$ in *trans*-$Cr(en)_2F_2^+$ [26]. The lowest excited state in this complex is a component of $^2T_1$ [35].

2.3.2. $Cr(tn)_3^{3+}$

In the first report of the $Cr(tn)_3^{3+}$ photoaquation both mono- and diaquo products were found [36]. Subsequently, it was

shown that $[Cr(tn)_2(H_2O)_2]^{3+}$ was formed by a secondary reaction [37]. The primary quantum yield was 0.14. In another study the photoaquation yield was nearly the same for $^4T_2$ and ^2E excitation, 0.15 and 0.16, respectively [38]. $f_D = 0.67$ with OH^- quenching and 0.78 by conductance measurements [37], leading to $\eta_D = 0.63$ or 0.73.

2.3.3. $Cr(NH_3)_6^{3+}$

Φ^T was quite reproducible, ranging from 0.44 to 0.47 [10,26,39–41]. There is more variation in f_D, 0.67–0.80 [10,26,39,40]. Waltz assumed that the intersystem crossing yield was η_{isc}, but his approach leads to Eq. (4) if η_{pisc} is included (supplement to Ref. [10]). Only one determination of η_D has been published, 0.69, based upon $\Phi^T = \Phi^E = 0.44$ and $f_D = 0.69$ [10].

2.3.4. Cis-$Cr(cyclam)(NH_3)_2^{3+}$

No fast reaction was observed in the photolysis of *cis*-$Cr(cyclam)(NH_3)_2^{3+}$ where $\Phi^T = \Phi^E = 0.15$ [42]. Both f_D and $\eta_D = 1$ for this complex. Many different combinations of η_{isc} and η_{bisc} will produce good fits to the measured reaction yields.

2.3.5. $Cr(CN)_6^{3-}$

The $^4T_2$–^2E gap is so large that $\eta_{bisc} = 0$ at ambient temperatures. All of the reaction in this complex occurs in $^4T_2$ prior to intersystem crossing and is unquenchable [43]. Consequently, f_D vanishes. $\Phi^T = 0.085$ in DMF and nonradiative return to the ground state is an important process.

Two sensitization procedures were used to obtain η_D for $Cr(CN)_6^{3-}$. In one method the 450 nm excitation radiation was only absorbed by the $Ru(bpy)_3^{2+}$ donor [20]. The $Cr(CN)_6^{3-}$ concentration was varied and the phosphorescence intensity extrapolated to high acceptor concentration. The directly excited ($\Phi_{P,direct}$) and $Ru(bpy)_3^{2+}$ sensitized ($\Phi_{P,sens}$) emission yields were then compared and $\eta_D = \eta_{isc}{}^s \Phi_{P,direct}/\Phi_{P,sens}$, where η_{et} is the energy transfer efficiency and η^s_{isc} refers to the donor molecules. In the second sensitization method both the donor and acceptor absorbed the 400 nm excitation radiation [19]. Corrections were made for the acceptor absorption and the donor emission. η_D was then computed from the same expression that was used in the first method. Good agreement between the two η_D determinations was obtained for $Cr(CN)_6^{3-}$, 0.5 and 0.57, assuming $\eta_{et}\eta^s_{isc}$ is unity. The second method was applied to a number of acceptor complexes.

The intersystem crossing yield by the sensitization technique in solution was smaller than the absolute quantum yield in a dilute crystalline powder of Cr^{3+}:$K_3Cr(CN)_6$, 0.8–1.0 [44]. As indicated above, the method for computing the phosphorescence yield of powders involves a number of assumptions and it is not certain if the value in the solid is really larger than in solution. Inhibition of photoreaction in crystals cannot explain the increase. Nonradiative decay might be inhibited. $\eta_D k_5$ for Cr^{3+}:$K_3Cr(CN)_6$ increases two-fold between 130 and 295 K [45]. The $^2E \Rightarrow {}^4A_2$ transition is symmetry forbidden in this crystal, as evidenced by the relative weakness of the 0–0 transition and much of this increase is due to thermally enhanced k_5. This view is supported by the near constancy of the ruby Φ_P and $k_5\tau$ from 77 to 300 K [46]. The origin line in ruby is the dominant feature. Incidentally, since $\Phi_P = 0.63$ and $k_5\tau \approx 1$, the ruby $\eta_D = 0.63$. None of the reaction is quenchable and $Cr(CN)_6^{3-}$ is definitely one complex where f_D and η_D are not equal.

2.3.6. $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$

The reaction yields and lifetimes of chromium polypyridyl complexes are sensitive to pH, concentration, and counterion. In contrast to the situation in the chromium amine complexes, the photoaquation yield in the polypyridyl complexes is increased in basic solution. A plateau occurs at high pH. The lifetimes of these two complexes are not reduced by concentration quenching in the absence of added anions [47]. In 1 M HCl concentration quenching is important in $Cr(phen)_3^{3+}$, but not in $Cr(bpy)_3^{3+}$ solutions. However, concentration quenching of $Cr(bpy)_3^{3+}$ is observed in 5 M HCl [48]. The sensitivity to so many factors makes it difficult to compare the results from different studies.

These complexes are of especial interest because the $^4T_2$–^2E gaps appear to lie between those of $Cr(CN)_6^{3-}$ and the other homoleptic complexes. This has led to considerable uncertainty in assigning the reactive states. In deaerated solutions at 295 K, Φ^T for aquation in 1.0 M NaCl are 0.18 (pH 9.8) and 0.006 (pH 10.4) for $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$, respectively [48]. When extrapolated to infinite dilution to eliminate substrate quenching Φ^T for $Cr(phen)_3^{3+}$ is increased to 0.028 [49,50].

$\eta_D = 0.94$ for $Cr(bpy)_3^{3+}$ by the sensitization method [19]. The corresponding value for $Cr(phen)_3^{3+}$ was only 0.2. Although Φ^T was very different for the two complexes, the very small η_D is unusual. The $Cr(phen)_3^{3+}$ measurement was made in a DMSO/H_2O solution and it has been shown that organic solvents reduce η_D [51]. Φ^E and Φ^T were compared for $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$ and it was found that the 0.2 value was incorrect [52]. It was inferred that η_D approached unity in both $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$.

$f_D = 0.98$ for $Cr(bpy)_3^{3+}$ [53] and 0.95 for $Cr(phen)_3^{3+}$ [50] in the photaquation reaction. It was asserted that the slow reaction occurred in ^2E. This conclusion was based upon the temperature dependence of the reaction yields and the involved argument depended on many assumptions. The strongest argument for the absence of back-transfer is the large magnitude of the $^4T_2$–^2E gap. Photoracemisation dominates in acid solution with $f_D = 0.86$ for $Cr(phen)_3^{3+}$ [54].

When the solvent is changed from H_2O to D_2O, the lifetime change is negligible for both complexes [55]. However Φ_P decreases fivefold for $Cr(bpy)_3^{3+}$. The refractive index is the same in both solvents and k_5 should not be affected by solvent deuteration. The unusual decrease of Φ_P in the deuterated solvent was ascribed to a reduction in $\eta_{isc,}$ which is now replaced by η_D. This could reflect diminution of either η_{pisc} or η_{isc}. In contrast, there is little solvent deuterium isotope effect in $Cr(phen)_3^{3+}$ solutions.

η_D was determined for a number of Cr(III) polypyridyl complexes by the photoacoustic method [24]. In $Cr(bpy)_3^{3+}$, $Cr(phen)_3^{3+}$, and $Cr(4,4'\text{-mebpy})_3^{3+}$ η_D was unity. It was only 0.73 in $Cr(5\text{-Cl-phen})_3^{3+}$.

2.3.7. Trans-Cr(en)$_2$(NCS)$_2^+$

Upon irradiation in ligand field bands this complex undergoes two photoaquation reactions, one associated with NCS^- release and the other initiated by the breaking of a Cr-en bond, The total photolysis yields at 288 K for both en and NCS^- reactions have been measured under unquenched, 0.25, and quenched conditions, 0.045 [56]. The individual yields of the two reactions were the same for direct and sensitized excitation, indicating that $\eta_D = f_D = 0.82$ (Eq. (8)). The ratios of the quantum yields for the two reactions were roughly the same in the fast and slow reactions leading to the conclusion that all of the reactions occurred in $^4T_2$.

The ratio of the phosphorescence yields under $^4T_2$ and ^2E excitation, the latter by Ru(bpy)$_3^{2+}$ sensitized energy transfer, was originally reported as 0.41, in conflict with the equality of η_D and f_D [19]. Subsequently, a much higher value was found in the same laboratory with Ru(bpy)$_2$(CN)$_2$ as the sensitizer and $\eta_D = 0.8$ was calculated, in accord with the photolyses results [56].

2.3.8. Trans-Cr(NH$_3$)$_2$(NCS)$_4^-$

$f_D = 0.5$ at 208 K in an alcohol–water solution [57] and the photoaquation yield in quenched solution was 0.005. The low temperature photosolvation yields in glycerol, ethanol, propanediol, and acetone were 0.005, 0.015, 0.01, and 0.02, respectively [58,59]. This yield, assumed to be Φ^T_{fast}, is constant in acetone between 183 and 223 K [58]. If this temperature invariance of the fast reaction continues to ambient temperatures f_D would exceed 0.9. $\Phi^T = 0.30$ at ambient temperatures in water [60].

There has been some controversy about the magnitude of η_D [61,62]. In both referenced papers the intersystem crossing efficiency was erroneously related to the reactive state, The room temperature η_D are essentially independent of solvent [60] and excitation wave length from 316 to 750 nm Since $\Phi^T = \Phi^E$, $\eta_D > 0.9$.

2.3.9. Ru(II) polypyridyl complexes

Excitation into the lowest spin-allowed excited state, ^{1}MLCT, is followed by intersystem crossing to the ^{3}MLCT state The value of η_D for Ru(bpy)$_3^{2+}$ is not only of intrinsic interest but is necessary for use in the sensitized determinations of intersystem crossing in other complexes [19,20]. As described above, η_D is assumed to be close to unity for this complex, but most references are ultimately traceable to the determination by Demas and Crosby [63]. This involved comparison of the phosphorescence yields excited by ^{1}MLCT $\Leftarrow {}^1A_1$ and ^{3}MLCT $\Leftarrow {}^1A_1$ absorption. Some uncertainty was expressed about the fraction of excitation that directly populated the ^{3}MLCT state. Reexamination of this question indicated that the intersystem crossing yield was indeed very close to unity [64]. Confirmation of the near unity value has been obtained by transient absorption [22] and total ground state depletion [65] methods.

Additional confirmation was obtained by a photochemical method involving the oxidation of Ru(II) by $S_2O_8^{2-}$ [66]. This technique yielded $\eta_D = 1$ for Ru(bpy)$_3^{2+}$ and Ru(phen)$_3^{2+}$. The photochemical method was applied to Ru(dimethylbipyridyl)$_2$(1,4-bis[2-(4′-methyl-2,2′-bipyrid-4-yl)ethenyl]benzene) and $\eta_D = 0.30$ [66].

η_D has been determined for six Ru(II) complexes coordinated by pyridine and heterocyclic groups [22]. The intersystem crossing efficiencies ranged from 1.0 to 0.24.

2.4. Wave length effects

Four excitation wave length dependent phenomena have been studied: (i) variation in the phosphorescence yield, η_D; (ii) changes in the overall reaction yield, Φ^T; (iii) alteration in the unquenchable fraction; (iv) variation in product composition. The emphasis here is on differences for excitation wave lengths within the $^4T_2$ state. Two domains are of interest, depending upon the location of the excitation energy relative to the $^4T_2$–^2E crossover point. Changes in η_D with excitation energy above this crossover could be due to a variation in either η_{pisc} or ϕ_{pr} [2,15]. An increase in ϕ_{pr} would decrease the quenchable reaction while an increase in η_{pisc} would increase the quenchable reaction. Excitation to a level below the crossover could lead to a reduced η_D since the transfer to ^2E would either be activated or have to tunnel through a barrier if the adiabatic model applies. In either case a change in η_D would be of interest. Changes accompanying excitation on the long wave length portion of the absorption spectrum has been called the red-edge effect. Kirk have suggested a source of red-edge effects wherein excitation at long wave lengths originates in high vibrational levels of the ground state [38].

The possible red-edge effect in Cr(en)$_3^{3+}$ has been subject to dispute. According to either the nonadiabatic picture (Fig. 2) or the adiabatic model of Kane-Maguire [13] (Fig. 3) it is possible for η_D to exhibit a wave length dependence. From Eq. (8) the results at two excitation wave lengths are related by

$$\frac{(\eta_D)_1}{(\eta_D)_2} = \left[\frac{(\Phi^T)_1}{(\Phi^T)_2}\right]\left[\frac{(f_D)_1}{(f_D)_2}\right] = \frac{(\Phi^T_P)_1}{(\Phi^T_P)_2} \quad (10)$$

The initial results showed that the relative phosphorescence yield upon 514 nm irradiation was only 63% of the 436 nm value [29]. The decrease in the phosphorescence yield was attributed to excitation below the $^4T_2$–^2E crossing point where η_D was reduced. In this study $(\eta_D)_{514}/(\eta_D)_{436} = 0.63$, $(f_D)_{514}/(f_D)_{436} = 0.65$ and the total reaction yields must be nearly the same at the two wave lengths, as observed [18]. A red-edge effect in η_D is consistent with constant photolyses yields. Smaller f_D and η_D imply a reduced Φ^T_{slow} and an increased Φ^T_{fast} if Φ^T is constant. Reducing η_{pisc} without changing any other parameters will also reduce η_D but Φ^T will not be affected. The red-edge effect on the phosphorescence was corroborated in aqueous solution, but was smaller in glycerol/H_2O solutions [67]. However, in later work, where acid solutions were used the phosphorescence yield reduction at 514 nm was less than 17% [68] and 7% [69]. f_D was invariant to excitation wave length in conductance measurements [30]. This implies a similar constancy in η_D. Impurity absorption or light scattering would lead to a reduced phosphorescence yield. Kirk discovered an artifact arising from the change of beam diameter with excitation wave

length and a concomitant geometry effect on the emission [69]. f_D is not affected by either of the aforementioned artifacts.

The constancy of f_D in the 436–488 nm range is noteworthy. Since the total photolysis yield is constant over a wide range of excitation wave lengths η_D will be constant over the same wave length interval and both η_{pisc} and ϕ_{Pr} will be unchanged even though $\eta_D < 1$. This point will be revisited below.

The putative red-edge effect of the *cis*/*trans* product ratio in the $Cr(tn)_3^{3+}$ fast reaction [39] was not confirmed subsequently [70]. There was a slightly different product ratio for the fast and total photoaquation reactions.

The wave length effect on the photoracemization yield of $Cr(phen)_3^{3+}$ has been explored [71]. It was concluded that the total and unquenchable yields decrease with increasing wave length on the red edge but in view of the above, these results should be viewed skeptically.

The *trans*-$Cr(en)_2(NCS)_2^+$ phosphorescence yield was wave length independent from 330 to 540 nm, but was reduced by a factor of 0.8 on the red-edge at 565 nm [56]. The NCS^- photolysis yield was constant in the same wave length interval.

$Cr(CN)_6^{3-}$ exhibits a red-edge effect in rigid media in which the phosphorescence yield increases [72]. This effect disappears in fluids and was attributed to solvate heterogeneity in rigid environments. There is no information on the constancy of η_D or Φ^T over a wide wave length interval in DMF at ambient temperatures where $\eta_D < 0.6$.

On balance, it appears that red-edge effects, if real, are small in fluid solutions.

3. Intersystem crossing rates

The emphasis above has been on the efficiencies of nonradiative processes between $^4T_2$ and ^2E or ^{1}MLCT and ^{3}MLCT. Efficiencies normally depend on more than one rate constant and it is the individual rate constants that are more fundamental. The fast rates ($>10^{12}$ s^{-1}) were associated with k_{pisc} and k_4 while the slow rates at low temperatures (10^9 s^{-1}) are approximately k_6. Since k_{pisc} refers to a process in a non-thermalized state it is difficult to relate k_{pisc} and k_{vr}. Moreover, the simplified expression for η_D obscures the details of the relaxation processes. Nevertheless, if $\eta_{pisc} < 1$ vibrational cooling or prompt reaction must compete with intersystem crossing.

In the thermalized limit the usual theoretical approach has been to represent the nonradiative rate constant in the weak coupling limit as a product of electronic (β) and vibrational overlap factors (F), $k_{nr} = \beta_0 F$ [73]. Is the difference between the fast and slow processes due to variations in the electronic or the vibrational factors? In particular, does a spin selection rule play a role?The electronic factor involves a promoting mode, ω_k [74]:

$$\beta_0 = C_k^2 \omega_k \left(\frac{\pi}{2}\right)^{1/2} \tag{11}$$

and C_k includes contributions from vibronic coupling and, in the case of spin-forbidden transitions, spin–orbit coupling. No successful calculation of the total nonradiative rate in a transition metal complex has been made because the electronic factor has defied evaluation. In contrast, F has been estimated successfully, at least in a relative sense. The vibrational factor depends upon accepting modes and in a single mode approximation is [75]:

$$F = \left(\frac{1}{\hbar\omega_M E}\right)^{1/2} \exp(-S_M) \exp\left(-\frac{\gamma E}{\hbar\omega_M}\right) \times \exp\left(\frac{\gamma+1}{\hbar\omega_M}\right)^2 \left(\frac{(\Delta\upsilon_{1/2})^2}{16\ln 2}\right) \tag{12}$$

and

$$\gamma = \ln\left(\frac{E}{S_M \hbar\omega_M}\right) - 1 \tag{13}$$

The parameters in Eqs (12) and (13) are E, a measure of the energy difference between the two states involved in the transition, S_M the Huang–Rhys factor which describes the displacement of the potential minima along the accepting mode coordinate, ω_M is the frequency of the dominant accepting mode, and $\Delta\upsilon_{1/2}$ is the full width at half maximum of the emission spectrum. These parameters can be extracted by fitting the emission spectrum [74].

In spite of the failure of any calculations to predict absolute values of k_6 the theoretical models do provide a framework for discussing trends in the slow nonradiative decay rates. The vibrational factor increases with the decreasing energy difference between the origins of the states involved, the energy gap effect, and increased S_M.

An alternate theoretical approach has been developed for the fast processes in which selection rules were extracted [2]. In this treatment the Born–Oppenheimer approximation was not used. A wave length dependence for k_{pisc} has been observed [8].

Since intersystem crossing involves a spin change, spin–orbit coupling is required to obtain a non-vanishing β_0. Three mechanisms for introducing the effect of spin–orbit coupling have been proposed; direct spin–orbit interaction, adiabatic spin–orbit coupling, and non-adiabatic spin–orbit coupling [76]. The last two contributions involve mixing between states of known energy [14]. In some cases these energies can be estimated from absorption and emission spectra, but often some of the transitions cannot be located experimentally. Efforts have been made to locate these hidden states by density functional theory (DFT) and ab initio calculations [77,78]. Quantitative calculations of β_0 have not been successful, but qualitative use of DFT and other theoretical results have proven useful for the interpretation of nonradiative decays. For example, the relatively small k_{pisc} in Cu(I) polypyridyl complexes compared to the Ru(II) analogues was not attributed to differences in the magnitudes of H_{so}, but rather to the reduction in the singlet–triplet state mixing due to geometric distortions [79]. The weak coupling limit was assumed to be applicable for all the intersystem crossing processes in the copper complexes. In another study, differences in triplet state lifetimes within a group of cyclic alkenes was attributed to variations in the vibrational rather than the electronic factor [80].

A different approach to estimating nonradiative rates involves a state hopping formalism to calculate excited state lifetimes [81].

3.1. Fast rates

Early attempts to measure directly the rates of ^2E formation in Cr(III) complexes with nanosecond techniques only revealed that these process were too fast to detect [33,82]. The first measurements in the ultrafast domain used picosecond excitation and could detect no risetimes > 5 ps for ^2E absorption in aqueous solutions of *trans*-$Cr(NH_3)_2(NCS)_4^-$, $Cr(NCS)_6^{3-}$, and $Cr(acac)_3$ [4]. Subsequently, risetimes of 16–22 ps were reported [7]. Later results from the same laboratory yielded somewhat shorter risetimes [6]. The results were interpreted by assuming that the risetime was due to intersystem crossing and that vibrational relaxation was at least as fast as intersystem crossing.

The preponderance of ultrafast rate measurements have employed pump and probe monitoring of transient absorption. It is first necessary to establish the origin of the transient. In Cr(III) complexes only absorption from ^2E and ground state depletion contribute to the time dependent signal. There are more possibilities in d^6 complexes that have low-lying charge transfer states. Faster time resolution with both picosecond and femtosecond lasers revealed no ^2E risetimes for aqueous solutions of *trans*-$Cr(NH_3)_2(NCS)_4^-$, $Cr(NCS)_6^{3-}$, $Cr(en)_3^{3+}$, $Cr(bpy)_3^{3+}$, $Cr(phen)_3^{3+}$ and $Cr(acac)_3$ slower than 1 ps [5]. The report of slow ^2E population in $Cr(bpy)_3^{3+}$ was shown to be an artifact of multiphoton absorption at high incident fluxes [83].

Polypyridyl complexes of Ru(II) have been the subject of extensive study with femtosecond excitation in the $^1MLCT \Leftarrow {}^1A_1$ transition. The ultrafast measurements have been reviewed by McCusker [8]. In addition to competition between intersystem crossing and vibrational relaxation, solvent motion and delocalized to localized excitation are possible dynamic changes that can affect excited state relaxation. Sorting out the several contributions requires more than one kinetic measurement. Both the dynamics of the transient absorption spectra and single wave length time changes were recorded. Verification that prompt intersystem crossing is important in $Ru(bpy)_3^{2+}$ comes from the appearance of transient absorption in ^3MLCT within 100 fs, with the complete transition in 300 fs [84]. Fluorescence up-conversion measurements established the lifetime of the Franck–Condon level in ^1MLCT as 40 fs [85]. The depletion of this level was the first step in intersystem crossing. The changes between 40 and 100 fs were ascribed to the delocalization to localization process in the ^3MLCT state which involved solvent motion [8,86]. Vibrational cooling in ^3MLCT is solvent dependent with relaxation times of 5 ps. In spite of the complicated processes involved, it is clear that $k_{pisc} = 25 \times 10^{15}\ s^{-1}$ and is faster than vibrational relaxation in ^1MLCT. This would lead to $\eta_{pisc} = \eta_D = 1$, independent of η_{isc}.

Excitation in a ligand field band of $Cr(acac)_3$ should lead to a simpler sequence of dynamic processes than are involved with MLCT states. However, the interpretation is actually more difficult because the transient absorption only changes the spectral width and not position as a function of delay time [87]. The ^2E level is populated within 100 fs. The narrowing of the transient spectrum at delay times exceeding 100 fs was due to vibrational cooling in ^2E with a relaxation time of 1.1 ps. The transient spectrum broadens with excitation energy indicating that intersystem crossing is faster than vibrational relaxation in $^4T_2$. This suggests that η_{pisc} and η_D are close to unity. These observations underline the interpretive difficulty encountered in the ultrafast measurements. The thermal relaxation rate for ^2E decay is best described by a biphasic Arrhenius plot [88]. Fitting over the range 77–208 K leads to a temperature invariant $k_4 = 4.1 \times 10^{14}\ s^{-1}$ and $\eta_{isc} = 0.89$.

Although k_{pisc} is definitely a fast process, direct measurement of k_4 has not been made. A rough estimate of k_4 can be made from measurements of k_{-4}. If back-transfer is the dominant thermal quenching process in $Cr(acac)_3$, an Arrhenius fit of the thermal decay rate [11], $(1 - \eta_{isc})k_{-4} = A \exp(-E_a/RT)$, can be combined with $k_{-4}/k_4 = \exp(-\Delta G/RT)$ where ΔG is the free energy difference between $^4T_2$ and ^2E. Depending on the relative values of ΔG and E_a and the magnitude of η_{isc}, k_4 can be larger or smaller than A. There is quite a spread in the A factors [12], but k_4 is in the 10^{12} to $10^{14}\ s^{-1}$ range for a wide variety of Cr(III) complexes. In particular, the room temperature ^2E lifetime of $Cr(en)_3^{3+}$ is 1.6 μs. With $E_a = 40$–$50\ kJ\ mol^{-1}$ good fits to Fig. 1 model requires a k_4 of 10^{12} to $10^{14}\ s^{-1}$ and η_{isc} close to unity. If this analysis is valid both the prompt and thermalized intersystem crossing rates are very large.

Since $\eta_{pisc} \leq \eta_D$ and $\eta_D \approx 0.7$ in $Cr(en)_3^{3+}$, k_{pisc} must compete with vibrational relaxation or prompt reaction in this complex. The same conclusion applies to $Cr(CN)_6^{3-}$. The observation of a difference in the $Cr(acac)_3$ excited state absorption spectrum with excitation wave length was interpreted to indicate that $k_{pisc} \gg k_{vr}$. This in turn requires $\eta_{pisc} = 1$.

Intersystem crossing rates for the $^1MLCT \Rightarrow {}^5T_2$ transition in low-spin Fe(II) polypyridyl complexes processes have been measured. After $^1MLCT \Leftarrow {}^1A_1$ excitation, absorption from the $^5T_2$ level appears within 700 fs for $Fe(tpen)^{2+}$ [89] and 80 fs in $Fe(tren(py)_3)^{2+}$ [90]. $Fe(tpen)^{2+}$ is a spin-crossover complex in which the high spin state is populated at room temperature. This makes it possible to assign the lowest excited state as $^5T_2$ in the absence of luminescence. It was initially thought that triplet ligand field states were part of the cascade [91], but the more recent interpretation is a one-step process wherein there is so much mixing between $^1T_1$, $^3T_2$, $^3T_1$, and $^5T_2$ that only the $^5T_2$ potential surface is well defined and the $^5T_2$ state is directly populated [89]. In Fe(II) complexes the $^5T_2$–$^1A_1$ gap is small and k_6 is near $10^9\ s^{-1}$ in several cases. The room temperature decay times of the $^5T_2$ states in $Fe(bpy)_3^{2+}$ and $Fe(phen)_3^{2+}$ are 676 and 685 ps, respectively [89]. Fe(II) polypyridyl complexes exhibit a decay rate that is typical of tunneling at low temperatures, but is activated at higher temperatures. The energy gap in Fe(II) polypyridyl complexes is smaller than the ^2E–$^4A_2$ gap in Cr(III) complexes and this, combined with the larger ΔQ in the Fe(II) complexes, would partially compensate for the $\Delta S = 2$ prohibition in the $^5T_2 \Rightarrow {}^1A_1$ transition.

Judged by the magnitude of Φ_{fast}^T, Φ_{pr} must be rather small in Cr(III) complexes and no excitation wave length dependence in Φ_{fast}^T has been reported. In contrast, the ultrafast dissociation of CO in organometallic complexes of zerovalent metals with CO ligands demonstrates competition between vibrational relaxation and prompt reaction prior to intersystem crossing in the ^1MLCT state [92–94]. The initially excited states in this group

are ^{1}MLCT. The rate constant for CO formation in $Cr(CO)_4(bpy)$ is 400 fs and the quantum yield decreases with increasing wave length [93,94]. Branching into two unreactive states is also wave length dependent. In Werner complexes the ^{1}MLCT states are usually unreactive and photoreactions occur in metal-centered states reached thermally from ^{3}MLCT after efficient intersystem crossing [12]. The presence of CO as spectator ligands can lead to competition between prompt intersystem crossing and other processes in the Franck–Condon state. This was attributed to mixing between ^{1}MLCT and proximate metal-centered states or continua. In the organometallic complexes with CO ligands the metal-centered states are closer to the ^{1}MLCT states than are the triplet d–d states to the ^{3}MLCT states in the Werner complexes.

3.2. Slow rates

The nearly universal $^2E \Rightarrow {}^4A_2$ luminescence from Cr(III) complexes at low temperatures has led to many measurements of $k_5 + k_6$ [95]. Fewer lifetime measurements have been made at ambient temperatures. The radiative rates, k_5, are generally in the 10^2 to 10^3 s^{-1} range, while k_6 seldom exceeds 10^6 s^{-1} at low temperatures. Lifetime decreases with temperature are mainly due to competitive processes that depopulate ^{2}E. These include back-intersystem crossing and chemical reaction in ^{2}E. A good approximation to the ^{2}E relaxation rate is

$$\tau_p^{-1} = k_5 + k_6 + (1 - \eta_{isc})k_{-4} \quad (14)$$

When back-intersystem is the dominant thermal decay pathway k_{-4} usually follows an Arrhenius dependence, $A\exp(-E_a/RT)$, where E_a is roughly equal to the $^4T_2$–^{2}E energy separation.

Thermal quenching in most Ru(II) polypyridyl complexes is mainly due to population of a ligand field state (^{3}MLCT $\Rightarrow$ d–d). $k_5 + k_6$ for ^{3}MLCT $\Rightarrow {}^1A_1$ is less than 10^7 s^{-1} [12].

The $^2E \Rightarrow {}^4A_2$ transition in Cr(III), the ^{3}MLCT $\Rightarrow {}^1A_1$ transitions in the d^6 complexes of Ru(II) and Os(III), as well as the $^3T_1 \Rightarrow {}^1A_1$ in Rh(III) are all characterized by relatively small rate constants [12]. The low temperature decay rates of these long-lived states are not usually affected by any processes that compete with the transition to the ground state. The magnitudes of the nonradiative $^2E \Rightarrow {}^4A_2$ rates at 77 K are, with few exceptions, less than 5×10^4 s^{-1}. The corresponding nonradiative rates for $^3T_1 \Rightarrow {}^1A_1$ are $<10^5$ s^{-1}. Thus the nonradiative rates for the prompt transition to the long-lived states are many orders of magnitude larger than the rates from the same thermalized states to the ground states.

The large number of lifetimes collected for luminescent complexes permits some generalizations about the effect of molecular structure on k_6 to be made. Two groups have been studied extensively; polypyridyl complexes of d^6 ions (Ru(II), Os(II), and Re(I)), and d^3 (Cr(III)) complexes. k_5 can be computed from the emission quantum yields and lifetimes (Eq. (9)) by assuming $\eta_D = 1$. Plots of $\ln k_6$ against the emission energy are quite linear for 33 Os(II) complexes [74]. This suggested that the electronic factor was not very different and the energy gap was the dominant factor in determining k_6 trends within a group of similar complexes. The transitions in this group originate in metal to ligand charge transfer states, ^{3}MLCT $\Rightarrow {}^1A_1$. The adequacy of the nonradiative transitions theory, embodied in Eqs. (12) and (13), for the calculation of the vibrational overlap was demonstrated by the linearity of the $\ln k_6$ versus $\ln F$ plots. Two thirds of the 33 calculations of $\beta_0 = k_6/F$ are within a five-fold range.

Analogous behavior was obtained for Ru(II) and Re(I) complexes [96–98].

The parameters in Eqs. (12) and (13) were obtained by fitting to the emission spectra of the d^6 complexes. Alternatively these parameters could be computed quantum mechanically in $Ru(bpy)_3{}^{2+}$ [98]. The only reported calculation of F in Cr(III) systems was for ruby [99]. This quantity was 10^{-26} and is consistent with a negligible k_6 as observed in ruby.

Another qualitative test of the theory was obtained for a group of Cr(III) complexes with coordination to six aliphatic nitrogen atoms. In this case, k_6 increased with the number of N–H bonds present, though not in a proportional manner [100,101]. Although the energy gap variation in the $^2E \Rightarrow {}^4A_2$ transition was small there was the expected dependence on this parameter. With few exceptions, $k_6 \gg k_5$ in Cr(III) complexes and quantum yield measurements are then unnecessary.

In order to avoid additional relaxation pathways the low temperature lifetimes were used in the correlations.

A number of $CrA_{6-n}B_n$ complexes were studied as a function of n. For $A = NH_3$ and $B = H_2O$, k_6 increases monotonically with n [102]. Apparently, O–H bonds are better quenchers than N–H bonds. However the ligands do not act independently, as demonstrated by the $Cr(NH_3)_{6-n}(D_2O)_n$, series where k_6 passes through a maximum as n is changed. Other series are: $A = ND_3$, $B = H_2O$; $A = NH_3$, $B = NCS^-$ [102]; $A = CN^-$, $B = H_2O$ [103]; $A = NCS^-$, $B = DMSO$ [104]. Empirically, NH_3, H_2O, and DMSO can be characterized as good quenchers while ND_3. D_2O, NCS^-, and CN^- are poor quenching ligands. The marked reduction of k_6 by deuteration of H_2O and NH_3 has been attributed to a reduction in ω_M and is characteristic of the nonradiative transitions in the weak coupling limit [105].

4. Discussion and conclusions

Is the classification into fast and slow intersystem crossing processes physically meaningful? In all measurements with ultrafast excitation, the fast rate exceeds 10^{12} s^{-1}. The slow rates for Cr(III), Ru(II), Os(II),and Rh(III) complexes are usually less than 10^6 s^{-1} at low temperatures, but in several Re(I) complexes can approach 10^8 s^{-1} [12,96]. Is the weak coupling model in which k_6 is represented by a product of electronic and vibrational factors adequate for both thermalized and prompt processes? It has been recognized that the parameters extracted from fitting the emission spectra are not unique [74], and rather different parameters were obtained for the same Re(I) polypyridyl complexes [96,97]. In these two calculations a factor of 10^6 was introduced into Eq. (12), but good concordance in $\ln F$ was obtained only by omitting this factor in one of the calculations. It is the constancy of β_0 that would indicate the lack of effective changes in spin–orbit coupling within each group of similar complexes.

The small k_6 magnitudes in the slow intersystem crossings support the designation of spin-forbidden, but no spin prohibition seems to be operative in the fast processes. Apparently mixing between states of differing spin is more important in k_{pisc} where the energy differences between states of different multiplicity are much less.

The qualitative predictions from the weak coupling limit are satisfied for both ^{2}E and ^{3}MLCT emitters. The energy gap law is operative in both cases, although the coupling strengths as measured by S_M are much different. The applicability of the same formalism for fast nonradiative transitions is questionable, but there are too few data to make a firm conclusion. The source of the difference between the fast and slow rates might be in the electronic or the vibrational factors. An analysis of F for ruby at 0 K lead to a difference of 25 orders of magnitude between k_4 and k_6 [99]. The electronic factors were assumed to be same for both the fast and slow processes.

In principle, k_{pisc} should vary with the energy of the Franck–Condon state because this rate is sensitive to the specific vibration excited [2]. However, vibronic band widths and overlapping vibronic energies may obscure this effect.

The assignment of the reactive state cannot be based solely on kinetic arguments. The most persuasive evidence that the slow reaction in Cr(III) complexes originates in the $^4T_2$ state after back-transfer is the same product distribution from both the fast and slow reactions. A good example is *trans*-$Cr(NH_3)_4(NCS)(CN)^-$ where three different photoaquation reactions are observed [106]. That the product ratios are the same for both the fast and slow reactions support the inference that both occur in the same state.

Although a unique fit to the measured quantities is not possible, no reasonable fit can be obtained when ϕ_{pr} is a major contributor to the fast reaction in any of the Cr(III) complexes. η_{pisc} cannot exceed η_{D}. Consequently, when η_{D} is less than unity vibrational relaxation in the initially excited state competes with intersystem crossing. No data on vibrational relaxation in complexes with $\eta_{\text{D}} < 1$ has been published. $Cr(en)_3{}^{3+}$ and $Cr(CN)_6{}^{3-}$ deserve attention in this respect. Is a reduction in η_{D} due to a decrease in k_{pisc} or an increase in the vibrational relaxation rate? A useful approach will be the determination of ultrafast rates for complexes with varying magnitudes of η_{D}. This will provide a test of the interpretation of the spectral dynamics.

Comparison of intersystem crossing rates and yields has been hampered by the lack of information on both quantities for the same complexes. The relative magnitudes of η_{pisc} and η_{isc} are uncertain. In principle, the relative contributions of k_{pisc} and k_4 can be determined from accurate risetimes of transient absorption. However, competition with vibrational relaxation will make such an analysis difficult. It might be possible to measure k_4 by trapping the excitation in $^4T_2$ below the crossover point at low temperatures. A question remains—is a thermalized distribution achieved in $^4T_2$ prior to reaching ^{2}E?

The question of a wave length effect on photoprocesses when excitation is confined to the same electronic state is still not definitively resolved. The claimed effects are small and the results insufficiently precise to reach reliable conclusions. More reliable results as a function of wave length are needed to assess the effect of the excitation energy on intersystem crossing rates and efficiencies.

At the present time, a simple three-state kinetic model is adequate for systematizing the results in transition metal complexes and searching for relations between molecular structure and dynamics. Since many intersystem crossing efficiencies have been determined for Cr(III) complexes and these span a wide range, a study of the intersystem crossing rates in these complexes might lead to a separation of the various contributions to the dynamics.

References

[1] G.A. Crosby, K.W. Hipps, W.H. Elfring Jr., J. Am. Chem. Soc. 96 (1974) 629.
[2] B.R. Hollebone, C.H. Langford, N. Serpone, Coord. Chem. Rev. 39 (1981) 181.
[3] A.D. Kirk, Chem. Rev. 99 (1999) 1607.
[4] A.D. Kirk, P.E. Hoggard, G.B. Porter, M.C. Rockley, M.W. Windsor, Chem. Phys. Lett. 37 (1970) 199.
[5] G.E. Rojas, C. Dupuy, D.A. Sexton, D. Magde, J. Phys. Chem. 90 (1986) 87.
[6] R. LeSage, K.L. Sola, R.W. Yip, C.H. Langford, Can. J. Chem. 61 (1983) 276.
[7] S.G. Pyke, M.W. Windsor, J. Am. Chem. Soc. 100 (1978) 6518.
[8] J.K. McCusker, Acc. Chem. Res. 36 (2003) 876.
[9] A. Vlček Jr., Coord. Chem. Rev. 200–202 (2000) 933.
[10] D.A. Friesen, S.H. Lee, R.E. Nashlem, S.G. Mezyk, W.L. Waltz, Inorg. Chem. 34 (1995) 4026.
[11] L.S. Forster, Adv. Photochem. 16 (1991) 215.
[12] L.S. Forster, Coord. Chem. Rev. 227 (2002) 59.
[13] N.A.P. Kane-Maguire, D.E. Richardson, C.G. Toney, J. Am. Chem. Soc. 98 (1976) 3996.
[14] C.T. Donnelly, T.J. Glynn, G.P. Morgen, G.F. Imbusch, J. Luminesc. 48/49 (1991) 283.
[15] C.H. Langford, Acc. Chem. Res. 17 (1984) 96.
[16] A.D. Kirk, Coord. Chem. Rev. 39 (1981) 225.
[17] M. Maestri, F. Bolletta, L. Moggi, V. Balzani, M.S. Henry, M.Z. Hoffman, J. Am. Chem. Soc. 100 (1978) 2694.
[18] A.D. Kirk, M.A. Rampi Scandola, J. Phys. Chem. 86 (1982) 4141.
[19] F. Bolletta, M. Maestri, V. Balzani, J. Phys. Chem. 80 (1976) 2499.
[20] N. Sabbatini, M.A. Scandola, V. Balzani, J. Phys. Chem. 78 (1974) 541.
[21] R. Fukuda, R.T. Walters, M. Mäcke, A.W. Adamson, J. Phys. Chem. 83 (1979) 2097.
[22] G. Orellana, A.M. Braun, J. Photochem. Photobiol. A 48 (1989) 277.
[23] X. Song, J.F. Endicott, Inorg. Chem. 30 (1991) 2214.
[24] D. Lynch, J.F. Endicott, Inorg. Chem. 27 (1988) 2181.
[25] R. Ballardini, G. Varani, H.F. Wasgestian, L. Moggi, V. Balzani, J. Phys. Chem. 77 (1973) 2947.
[26] W.L. Waltz, J. Lilie, S.H. Lee, Inorg. Chem. 23 (1984) 1768.
[27] X. Yang, C.A. Sutton, C. Kutal, Inorg. Chem. 21 (1982) 2893.
[28] V. Balzani, R. Ballardini, M.T. Gandolfi, L. Moggi, J. Am. Chem. Soc. 93 (1971) 339.
[29] N.A.P. Kane-Maguire, J.E. Phifer, C.G. Toney, Inorg. Chem. 15 (1976) 593.
[30] W.L. Waltz, R.T. Walters, R.J. Woods, Inorg. Chim. Acta 46 (1980) L153.
[31] C.M. Cimolino, R.G. Linck, Inorg. Chem. 20 (1981) 3499.
[32] F. Castelli, L.S. Forster, Chem. Phys. Lett. 30 (1975) 465.
[33] F. Castelli, L.S. Forster, J. Phys. Chem. 81 (1977) 403.
[34] G. Irwin, A.D. Kirk, I. Mackay, J. Nera, Inorg. Chem. 41 (2002) 874.
[35] A.F. Fucaloro, L.S. Forster, S.G. Glover, A.D. Kirk, Inorg. Chem. 24 (1985) 4222.
[36] E. Gowin, F. Wasgestian, Inorg. Chem. 24 (1985) 3106.

[37] A.D. Kirk, A.M. Ibrahim, Inorg. Chem. 27 (1988) 4567.
[38] A.D. Kirk, A.M. Ibrahim, Inorg. Chem. 29 (1990) 4848.
[39] H.H. Krause, F. Wasgestian, Inorg. Chim. Acta 29 (1978) 231.
[40] H.H. Krause, F. Wasgestian, Inorg. Chim. Acta 49 (1981) 231.
[41] K. Angermann, R. van Eldik, H. Kelm, F. Wasgestian, Inorg. Chem. 20 (1981) 955.
[42] D.A. Friesen, S.H. Lee, J. Lilie, W.L. Waltz, L. Vincze, Inorg. Chem. 30 (1991) 1975.
[43] H.F. Wasgestian, J. Phys. Chem. 76 (1972) 1947.
[44] F. Castelli, L.S. Forster, J. Phys. Chem. 78 (1974) 2122.
[45] F. Castelli, L.S. Forster, J. Phys. Chem. 81 (1977) 403.
[46] D.F. Nelson, M.D. Sturge, Phys. Rev. A 137 (1965) 1117.
[47] M.A. Jamieson, N. Serpone, M.Z. Hoffman, F. Bolletta, Inorg. Chim. Acta 72 (1983) 247.
[48] N. Serpone, M.A. Jamieson, R. Sriram, M.Z. Hoffman, Inorg. Chem. 20 (1981) 3983.
[49] M.A. Jamieson, N. Serpone, M.S. Henry, M.Z. Hoffman, Inorg. Chem. 18 (1979) 214.
[50] F. Bolletta, M. Maestri, L. Moggi, M.A. Jamieson, N. Serpone, M.S. Henry, M.Z. Hoffman, Inorg. Chem. 22 (1983) 2502.
[51] M.S. Henry, M.Z. Hoffman, Adv. Chem. Ser. 168 (1978) 91.
[52] N. Serpone, M.A. Jamieson, M.Z. Hoffman, J. Chem. Soc. Chem. Commun. (1980) 1006.
[53] M.A. Jamieson, N. Serpone, M.Z. Hoffman, J. Am. Chem. Soc. 105 (1983) 2933.
[54] N.A.P. Kane-Maguire, C.H. Langford, J. Am. Chem. Soc. 94 (1972) 2125.
[55] R. Sriram, M.Z. Hoffman, N. Serpone, J. Am. Chem. Soc 103 (1981) 997.
[56] D. Sandrini, M.T. Gandolfi, L. Moggi, V. Balzani, J. Am. Chem. Soc. 100 (1978) 1463.
[57] S.N. Chen, G.B. Porter, Chem. Phys. Lett. 6 (1970) 41.
[58] L.S. Forster, J. Vandermark, J.V. Rund, Inorg. Chim. Acta 202 (1992) 141.
[59] L.S. Forster, Inorg. Chim. Acta 247 (1996) 1.
[60] E.E. Wegner, A.W. Adamson, J. Am. Chem. Soc. 88 (1966) 394.
[61] A.R. Gutierrez, A.W. Adamson, J. Phys. Chem. 82 (1978) 902.
[62] Y.S. Kang, L.S. Forster, J. Phys. Chem. 83 (1979) 2368.
[63] J.N. Demas, G.A. Crosby, J. Am. Chem. Soc. 93 (1971) 2841.
[64] J.N. Demas, D.G. Taylor, Inorg. Chem. 18 (1979) 3177.
[65] R. Bensasson, C. Salet, V. Balzani, Comput. Rend. Acad. Sci. 289 (1979) 41.
[66] F. Bolletta, A. Juris, M. Maestri, D. Sandrini, Inorg. Chim. Acta 44 (1980) L175.
[67] C. Conti, F. Castelli, L.S. Forster, Inorg. Chim. Acta 33 (1979) L171.
[68] N.A.P. Kane-Maguire, N. Helwic, J.M. Derrick, Inorg. Chim. Acta 102 (1985) L21.
[69] A.D. Kirk, C. Namasivayam, Inorg. Chem. 22 (1983) 2961.
[70] A.D. Kirk, S.R.L. Fernando, Inorg. Chem. 33 (1994) 4435.
[71] R. Sasseville, C.H. Langford, J. Am. Chem. Soc. 101 (1979) 5834.
[72] F. Castelli, L.S. Forster, J. Am. Chem. Soc. 95 (1973) 7223.
[73] R. Englman, Non-radiative Decay of Ions and Molecules in Solids, North-Holland, Amsterdam, 1979.
[74] E.M. Kober, J.V. Caspar, R.S. Lumpkin, T.J. Meyer, J. Phys. Chem. 90 (1986) 1722.
[75] P. Chen, T.J. Meyer, Chem. Rev. 98 (1998) 1439.
[76] W. Siebrand, Z. Zgierski, Chem. Phys. Lett. 35 (1975) 153.
[77] C.A. Daul, Chimia 58 (2004) 36.
[78] C. Daniel, Coord. Chem. Rev. 238/239 (2003) 143.
[79] Z.A. Siddique, Y. Yamamoto, T. Ohno, K. Nozaki, Inorg. Chem. 42 (2003) 6366.
[80] M. Woeller, S. Grimme, S.D. Peyerimhoff, J. Phys. Chem. A 104 (2000) 5366.
[81] N.L. Doltsinis, D. Marx, Phys. Rev. Lett. 88 (2002) 166402.
[82] S.A. Pollack, IEEE Quant. Electron. QE4 (1968) 703.
[83] G.E. Rojas, D. Magde, J. Phys. Chem. 91 (1987) 689.
[84] N.H. Damrauer, G. Cerrullo, A. Yeh, T.R. Boussie, C.V. Shank, J.K. McCusker, Science 275 (1997) 54.
[85] A.C. Bhaskuttan, M. Suzuki, S. Nakashima, T. Okada, J. Am. Chem. Soc. 124 (2002) 8398.
[86] A.T. Yeh, C.V. Shank, J.K. McCusker, Science 289 (2000) 935.
[87] E.A. Juban, J.K. McCusker, J. Am. Chem. Soc. 127 (2005) 6857.
[88] W. Targos, L.S. Forster, J. Chem. Phys. 44 (1966) 4342.
[89] J.K. McCusker, K.N. Walda, R.C. Dunn, J.D. Simon, D. Magde, D.N. Hendrickson, J. Am. Chem. Soc. 115 (1993) 298.
[90] J.E. Monat, J.K. McCusker, J. Am. Chem. Soc. 122 (2000) 4092.
[91] M.A. Bergkamp, C.R. Chang, T.L. Netzel, J. Phys. Chem. 87 (1983) 4441.
[92] A. Vlček Jr., Coord. Chem. Rev. 177 (1998) 219.
[93] D. Guillaumont, A. Vlček Jr., C. Daniel, J. Phys. Chem. A 105 (2001) 1107.
[94] I.R. Farrell, P. Matousek, M. Towrie, A.W. Parker, D.C. Grills, M.W. George, A. Vlček Jr., Inorg. Chem. 41 (2002) 4318.
[95] L.S. Forster, Chem. Rev. 96 (1991) 321.
[96] L.A. Worl, R. Duesing, P. Chen, L.D. Ciena, T.J. Meyer, J. Chem. Soc., Dalton Trans. (1991) 849.
[97] V.I. Baranovskii, O.O. Lublimova, Chem. Phys. Lett. 370 (2003) 636.
[98] V.I. Baranovskii, O.O. Lublimova, Opt. Spectry 94 (2003) 502.
[99] W.H. Fonger, C.W. Struck, Phys. Rev. B 11 (1975) 3251.
[100] K. Kühn, F. Wasgestian, H. Kupka, J. Phys. Chem. 85 (1981) 665.
[101] L.S. Forster, O. Mønsted, J. Phys. Chem. 90 (1986) 5131.
[102] A. Fucaloro, L.S. Forster, J.V. Rund, S.H. Lin, J. Phys. Chem. 87 (1983) 1796.
[103] A. Ghaith, L.S. Forster, J.V. Rund, Inorg. Chim. Acta 116 (1986) 11.
[104] W. Strek, E. Lukowiak, B. Jeźowska-Trzebiatowska, J. Luminesc. 15 (1977) 437.
[105] K. Maruszewski, K. Bajdor, D.P. Strommen, J.R. Kincaid, J. Phys. Chem. 99 (1995) 6286.
[106] P. Riccieri, E. Zinato, A. Damiani, Inorg. Chem. 26 (1987) 2667.