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# DIPOLE-FORBIDDEN ENERGY TRANSFER PROCESS IN SOLUTION

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## ABSTRACT

The transfer of electronic excitation energy to or from d-d excited states of transition metal compounds is formally dipole forbidden and is allowed by an electron exchange mechanism. In this limit, the quenching rate constant may be factored into contributions of an electronic term and a Franck-Condon, or nuclear term. A formalism based on non-radiative relaxation of electronic excited states is used to identify important features of the Franck-Condon term in the strong coupling and the weak coupling limits. Many of the systematic studies so far reported in fluid solution have involved the $^4A_2 \leftrightarrow {}^2E$ electronic transition of Cr(III) in either the donor or acceptor and such systems often correspond to the weak coupling limit. The behavior observed in this limit has been thought to deviate from expectation, but the proper accounting for the vibrational modes available to accommodate the excess energy in a weak coupling formalism accounts for the observed gap dependencies. When ($^2$E)Cr(III) excited states are employed with ($^1A_1 \rightarrow {}^3T_1$)Co(III) acceptors, a strong coupling formalism may be employed to extract information about the electronic factor from variations in the quenching rates. The strong coupling and weak coupling formalisms, based on unimolecular radiationless transitions, have successfully described many aspects of bimolecular reactions, but several issues remain. Some of these issues will require observations on metal-to-metal energy transfer in multimetal molecules. A few pertinent studies are becoming available.

## INTRODUCTION

The transfer of electronic excitation energy between molecular centers is one of the simplest and most fundamental classes of light initiated processes. When the molecular species are transition metal complexes in fluid solutions and when metal centered ligand field (or d-d) excited states are involved, the basic principles for description of the energy transfer reaction coordinate are not altogether clear. Thus the much studied and well understood dipole-dipole, or Förster mechanism for energy transfer (refs. 1-3) is not applicable when Laporte (e.g., ligand field) or spin forbidden excited states are involved. For such systems, short range, collisionally activated energy transfer mechanisms must be operative. If the electronic transition within the donor is dipole allowed, then a dipole-multipole mechanism may be

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important, if not, the energy transfer process is presumed to depend upon exchange coupling of the donor and acceptor (ref. 3). In the limit of an exchange mechanism, the formal description of the rate constant for energy transfer (ref. 3) is similar in a general way to descriptions of the rate constant for outer-sphere electron transfer processes (e.g., see ref. 4). Thus the formalisms used to describe the rates of electron transfer processes have been applied to describe the rates of energy transfer between transition metal complexes (ref. 5), and it has been argued that energy transfer processes can provide useful insight into novel aspects of the factors governing electron transfer rates (refs. 6,7).

A number of systematic experimental studies of energy transfer involving transition metal complexes have appeared in the past few years (e.g. see refs. 5-11). These studies can be approximately classified by the types of donor and acceptor excited states: (a) organic triplet donor--d-d acceptor; (b) metal to ligand charge transfer (MLCT) donor--d-d acceptor; (c) d-d donor--d-d acceptor. Each class of energy transfer reactions raises slightly different issues and illustrates slightly different points. Several of these issues will be considered below in the light of available information and pertinent models for the energy transfer process.

## GENERAL MECHANISTIC CONSIDERATIONS FOR ENERGY TRANSFER INVOLVING TRANSITION METAL COMPLEXES.

Dipole-multipole mechanisms have to be considered for charge-transfer or ligand centered excited states of heavy metal donors in which spin orbit coupling makes spin a poorly defined quantum number. This issue has been addressed for energy transfer reactions of ruthenium(II)-polypyridyl MLCT donors with chromium(III) acceptors (ref. 12). Since no correlation could be found between the spin allowed acceptor transitions and the rates of the energy transfer reactions, this study inferred that the dipole-multipole mechanism was not a major factor in the observed reactivity patterns.

It is more useful to consider the energy transfer processes as radiationless transitions within a collision complex. In this approach the energy transfer rate may be formulated, within the context of the Fermi Golden Rule, as,

$$k_q/K_o = (2\pi/\hbar)\langle V\rangle^2 N\rho \qquad (1)$$

where $\rho$ is a density of states parameter and the variations in the energy transfer rate ($k_q/K_o$) in the collision complex are attributed to variations in a nuclear, or Franck-Condon factor (N) and/or to variations in the electronic matrix element, $\langle V\rangle$ (ref. 3) (for $k_q$ the bimolecular rate constant and $K_o$ an equilibrium constant for formation of the collision complex). Insofar as the Born-Oppenheimer approximation is valid, (1) allows one to discuss the reaction coordinate in terms of reactant and product potential energy surfaces based on the nuclear factor (N), and the effectiveness of the coupling of those surfaces, based on the electronic factor <V>. Very similar approaches have been used to describe simple electron transfer reactions (e.g. refs. 13,14).

## Reaction Categories

Two qualitatively distinct limits can be distinguished for radiationless transitions (ref. 15):

1. *The activated surface crossing limit (strong coupling)*. In this limit, the initial and final states of the system differ considerably in bond lengths or bond angles. This results in an intersection of the potential energy surfaces and a classical activation energy for the transition:

$$E_a \approx (\lambda/4)(1 + \Delta E/\lambda)^2 \qquad (2)$$

where the minima of the two surfaces differ by $\Delta Q_o$ in their nuclear coordinates, $\lambda = (f/2)(\Delta Q_o)^2$, f = a mean force constant for normal modes associated with $\Delta Q_o$, and $\Delta E$ is the difference in the zero point potential energy of the initial state and final state (see Fig. 1a). This is the

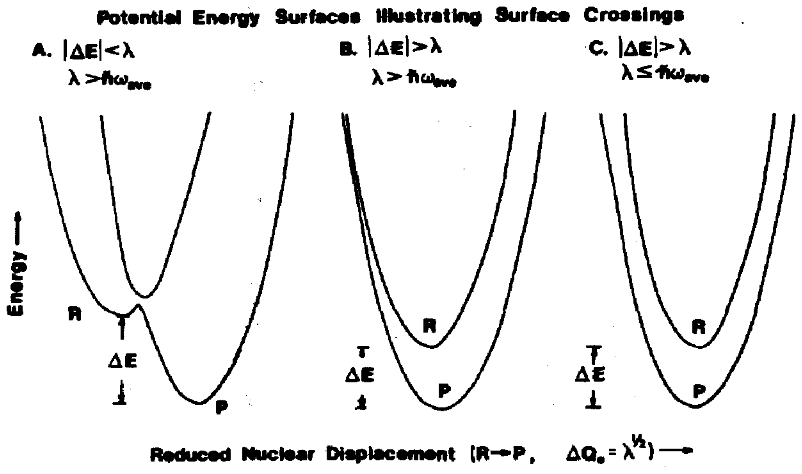

Fig. 1. Qualitative potential energy surfaces illustrating surface crossings. (a) Category I (strong coupling limit). (b) Category III (intermediate strong coupling). (c) Category II (weak coupling limit).

limiting condition most appropriate to simple electron transfer reactions. For $\omega_{ave}$ the mean vibrational frequency associated with the surface crossing, the conditions for this limit are: (a) $|\Delta E| \leq \lambda$; (b) $\lambda >> \hbar\omega_{ave}$.

2. The nested surface limit (weak coupling). In this limit the nuclear coordinates of the initial and final states are very similar. In such a situation, the non-radiative transition between surfaces depends entirely on nuclear and electronic "tunneling," the transition rate is very nearly temperature independent (see Fig. 1c) and decreases with increasing $|\Delta E|$. The low temperature $^2E_g \rightarrow {}^4A_{2g}$ relaxation rates of Cr(III) complexes appear to approach this limit. The conditions for this limit are: (a) $|\Delta E| > \lambda$; (b) $\lambda \sim \hbar\omega_o$.

Not all real systems can be conveniently described by these limits and some behavior intermediate between them should be considered:

3. Large displacement-large gap ("inverted region") behavior. This is the most commonly encountered intermediate situation. It has been extensively discussed, mostly within the context of electron transfer reactions (e.g., refs. 4,5,16,17), and has been referred to as the inverted region since the usual (strong coupling limit) electron transfer formalism predicts a decrease in rate with $|\Delta E|$ when the gap is sufficiently large. If the displacement of initial and final state surfaces is also large, there should be a formal intersection of the zero order potential energy surfaces, and some features of an activated crossing might be retained. (Fig. 1b). This behavior corresponds to: (a) $|\Delta E| > \lambda$; (b) $\lambda > \hbar\omega_{ave}$.

4. Small displacement-small gap behavior. In energy transfer reactions one frequently encounters very small initial state-final state energy gaps. As a result, intermediate situations can arise, which in principle derive from limit 2, above. Such situations have received very little attention. The conditions for this kind of intermediate behavior, are: (a) $|\Delta E| < \lambda$; (b) $\lambda \leq \hbar\omega_{ave}$.

While the above reaction categories can be reasonably and straightforwardly discussed for radiationless transitions in molecules, there are some complicating aspects in bimolecular reactions that need to be carefully examined. The major concerns relate to the nuclear reorganizational parameter, $\lambda$, and the electronic matrix element. These issues will be discussed in turn below.

## The nuclear reorganizational parameter ($\lambda$).

In the limit of strong coupling, categories 1 and 3, and for harmonic potential energy functions, the nuclear reorganizational parameter for a cross reaction can be represented by the mean of the reorganizational parameters for the component exciton exchange reactions,

$\lambda = (1/2)\ (\lambda_D + \lambda_A)$ (3)

For energy transfer reactions, where the cross reaction is of the form,

$*D + A \rightarrow D + *A$

the exciton exchange reactions are

$*D + D' \leftrightharpoons D + *D'$ $(\lambda_D)$

$A + *A' \leftrightharpoons *A + A'$ $(\lambda_A)$

where the asterisk indicates an electronically excited molecule and the prime designates an arbitrary (e.g., isotopic) label used to distinguish different molecules of the same chemical species.

Use of eq. (3) is difficult to justify when one or both of the degenerate exciton exchange reactions falls into either category 2 or 4. Since the energy transfer rates in the weak coupling limit depend on nuclear and electronic tunneling coefficients, there is no simple way to partition the kinetic parameters into separate donor and acceptor contributions. Even for $|\Delta E|$ large and $T \rightarrow 0$, the weak coupling limit leads to an expression of the form (refs. 15,18),

$-\ln(k_q/K_oD) \approx +(\lambda/\hbar\omega_{ave}) + \gamma(\Delta E - \hbar\omega_k)/\hbar\omega_M$ (4)

(where D is a vibronic frequency term, $\gamma$ is a slowly varying function of $\Delta E$ and the contributions to $\Delta E$ from high frequency vibrational modes ($\omega_M$), and for $\omega_k$ a promoting mode). In this limit, an "intrinsic" parameter based on the gap independent contributions to $k_q$ is approximately $[\lambda/\hbar\omega_{ave} - \gamma\hbar\omega_k/\hbar\omega_M]$ compared to $[\lambda/4RT]$ from equation (2). When $\hbar\omega_k \sim k_BT$, population of the promoting modes will lead to a positive contribution of these modes for the "intrinsic" parameter. The situation for $\Delta E \rightarrow 0$ in the weak coupling limit has not received much experimental or theoretical attention.

Energy transfer between $(^2E)Cr(III)$ donors and $(^4A_2)Cr(III)$ acceptors will correspond to the weak coupling limit ($\lambda \sim 0$) with $\Delta E$ small or approaching zero. There are a few scattered observations. Energy transfer between Cr(III) complexes in the solid state does occur, but it is relatively inefficient (refs. 19,20). There have been a few pertinent studies of polypyridyl (PP) chromium(III) complexes in solution. Thus, reactions of the type,

$(^2E)Cr(PP)_3{}^{3+} + (^4A_2)Cr(PP')_3{}^{3+} \rightarrow (^4A_2)Cr(PP)_3{}^{3+} + (^2E)Cr(PP')_3{}^{3+}$ (5)

have not been detected and $k_q \leq 10^7\ M^{-1}s^{-1}$(20). In contrast, the "self-quenching" reactions,

$(^2E)Cr(phen)_3{}^{3+} + (^4A_2)Cr(PP)_3{}^{3+} \rightarrow (^4A_2)Cr(phen)_3{}^{3+} + (^4A_2)Cr(PP)_3{}^{3+}$ (6)

do occur with $k_{sq} \sim 10^7\ M^{-1}s^{-1}$ (21). Since $|\Delta E|$ is very large for (6) and very small for (5), but $\lambda \sim 0$ for both reactions, consideration of eq. (4) suggests that the "intrinsic" Franck-Condon parameters are smaller and/or the electronic factor ($\langle V \rangle$) is larger for (6) than for (5). The very limited available information indicates that the rates of reaction (6) are more dependent on the spatial extension of the ligand π-systems than on the reactant-product energy gap, and this is suggestive of a dominant electronic factor. The issues of possible promoting modes and accepting modes have not been addressed.

If there is any significant Stokes shift in the excited state emission, the corresponding degenerate energy transfer reactions fall into category 1. For example this should be so for (*CT)Ru(II)-($^1A_1$)Ru(II) reactions and for ($^1A_1$)Co(III)-($^3T_1$)Co(III) reactions. For such systems, the nuclear reorganizational parameter can be considered a well defined quantity which is transferable to any category 1 or 3 cross energy transfer reaction.

Most cross energy transfer reactions will have appreciable energy gaps and many will fall into categories 2 or 4, even though one or both of the component exciton transfer reactions may fall into category 1. When this is the case, $\lambda_A$ and $\lambda_D$ in eq.(3) are not simply related to measurable parameters from the exciton exchange reactions. The experimentally inferred reorganizational parameters have different physical meanings for reactions in the different limiting categories.

## SURVEY OF SELECTED ENERGY TRANSFER STUDIES

### The Franck-Condon contributions found in energy transfer reactions.

The problems of interpreting experimental observations will also be present in the different intermediate energy transfer categories. Thus, a series of reactions could exhibit a normal gap dependence, characteristic of category 1 behavior, and approach a limiting value of $k_q$ as $N \rightarrow 1$ for very large gaps. Such a situation is illustrated by the data in Figure 2. The form of the Franck-Condon factor in the region in which $|\Delta E| \gtrsim \lambda$ has received much theoretical and experimental attention (refs. 4,5,8-11, 14-18), and the limiting values of $k_q$ (for $N \sim 1$) have formed the experimental basis for discussions of the nature of the electronic matrix element (refs. 5-12). If any of these reactions happened to fall into categories 2 or 4 one would expect a relatively shallow gap dependence, with $k_q$ decreasing as $|\Delta E|$ increases (refs. 15,18). In contrast, the several systems so far examined have tended to have values of $k_q$ which either appear to be gap independent or to increase with $|\Delta E|$. These systems will be considered in turn below. This work has involved either Cr(III) donors or Cr(III) acceptors for which $\lambda_{Cr} \sim 0$.

Energy transfer to Cr(III) acceptors.

Chromium(III) acceptors have been used in systematic studies with organic triplet (ref.11) and with MLCT-ruthenium-polypyridyl (refs. 8,10,12) donors. The nature of the acceptor electronic state in these complexes is not absolutely clear. The lowest energy doublet state, for simplicity called "$^2E$", is a well characterized state, with the same molecular geometry as the gound state. Somewhat higher in energy is a second collection of doublet states, for simplicity called "$^2T_1$", which have the same orbital populations. In $Cr(NH_3)_6^{3+}$, $E(^2T_{1g}) - E(^2E_g) \sim 700$ cm$^{-1}$ (ref. 23). In complexes of lower symmetry some or all of the degeneracies are removed and there can be up to 5 possible acceptor states spanning a range of $\sim 1 \times 10^3$ cm$^{-1}$ above the lowest doublet component. The gap dependence for any energy transfer reactions falling into category 2 will tend to favor the highest energy of these possible acceptor states. The large number of possible acceptor states, scattered over an appreciable energy range, compared to $\Delta E$, is probably an important factor in the experimentally observed dependence (or independence) of $k_q$ on the energy gap.

Using a series of organic triplet donors with each of two closely related Cr(III) acceptors, Wilkinson and Tsiamis (ref.11) have shown: (1) a limiting value of $k_q$ is reached near the energy of the $^2T_1$ acceptor state; (2) that the limiting value of $k_q$ depends on the acceptor, being much nearer the diffusion limit (as corrected by a spin statistical factor of 1/6) for the smaller complex, $Cr(acac)_3$, than for the larger $Cr(dpm)_3$ (dpm = 2,2,6,6-tetramethyl-3,5-heptanedionate); and (3) the limiting values of $k_q$ were nearly independent of $\Delta E$. These observations, Fig. (2a), suggest a very small empirical reorganizational parameter ($\lambda$) for these systems. Complementary studies using a single donor and several Cr(III) acceptors (Fig. 2b) support this inference. These small values of $\lambda$ should lead to category 2 behavior and smaller values of $k_q$ for very large $|\Delta E|$. That this is not the case can be attributed to the combined effect of the several acceptor doublet electronic states and the contributions of different collections of high frequency vibrational mode ($\hbar\omega_M$) for the large values of $|\Delta E|$ than for the small values of $|\Delta E|$. This interpretation is discussed in more detail below.

Several studies of (*CT)Ru(II)-Cr(III) energy transfer systems have been reported (refs. 8,10,12), where the donor is a MLCT excited state of polypyridyl-ruthenium(II) species. The donor emission overlaps significantly with the Cr(III) acceptor ($^4A_2 \rightarrow {}^4T_2$) absorbance in many of these studies (ref. 12). Since spin-orbit coupling is often considered to make the triplet state designation inappropriate for the (*CT)Ru(II) excited states (refs. 8,10,24), the appreciable donor-acceptor overlap raises the possibility of a dipole-

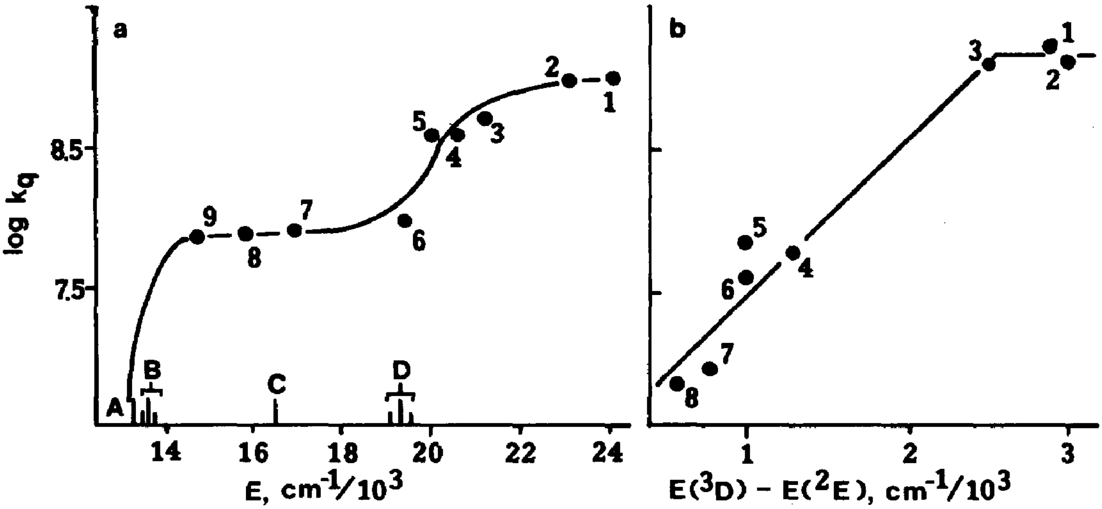

Fig. 2. Energy gap dependence of $^3$(organic) + Cr(III) energy transfer reactions. (a) ($^4A_2$)Cr(dpm)$_3$ acceptor with organic donors: 1, benzophenone; 2, triphenylene; 3, naphthalene; 4, 2-acetonaphthone; 5, chrysene; 6, coronene; 7, pyrene; 8, acridine; 9, anthracene (based on ref. 11). Energies of potential acceptor excited states are indicated: A, $^2$E; B, $^2$T, (short lines allow for typical splittings); C, $^4T_2$; D, $^2T_2$. (b) $^3$(acridine) with several Cr(III) acceptors: 1, Cr(NCS)$_6^{3+}$; 2, Cr(acac)$_3$; 3, Cr(NH$_3$)$_2$(NCS)$_4^-$; 4, Cr(C$_2$O$_4$)$_3^{3-}$; 5, Cr(NH$_3$)$_5$Br$^{2+}$; 6, Cr(NH$_3$)$_5$Cl$^{2+}$; 7, Cr(en)$_3^{3+}$; 8, Cr(NH$_3$)$_6^{3+}$ (based on ref. 22).

multipole contribution to the (*CT)Ru(II)-Cr(III) energy transfer mechanism. This issue has been considered (ref.12), but no correlation has been found between the quartet excited state parameters, and the quenching rates and the contributions of such a mechanism seem unlikely. Consideration of energy transfer rates in (*CT)Ru(II)-Cr(III) systems in which there is no significant spectral overlap indicates that there is a shallow, but category 1-type energy gap dependence (e.g., see Fig. 3). Such a correlation can be generated for either $^2$E or for $^2T_1$ acceptor excited states, but the small values of $\lambda$ and relatively large values of $|\Delta E|$ would place the (*CT)Ru(II) → ($^2$E)Cr(III) energy transfer within the category 2 regime. If no other factors intervened, one would expect the $^2$T, to be the favored acceptor state, and $k_q$ should decrease with $|\Delta E|$. However, the values of $|\Delta E|$ are small enough that the effects of several "high frequency" acceptor modes have to be considered; e.g., for $|\Delta E| \geq 3\times10^3$ cm$^{-1}$, the C-H stretching modes will make the dominant contribution to $\hbar\omega_M$. The net result of the contributions of the two sets of acceptor electronic states ($^2$E and $^2T_1$) and potential contributions to $\hbar\omega_M$

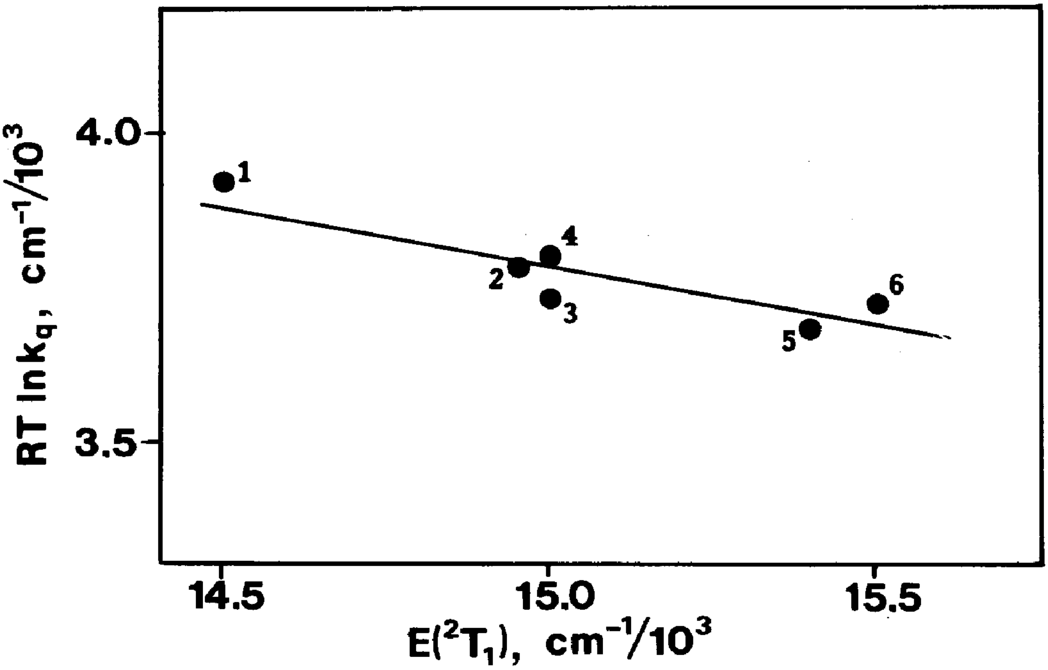

Fig. 3. Variation of quenching rate with energy gap for (*CT)Ru(bpy)$_2$(CN)$_2$ -Cr(III) reactions in which the only accessible acceptor states are doublets. Acceptors: 1, *trans*-Cr([14]aneN$_4$)(CN)$_2$$^+$; 2, Cr(chda)$_3$$^{3+}$; 3, Cr(NH$_3$)$_5$CN$^{2+}$; 4, Cr(en)$_3$$^{3+}$; 5, Cr(NH$_3$)$_6$$^{3+}$; 6, Cr(NH$_3$)$_5$OH$_2$$^{3+}$. Values of $k_q$ have been corrected for variations in $K_o$. Based on ref. 12.

from vibrational modes (of the quenched donor) in distinctly different energy ranges will be a very shallow, if any, dependence of $k_q$ on $|\Delta E|$. The slope will depend on the detailed relationships between the energy range spanned by the acceptor electronic states and the frequency ranges spanned by modes contributing to $\hbar\omega_M$. A very approximate illustration of the expected behavior is shown in Fig. 4. In order to generate this figure only the highest frequency modes contributing to $\hbar\omega_M \leq |\Delta E|$ have been considered, it has been assumed that $E(^2T_1) - E(^2E) = 700$ cm$^{-1}$, and these acceptor electronic states have been assumed to have similar values of $\langle V \rangle$. This approach can clearly account for an extended range of observed gap independence for many reactions falling in category 2.

The Cr(III) complexes containing halide or pseudohalide ligands are relatively good quenchers of the (*CT)Ru(II) excited states (refs. 8,10,12), although the rates observed are less than a factor of 10 greater than those

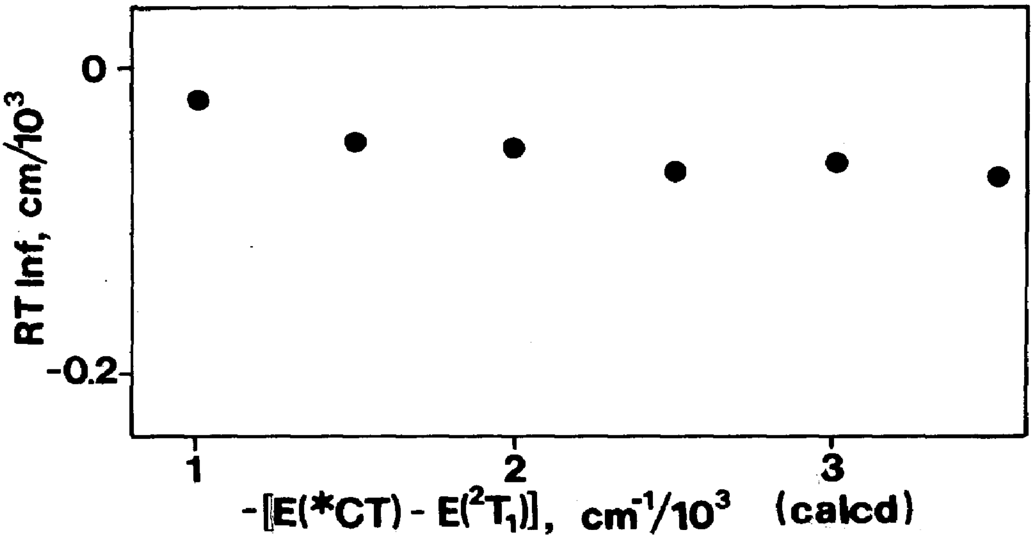

Fig. 4. Gap dependence predicted for (*CT)Ru(II) - $(^4A_2)$Cr(III) energy transfer. Assumes category 2 behavior (weak coupling), $\hbar\omega_M \sim (1.2 \pm 0.2) \times 10^3$ or $(3.0 \pm 0.2) \times 10^3$ cm$^{-1}$ for $(^1A_1)$Ru(II) and $E(^2T_1) - E(^2E) \approx 0.7 \times 10^3$ cm$^{-1}$ for acceptor states on Cr(III). $f = \sum(\Delta E_i \hbar\omega_{M,i})^{-\frac{1}{2}} \exp(-\Delta E_i/\hbar\omega_{M,i})$. Only the largest values of $\hbar\omega_M \leq |\Delta E|$ have been considered. Sum is over both acceptor states and the appropriate values of $\hbar\omega_M$.

predicted based on energy gap correlations such as that in Fig. 3 (ref. 12). These enhanced quenching rates could, in principle, be attributed to: (a) a nephelauxetic effect which expands the acceptor d-orbital wave functions, giving enhanced donor-acceptor overlap, bigger values of ⟨V⟩ and, thus, larger values of $k_q$ (refs. 8,10,25); or (b) an intermolecular, charge-transfer perturbation which has the effect of increasing ⟨V⟩ (refs. 7,12); (c) a significant change in the energy range spanned by components of the $^2E$ and $^2T_1$ states in these relatively low symmetry complexes.

The nephelauxetic parameter, $\beta = B/B_0$ (B and $B_0$ are Racah parameters for the complex and the free ion, respectively), is a measure of the different effects of electron repulsion on the complex and free ion d-orbitals (refs. 26,27). Different values of β and B are required for the quartet and the doublet excited states (refs. 23,26,27). The doublet state parameters, $\beta_{55}$ and $B_{55}$, are often interpreted in terms of σ-bonding parameters (refs. 23,26,27) and do not vary much when one or two ligands are substituted in amine complexes (ref. 12); i.e., $\beta_{55} \approx 0.81 \pm 0.01$ for the Cr(III) acceptors used in references 8,10, and 12. An approximate MO argument has been used to suggest that $\langle V\rangle \sim (1 - \beta^{\frac{1}{2}})$ (ref. 8) and there may be some tendency for $k_1$ to increase with $(1 - \beta_{55}^{\frac{1}{2}})^2$ for the $(^*CT)Ru(bpy)_2(CN)_2 - Cr(Amine)_6^{3+}$ reactions (ref. 12). However, the doublet state energies are strong functions of $\beta_{55}$ and the correlation in Fig. 3 guarantees that there will also be a crude correlation with $(1 - \beta_{55}^{\frac{1}{2}})^2$. Variations in $\beta_{55}$ do not account for variations of $k_q$ for both the hexamine-type and the haloamine-type acceptors. While the total pattern of variations in $k_q$ cannot be attributed to the nephelauxetic parameter, some contributions of $\beta_{55}$, in combination with other factors, cannot be unequivocally excluded at this time. However, no clear correlation has emerged. Furthermore, it seems very unlikely that the electronic matrix element can be so neatly factored into individual contributions of donor and acceptor as a correlation of $k_q$ with $(1 - \beta_{55}^{\frac{1}{2}})^2$ would require.

A small charge-transfer perturbation of $\langle V \rangle$, arising because the donor ($^*$CT)Ru(II) excited states are good oxidants and the halide and pseudo-halide ligands are ionizable, could account for many of the deviations of $k_q$ from simple correlations with $\Delta E$. The small size of the effect for these systems, possibly an order of magnitude smaller than found in $(^2E)Cr(PP)_3^{3+}$ - Co(III) systems (refs. 7 and 28), is attributable to the more weakly oxidizing ruthenium (than $(^2E)Cr(PP)_3^{3+}$) excited states. Thus the overall behavior of ($^*$CT)Ru(II)-Cr(III) seem best described by a combination of Franck-Condon and electronic factors in the weak coupling regimes (categories 2 or 4). The detailed origins of many of the small rate variations are not at present clear.

### Energy transfers for $(^2E)Cr(PP)_3^{3+})$ donors

There have also been systematic studies of the $(^2E)Cr(PP)_3^{3+}$ - Co(III) energy transfer systems. These systems contrast with those discussed in the preceeding section in that there is a very large distortion associated with population of any of the acceptor excited states. The best characterized of the acceptors is $Co(NH_3)_6^{3+}$, for which the low temperature, single crystal absorption spectra indicate a tetragonal distortion of the $^3T_1$ excited state: a 12 pm expansion of four equatorial Co-N bonds and a 4 pm axial compression (ref. 29). The Stokes shift for the $^1A_{1g} \leftrightarrow {}^3T_{1g}$ transition is ~ 6 x 10$^3$ cm$^{-1}$, so for the degenerate exciton exchange transfer reaction,

$$(^3T_{1g})Co(NH_3)_6^{3+} + (^1A_{1g})Co'(NH_3)_6^{3+} \rightarrow (^1A_{1g})Co(NH_3)_6^{3+} + (^3T_{1g})Co'(NH_3)_6^{3+}$$

$\lambda \sim 6 \times 10^3$ cm$^{-1}$. This, and $\lambda_D \sim 0$ lead to $\lambda \sim 3 \times 10^3$ cm$^{-1}$ for category 1 or 3 behavior of,

$$(^2E)Cr(PP)_3^{3+} + (^1A_{1g})Co(NH_3)_6^{3+} \rightarrow (^4A_2)Cr(PP)_3^{3+} + (^3T_{1g})Co(NH_3)_6^{3+}$$

The $(^2E)Cr(PP)_3{}^{3+}$ - Co(III) energy transfer reactions exhibit several features anticipated for category 3 behavior (refs. 6,7,9,28): (a) estimated energy gaps are $(1 - 4.5) \times 10^3$ $cm^{-1}$, so for many of the reactions $|\Delta E| \sim \lambda$; (b) over this range of $\Delta E$, $k_q$ is found to be insensitive to the donor-acceptor energy gap, (c) $Co(NH_3)_6{}^{3+}$ and $Co(ND_3)_6{}^{3+}$ have nearly the same values of $k_q$ (indicating that Co-N nuclear tunneling does not make a significant contribution).

Despite all the evidence that $E_a \sim 0$, the Co(III) acceptors are inefficient quenchers of $(^2E)Cr(PP)_3{}^{3+}$. For example, $k_q = 1.4 \times 10^6$ $M^{-1}s^{-1}$ for the $(^2E)Cr(phen)_3{}^{3+}$ - $Co(NH_3)_3{}^{3+}$ reaction (25° C, 1 M $NaCF_3SO_3$), a value only about 0.1% of the diffusion limited collision frequency. This inefficiency of $(^2E)Cr(PP)_3{}^{3+} \rightarrow Co(III)$ energy transfer has been attributed to contributions of the electronic matrix element, <V> (refs. 6,7,9,28). Since there seem to be relatively few ambiguities concerning these systems and since $k_q$ appears to be insensitive to Franck-Condon factors, the $(^2E)Cr(PP)_3{}^{3+} \rightarrow Co(III)$ energy transfer systems can provide relatively direct experimental information about the contributions to <V> and how they affect simple bimolecular reactions. Thus $k_q$ for these systems has been found to decrease with increasing size of the donor and acceptor (refs. 6,28) and to increase as the energy of charge transfer excited states becomes smaller (refs. 7,28). These points are elaborated below. There has also been some speculation that $k_q$ in $(^2E)Cr(PP)_3{}^{3+} \rightarrow Co(III)$ systems can be correlated with nephelauxetic parameters (ref. 9), but no clear correlation has been demonstrated.

### Other $(^2E)Cr(III)$ - acceptor systems

A variation on the approaches described above is to vary the acceptor electronic structure while keeping other factors (ligands, medium, etc.) constant. A few efforts in this direction are summarized in Table I. A relatively trivial point, emphasized by the observations in Table I, is that the only coordination complexes which are at all effective as quenchers of $(^2E)Cr(PP)_3{}^{3+}$ are those with accessible excited electronic states. A second point reinforces some comments made above: one expects $\beta_{55}$ to depend more on the ligands and the charge type of the quencher than on the specific metal (refs. 23,26,27), and there is no correlation of $k_q$ with such factors. The estimated energy parameters in Table I are for the spin allowed quenching processes, and there may be some tendency for $k_q$ for the $M(OH_2)_6{}^{2+}$ complexes to decrease as $\Delta E$ becomes more negative. Since Stokes shifts are unknown for most of these acceptors, since estimates of the equilibrated excited state energy are very approximate, and since there are only a few available systems, definitive correlations are not possible at this time.

Table I.

Variations in $(^2E)Cr(III)\text{-}ML_6$ Energy Transfer Rates with Metal

| Quencher | $k_q^a, M^{-1}s^{-1}/10^6$ | Acceptor State[b] $E_{max}, cm^{-1}/10^3$ | $\sim\Delta E^c$ $cm^{-1}/10^3$ |
|---|---|---|---|
| $Cr(OH_2)_6^{3+}$ | <0.01 | 14.8 | +1.0 |
| $Fe(OH_2)^{3+}$ | 0.4 | 12.6 | -3.7 |
| $Co(OH_2)_6^{3+}$ | 3.7 | (8) 12.5 | -3.8 |
| $Mn(OH_2)_6^{2+}$ | <0.004 | 18.7 | +4.9 |
| $Co(OH_2)_6^{2+}$ | 0.005 | ~10 | -5.5 |
| $Ni(OH_2)_6^{2+}$ | 1.9 | $8.5^d, 15.2^e$ | $-1^e$ |
| $Cu(OH_2)_6^{2+}$ | 0.36 | 8,11,13 | -3.8 |
| $Ru(NH_3)_6^{3+}$ | <0.2 | 23 | +6.2 |
| $Co(NH_3)_6^{3+}$ | 3.5 | 13 | -3.3 |
| $Co(NH_3)_5Cl^{2+}$ | 41 | ~12 | ~-4.3 |
| $Rh(NH_3)_5Cl^{2+}$ | <02. | 29 | +10.7 |

**Notes:** a) 25°C, 1 M ionic strength ($HClO_4$, $NaClO_4$ or $NaHSO_4$); refs. 6,28. b) Based on ref. 23. States for which $\Delta S = 0$ in the energy transfer process. c) Vibrationally equilibrated acceptor state energies assume a $5 \times 10^3$ $cm^{-1}$ Stokes shift for distorted excited states. d) Triplet state. e) Singlet state.

The $(^2E)Cr(PP)_3^{3+}$ species are quenched by $O_2$ with $k_q(O_2) \sim 10^7$ $M^{-1}s^{-1}$ (ref. 30). In contrast, the oxygen insensitivity of $(^2E)Cr([14]aneN_4)(CN)_2^+$ (ref. 31) implies that for this complex $k_q(O_2) < 10^3$ $M^{-1}s^{-1}$. Such gross differences in behavior are yet to be explored carefully, but they could relate to the low energy charge transfer transitions present in $(^2E)Cr(PP)_3^{3+}$ but not in $(^2E)Cr([14]aneN_4)(CN)_2^+$.

## Unimolecular Analogs

There have been a few studies of energy transfer between transition metal centers in polymetallic molecular species. However, the work to date has largely involved sensitized photochemistry (e.g., refs. 32,33), and little photophysical information is available about energy transfer pathways.

Some interesting features have begun to emerge from studies of mixed metal, uranyl polyketonate complexes (ref. 34). The absorption spectra of these complexes are dominated by ligand to metal charge transfer (LMCT) bands. These bands move to progressively lower energies as the number of ketonate moieties increase. Thus $\lambda_{max}$ = 365 nm for $UO_2(acac)_2$, 405-424 nm for $UO_2M(triketonate)_2$ (M = Co,Ni,Pd), and 475-480 nm for $(UO_2)_2M(tetraketonate)_2$ (M = Co,Ni,Fe,Cu,Zn) (refs. 35-37). The absorption of the uranyl moiety in obscured by the LMCT transitions in these systems, but the characteristic,

Table II

Photophysical Parameters for Mixed Metal-Uranyl Polyketonate Complexes

| Complex[a] | $\Phi_{em}$[b] | $\tau$,μs[c] | Relative Transfer Efficiency[d] | $\varepsilon$(at 386 nm) $M\ cm^{-1}/10^4$ |
|---|---|---|---|---|
| $UO_2(acac)_2 \cdot H_2O$ | 0.67 | 300 | 1 | 0.17 |
| $UO_2H_2(DBA)_2 \cdot CH_3OH$ | 0.083 | 140 | 0.27 | 2.51 |
| $UO_2Co(DBA)_2 \cdot 3H_2O$ | 0.023 | 120 | 0.09 | 3.74 |
| $UO_2(DBA)_2 \cdot 3H_2O$ | 0.072 | 125 | 0.26 | 1.89 |
| $UO_2Pd(DBA)_2 \cdot H_2O$ | 0.041 | 180 | 0.1 | 2.91 |
| $(UO_2)_2Fe(DBAA)_2 \cdot 4py$ | 0.15 | 125 | 0.55 | 2.15 |
| $(UO_2)_2Co(DBAA)_2 \cdot 4py$ | 0.003 | 302 | 0.005 | 3.76 |
| $(UO_2)_2Cu(DBAA)_2 \cdot 4py$ | 0.006 | 200 | 0.014 | 1.72 |

a) acac = acetylacetonate; DBA = dibenzoylacetonate; DBAA = dibenzoylacetylacetonate. b) Yields relative to $UO_2(NO_3)_2$ at 77 K in 2-methyl-tetrahydrofuran glass. c) 77 K EPA glass. d) Based on $\eta \cong \Phi_{em} \tau^{-1} k_{rad}$; $k_{rad}$, constant.

structured uranyl luminescence is observed in glasses at 77 K, and the zero-zero transition is ~ 520 nm in the polyketonate complexes (ref. 34). Thus, the equilibrated LMCT excited state lies at higher energy than the $UO_2$ excited state in the di- and tri-ketonate complexes, but at lower energy in the tetraketonates. The uranyl emission is observed at 77 K for all these complexes, the luminescence lifetimes change only a little, but the relative luminescence quantum yields change a great deal (Table II). The implication is that transfer of electronic excitation energy into and out of the uranyl moiety is inefficient. For example, assuming that the radiative lifetime ($k_{rad}$) is invariant in these complexes, one can estimate the relative efficiency, $\eta_{ic} \approx \Phi_{em}\,\tau^{-1}k_{rad}$, for populating the uranyl excited state following 385 nm (≥ 90% LMCT) absorption. For most of the complexes with strong LMCT absorptions at 386 nm, $\eta_{ic}/\eta_{ic}(UO_2(acac)_2) \ll 1$. In view of this and the fact that the lower energy LMCT state does not quench the uranyl emission in tetraketonates, there must be an appreciable barrier to entry into or exit from this state at 77 K. In view of the appreciable Stokes shift of the uranyl emission, a considerable distortion along the $O{=}U{=}O$ axis is implicated (ref. 38). Thus the isolation of the uranyl excited state, from other states of the polyketonate complexes, is most readily attributed to a substantial Franck-Condon barrier for surface crossing into, or out of, the uranyl excited state potential energy surface. Unfortunately, the uranyl polyketonates are relatively labile, and complicated photoinduced chemical degradation precludes investigation of the surface crossings at higher temperature (ref. 34).

## GENERAL DISCUSSION

Systematic studies of energy transfer processes involving the Laporte forbidden transition metal excited states are relatively few. The existing studies have provided some insights into the factors affecting the electronic matrix element. They also raise a number of fundamental questions to be addressed in future studies.

### Concerning the applicabiltiy of unimolecular relaxation models to bimolecular processes.

Unimolecular and bimolecular processes appear to be very nicely described by very similar formulations in the strong coupling limit. Within the constraints of this limit, as in categories 1 and 3 above, one can design experiments which probe the interactions between reactive molecules, thus obtaining experimental information about the electronic matrix element for simple bimolecular reactions.

The situation is not so satisfactory for bimolecular systems which can be described as at or near the weakly coupled limit. The studies now available seem to show that those bimolecular energy transfer reactions which can be described as falling into categories 2 or 4 have rates which are either independent of or increase slightly with $|\Delta E|$, rather than the expected decreases of $k_q$ with increasing $|\Delta E|$. It now seems likely that this feature is related to the distribution of high frequency vibrational modes which are available to span $|\Delta E|$, and the energy range spanned by potential acceptor electronic states. Further studies are needed to explore more critically the relationship between the high frequency vibrational modes available in the electronically relaxed donor, the several possible acceptor electronic states, and the efficiency of bimolecular energy transfer processes. At the present time, formalisms based on umimolecular processes seem to provide an adequate basis for interpreting observations on bimolecular systems.

## Observations on the nature of the electronic matrix element

In the limit that the donor and acceptor states are coupled by the electron exchange operator, the electronic matrix element is given approximately by (ref. 3), $\langle V \rangle \sim A \exp(-2\alpha r_{DA})$ where $r_{DA}$ is the donor-acceptor separation, $\alpha$ is an inverse radial parameter (where the exponential is a crude donor-acceptor overlap term), and A is a collection of Hamiltonian coupling terms. By using substituted polypyridyl ligands, simple cobalt(II) amine complexes, and van der Waal's contact distances for $r_{DA}$, $2\alpha$ has been found to be 11±1 $\mathrm{nm}^{-1}$ for the $(^2E)Cr(PP)_3^{3+}$ - Co(III) energy transfer reactions (refs. 6,28). This leads to $\alpha^{-1} \sim 1.8$ Å, which seems a reasonable magnitude for a mean d-orbital radius. The Co(III) complexes become better quenchers of $(^2E)Cr(PP)_3^{3+}$ when there are low energy charge transfer states in the donor-acceptor system. For this class of reactions, the dominant contribution is for intermolecular charge transfer transitions of the type,

$$\left\{ (^2E)Cr(PP)_3^{3+},\ (^-X\ )Co(III) \right\} \xrightarrow{h\nu(CT)} \left\{ Cr(PP)_3^{2+},\ (\cdot X)Co(III) \right\}$$

where the brackets indicate a donor-acceptor collision and $X^-$ is an ionizable ligand of the Co(III) acceptor. The effect of such low energy CT transitions can be interpreted in terms of an induced dipole moment which has the effect of increasing $\alpha^{-1}$ (ref. 7).

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