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MULTIPLE STATE EMISSION AND RELATED PHENOMENA IN TRANSITION METAL COMPLEXES

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CONTENTS

A. INTRODUCTION

The relaxation of electronic states for complex organic molecules is determined by (1) the radiative-nonradiative competition and (2) the pathway (spin-forbidden or spin-allowed) of the relaxation processes. From the combination of emission and absorption spectra, decay times and quantum yields, detailed theories [1—5] elaborating the relaxation process with emphasis upon the role of molecular vibrations have been developed. These theories have been supplemented by results that define nonradiative selection rules [6,7] between distinct orbital configurations.

From these data and theories, some simple and useful generalizations concerning relaxation of excited states of organic aromatics have been developed:

(1) Fluorescence (spin-allowed emission) typically occurs from the lowest vibrational state of the lowest excited singlet level (and only this state) regardless of the excitation energy.

(2) A single phosphorescence (spin-forbidden emission) typically occurs from the lowest vibrational state of the lowest excited triplet state.

(3) Intersystem crossing (singlet to triplet nonradiative processes) usually occurs only from the lowest singlet electronic state, since vibrational relaxation from higher excited singlets, called "internal conversion", is extremely rapid. As a consequence, emission quantum yields are typically wavelength independent.

The first two statements are the essence of Kasha's rule [8] and have proved accurate in the descriptions of most luminescent organic systems. The dual fluorescence from azulene and its derivatives is the best known and most completely documented example among the bona fide exceptions to Kasha's rule [2,5].

The relaxation of excited electronic states for transition metal chelates can, as for organic molecules, be investigated by luminescence spectroscopic techniques including pulsed excitation and photoselection methods. From the array of spectral and efficiency data, emission assignments (spin multiplicity and orbital origin) and kinetic parameters can be determined [9—11]. These data have been accumulated for a substantial number of d^3 ($\mathrm{Cr^{III}}$) and d^6 ($\mathrm{Ru^{II}}$, $\mathrm{Rh^{III}}$ and $\mathrm{Ir^{III}}$) complexes and provide some interesting contrasts to the organic emitter systems:

(1) Phosphorescence is the predominant form of emission with only a few bona fide fluorescence cases known [9,10].

(2) This phosphorescence frequently occurs at room temperature with substantial efficiency, (the radiative k_r is relatively large for these systems).

(3) Emission polarization spectra for d^6 emitters do not exhibit vibronic structure [12,13].

(4) Emission quantum yields can show an excitation wavelength dependence [14,15].

The first three observations can be related to the large spin-orbit coupling possible for these metal complex systems while the last observation is probably a reflection of the anisotropic nonradiative coupling that exists between states of different orbital origin. That is the dd^*, $d\pi^*$, $\pi\pi^*$, etc. states that occur, can result in a variety of coupling schemes, i.e., $\pi\pi^* \longrightarrow d\pi^* \longrightarrow dd^*$, etc., which are not all equally allowed.

The phenomenon of "multiple state emission" observed for a number of d^6 complexes is perhaps the most unusual and distinctive aspect of the relaxation of transition metal complex excited states and has not, to date, been completely rationalized. The first such multiple state emission was reported [16] for the mixed ligand complexes $[\mathrm{Rh(bpy)_2phen}]^{3+}$ and $[\mathrm{Rh(phen)(bpy)_2}]^{3+}$ and was characterized by decay curves and emission spectra that could be deconvoluted to produce two lifetimes and two emission spectra characteristic of the parent $[Rh(phen)_3]^{3+}$ and $[Rh(bpy)_3]^{3+}$ complexes. This multiple phosphorescence emission can be categorized as spatially isolated emission and does indicate that the wave function for the emitting excited state is localized on a single chelate ring and that these emitting states are not thermally equilibrated. Characterization of this emission as "single (chelate) ring" type does indeed suggest that the parent complex emission ($[RhL_3]^{3+}$) may be of the same type. More recently, emission reported by Watts et al. [17,18] for heterochelated bis Ir^{III} chelates appears to have the same essential origin, i.e., spatially isolated excited states, since multiple lifetimes and composite emission spectra characteristic of the parent homo bis chelates can be measured. The likelihood is that these multiple emissions are not true violations of Kasha's rule but are best considered as "composite molecule" emissions.

A second type of non-thermally equilibrated multiple emission from transition metal complexes in which emission occurs from states of distinct orbital origin, i.e., dd^* and $d\pi^*$ or dd^* and $\pi\pi^*$, may be more common than the spatially isolated emission. Such a multiple emission was first reported by Watts et al. [19,20] for the $[Ir(phen)_2Cl_2]^+$ complex and was subsequently corroborated in our laboratory by photoselection spectroscopy [12]. Other examples of distinct orbital multiple state emission from d^6 complexes include the dd^* and charge transfer emission from each of four tris sulfur chelates (two Rh^{III} and two Ir^{III}) [21] and charge transfer and $n\pi^*$ emission for Re^I carbonyl complexes [22,23]. Distinct orbital multiple state emission may also occur for Cu^I complexes [24].

A thermally equilibrated multiple state emission apparently occurs for $[Ru(bpy)_3]^{2+}$ [11], and the series of related Ru^{II} complexes [25,26]. The origin of this unique emission is as yet uncertain. One model developed by Crosby and coworkers [27—29] to explain the temperature dependent quantum yield and lifetime data postulates a strong spin-orbit coupling to rationalize an emission that occurs from a closely spaced manifold of three spin-orbit coupled states, one of which is assigned as an E (doubly degenerate) state. Such an emission model is consistent with the relatively larger absorption intensity observed for the overlap region for these materials and would imply that the spin quantum number, S, has limited validity.

Additional examples of thermally equilibrated multiple emitters are found for Cr^{III} complexes where both metal localized fluorescence (${}^4T_2 \rightarrow {}^4A_2$) and phosphorescence (${}^2E \rightarrow {}^4A_2$) can be measured [30—35]. A unique multiple state emission in which the emission spectra have a hybrid appearance indicating a substantial mixing of the quartet and doublet emitter states occurs for the $Cr(dtc)_3$ (dtc = diethyldithiocarbamate) complex [32]. In those few cases where the broad structureless fluorescence and the narrow structured phosphorescence have been observed for molecular species, only a single decay time has been reported [35], but multiple decay times have been measured for the ionic $MgO : Cr^{3+}$ system [34].

Thus, a quantity of data accumulated for a range of multiple state emitter

d^6 and d^3 complexes has raised some general questions:

(1) What is the origin of the multiple state emission? (Is Kasha's rule violated for these transition metal complexes or can the systems be treated as composite molecules?)

(2) Do "spatially isolated" and "distinct orbital" emission have a common rationale, i.e., absence of appropriate vibrations to couple the emitter states?

(3) Why are some "multiple emitting states" "thermally equilibrated" and others "non-equilibrated"? Are differences related to the magnitude of the coupling interaction or perhaps the amount of *d* orbital character?

B. EMISSION RESULTS

(i) Some caveats

Certainly a unique phenomenon such as multiple state emission requires that substantial experimental precaution be taken prior to the report of results. Indeed, the recognition that small amounts of impurity can result in luminescence do necessitate that strenuous efforts be made in the purification of these multiple state emitters. Such precautions can be illustrated for the $[Rh(bpy)_2phen]^{3+}$ complex synthesized from $[Rh(bpy)_2Cl_2]^+$ and stoichiometric amounts of phen [16]. Compound purity was assured by the absence of $[Rh(bpy)_3]^{3+}$ from the starting material $[Rh(bpy)_2Cl_2]^+$, the nonlability of the complex, the elemental analysis and the absorption and emission spectra. Recrystallization and chromatographic methods would, of course, not have provided satisfactory separation of $[Rh(bpy)_2phen]^{3+}$ and $[Rh(bpy)_3]^{3+}$ since solubility, charge, etc. are comparable. The absorption spectra for this material (and the analogous $[Rh(phen)_2bpy]^{3+}$ complex) were appropriately weighted averages of the $[Rh(phen)_3]^{3+}$ and $[Rh(bpy)_3]^{3+}$. Absorption spectra thus are inconsistent with the presence of small impurity amounts of $[Rh(phen)_3]^{3+}$ and $[Rh(bpy)_3]^{3+}$. Though the materials were known to be non-labile, the possibility of ligand scrambling was tested by attempts to produce mixed ligand complex from solutions of $[Rh(bpy)_3]^{3+}$ and phen ligand. No detectable amounts of mixed ligand complexes were noted with these attempts, thus verifying the purity of this material beyond reasonable doubt. Nevertheless, doubts [36] apparently did remain in the minds of some researchers for some years following report of this multiple state emission.

The unique sensitivity of the luminescence method has been used as the basis of a technique to monitor purity and thus verify a multiple emission. The original report of multiple emission [19] for $[Ir(phen)_2Cl_2]^+$ was complicated by the presence of a persistent luminescent impurity. Balzani and coworkers [37] did utilize a repetitive sequence of recrystallization purification until a constant emission spectrum was obtained. Such a repetitive procedure utilizing recrystallization, column chromatography or thin layer chromatography used in conjunction with elemental analysis and routine spectral techniques (NMR, IR) can generally assure proper identification and purity of the complex. Use of elemental analysis and NMR spectra or IR spectra alone cannot be expected properly to verify purity when the phenomenon of interest is luminescence.

After exclusion of the impurity emission possibility, other rationale must be considered prior to assignment of the emission as a genuine multiple state emission. One possibility, that of solvent heterogeneity, has been observed for Cr^{III} complexes and suggested for Ru^{II} and Os^{II} complexes [35,38,39]. Heterogeneity may result in multiple spectra and multiple lifetimes due to slightly different solvent environments for the distinct sites. This effect may be distinguished by solvent and temperature variations. For example, multiple emission will resolve to a single emission in fluid solution. Moreover, cycling the sample from glassy to fluid to glassy solution will typically result in changes in the relative intensity of the different site emission bands.

The identification of a multiple emission, subsequent to careful purification of the materials, has depended in a large part upon pulsed excitation measurements. For the majority of the multiple state emitters discussed here, the emitting states are nearly degenerate and, in the case of spatially isolated emitters, have comparable spectral shapes. Thus energy resolution of the overlapped bands is difficult. However, time resolved spectra where emission spectra are determined at specific times following pulsed excitation can provide the necessary verification of multiple emission. Such measurements, done with a variable speed rotating chopper or a boxcar integrator, can resolve the near degenerate multiple emission if the lifetimes of the two emission bands differ by at least a factor of three [21]. For degenerate emitter systems in which the lifetimes are approximately equal, time resolved spectra cannot be acquired; however polarization spectra [21] can be used to verify the presence of emission from such non-equilibrated emitting states.

(ii) Single ring multiple emission

The first example of a multiple emission was that found for the mixed ligand complexes $[Rh(phen)_2bpy]^{3+}$ and $[Rh(bpy)_2phen]^{3+}$ (Fig. 1). Here, the phenomenon is readily apparent in the decay experiments (Fig. 2) which indicate a definite non-exponential decay curve that can be deconvoluted to give two lifetimes, τ_{bpy} and τ_{phen}, whose magnitudes are identical, respectively, to those measured for the pure precursor compounds $[Rh(bpy)_3]^{3+}$ and $[Rh(phen)_3]^{3+}$. Additionally, the vibronic patterns of the emission for $[Rh(phen)_3]^{3+}$ and $[Rh(bpy)_3]^{3+}$ are distinguishable, and use of a rotating chopper with the mixed ligand emission permitted time resolution of the overlapped emission spectra present for the mixed ligand complexes (Fig. 1). Apparently, the ligand localized (π—π^*) emission from the mixed ligand complexes occurs from states essentially characteristic of a single chelate ring, i.e., the phen or bpy system. Such behavior is analogous to that observed for non-conjugated organic chromophores, i.e., spirans [40] in which the chromophores have fixed distances and orientations. The similarity of the absorption spectra have thusfar precluded study of the intramolecular transfer of

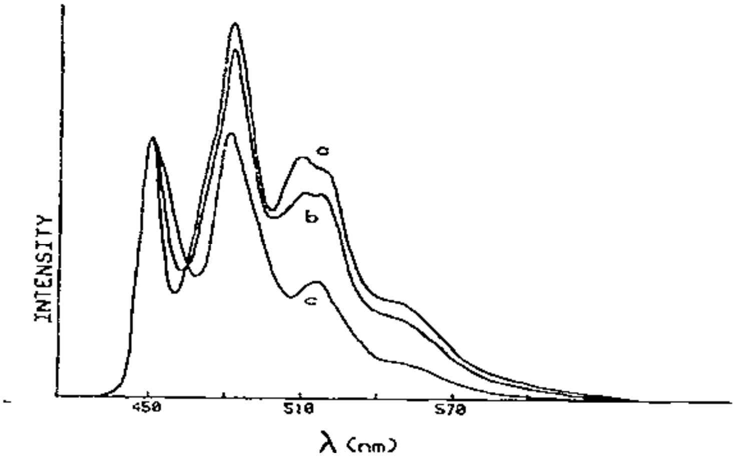

Fig. 1. Emission spectra of (a) $[Rh(bpy)_3]^{3+}$, (b) $[Rh(bpy)_2(phen)]^{3+}$ and (c) $[Rh(phen)_3]^{3+}$ in ethanol at 77 K.

energy between the phen and bpy chelate ring systems in the metal complexes. However, the fact that the two lifetimes measured for the mixed ligand complexes are nearly identical to those of the parent $[RhL_3]^{3+}$ com-

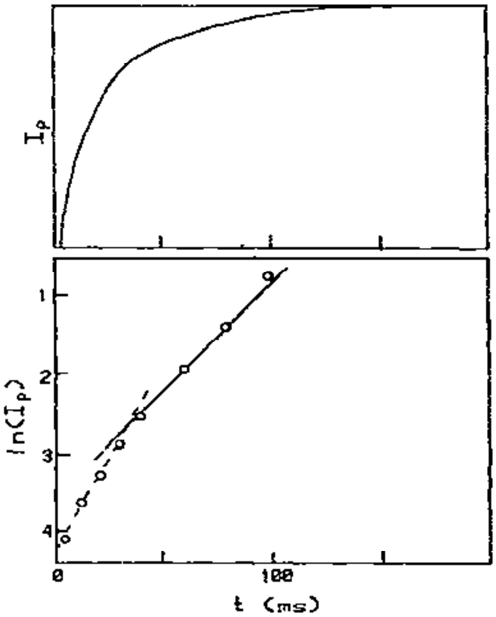

Fig. 2. Emission decay curve and ln (emission intensity) as a function of time for $[Rh(phen)_2(bpy)]^{3+}$ in ethanol at 77 K.

pounds implies that the energy transfer rate cannot be greater than the reciprocal of the lifetime, 2.3 μsec, for the $[Rh(bpy)_3]^{3+}$ complex. The apparent lack of coupling between the emitter systems is unexpected in view of the proximity of the chromophores and the fact that the transition moments of the individual chelate rings are not orthogonal.

The nearly accidental degeneracy of the emitter levels for the mixed ligand complexes of Rh^{III} implies that the π–π^* emission of the $[Rh(bpy)_3]^{3+}$ and $[Rh(phen)_3]^{3+}$ complexes may also be effectively single chelate ring followed by a hopping of the excited state from chelate ring to chelate ring. Recent efforts [13] to clarify this point have utilized the emission photoselection techniques [41]. The technique utilizes polarized excitation to select a set of particularly oriented molecules from the randomly oriented group of frozen molecules, then monitors the resultant emission with a polarizing analyzer (Fig. 3). The technique permits measurement of the relative orientations of emission and excitation oscillators and consequently provides information about the symmetry of the excited states. Monitoring of the excitation polarization in the region of absorption and emission overlap is particularly useful in determining whether the emitting state is non-degenerate (linear oscillator) or degenerate (planar oscillator) since the limiting P values for such cases should be, respectively, 0.50 and 0.14 [42] (Table 1). Sometimes this information alone can provide details of the effective molecular symmetry [13]. The excitation polarization spectra at 77 K for the two

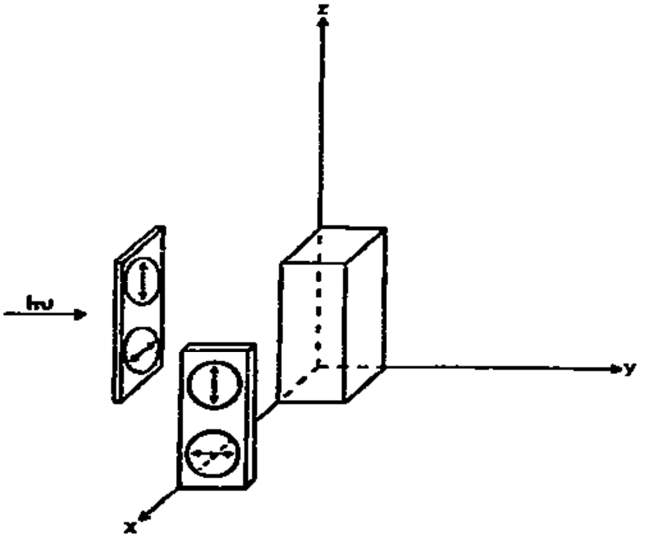

Fig. 3. Orientation of excitation and analyzing polarizers in a photoselection spectrometer.

TABLE 1

Limiting polarization values

Absorption oscillator	Emission oscillator	Polarization, P
Linear (z)	Linear (z)	+1/2
Linear (z)	Linear (x)	−1/3
Linear (z)	Planar (z, x)	+1/7
Linear (z)	Planar (x, y)	−1/3
Planar (x, y)	Linear (z)	−1/3
Planar (x, y)	Planar (x, y)	+1/7

parent tris diimine complexes of Rh^{III} is substantially depolarized (P = ca. 0) throughout the high energy π—π^* absorption region and only increases to ca. 0.12 in the low energy, low intensity absorption region. Such results can be interpreted as deriving from the slow hopping of the excitation from ring to ring competitive with the radiative deactivation of the excited state (effective C_{2v} symmetry). The possibility also exists that the polarization value of 0.12 in the overlap region signifies a planar emitter (E) oscillator (effective D_3 symmetry) and that a small trigonal field splitting of the E and A produces overlapping bands resulting in the near zero polarization values at higher energy. In either interpretation, the likelihood is that the molecule can be moved to the C_{2v} (single ring) limit by application of a small perturbation, (i.e. decrease in temperature, small structural change, etc.).

Another set of mixed ligand complexes, the $[Ir(LL')Cl_2]^+$ (L = phen, L′ = 5,6-mephen and L = phen, L′ = 4,7-mephen) species, also show multiple emission [17,18] characteristic of a single chelate ring. In these molecules the orbital origins of multiple emission are characterized as ligand $\pi\pi^*$ and charge transfer $d\pi^*$ type. For the $[Ir(phen)(5,6\text{-mephen})Cl_2]^+$ system the two lifetimes resolved (τ_1 = 9.5 μsec and τ_2 = 65 μsec) from the non-exponential decay curve are, for the Rh^{III} compounds, quite similar to the parent $[Ir(phen)_2Cl_2]^+$, (τ = 6.95 μsec), and $[Ir(5,6\text{-mephen})_2Cl_2]^+$ (τ = 65 μsec). Moreover, a time resolved emission spectrum ($t > 2$ μsec) obtained with a boxcar integrator is quite similar to that of the $[Ir(5,6\text{-mephen})_2Cl_2]^+$. The non-exponential decay [18] for the $[Ir(phen)(4,7\text{-mephen})Cl_2]^+$ complex has been interpreted by Watts et al. as deriving from superposition of 3 exponentials having decays of 6.0, 8.7 and 22 μsec. However, our own difficulty in deconvoluting decay curves for which the convoluted exponentials are within a factor of 4—5 of one another implies that a two level model suggested by Watts et al. is perhaps more consistent with the deconvolution method and results obtained for the other mixed ligand complexes. With this interpretation, the two emissions are readily associated with states primarily localized on the phen and 4,7-phen ring system and earlier assigned as $d\pi^*$(phen) and mixed parentage $d\pi^*$—$\pi\pi^*$ (4,7-mephen) states. As for the Rh^{III} complexes, the

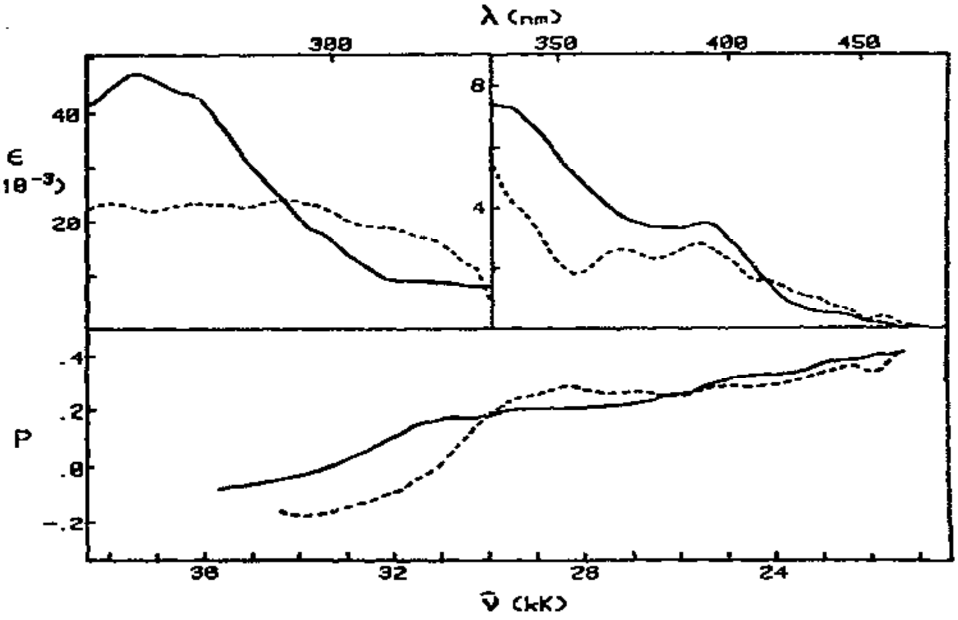

Fig. 4. Absorption and excitation polarization spectra of [Ir(bpy)$_2$Cl$_2$]$^+$ (- - - - - -) and [Ir(phen)$_2$Cl$_2$]$^+$ (———) in 4 : 1 ethanol/methanol at 77 K.

possibility exists that the parent complexes, i.e., [Ir(bpy)$_2$Cl$_2$]$^+$, [Ir(phen)$_2$Cl$_2$]$^+$ etc. do also show single ring emission.

However, polarization spectra for these Ir complexes (Fig. 4) cannot be used to verify this supposition since the molecular symmetry of the complex is C_2 while the single chelate ring has an effective C_{2v} symmetry, and both point groups possess only non-degenerate representations, i.e. linear absorption and emission oscillators. The large polarization value (ca. 0.42) measured in the overlap region implies that the single ring limit, if it occurs, is not accompanied by rapid energy transfer between the chelate rings. Alternatively, the [Ir(bpy)$_3$]$^{3+}$ complex whose emission has been assigned as $\pi\pi^*$ type has an excitation polarization spectrum like that of the [RhL$_3$]$^{3+}$, i.e., depolarized (P = ca. 0) in the high energy $\pi\pi^*$ absorption region but approaching the planar oscillator limit in the low energy, low intensity overlap region. Therefore, either a multiring effective D_3 symmetry or a single ring (C_{2v}) with hopping could account for P values considerably less than the $P = 0.50$ limit. Unfortunately, mixed ligand tris Ir^{III} complexes have not been synthesized; thus relevant τ and polarization spectra are not available here.

Emission spectra determined for mixed ligand Ru^{II} complexes, [Ru(bpy)$_2$phen]$^{2+}$ and [Ru(phen)$_2$bpy]$^{2+}$, appear to give a single emission [36]; but the similarity of the spectra for [Ru(phen)$_3$]$^{2+}$ and [Ru(bpy)$_3$]$^{2+}$ and the short and comparable magnitude ($\tau_{\text{phen}} = 9.8$ μsec, $\tau_{\text{bpy}} = 5.2$ μsec) for these two complexes [25,26] make it feasible that single ring emission from two states can occur but not be detectable.

(iii) Distinct orbital multiple emission

In all cases above, whether $\pi\pi^*$ charge transfer or $d\pi^*$ charge transfer emission, the emitting states derive from a delocalized orbital configuration, one in which the optical electron exists in an orbital delocalized over many atoms. The reports [19,20] by Watts and coworkers of two emissions, one from a $d\pi^*$ charge transfer state (delocalized orbital type) and a second from localized (centered on a single atom) dd^* state for $[Ir(phen)_2Cl_2]^+$ and $[Ir(5{,}6\text{-mephen})_2Cl_2]^+$ are the first documented cases of multiple emission from states having distinct orbital origin. The verification of the true multiple emission was complicated by the presence of a persistent trace luminescent impurity (see Experimental). Thus, both multiple emission and an earlier exciplex emission for $[Ir(phen)_2Cl_2]^+$ were attributed by Balzani and coworkers [37] to this trace impurity; however, Watts and Missimer [20] have utilized the Balzani "iterative" purification method to verify the purity of samples of $[Ir(phen)_2Cl_2]^+$.

Subsequently, variable temperature emission spectra using a red sensitive pm tube detection in DMF and glycerol verify the growth of a broad red emission for both compounds as the temperature increases (Fig. 5) and the solution becomes fluid. Lifetime measurements for the two emission bands give essentially identical values at room temperature and in fluid solution, but in solid solutions the decay curves of the red (dd^*) and green ($d\pi^*$)

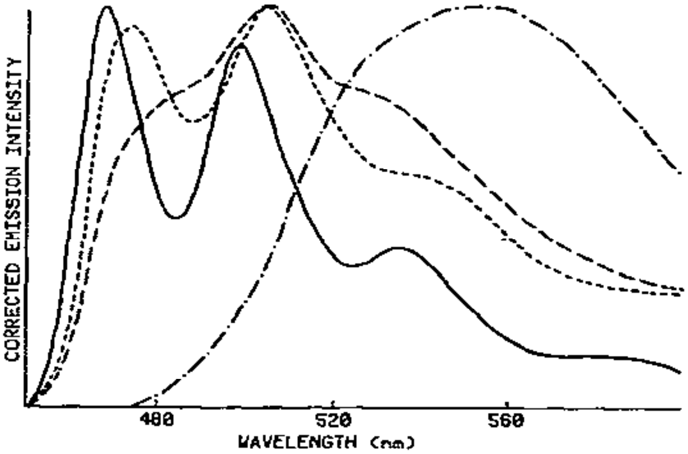

Fig. 5. Steady state luminescence spectra of $[Ir(phen)_2Cl_2]Cl$ in glycerol at −196°C (———), −130°C (- - - - - -), −95°C (— — —) and 0°C (· — · — ·). From Watts et al. [19].

emissions are distinct with the decay curves for each emission non-exponential. The decay curve behavior is comparable in glycerol with the addition that a distinct risetime can now be observed for the *dd** emission. Using emission data for these complexes and estimates from data for other Ir^{III} complexes, Watts placed the *dd** excited minima at lower energy than the $d\pi^*$ state, consistent with the observation of *dd** photochemistry for the $[Ir(phen)_2Cl_2]^+$ complex [43].

Other examples of multiple emission from states of distinct orbital origin have been described for Re(I) complexes [22,23] of general formula $XRe(CO)_3L_2$, where X = Cl, Br and I and L = 3-benzoylpyridine. Here, the emission band at 77 K can be time resolved with a phosphoroscope since the two emissions have lifetimes differing by two orders of magnitude. The emissions have been assigned here as charge transfer ($d\pi^*$) and $n\pi^*$ type with the charge transfer emission visible at room temperature. Wrighton and coworkers [22,23] have also reported multiple emission at 77 K for $[SRe(CO)_3L]^+$ species where S = CH_3CN, PhCN, pyridine, piperidine and L = 1,10 phenanthroline where now the two emission bands are described as $d\pi^*$ charge transfer and phen ligand localized $\pi\pi^*$ transitions.

Observation of multiple emission for the series of bidentate sulfur chelates [21] with Rh^{III} and Ir^{III} verifies that the phenomenon can occur for heavy metal complexes with ligands other than the bidentate diimine complexes. Here, the dual emission is less obvious since the multiple state emission spectra in addition to being isoenergetic (as for the other cases) are both broad

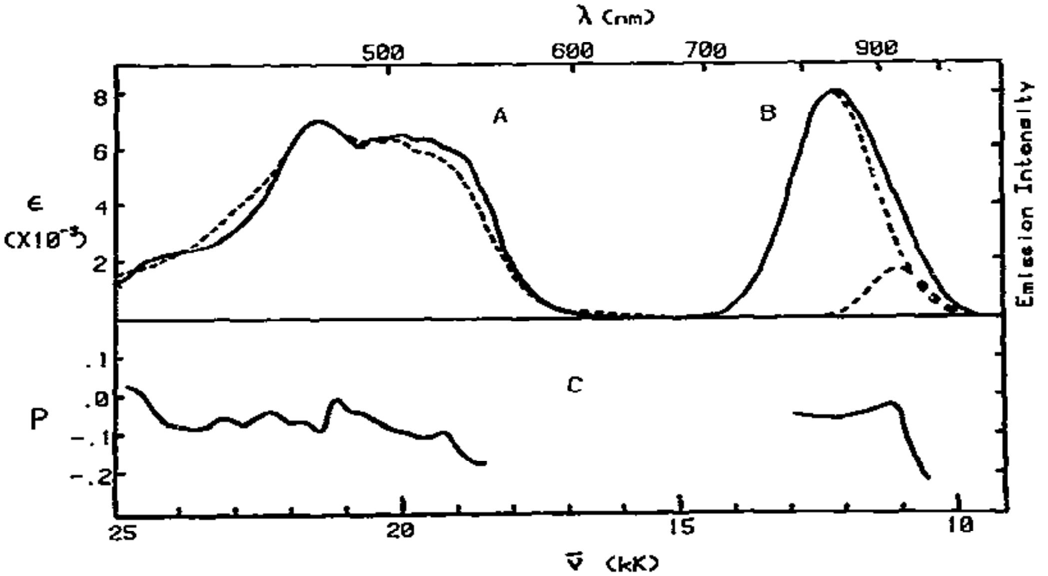

Fig. 6. 77 K corrected excitation (A, ———); absorption (A, - - - - -); emission (B, ———) and excitation and emission polarization spectra (C) for $Ir(SacSac)_3$. The deconvolution of the emission into two Gaussian curves is shown.

TABLE 2

Multiple emitter types for some transition metal complexes

Spatially isolated	Distinct orbital
$[Rh(bpy)_2phen]^{3+}$	$[Ir(phen)_2Cl_2]^+$
$[Rh(phen)_2bpy]^{3+}$	$[Ir(5,6\text{-}mephen)_2Cl_2]^+$
$[Rh(bpy)_3]^{3+}$	$XRe(CO)_3L_2$ (X = halide, L = 3-benzoylpyridine)
$[Rh(phen)_3]^{3+}$	
$[Ir(phen)(5,6\text{-}mephen)Cl_2]^+$	
$[Ir(phen)(4,7\text{-}mephen)Cl_2]^+$	$[SRe(CO)_3L]^+$ (S = CH_3CN, PhCN, pyridine, piperidine and L = phen)
$[Ir(bpy)_3]^{3+}$	
$[Ru(bpy)_2phen]^{2+}$	
$[Ru(phen)_2bpy]^{2+}$	IrL_3 (L = SacSac, SSBB)
$[Ru(phen)_3]^{2+}$	RhL_3 (L = SacSac, SSBB)
$[Ru(bpy)_3]^{2+}$	$Cu(P\phi_3)_2L$ (L = phen, bpy)

and structureless, amenable to gaussian deconvolution, but not readily time resolved since lifetimes determined from measurements at various wavelengths are short and of comparable magnitude. Therefore, photoselection spectroscopy has been used to resolve and verify the multiple emission (Fig. 6). For all four compounds, the presence of oppositely polarized emission bands verifies the two Gaussian curve analysis for the complexes. The two emissions, overlapping the absorption, are assigned as dd^* and πd^* type. Moreover, excitation spectra (Fig. 6) for the complexes suggests that the emitting states are populated by different pathways.

The previous examples demonstrate the characteristics and occurrence of multiple state emission for a variety of nominal d^6 second and third transition series complexes (Table 2). Among the first series, only Cu^{II} complexes of formula $[Cu(P\phi_3)_2L]$, (L = phen, bpy) are reported [24] to exhibit multiple emission, here tentatively assigned as phosphorescence having $\pi\pi^*$ ligand localized and $d\pi^*$ charge transfer orbital origin.

C. RELATED PHENOMENA

For both types of multiple emission, "single ring" and "distinct orbital" type, a degree of spatial localization of the excited states is apparent. Such a circumstance is also manifest in a variety of other experiments, substantiating the distinctive molecular orbital character for these molecules.

(i) Electrochemical measurements

Cyclic voltammetry and coulometry data [44—55] have been utilized to establish the electron transfer sequence (n value, $E_{1/2}$, number of waves) for a number of nominal d^6 transition metal complexes of structure $[ML_3]^{n+}$, $[ML_2X_2]^{n+}$, $[ML_2]^{n+}$ where M = Fe^{II}, Ru^{II}, Os^{II}, Co^{III}, Rh^{III}, Ir^{III}, L = bpy,

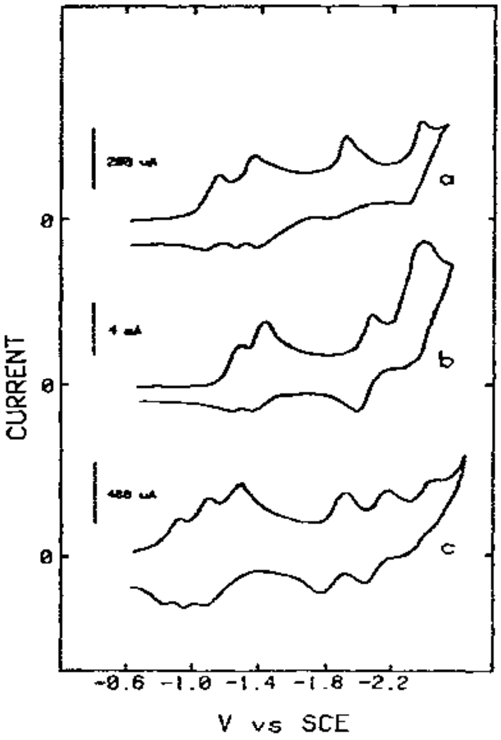

Fig. 7. Cyclic voltammograms of (a) 6 × 10^{-4} M $[Ir(bpy)_2Cl_2]^+$ at 3 V s^{-1}, (b) 1 × 10^{-3} M $[Fe(terpy)_2]^{2+}$ at 1 V s^{-1} and (c) 4 × 10^{-4} M $[Ir(bpy)_3]^{3+}$ at 9 V s^{-1}.

phen, 5,6-mephen, terpy, etc. and X = halogen. The most common electron transfer sequence is a series of simple one electron transfer processes producing species stable on the cyclic voltammetry and coulometry time scale. The redox orbitals associated with the successive species are, for most species, the same type (see below) and can be characterized as "delocalized orbital" type as opposed to "localized (*d*) orbital" type. Moreover, the spacing, three and three pattern of redox waves for the bidentate tris Ir complexes (Fig. 7) and the two and two pattern for the C_{2v} bidentate bis complexes and the tridentate D_{2d} terpy complexes, suggests redox orbitals characteristic of a single chelate ring. Such a circumstance would imply that the effective molecular symmetry for $[ML_3]^{n+}$ complexes is C_{2v} rather than D_3.

The molecular orbital diagrams illustrate the highest filled and lowest empty orbitals for two limiting cases. In Fig. 8, the diagrams are appropriate to systems in which the molecular orbitals span multiple ligands, i.e. delocalization of the wave functions is maximum. Figure 8(a) indicates the scheme for D_3 complexes. Such a diagram in which the highest filled orbital is a localized metal orbital and the lowest empty orbital is a delocalized ligand type orbital is possible for the majority of the D_3 species examined. (Excep-

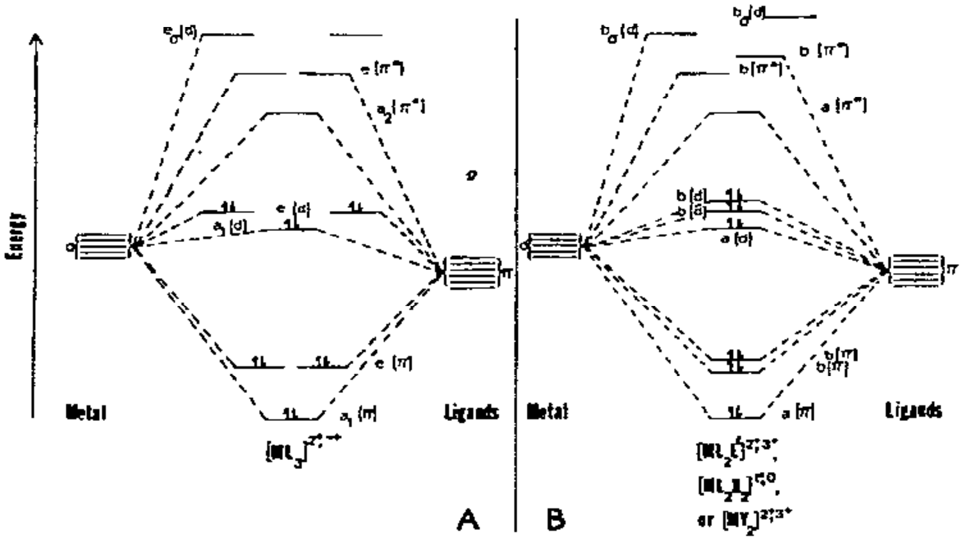

Fig. 8. Multi-ring molecular orbital diagram for (A) D_3 symmetry tris complexes and (B) C_2 symmetry bis complexes.

tions are the Co^{III} case, where an "orbital crossover" anomaly occurs). Figure 8(b) illustrates a possible molecular orbital sequence for the C_2 complexes having delocalized orbitals encompassing multiple rings (multiring

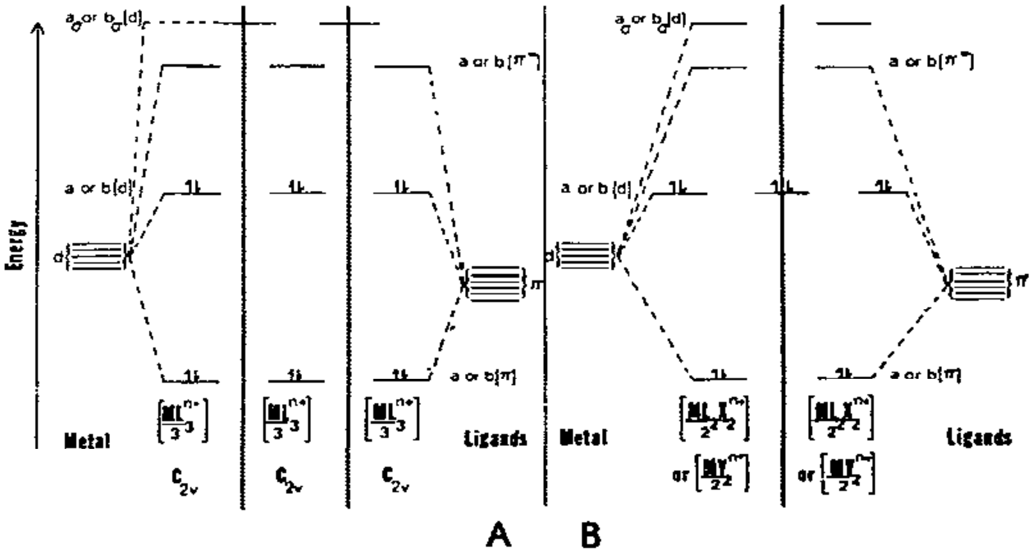

Fig. 9. Single ring molecular orbital diagrams for (A) tris complexes and (B) bis complexe

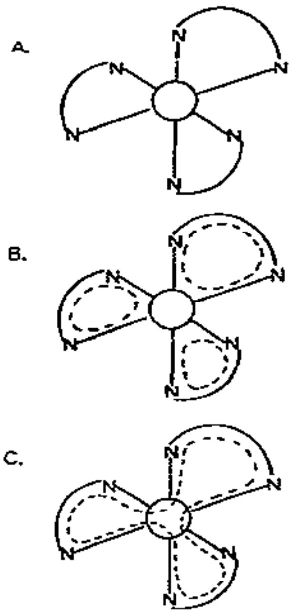

Fig. 10. Delocalization models for (A) no delocalization, (B) single ring delocalization and (C) multi-ring delocalization.

orbital). The relative magnitude of the orbital splitting and spin pairing energies would, in most cases, determine the orbital in which the redox electron enters. Figure 9 illustrates another limiting case and, perhaps, the preferred molecular orbital description for some of these materials. This diagram represents molecular orbitals that are not substantially delocalized, i.e., minimum interaction between the three or two ligands is occurring (single ring delocalized orbital). Such a diagram implies that the electrochemical or chromophoric unit is a single chelate ring containing the coordinated metal and having C_{2v} symmetry, a kind of metal containing heterocycle. A small splitting of the accidental three-fold degeneracy is possible but is probably smaller than that for the C_2 case of Fig. 8(b). This limit, as indicated in Fig. 9, can be pictured as an "insulation" of the chelate ring systems from one another caused by the presence of a node at the metal ion (Fig. 10). The node reflects a vanishing metal—ligand interaction for this orbital and presumably could occur for those nominal d^6 complexes in which the lowest excited state is either an essentially pure $\pi\pi^*$ type ($[\mathrm{Rh(bpy)_3}]^{3+}$) or a $d\pi^*$($[\mathrm{Ru(bpy)_3}]^{2+}$).

If Koopmans' theorem [56] is valid for the "d^6" starting species and, at least, the reduced species with one additional electron, then the electrochemical data and the luminescence spectra can be presumed to reflect the characteristics (localized or delocalized, single ring or multiring) of the lowest empty orbital for the parent d^6 complex. Such a correlation does imply, for example, that the excited state $^*[Ru(bpy)_3]^{2+}$ would possess an optical orbital that is, in the zeroth order approximation, similar to that of the redox orbital for $[Ru(bpy)_3]^+$. The optical (d^6) species could be represented as a $[Ru^{III}(bpy)^{1-}(bpy)_2]^{2+}$ species while the reduced (d^7) species would be represented as a $[Ru^{II}(bpy)^{1-}(bpy)_2]^+$ species; thus the single ring orbitals for the two cases should only differ in the effective metal ion charge that each sees. For $[Ir(bpy)_3]^{3+}$ where the optical excitation for the emitting state is assigned as a $\pi \rightarrow \pi^*$ rather than a $d \rightarrow \pi^*$, the redox orbital and the optical orbital would differ in an analogous way with the redox orbital seeing an effective smaller charge than the optical orbital.

Interaction between the rings is expected to arise from two sources: (1) a direct π cloud interaction and (2) an interaction through the metal, probably a d orbital interaction.

To the extent that the presence of a charge transfer optical transition is a reflection of a metal d and ligand π interaction, complexes such as the $[Ru(bpy)_3]^{2+}$ species in which the lowest excited state is $d\pi^*$ might be expected to show a relatively larger interaction between rings than $[Rh(bpy)_3]^{3+}$ for which the lowest excited state is the $\pi\pi^*$ type. However, the magnitude of the interaction between the rings as reflected by the separation between the successive redox couples (ca. 0.020 V) is roughly comparable for the $[Ru(bpy)_3]^{2+}$ and the $[Ir(bpy)_3]^{3+}$ complexes, in spite of the fact that the emissions of the compounds are assigned, respectively, as charge transfer $d\pi^*$ and $\pi\pi^*$. Since the optical assignments are probably correct, this suggests that the presence of a lowest charge transfer excited state does not necessarily imply a significant ligand—ligand interaction via metal d orbitals.

In any case, the observation of distinct waves for the successive electron transfers in the complexes does imply that a small but finite interaction must occur between the rings. The formal potentials for the first and last pair of oxidation states for molecules containing n reducible multiple noninteracting centers are predicted to be separated by $2(RT/F) \ln n$ [57]. For the tris systems considered here, a spacing of 35 mV between the first two waves and 21 mV for the separation of the second and third waves is predicted. The magnitude of the separation observed for the tris chelates is typically 150—200 mV, much larger than that predicted by the simple model. However, the model as formulated takes no account of the differing charges of the redox centers for the successive processes. Those non-interacting systems used to test the model have typically been polymeric systems (polyvinylferrocene [58]) in which the separations between redox centers are considerably larger than those here in the metal chelate systems; consequently charge differences might be expected to increase the spacing for the metal chelate molecules.

(ii) ESR spectra of reduced species

The observation of electron spin resonance (ESR) spectra for the electrochemical reduction products affords the opportunity to directly verify the character of the redox orbital for these systems, i.e., is the redox orbital metal localized or chelate ligand delocalized? Also if the orbital is the delocalized type, is it a single ring or a multiring orbital? The redox orbital of the one electron reduction product obviously is most likely to correlate with the optical orbital from metal complex luminescence data; but spectra for two, three, etc. electron reduction products can provide details pertinent to the rationale of the one electron redox orbital. The first such data were reported by Tanaka et al. [59] for the $[Fe(bpy)_3]^{+,0,-}$ species in acetonitrile at room temperature. Our extension [60] of these experiments to include variable temperature spectra do verify the Japanese workers room temperature results while providing some enlightening new data. Table 2 indicates *g* values reported for the one, two, and three electron reduction products for the $[Fe(bpy)_3]^{2+}$ starting material. The *g* factors measured indicate that the redox orbitals for the one and three electron products are effectively "delocalized" (ligand) type while that redox orbital of the two electron species is a "localized" (metal) type. Moreover, the magnitude of the *g* shift for the one and three electron species is the same suggesting that the extent of delocalization per electron is comparable for the one and three electron species. Most importantly, the peak-to-peak line width for the one electron species (Table 3) is broad (100 G) at room temperature and does narrow to ca. 20 G at 77 K (frozen solution) while the peak to peak line width (ca. 14 G) for the three electron product is invariant to temperature.

These results can be understood if the redox orbitals for both species are single ring type rather than multiring type. A hopping of the electron from ring to ring explains the temperature dependent line width of the one electron product, i.e., the hopping can be pictured as a pseudo rotational motion whose rate increases as the temperature increases. The absence of this line broadening for the three electron product implies that this pseudorotation does not occur for this species. This phenomenon can be understood by con-

TABLE 3

ESR data for electrolytically generated imine complexes of Fe and Ru in acetonitrile

	Room temperature		Low temperature [a]		
	g_{iso}	Linewidth (G)	g_{iso}	Linewidth [b] (G)	Hyperfine [c] (G)
$[Fe(bpy)_3]^+$	1.996	100	1.996	20	4
$[Ru(bpy)_3]^+$	1.998	140	1.996	40	
$[Fe(bpy)_3]^0$	2.08	ca. 500			
$[Ru(bpy)_3]^0$	2.23	ca. 250			
$[Fe(bpy)_3]^-$	1.995	12		12	4
$[Ru(bpy)_3]^-$	1.996	15	1.994	20	

[a] 77 K. [b] Linewidth constant at ca. 200 K. [c] Hyperfine resolved at ca. 200 K.

sideration of the molecular orbital diagram of Fig. 9. The diagram for the three electron species would indicate that one electron is placed in each of the three accidentally degenerate single ring orbitals. Consequently, electron hopping necessarily must produce a paired electron configuration, which is energetically unlikely, or a pairwise exchange of electrons which is statistically (and therefore energetically) unlikely.

Additional verification of the single ring character for these two species is provided by the observation of nitrogen atom hyperfine structure at ca. 200 K, just below the freezing point of the solvent. The five line hyperfine pattern observed indicates that the unpaired electron(s) does see two equivalent nitrogens rather than the six equivalent nitrogens expected for a multiring redox orbital.

The ESR spectrum obtained for the two electron species implies that the orbital order of the two metal σ type and the three π ligand type orbitals invert upon addition of one electron to the one electron product and that this orbital order inverts again upon addition of the third electron. These results are quantitatively consistent with the fact that the redox orbital for the one electron species does not correlate with the optical orbital for the Fe^{II} d^6 starting material. The lowest excited state for $[Fe(bpy)_3]^{2+}$ is a dd^* state [61] which thus rationalizes the absence of a charge transfer emission for this compound as found for the isoelectronic $[Ru(bpy)_3]^{2+}$. This "crossover anomaly" can be interpreted to indicate that empty d^* orbitals lie close to the empty π^* orbitals for the parent d^6 species, thereby accounting for the inversion of the d^* and π^* orbitals with the decrease in charge. Alternatively, the possibility does exist that the primary product of the addition of two electrons is, as for the one electron product, a ligand π type species; but this primary product relaxes to the more stable dd^* species. The magnitude of k_s for the addition of the second electron is consistent with this latter interpretation [55].

The phenomenological similarity of the electron transfer patterns for the $[Fe(bpy)_3]^{2+}$ and $[Ru(bpy)_3]^{2+}$ complexes suggests that the redox orbitals of the $[Ru(bpy)_3]^{+,0,-}$ species should also be characterized via ESR since the redox and optical orbitals for this complex should correlate. The spectra for $[Ru(bpy)_3]^+$ and $[Ru(bpy)_3]^0$ are similar to those of $[Fe(bpy)_3]^+$ (Table 3). Moreover $[Ru(bpy)_3]^+$ exhibits temperature dependent linewidths comparable to those of $[Fe(bpy)_3]^+$. The ESR spectra for the three electron Ru^{1-} species could not be determined. Nevertheless, the similar ESR data for the one and two electron species coupled with the ESR of the three electron $[Fe(bpy)_3]^-$ and the luminescence of $[Ru(bpy)_3]^{2+}$ make it reasonably certain that single ring redox ($[Fe(bpy)_3]^+$, $[Ru(bpy)_3]^+$) and optical ($[Ru(bpy)_3]^{2+}$) orbitals exist for these materials. The identification of a σ type radical for the two electron reduced species implies that the parent d^6 complexes (Fe^{II} and Ru^{II}) do have an empty low lying d orbital. Such results are consistent with the photochemical results obtained by Creutz et al. [61] and by Meyer and coworkers [62] in which flash photolysis and photochemical results with $[Ru(bpy)_3]^{2+}$ produces results consistent with a low lying dd^* state. Recent ESR results [62] for the tridentate $[Fe(terpy)_2]^{2+}$ and $[Ru(terpy)_2]^{2+}$ complexes appear to be consistent with those data for the bpy complexes.

(iii) Resonance Raman studies

Elegant time resolved resonance Raman (RR) studies by Dallinger and Woodruff [63,64] of the luminescent charge transfer excited state of $[Ru(bpy)_3]^{2+}$ has produced yet another verification of the single ring character of the optical orbital. In this experiment, the shifts (from the ground state values) of seven symmetric vibrational frequencies associated with the lowest excited state (emitting state) were measured and compared. The magnitude of the shifts (ca. 60 cm^{-1}) is as large or larger than those observed for the one electron reduction of the free ligand to the radical anion, and therefore has been interpreted to indicate that the optical electron is localized on a single ligand (i.e., $^*[Ru^{III}(bpy)^{1-}(bpy)_2]^{2+}$) rather than delocalized through all three ligands ($^*[Ru^{III}(bpy^{1/3-})_3]^{2+}$).

(iv) MCD spectra

A series of circular dichroism studies by Mason and coworkers for $[ML_3]^{n+}$ (D_3) and $[ML_2L']^{n+}$ (C_{2v}) diimine complexes [65—67] have attempted to rationalize the splittings and intensities of MCD and isotropic spectra using a simple exciton theory. Mason did adequately rationalize the CD spectra, finding that direct ring interaction or interaction through the metal did not improve the fit. While the magnitude of the exciton splitting measured from the overlapped CD and absorption spectra and that calculated from the theory are the source of dispute [68], the accuracy of the measured splitting is not great. Nevertheless, the essential point of the CD work that a simple dipole exciton model can rationalize the spectra lends credence to the view that single ring orbitals exist for these systems. Indeed, if the weak coupling exciton limit, in which the excitation energy relaxes to the equilibrium nuclear configuration prior to transfer of excitation energy is utilized [68], rather than the intermediate and strong coupled limits preferred by Mason and coworkers, these data would seem to result in an orbital picture consistent with that of the other data.

D. MODEL SYSTEMS

Spectroscopic data from the MCD, resonance Raman and photoselection techniques provide evidence that at least the lowest excited states for a number of heavy transition metal complexes have characteristic single chelate ring orbitals, implying that minimal interaction (communication) occurs between the π electron systems associated with the individual chelate rings. Additionally, the multiple emission classified as "distinct orbital origin" type does also illustrate a kind of minimal interaction between potential surfaces of two excited states. To attempt to provide a unified framework for rationale of these unusual phenomena, a re-examination of some multiple emission phenomena for organic (light atom) and Cr^{III} systems will now be presented.

(i) Organic multiple state emitters

The classic case of a multiple emission (non-equilibrated) from an organic π system is the multiple fluorescence from S_2 and S_1 of azulene. Here, the large separation of the lowest excited singlet S_1 from the next higher singlet S_2 results in two fluorescence emissions with distinct lifetimes. However, the two emission bands occur at greatly different energies, and hence obviously have little relevance to the multiple state emission phenomena of the metal complexes. The equilibrated dual fluoresence emission that occurs for a number of aromatic compounds having close lying S_2 and S_1 states can be considered to be analogous to that occurring for the d^3 Cr^{III} complexes in which both fluorescence and phosphorescence occur but only a single lifetime is measured. Such a thermally equilibrated dual emission is analogous to the so-called E-type delayed fluorescence [69,70]. Therefore, the multiple emission observed for the mixed ligand Rh^{III} and Ir^{III} must differ, at least, in degree since the zero point energy levels of the multiple emission are quite close in energy, yet two distinct decay times can be measured for the emission. However, the multiple emission occurring for so-called "di-aromatic" molecules (X—A—Y) which contain at least two distinct aromatic groups X and Y separated by an alkane chain does bear a resemblence to that deriving from the mixed ligand complexes, $[ML_2L']_3^{n+}$. Here, the absence of substantial interaction between X and Y is verified by the absorption spectrum which typically is a composite of those of the two chromophores X and Y.

The dual emission occurring for the so-called homopolar diaryl molecules, such as 1,1′-binaphthyl [71], 2,2′-binaphthyl [72] and 9,9′-dianthryl [73] may have a relevance to the distinct orbital emission observed from transition metal complexes. For these organics, two fluorescence emission spectra are observed with one (F_1) the mirror image of the absorption transition and similar to the fluorescence of X while the second, F_2, is structureless and occurs at lower energies. Of substantial significance here is the viscosity dependence of these two emissions. At high viscosities and in solid solution, only F_1 is observed while as the viscosity is reduced, the ratio of the F_2 to F_1 intensities increases. This behavior has been interpreted as deriving from steric hindrance to twisting about the bond linking the chromophores. The net effect is that the two minima occur for the excited state, only one of which lies vertically above the ground state equilibrium configuration. More recently Rotkiewicz and coworkers [74—76] have studied the dual fluorescence of *p*-substituted dialkylanilines. They concluded that the second emission occurs from a state created by twisting of the amino group relative to the benzene ring, a "twisted internal charge transfer" (TICT) state. Although the steric origin of this multiple state emission phenomenon is different from that of the metal complex distinct orbital case, the phenomena observed should be quite similar. The viscosity effects noted by Watts and Missimer [20] and Giordano et al. [22] are quite reminiscent of those described for the biaryls and the dialkylanilines. For the distinct orbital origin emitter systems, the double minima excited states have their origin in the near accidental degeneracy of two excited state minima, one deriving from a transition occurring to a ligand π state having an equilibrium internuclear geometry comparable to that of the ground state while the second and displaced minimum arises from a transition to an antibonding σ^* state localized on the metal atom.

The multiple phosphorescences occurring for the phenylalkylketones [77,78] are phenomenologically similar to those dual fluorescences observed for the biaryls. A short lived intense emission assigned as $n\pi^*$ emission dominates in rigid solution, with a long lived and lower energy emission increasing its contribution as the viscosity decreases. The short lived higher energy emission has been assigned to the excited state triplet in a configuration vertically above the ground state configuration. The long lived lower energy emission is then presumed to occur from a triplet molecular configuration that has relaxed and is displaced relative to the ground state.

(ii) Chromium(III) multiple state emitters

The dual emission ($^4T_2 \rightarrow {}^4A_2$ and $^2E \rightarrow {}^4A_2$) from Cr$^{\text{III}}$ complexes, although not a true "multiple state" emission since one emission presumably has a spin allowed origin and the other a spin forbidden origin, can be useful to our understanding of the heavy transition metal multiple emission, in particular the distinct orbital origin type (Fig. 2). The orbital origin ($t_{2g} \rightarrow t_{2g}$ in O_h symmetry) of the Cr$^{\text{III}}$ phosphorescence determines that the phosphorescence band has vibronic structure similar to that of the ligand localized and charge transfer type d^6 distinct orbital multiple emission. The orbital description ($e_g \rightarrow t_{2g}$ in O_h) of the Cr$^{\text{III}}$ fluorescence emission results in a broad structureless emission as does the metal localized component of the d^6 distinct orbital multiple emission. It is likely that the difference in the formal spin character of the Cr$^{\text{III}}$ transition (spin allowed) and the d^6 complexes (spin forbidden) does not affect the comparison, particularly in view of the large spin orbit coupling and the consequent mixing of the spin states for the heavy metal d^6 systems. Examination of the few cases [30,31] for which Cr$^{\text{III}}$ fluorescence and phosphorescence occur suggests that only in the case of the near degeneracy of the zero point levels for the $^4T_2$ and ^2E states does the "multiple emission" occur. For most cases, only a single lifetime characteristic of the ^2E emission has been measured suggesting that either equilibration occurs or that thermal population of the $^4T_2$ is the origin of the fluorescence emission. Therefore, the suggestion that a single potential surface with distinct minima exists for the ^2E and $^4T_2$ states would seem quite reasonable [79,80]. The unique emission spectra obtained for the Cr(dtc)$_3$ [32] complex is perhaps the best example yet provided to verify this view. Here, the emission spectra ob-

TABLE 4

Representative emission data [a] for Cr^{III} complexes (energies in 10^3 cm^{-1})

Complex [b]	Emission type	$\overline{V}_{max}$	$\Delta\overline{V}_{1/2}$	Stokes shift [c]	$\tau(\mu_{sec})$	Ref.
$Cr(dtc)_3$	Hybrid	12.5	0.80	0.6	118	32
$Cr(dmtc)_3$	Hybrid	12.5	0.82	0.6	128	32
$Cr(exan)_3$	Phos.	12.8	0.41	0	380	32
$[Cr(urea)_6]^{3+}$	F	12.6	1.7	3.8		78

[a] All emission maxima ($\overline{V}_{max}$), half widths ($\Delta\overline{V}_{1/2}$), Stokes shift and lifetimes in glassy solvent. [b] Abbreviations: dtc, diethyldithiocarbamate; dmtc, dimethyldithiocarbamate; exan, ethylxanthate. [c] Calculated as peak to peak separation between emission maximum and corresponding absorption maximum.

served is neither the characteristic structured narrow phosphorescence type emission nor the broad structureless type typically observed for the fluorescence but is something of a hybrid, narrower and more structured than pure fluorescence but broader and more diffuse than pure phosphorescence (Table 4). Such a spectrum could imply that the barrier between the "phosphorescence" and "fluorescence" minima on the excited state potential surface is small (relative to the active vibrational modes); consequently the unique emission occurs.

(iii) Perspective

Thus, the multiple state emission occurring for the nominal d^6 transition metal complexes, although apparently a more common occurrence than for the aromatics, does have some parallels among the multiple emission of aromatics. The spatially isolated multiple emission of the mixed ligand $[RhL_2L']^{3+}$ and $[Ir(LL')Cl_2]^+$ does differ from that of the heteropolar diaromatic molecules in degree (if not type) since the luminescent chromophores are separated by only a single atom (the metal atom). Furthermore, the insulating character of the metal atom is surely not total in every case, since unlike the diaromatic molecules, the emitting levels of the mixed ligand complexes of Rh(III) [16] are known to have nearly degenerate zero point energy levels. Further, ESR, resonance Raman and electrochemistry data suggest that the spatially isolated orbitals exist for the homoligand $[RuL_3]^{2+}$ and $[IrL_3]^{3+}$ complexes, materials in which the metal d orbital may provide some minimal interaction with the π electron systems of the rings.

Pertinent to this latter point is the work of Ferguson and coworkers [81] who have reported single crystal absorption and MCD spectra for $[M(bpy)_3]^{2+}$ complexes (M = Fe^{II}, Ru^{II}, Os^{II}). They dispute the spin-orbit origin of the lowest set of states for Os^{II} and Ru^{II} using relative intensity arguments to argue that the lowest states (for Ru^{II}, Os^{II}) are bona fide triplet states ($\pi\pi^*$

and $d\pi^*$). Moreover, these workers assign the closely spaced (ca. 1500 cm^{-1}) components of the lowest energy singlet transitions to states of distinct electronic origin rather than a vibronic progression as do others. This latter finding is particularly interesting when compared with the resonance Raman excitation profile for the $[Fe(L)_3]^{2+}$ (L = bpy, phen) obtained by Clark et al. [82]. Clark et al. [82], in agreement with others, note that the lowest energy intense absorption band peak is assigned as an $^1E \leftarrow {}^1A_1$ charge transfer transition. Since the excitation profiles across this band are dominated by the A_1 modes, these authors argue that the B term and thus the coupling term, $\langle e|h_a|S\rangle$, (where e and S are two excited electronic states and h_a is the vibrational coupling operator) cannot be contributing to the resonance Raman spectra obtained for the region of the shoulder. Therefore, these authors conclude that this shoulder must be of vibronic origin, a conclusion in contradiction to that of Ferguson et al. [83].

The rationale of these apparently contradicting conclusions may lie with the following interpretation of the two sets of experimental data (resonance Raman and single crystal absorption): the distinct electronic states required by the Ferguson data could have their origin in weak coupled exciton states. Now, the absence of resonance Raman enhancement of the vibrational modes in the region of the shoulder would mean that the small magnitude of the matrix elements $\langle e|h_a|S\rangle$ simply reflects the minimal (weak coupled) interaction between two electronic states of exciton origin. Although the states involved here are apparently the singlet portion of the $d \rightarrow \pi^*$ orbital transition, the emitting triplet manifold does have the same orbital origin, and therefore should have the same fundamental character, i.e. single ring orbitals.

Recent luminescence polarization data of Ferguson et al. [83] directly illustrates the localization in a single chelate ring for two $[Ru(bpy)_2L]^{2+}$ type complexes. Although the structural perturbation here is not as small as for the other mixed ligand complex, the results again imply that single ring orbitals exist for the parent $[Ru(L_3)]^{2+}$ complexes.

Although the vibrational pattern of the absorption for $[Ru(bpy)_3]^{2+}$ cannot be readily interpreted to indicate exciton coupling, the change in the lifetime and quantum yields over the 77—4 K range could be conceived to be consistent with a weak exciton model. Thus, the three level splitting obtained for this system could be the result of a weak exciton splitting rather than the proposed strong spin-orbit splitting. Further, preliminary high resolution polarization data [84] recently obtained in the overlap region for the $[Ru(bpy)_3]^{2+}$, $[Ru(phen)_3]^{2+}$ and $[Os(bpy)_3]^{2+}$ complexes might be interpreted to imply hopping from ligand to ligand. Such an interpretation could be consistent with the localized exciton model. This interpretation is afforded further credibility by the resonance Raman data previously discussed. Certainly, the occurrence of vibronic emission patterns (relative intensity and band widths) for $[Rh(bpy)_3]^{3+}$ and $[Ir(bpy)_3]^{3+}$, altered from those of the free ligands may also be rationalized by such an exciton model. For the $[Rh(bpy)_3]^{3+}$ and $[Rh(phen)_3]^{3+}$ complexes [16], two origins, separated by 400 cm^{-1}, can be located for the dominant ca. 1400—1500 cm^{-1} mode present in the emission pattern suggestive of an exciton splitting.

The distinct orbital emission with its viscosity dependence and differences in vibrational structure is formally similar to that found for some aromatic systems (diaryls and dialkylanilines) and the Cr^{III} complexes that fluoresce and phosphoresce. It may therefore be amenable to further experimental and theoretical elaboration as detailed by Grabowski, Hochstrasser and others [71—78].

(iv) Potential surface models

The two types of emitters (spatially isolated and distinct orbital) are similar in that both involve excited state potential surfaces having potential minima separated by barriers. The origin of these distortions (the barrier) is, in the one case, the localization of wavefunctions on a single chelate ring (localized exciton) while the second type of distortion (barrier) derives from a displacement in configuration space along a metal—ligand vibrational coordinate. Critical to both cases are the vibrational modes coupling the separate potential minima since failure to activate these modes is crucial to the observation of the multiple emission for both cases. The two cases would have distinctive excited state configurations with the spatially isolated function for the tris system exhibiting triply degenerate minima (Fig. 11) while the distinct orbital emitter possesses a double minima at low temperatures (Fig. 12). The possibility of a stable ground state minimum, corresponding to the displaced excited state, appears slight since the *dd** emission is most intense for the low viscosity condition, a circumstance where the extended bond lengths of the *dd** excited state would be unstable relative to the ground state configuration.

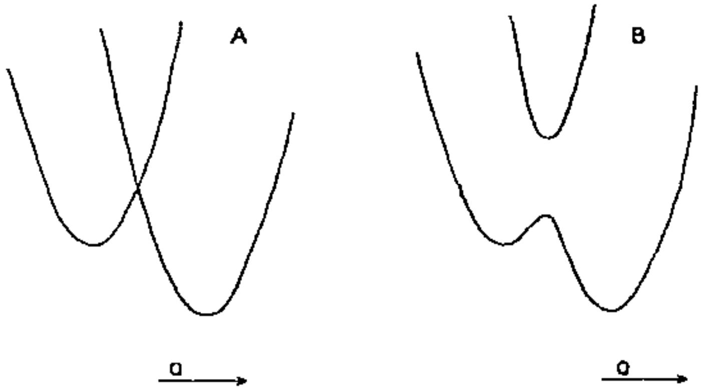

Fig. 11. Potential energy diagrams for spatially isolated emitters ignoring (A) and including (B) exciton interactions.

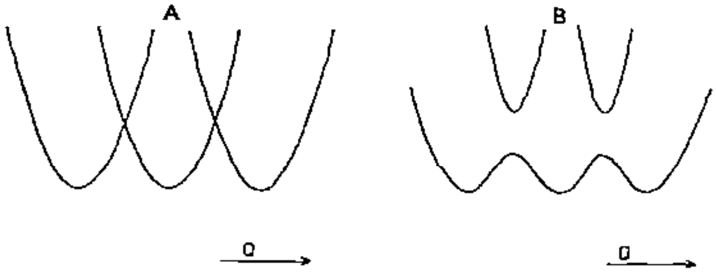

Fig. 12. Potential energy diagrams for distinct orbital emitters ignoring (A) and including (B) exciton interactions.

The model of Gouterman and coworkers for dimer and trimer molecules affords a substantial framework [85—87] for examination of the spatially isolated multiple state emitter. The Gouterman model demonstrates the fundamental equivalence of the excitonic spectral problem and the vibronic coupling problem (Jahn—Teller and vibronic intensity borrowing), a point to which we shall return below. The model utilizes two parameters, ϵ, an electronic energy parameter and λ, a nuclear displacement parameter to define the weak ($\lambda >> \epsilon$) exciton coupling and strong ($\lambda << \epsilon$) exciton coupling. The ϵ parameter, which defines the magnitude of the exciton splitting, has typically been the focus of the coupled exciton problem while the λ parameter defining the potential surface displacement is typically the emphasis of the Jahn-Teller or vibrational borrowing problem. For the weak coupled limit, the interpretation is that vibrational relaxation to the equilibrated state occurs prior to transfer of the electronic energy while for the strong coupled limit, the electronic excitation energy is considered to be transformed from ligand to ligand prior to vibrational relaxation (i.e. the excitation is delocalized). Further, for the weak coupling (localized exciton) trimer system both a Jahn-Teller effect for the degenerate electronic state and a pseudo Jahn-Teller effect between the E pair and the close lying third non-degenerate level can occur. The net effect of these interactions is that both degenerate and the non-degenerate surfaces can be distorted. In addition to the low temperature effects associated with the presence of the barrier, Gouterman has calculated absorption and emission spectra expected for dimer and trimer molecule systems over a range of parameters from the strong to the weak coupled limit. Within the limits of the assumptions used (a single vibrational mode is assumed for each unit) at least two experimental results can be expected for molecular systems lying within Gouterman's weak to intermediate coupled limits. The first is that vibronic structure occurring in the absorption pattern may be expected to broaden and alter (spacings, relative intensity of peaks). Furthermore, emission patterns and lifetimes may vary as a function of temperature. The origin of these effects is the exciton splitting which necessitates that the oscillator strength is not equally divided among the components of the split states.

The vibronic wave functions for the single ring orbital tris complexes would have the form

$$\Psi_0 = \psi_0 \cdot \phi_0 \tag{1}$$

with

$$\psi_0 = \psi_A\psi_B\psi_C \tag{2}$$

and

$$\Psi = \psi_a\phi_a + \psi_b\phi_b + \psi_c\phi_c \tag{3}$$

with

$$\psi_a = \psi'_A\psi_B\psi_C \tag{4}$$

For these equations, ψ_A, ψ_B and ψ_C are the ground state electronic wave functions for identical ligands A, B and C. The excited electronic state localized on a single ligand is designated by ψ'_i where i = A or B or C. The symbol ϕ_0 represents a vibrational function for a monomeric unit and ϕ_a, ϕ_b and ϕ_c represent vibrational wavefunctions for the excited state when the respective monomer unit is excited. These functions presume the validity of the adiabatic approximation.

For the D_3 symmetry species of interest, an E symmetry state and an A_1 or A_2 state are possible; consequently the linear combination must be properly symmetrized and normalized. In this case, nonsymmetric vibrations may couple the excited states.

For the distinct orbital multiple state emitters, Watts [20] has utilized the model of Dellinger and Kasha [88,89] to explain the temperature and solvent dependence of the dd^* and charge transfer emissions for the $[\text{Ir(phen)}_2\text{Cl}_2]^+$ and $[\text{Ir(5,6-mephen)}_2\text{Cl}_2]^+$ complexes. This model treats the solute—solvent interaction as a Born-Oppenheimer type approximation, noting that in the high viscosity range solvent relaxation occurs more rapidly than viscosity dependent intramolecular (diffusion) relaxation processes. Consequently, relaxation of the molecular configuration from excited states attained as a result of excitation of an electron from a bonding orbital (t_2) to an antibonding (e) orbital may be slowed because of the viscosity dependent barrier (Fig. 12). This additional term added to the Hamiltonian to represent the intermolecular perturbation has been used to generalize a number of related viscosity dependent phenomena, among which, the pseudo Jahn-Teller effect and the periodic potential (as observed for conformational isomers) are of interest. At present, data distinguishing between a pseudo Jahn-Teller or a periodic potential are not available; however, as noted previously, the probability of a significant ground state barrier (periodic potential) corresponding to the dd^* excited state seems small.

The exciton model has been utilized by Mason and coworkers [65—67] to attempt to quantitatively rationalize CD and vibronic structure for optical isomers of tris phen and bpy metal complexes (including Ru^{II}, Rh^{III}). These workers concluded that the data for $\pi\pi^*$ bands of $[Ni(bpy)_3]^{2+}$ and $[Fe(bpy)_3]^{2+}$ imply that the intermediate or strong coupling limit is appropriate [67]. However, the calculated magnitude of the exciton splitting of the A and E states appears relatively insensitive to the model parameters (exciton splitting parameter, potential surface displacement, and vibronic band width) utilized by Mason and coworkers. Thus, Hawkins and coworkers [68] utilized the Perrin-Gouterman trimer model [87] to calculate the absorption and CD spectra for $[Ni(bpy)_3]^{2+}$ and found what appears to be a good match between theory and experiment using the weak coupling limit parameters. These conclusions are disputed by Mason et al. [67] who have utilized the "dissymmetry factor" (ratio of CD to isotropic absorption) to calculate the degree of overlap of the rotational strengths.

All of these estimates of the appropriate model limit are, to some extent, matters of interpretation of the overlapped CD spectra and necessarily create considerable ambiguity. In any case, these data tend to focus more upon the symptoms of the phenomenon, i.e. the presence of vibronic structure and the width of absorption bands, rather than the phenomenon itself. The essence of the exciton model, as previously noted, is the rate of transfer of the electronic excitation vs. the vibrational relaxation. Strong coupling results in an excitation delocalized over all three chelate rings and weak coupling results in excitation characteristic of a single chelate ring which is accompanied by hopping of the excitation from ring to ring. Consequently, the data reported for the d^6 diimine complexes (resonance Raman, electrochemistry, etc.) suggest that these materials are generally better described by the weak coupling limit.

The various experimental perturbations (symmetry, electronic, temporal, temperature) afford an opportunity to determine the relative magnitude of the parameters λ and ϵ for the parent D_3 complexes. A relative interaction scale in which a very large separation of the E pair of orbitals from the A orbital is chosen as the one extreme and the zero splitting of the three levels is chosen as the other extreme is defined. These limits correspond, respectively, to strong exciton coupling and a delocalized ψ function and a weak exciton coupling and single ring localized function. The various perturbations can be placed on the scale, providing at least a qualitative estimate of interaction magnitude. For example, the substitution of one phen for a bpy in $[Rh(bpy)_3]^{3+}$ complex to produce a mixed ligand complex, does result in a molecule that definitely lies close to the weak coupling limit. Consequently, since this symmetry perturbation is small, the parent compound can also be considered to be close to the weak coupling limit. The energies of the emitting states for the $[Rh(bpy)_3]^{3+}$ and $[Rh(phen)_3]^{3+}$ have been estimated to differ by ca. 200 cm^{-1}. If this difference approximates the separation of emitting states in the mixed complexes and is smaller than or equal to the exciton splitting estimated between the E and A states (assuming D_3 symmetry) of the parent compounds, then the above rationale is probably appropriate. Certainly, measurement of emitting state properties for a small symmetry perturbation such as $[RhL_2L_D]^{3+}$ (where L_D is a perdeuterated diimine ligand) would afford an opportunity to minimize the exciton splitting for the parent while providing a probe, the decay time, to verify that the system does approach the weak coupling limit. The electrochemical (electronic perturbation) results for $[RhL_3]^{3+}$ have been interpreted to imply that this structural (electron charge) perturbation indicates proximity to the weak coupling limit. However, low temperature ESR data must be acquired for the $[RhL_3]^{2+}$ species to verify that the room temperature instability derives from localization of the excess electron charge on a single chelate ring.

While recognizing that addition of an electron to the parent compound (as in the electrochemistry) to simulate the optical excited state may be a relatively large perturbation to the parent, the electrochemical ESR results previously detailed for $[Ru(bpy)_3]^{2+}$ provide a strong argument that this material does lie near the weak coupling limit. Although the mixed ligand perturbation does not verify this limit, the resonance Raman result implies that, at least on the time scale of the Raman experiment (10^{-15} sec) the excited state is localized on a single ring. Decay of emission polarization for these Ru^{II} compounds would certainly provide an additional vantage point for this material by permitting an estimate of the exciton hopping rate.

For all perturbations the magnitude of the barrier between the different potential minima is critical to the determination of the appropriate limit for a complex. Therefore, the freezing out of vibrational coupling modes for a particular system can change the chemical system from strong coupled to weak coupled. Thus far no systematic effort to examine this limit and to quantitate the barriers has been reported for the spatially isolated emitter systems.

The previous discussion has emphasized the spatially isolated systems; however, to the extent that the model for the distinct orbital emitters involves distorted potential surfaces with moderate height potential barriers, such perturbation probes as "temperature" can be used to determine the degree of mixing of the distinct orbital emitter states. Moreover, as indicated, the fact that the barrier for these systems is an "environmental barrier" permits the possibility of an additional kind of perturbation, i.e. the solvent.

E. FURTHER EXPERIMENTS

While the multiple emission phenomenon has been demonstrated for a number of heavy metal molecule systems and a variety of related phenomena detailed, the total understanding of these related phenomena does require a variety of additional information, some of which are suggested above. Discovery of additional examples of multiple emission must be one of the focuses of future research. Along with additional solvent and temperature dependent spectra and lifetime data, a major emphasis must be directed to acquiring vibrational details, in particular high resolution vibronic data, for the excited state and the ground state. The difficulty in obtaining high resolution vibronic data for transition metal systems is well known; however standard IR techniques as well as resonance Raman methods may afford opportunities to identify the vibrational modes critical both to the potential surface distortion and to the excited state deactivation.

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