Spectroscopic Investigations of Excited States of Transition-Metal Complexes

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Photoluminescence spectroscopy has been a standard method of inquiry for the investigation of excited states of organic materials for over 30 years. Complemented by theoretical developments, analyses of fluorescence and phosphorescence phenomena have led to orbital and spin classifications of excited states, symmetry assignments, and an enormous amount of detailed information about rate constants, energy levels, vibrational structures, and relaxation phenomena.[1,2] Moreover, the information obtained from luminescence measurements on organic materials has laid a firm foundation for the magnificent developments in organic photochemistry[3,4] and the use of organic materials as probes for studying energy transfer in gases, solutions, and solids. Luminescence is a primary tool for unraveling the details of relaxation processes occurring in large molecular systems.

The use of emission spectroscopy for probing the excited states of inorganic complexes containing organic ligands is of relatively recent origin. First extensively applied to rare earth chelates[5] and chromium compounds,[6] the power of emission techniques has only recently been demonstrated in the quest to define the full range of types and properties of the excited states of transition-metal complexes. Reasons for this late development are not difficult to find. Unlike organic molecules, notably the aromatics, that have electronic structures virtually ensuring the incidence of easily observable photoluminescence, many of the common transition-metal complexes possess electronic structures that promote rapid radiationless loss of absorbed energy and thus produce no emission. This statement holds for the bulk of complexes of the first transition series, and these are precisely the elements where the chemistry is best defined. Luminescent complexes of the 3d elements are known, but the number is relatively small. Moreover, the observed luminescence from a series often owes its origin to a state or states arising from a particular electronic configuration of the metal atom that is common to the entire group of active materials.[7]

A second important factor retarding the study of transition-metal complexes by emission techniques is the requirement of specialized optical and cryogenic equipment. Although some transition-metal complexes emit in the visible region, the bulk of them luminesce in the red or near-infrared region of the spectrum where sensitivity is low and, for many materials, the quantum yield also is low. Frequently, complexes achieve good luminescence efficiencies only at sub-77 K temperatures, ranges not yet routinely available in many laboratories.

## Structural Prerequisites for Photoluminescence

If one accepts a nominal minimum energy difference of 10 kK between ground and emitting states as a practical condition for the observation of luminescence, then probable candidates for the emission experiment can be selected by electronic considerations. One is also guided by the rule: "In the absence of photochemistry from upper excited states, emission from a transition-metal complex with an unfilled d shell will occur from the lowest electronic excited state in the molecule or from those states that can achieve a significant Boltzmann population relative to the lowest excited state". This generalization, originally inferred from sparse evidence on d^3 and d^6 complexes, appears to be withstanding the test of new experimental data as long as conventional light sources are employed and one's purview is restricted to chemical complexes and does not include ions imbedded in hard lattices.[8]

The Utility of the nd^6 Configuration

The requirement of a large energy gap between ground and excited state is rarely satisfied by complexes of the first transition row. If one moves to the second and third transition series, however, and confines attention to complexes with metal ions having nd^6 configurations, the basic requirement is generally met. Furthermore, by a judicious choice of ligands and central metal ions, one has the capability of designing series of complexes in which the nature of the lowest excited state(s) can be stipulated. According to the rule enunciated above the emission will originate from the lowest excited level(s), and thus the properties of the excited state(s) can then be revealed through a detailed investigation of the observed luminescence.

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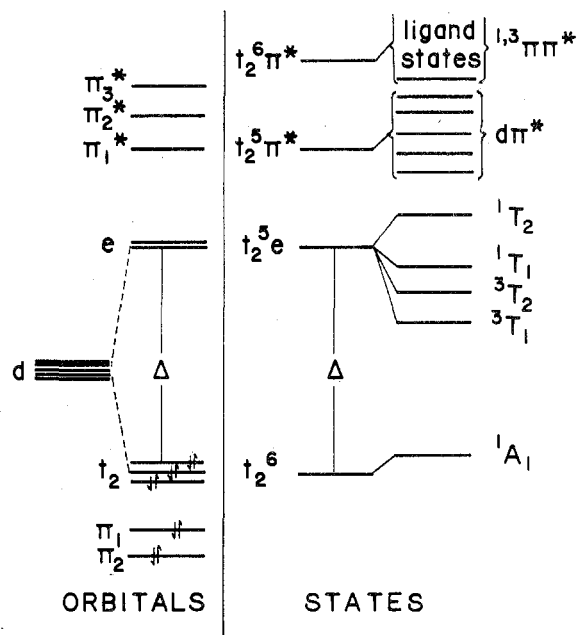
Figure 1. Schematic orbital and state diagram for a d^6 electronic system perturbed by an octahedral environment. A strong-field description is assumed. Shown also are bonding and antibonding π orbitals located on the ligands. Splitting due to spin–orbit coupling has been ignored.

A schematic representation of the electronic situation for nd^6 complexes is depicted in Figure 1 where, for simplicity, octahedral microsymmetry has been assumed. One visualizes a central metal ion surrounded by six negative groups supplied by the ligands. It is important to realize that most of the systems investigated are not octahedral and the symmetries range from C_s to O_h. Many different elements in various oxidation states can occupy the central coordination site, and the spin–orbit coupling constants can range from ~0.5 kK (Co^{3+}) to ~4 kK (Ir^{3+}).[9] Chemically, the luminescent species range from anions through molecular species to highly positively charged cations. Common to all the species considered here, however, are a metal ion with a d^6 spin-paired electronic configuration and a ligand system containing at least one moiety with a π structure. The two electronic systems are depicted in Figure 1. In the ground state all electrons are generally paired as indicated.

Formal descriptions of the low-lying excited states of nd^6 complexes can be derived from successive one-electron promotions. There are basically four orbital types expected. For clarity we use the scheme based on octahedral microsymmetry.

dd States. These can be visualized as arising from promotions of an electron from t_2 to e, an excitation confined (essentially) to the metal ion. The promoted electron either has its spin parallel or antiparallel to the spin of its partner remaining in the t_2 core. Configurational energy is determined by Δ, the octahedral ligand-field parameter. Δ is a function of the ligand strengths, the position of the metal ion in the periodic table, and the oxidation state of the ion.[10] *Thus, to a degree, Δ is at our command,* and the average energy of the cluster of ligand-field states can

be chemically controlled. The splitting into the four T states is a measurement of interelectronic repulsion and is usually given in terms of Racah parameters.

$d\pi^*$ States. These arise from the excitation of a metal (t_2) electron to a π^* antibonding orbital located on the ligand system. One can view this process as a transfer of electronic charge from the central ion to the ligands, i.e., as an incipient oxidation of the metal ion. From this point of view one expects such states to be related to the redox potential of the complex— the more easily oxidized, the lower should lie the $d\pi^*$ transitions. Thus, a change of metal ion, while preserving the d^6 configuration, will drastically affect the position of the $d\pi^*$ states.

$\pi\pi^*$ States. States of this description are associated with the promotion of an electron in a π bonding orbital of the ligand system to a π^* antibonding orbital also on the ligand system. These, as depicted in Figure 1, usually lie at relatively high energies and are substantially of ligand character. The metal ion plays a minor role in the definition of their energies but can affect other sensitive properties such as decay times and quantum yields.

πd States. Formally, such states are expected to arise from a promotion of electronic charge from the ligand π system to the metal (e) orbital. For the complexes investigated in the author's laboratory no firm evidence for them has been acquired,[11] and they have not been included in the level system depicted in the figure.

Thus, simple model considerations delineate the orbital types of excited states expected in metal complexes. Complemented by spin-coupling rules, they also define the possible spin labels for the electronic terms. For nd^6 complexes both singlet and triplet states are expected to arise from each excited configuration, and appropriate multiplicity symbols have been attached to the dd and $\pi\pi^*$ states in the figure. For the $d\pi^*$ states no spin label has been included, since there is strong evidence that S is not even approximately a "good" quantum number for most complexes.[12] For the heavier elements S loses meaning as a label for dd states as well. We will return to this point later. A complete labeling of an excited state would include the final symmetry label of the irreducible representation of the symmetry group to which the complex belongs.

The energy-level sequence in Figure 1 is schematic only. The relative ordering can be altered by switching metal ions, exchanging ligands, modifying the ligands, or varying the geometry, i.e., by employing chemistry. There are also distinct possibilities of perturbing level structures by solvent effects, pressure variations, magnetic and electric interactions, etc. Thus, one has available a wide range of chemical and physical means to modify the electronic properties in predictable ways. The final descriptions of the states of a particular complex rest, as always, with experiment. We reiterate that the important feature to notice is that the *lowest excited states*, i.e., those that are responsible for the luminescence, can be specified

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chemically. Then, the powerful tools of luminescence spectroscopy become available for defining their properties.

Goals of Current Research

In the author's laboratory the research effort has encompassed chemical synthesis, physical measurements, and the construction of theoretical models. The guiding philosophy has been to focus on the general problem of defining the nature of the excited states of transition-metal complexes as revealed by spectroscopic measurements, primarily photoluminescence. The immediate goals have been (a) to develop experimental methods commensurate with the task of determining energy-level splittings, symmetries, radiative and radiationless rate constants, geometrical parameters, spin labels, magnetic characteristics, etc. of the excited states of transition-metal complexes, (b) to formulate criteria that will allow the lowest excited states of transition-metal complexes to be characterized empirically by orbital type and spin label from a study of optical properties, (c) to generate quantitative models of the excited states that will not only correlate data deduced from diverse experimental methods but will have genuine predictive capability, and (d) to arrive at a degree of sophistication of the descriptions of excited states such that their roles in photochemical, electrochemical, and chemical transformations can be understood.

The ultimate goal of the research has been to arrive at a degree of understanding such that metal complexes can be engineered to possess desirable optical, electrooptical, photochemical, electrochemical, and chemical properties.

Principal Experimental Methods

Absorption Spectroscopy. This is especially valuable if the spectra are measured at 77 K where better resolution of band structure is frequently noted. The measurement of absorption spectra as a function of solvent polarity is also an important diagnostic tool for recognizing the natures of excited states. Standard equipment is used, and cell designs for low-temperature measurements are available.[13]

Emission Spectroscopy. The basic apparatus requires (1) source of uv-visible light for excitation and either a filter train or a small monochromator for limiting the bandpass, (2) a detection system consisting of a scanning monochromator and a photomultiplier. For most materials a red-sensitive sensor and phase-locked electronics are highly desirable. The emission intensity vs. wavelength is usually displayed on a chart recorder and is frequently corrected for instrument response and reported linear in frequency. The sample is usually a solution of the complex in a solvent that forms a rigid glass at 77 K. For certain types of emission the solid material can be suspended in liquid nitrogen and excited directly. Emitted light is sometimes observed at room temperature, but the luminescence efficiency almost invariably improves as the temperature is lowered to 77 K. For some substances considerable improvement in resolution and large spectral changes occur at still lower temperatures. Sub-4.2 K data may be necessary to provide detailed descriptions of some systems.

Quantum Yield Measurements. In principle the quantum yield is a simple luminescence efficiency measurement. One counts the number of photons emitted by the sample and compares this with the number of photons absorbed from the source. Basically the apparatus employed for this determination is the same as that used for standard emission measurements. Considerably more calibration, data reduction, stabilization, and standardization are required.[14,15]

Decay Time Measurements. In this experiment a short burst of radiation is used to excite the sample, and the transient emitted light is monitored electronically. The exponential signal is frequently displayed on an oscilloscope, photographed, and plotted on a semilogarithmic scale. The slope yields the mean decay time for the ensemble. For transition-metal complexes the measured decay times are frequently in the microsecond range, and the nitrogen laser has provided a convenient source of pulsed (fwhh, ~20 nsec) uv (337 nm) radiation.

Temperature-Dependent Measurements. Since the spectra obtained from transition-metal complexes are usually quite diffuse, direct measurement of term splittings is often impossible. Valuable information on electronic excited states can be obtained from monitoring emission spectra, quantum yields, and decay times as a function of temperature and employing computer techniques to extract molecular parameters. Indeed, for closely spaced excited states (~10 cm^{-1}) it is often necessary to achieve quite low temperatures (~1.5 K) to obtain energy-level splittings and rate constants for individual levels. A variable temperature helium dewar with the sample in contact with the escaping gas must be employed if data accurate enough for computer analysis are to be acquired.[16]

Other Methods. In principle those experimental techniques commonly employed for the investigation of the excited states of organic materials could be used on inorganic complexes. These include excited-state EPR,[17] phosphorescence microwave double resonance,[18] excited-state electronic absorption spectroscopy,[19] polarization measurements,[20] and infrared optical double resonance.[21] Few complexes have been investigated by these methods, and the field is ripe for exploitation.

Often the use of several techniques is required to unravel the nature of a given set of energy levels producing luminescence in a transition-metal complex or a series of complexes. The point of view adopted in the rest of this short review will be to proceed from a coarse classification of excited states, as demanded by the simpler measurements, to a final brief description of the types of information available with the use of more complicated techniques. There will be a con-

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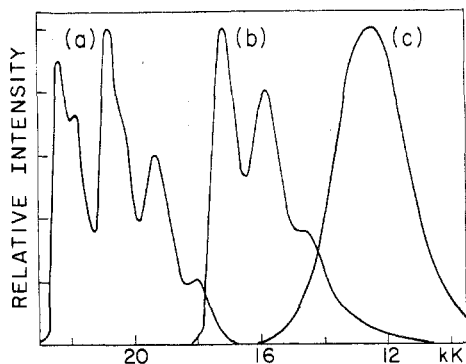
Figure 2. Luminescence from transition-metal complexes at 77 K exemplifying $^3\pi\pi^*$, $d\pi^*$, and ^3dd origin, respectively. (a) [Rh-(phen)$_3$](ClO$_4$)$_3$ in water–methanol glass, (b) [Ru(bpy)$_3$]Cl$_2$ in ethanol–methanol glass, (c) solid [RhCl$_2$(phen)$_2$]Cl.

comitant rise in sophistication of the models employed to rationalize the observations.

Experimental Classification of Excited States

Since the orbital and spin characteristics of the lowest lying excited states in transition-metal complexes not only govern the emission spectroscopy but are most probably involved in controlling the photochemical and some chemical properties as well,[22,23] a key problem is the formulation of experimental criteria for assigning appropriate labels to observed excited states. The approach has been to synthesize complexes whose lowest excited configurations are fairly certain on general structural grounds and to use the spectroscopic properties to formulate rules for recognizing analogous configurations and states in more complex situations. These investigations have been carried out systematically on d^6 ions, and the criteria have been formulated for experiments carried out at the convenient temperature of 77 K.[24]

^{3}**dd Excited States.** If the average ligand-field parameter is sufficiently small and the oxidation potential of the metal ion is high, one has a disposition of lowest states pictured in Figure 1. The lowest excited configuration is dd, and one expects luminescence to arise from the lowest term, formally $^3T_1$. These conditions are satisfied by [RhCl$_2$(phen)$_2$]$^+$ (phen = 1,10-phenanthroline) whose spectrum is displayed in Figure 2. The spectroscopic behavior of this ion is typical of a broad class of complexes whose lowest (emitting) excited state has been classified as ^{3}dd.[25,26]

Emission is broad and structureless. It is relatively matrix independent but is rarely observed at room temperature. After flash excitation, the mean decay time ranges from 10 to 500 μsec and is temperature dependent. The emission is characterized by a low quantum yield that can be enhanced considerably by eliminating high-frequency vibrations from the coordination sphere.[27] The energy of the luminescence is

a function of the average ligand-field strength about the central ion.[25]

dπ^* Excited States. By switching to an ion of the 4d or 5d transition series and choosing one that is easily oxidized, one modifies the energy-level sequence to produce a dπ^* configuration lowest. The prototype systems are ruthenium(II) complexes containing 2,2'-bipyridine (bpy) or 1,10-phenanthroline (phen) as coordinated ligands.[28] The well-studied spectrum of [Ru(bpy)$_3$]$^{2+}$ is shown in Figure 2. Extensive studies of emission spectra from states arising from a dπ^* configuration have identified the following characteristic features at 77 K.

The emission is intense and highly structured. Often a single vibrational progression is the dominant feature of the band. Frequently the luminescence is observable at room temperature in a rigid matrix and sometimes in fluid solution.[29] The decay time is ~1–10 μsec at 77 K. Usually the emission lies in the tail of a strong absorption region and suffers strong reabsorption when the pure solid material is excited. The quantum yields often exceed 1,[30] and thus a short radiative life (<100 μsec) is indicated. If the complex possesses a dipole moment, the emission can be shifted substantially by varying the hydroxylic content of the rigid glass.[31] Because of the dominant role played by spin–orbit coupling, no spin label is meaningful.[12]

$^3\pi\pi^*$ **Excited States.** These states are easily observed from complexes containing metal ions with closed shells.[32] They are also the emitting levels in rare-earth complexes of trivalent lutetium, lanthanum, and gadolinium.[33,34] To engineer a complex possessing an open d shell that has $^3\pi\pi^*$ states lowest, one must choose a system with a large value of Δ and a metal ion that is difficult to oxidize. Rhodium(III) complexes of bipyridine and phenanthroline satisfy these requirements. Both the dπ^* and dd states are raised in energy sufficiently such that the lowest (emitting) states in the complexes become $^3\pi\pi^*$.[25,26]

Emission spectra originating from $^3\pi\pi^*$ states in complexes often resemble those emanating from the uncoordinated ligands both with regard to energy and to band structure. In the complex the band is generally red shifted ($\leq$1 kK) from its position observed from the corresponding ligand.[25,35] The decay time at 77 K is usually in the millisecond range and is considerably shorter (~10^2) than the decay of the uncoordinated ligand phosphorescence. The energy of the emission is not highly solvent dependent. [Since coordination drastically affects the nonbonding electrons of the ligands, a ligand exhibiting $^3n\pi^*$ phosphorescence would be expected to produce a complex exhibiting $^3\pi\pi^*$ emission. The similarities noted

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above could well disappear.]

A Case History. Use of the listed criteria to assign the lowest excited states of a related set of complexes is exemplified by the case of the three related $5d^6$ iridium(III) complexes.[24] The luminescence from cis-[IrCl$_2$(5,6-Mephen)$_2$]$^+$ has a measured decay of 190 ± 5 µsec in an alcoholic glass, possesses pronounced structure, and is slightly red shifted from the emission from the 5,6-dimethyl-1,10-phenanthroline molecule itself. It is assigned to a $^3\pi\pi^*$ origin. The characteristic structure of the emission from cis-[IrCl$_2$(phen)$_2$]$^+$, the short decay time (~7 µsec), and the high quantum yield (0.50) label the luminescence as dπ^* in origin. By the criteria stated above, the broad structureless emission emanating from [IrCl$_4$(phen)]$^-$ in the solid state is clearly ^{3}dd in origin.

The assignments of the lowest excited states of the three iridium(III) complexes show the efficacy of using complementary experimental methods for arriving at a unique orbital labeling of excited states for well-defined configurations. When significant configurational mixing occurs, the state assignment problem becomes considerably more complicated, and more interesting.

Manifestations of Configuration Interaction

In the previous section it was implicitly assumed that an excited state could be assigned a unique orbital label. In the dd and $\pi\pi^*$ cases a spin labeling was also considered to be meaningful for the lowest excited configuration. This situation obtains when the emitting states are relatively isolated from electronic states arising from other configurations. Complexes have been synthesized, however, whose spectroscopic properties indicate that significant dπ^*–$\pi\pi^*$ interaction is occurring.[35,36] Its incidence is signalled by a near-coincidence of uncoordinated ligand $^3\pi\pi^*$ emission and complex emission and a strong dependence of measured decay time (77 K) on the polarity of the rigid glass medium. When a $^3\pi\pi^*$ level lies lowest but is strongly perturbed by dπ^* states lying nearby, configuration interaction is most easily recognized and can be treated in a semiquantitative way. For [IrCl$_2$(5,6-Mephen)$_2$]$^+$ a factor of 7 in measured decay time has been introduced simply by switching solvents. This has led to a semiquantitative model of dπ^*–$\pi\pi^*$ interaction and established a criterion for deciding upon the appropriateness of attaching a single configuration label to the emitting levels. Cases where this is manifestly impossible have been described.

Clearly one expects dd–dπ^* and dd–$\pi\pi^*$ configuration interaction to occur in complexes and indeed to be of major importance in those systems where a near-coincidence of two zero-order configurational energies occurs. The observable spectroscopic manifestations should be a "mixing" of band types, subtle changes in emission characteristics with changes in solvent, and values for excited-state parameters that lie intermediate between those characteristic of "pure" states. Evidence for dd–dπ^* configuration interaction exists,[37] but no systematic spectroscopic study has yet been reported. A clear case of dd–$\pi\pi^*$
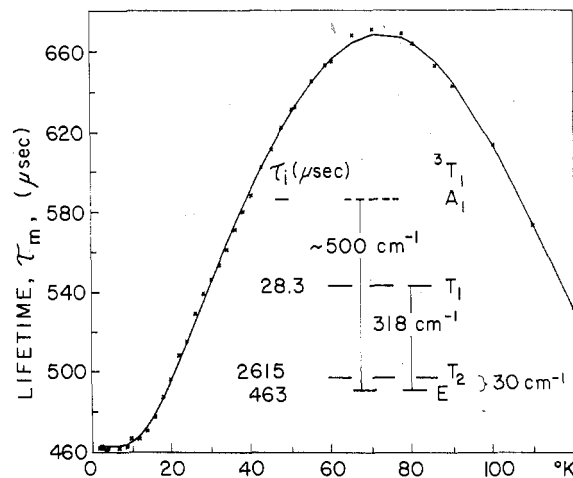
Figure 3. Measured decay times of solid K$_3$Co(CN)$_6$ as a function of temperature. ×, data points; —, computer fit. Decay constants and energy gaps obtained by a least-squares fit of the equation $\tau_m = [2 + 3e^{-\epsilon T_2/kT} + 3e^{-\epsilon T_1/kT}]/[(2/463) + (3/\tau_{T_2})e^{-\epsilon T_2/kT} + (3/\tau_{T_1})e^{-\epsilon T_1/kT}]$. (See ref 38.)

interaction has not yet been seen by the author. The recent photochemical results of Balzani et al. strongly point toward a near-coincidence of several types of states.[22] It is important to emphasize that configuration interaction may be revealed only in subtle changes of experimentally measured quantities, and detailed experimentation and data reduction may be required to achieve a quantitative measure of it.

In our discussion of state labeling and classifying we have formulated criteria explicitly based on data obtained at 77 K, since most information is available for that temperature. As shown later, the "states" are really clusters of levels with populations controlled by Boltzmann statistics. Nonetheless, the criteria still remain valid for the reason that splittings for many complexes turn out to be smaller than kT at 77 K, and thus an average property is displayed. This statement is justified a fortiori in the later sections where the detailed splittings and properties of individual electronic levels are described.

Quantification of Excited State Properties

Level Splittings, Rate Constants, and Symmetry Assignments. Once the configurational identity (and sometimes the spin label) for an emitting term has been verified, considerable additional detailed information about the emitting states can be acquired by a study of the temperature dependences of the band structure, the decay time, and the quantum yield of the luminescence. The matching of these experimental results through computer analyses to theoretical models has begun to generate quantitative descriptions of the excited states.

Ligand-Field States. In Figure 3 is a plot of the measured decay time of the luminescence of K$_3$Co(CN)$_6$ as a function of temperature.[38] Not only is the mean life of the luminescence highly temperature dependent, but the observed decays are exponential at all temperatures reached. This behavior strongly points toward a manifold of excited states producing the emission whose occupation numbers are controlled by equilibrium statistics at all temperatures. Computer analysis of the emitted light under

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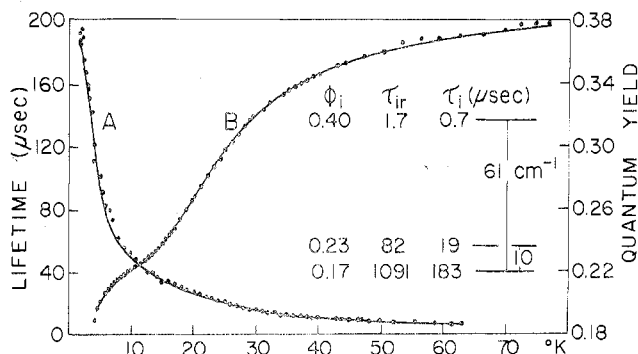
Figure 4. Temperature dependence of the calculated (—) and observed (···) lifetime and quantum yield of $[Ru(bpy)_3]^{2+}$ in poly-(methyl methacrylate). Lifetimes, curve A, are read from the left ordinate; quantum yields, curve B, from the right. Energies, quantum yields, and decay constants obtained by computer fit of the experimental data. (See ref 40.)

these assumptions has produced energies and decay parameters for the individual levels. Comparison with simple crystal-field calculations supplied the final group theoretical labels for the states that are included in the figure. Thus the $^3T_1$ term pictured in Figure 1 is interpreted to be a cluster of levels split by spin–orbit coupling, each possessing unique decay parameters. A value for the spin–orbit coupling constant for diamagnetic cobalt(III) has also been obtained. When temperature-dependent quantum-yield data are available for a system (see below), highly important additional information on both radiative and radiationless processes can be extracted.

Computer analysis of the temperature dependence of the emission decay time of ruthenocene, which also displays dd luminescence, has also been carried out in the 4.2–77 K temperature range.[39] The derived level pattern has been rationalized on the basis of a $^3E_1$ (dd) term (D_5), split by ~0.5 kK by spin–orbit coupling into $A_2 + A_1 + E_1 + E_2$ components in order of increasing energy. Information on the degree of covalency in the molecule in the excited configuration has also been furnished by the analysis.

Charge-Transfer States. The temperature dependences of both the quantum yield and the decay time of the intense luminescence of $[Ru(bpy)_3]^{2+}$ are displayed in Figure 4. One sees that the decay time increases monotonically with decreasing temperature below 77 K, a behavior exactly opposite to that for $K_3Co(CN)_6$. The emission from the former ion, now firmly established as arising from a $d\pi^*$ configuration, has been subjected to detailed investigations.[40–46] Simultaneous computer analyses of both the quantum yield and decay curves displayed in Figure 4 have produced level splittings and both radia-

tive and radiationless decay parameters for the individual levels. They are included in the figure.

Geometrical Distortions of Excited States. Although vibronic analyses of band structures have been carried out for numerous diatomic molecules and organic substances, subjecting emission bands of transition-metal complexes to detailed analyses has just begun. The lack of effort is a result of the paucity of emission spectra and the general diffuseness of most observed emission bands. Because of the huge geometrical changes that may occur upon excitation, especially $t \rightarrow e$ excitation, and the probable role of excited states in controlling photochemistry (and chemistry), it is of considerable interest to measure excited-state geometries quantitatively.

The emission spectrum of $K_3Co(CN)_6$, which is devoid of detail at 77 K, displays considerable vibrational structure at 4.2 K, where the emission originates from the *lowest* (E) spin–orbit component of the $^3T_1$ term.[38] An analysis of this band has been carried out by the use of a simple spectral fitting technique. Relative intensities of the vibronic transitions were assigned by the use of Franck–Condon factors obtained from harmonic oscillator models of the ground (A_1) and excited (E) states. The analysis has yielded the approximate geometry of the excited complex and a quantitative measure of its expanded geometry. It has also yielded a measure of the weakening of the (M–CN) harmonic force constant in the excited state and has located the probable frequency of the nonvertical $A_1 \rightarrow E(^3T_1)$ transition.

A similar analysis of the band contour of the luminescence observed from ruthenocene has also been completed.[39] Detailed information on the lowest excited level has been obtained. Other molecules are under investigation. Because of the huge Stoke's shifts exhibited by these and many other complexes, such studies should play a key role in establishing a connection between spectroscopic properties and photochemical reactivities.

Excited-State Charge Distributions. Systematic investigations of the emitted light from series of related complexes of ruthenium(II) with bipyridine and phenanthroline have not only permitted group theoretical labels for the emitting levels to be inferred but also have led to the development of a coupling model for $d\pi^*$ excited states. The model appears to be applicable to a broad class of complexes and is capable of correlating information derived from diverse experimental methods.[40,41]

The ion (parent) coupling model views the $d\pi^*$ excited states of a d^6 complex as the result of coupling the low-lying electronic states of the corresponding d^5 complex (obtained from a one-electron oxidation) with an optical electron residing in an antibonding orbital on the ligand π system. The coupling scheme has been quantified mathematically.[44] The observed splittings of the lowest group of $d\pi^*$ emitting states are determined by exchange integrals and a mixing parameter that is dependent on the spin–orbit coupling parameter of the central metal ion in the complex. Comparison of the experimentally derived splittings with the theoretical parameters has allowed a quantitative measurement to be made of the relative importance of spin–orbit vs. electrostatic interactions in defining the final electronic states. Moreover, since

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the spin–orbit contributions are, in principle, obtainable from EPR measurements on the oxidized complex, then the formalism provides a mechanism for relating the excited-state properties of a given complex with the ground-state properties of the species generated by a one-electron oxidation. If one then exploits known trends in spin–orbit coupling and crystal-field parameters with oxidation state and position in the periodic table, the way is open to draw generalizations about the optical and magnetic properties of excited states applicable to large numbers of transition-metal complexes.

Excited-State Interactions

Vibronic Coupling. The lowest state of the $d\pi^*$ emitting manifolds of trigonal ruthenium(II) complexes has been assigned A_1 symmetry in the group D_3.[41] Transitions to the ground state from an A_1 state are electronically forbidden, and the coupling mechanism leading to the finite radiative life can be inferred from the behavior of the luminescence at very low temperatures. Figure 5 shows the luminescence from $[Ru(bpy)_3]^{2+}$ doped in $[Zn(bpy)_3]SO_4$ lattice at 4.2 K and at 1.65 K. The intense, short-lived, Franck–Condon allowed band observed at 4.2 K (assumed to come from E) is replaced by a less intense, long-lived band at 1.65 K whose first peak is displaced 415 cm^{-1} toward lower frequencies from the 4.2 K spectrum. We have interpreted this behavior in terms of a vibronic coupling mechanism lending intensity to the formally forbidden A_1 state, which is essentially the only state populated at the lowest temperature.[45] The proposed explanation is indicated in insert a in Figure 5. Although the experiments have not been carried out, it is obvious that linear polarization measurements at very low temperatures should yield valuable information on vibronic coupling in molecules containing heavy metal ions.

Magnetic Field Interactions. As indicated in Figure 5 an external field applied along the trigonal axis of a complex should induce a first-order splitting of the E level and cause a second-order mixing of the A_1 and A_2 levels. These effects should produce a qualitative dependence of both the observed spectrum *and* the measured decay times on magnetic field strength. The spectral changes are shown in Figure 5 where the spectrum observed at 1.65 K can be essentially switched back to that observed at 4.2 K by the application of a 75-kG field *without* changing the temperature.[45]

The decay time of the photoluminescence is also magnetic field dependent. A monotonic decrease in the measured life of the emission at a fixed temperature occurs as the external field is increased. These results have been treated quantitatively and provide detailed information on the eigenkets of the excited states.[46]

Magnetic effects of these magnitudes have threefold importance: (a) they show that the optical properties can be modulated with external fields and thus provide impetus for additional investigations of complexes for possible uses as electrooptical materials, (b) they provide a means of supplying quantitative experimental tests of the validity of proposed theoretical models for excited states in complexes con-
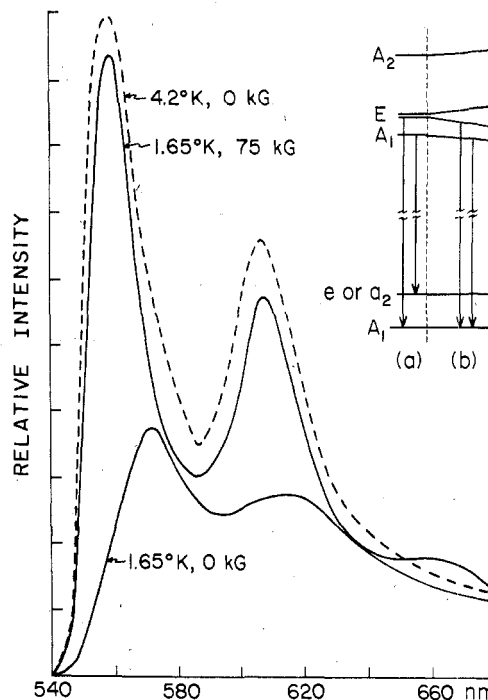
Figure 5. Emission spectra of $[Ru(bpy)_3]^{2+}$ in $[Zn(bpy)_3]SO_4\cdot 7H_2O$ crystal lattice in zero magnetic field at 1.65 and 4.2 K and in 75-kG field at 1.65 K. (a) Energy-level diagram of $[Ru(bpy)_3]^{2+}$; (b) magnetic field dependence of the emitting levels with magnetic field parallel to principal axis. $\downarrow$, allowed transitions. (See ref 45).

taining heavy metal ions, and (c) they provide a means for obtaining g values for excited-state parameters that are not easily measured by standard resonance methods.

Research Trends

From a perusal of current research publications one can recognize several distinct lines of investigation and also discern areas where a modest effort could yield substantial progress.

Investigations of Mechanisms and Models. The validity of current models for describing the excited states of transition-metal complexes should be subjected to much further experimental verification. In particular, the role of spin–orbit coupling in controlling excited-state properties has not received adequate attention. The spin-based language developed for organics[47] may not even be appropriate at all for certain types of states possessing highly interesting and unusual spectroscopic, photochemical, and chemical properties. Mechanistic studies of relaxation phenomena in complexes are receiving attention.[26,48] Attempts to correlate radiative and radiationless properties with theoretical models have met limited success, but the real problem is lack of systematic data derived from numerous systems. The interpretation of relaxation rates in complexes in terms of current theories of radiationless processes is complicated by the still uncertain role of spin–orbit coupling and configuration interaction in dictating the gross features of the optically probed states. Subtle changes, such as deuterium substitution,[27] indicate that much can be learned from the use of luminescence as a tool, but few detailed investigations have been carried out.

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Extension to Other Ions and Configurations. The bulk of the detailed information on excited states of transition-metal complexes has been derived from d^6 and d^3 configurations. The data from complexes with ions of other electronic configurations are relatively sparse. Nonetheless, many d^5, d^8, and d^{10} complex ions, for example, are highly luminescent, and use of a variety of experimental techniques holds high promise for elucidating the natures of their excited states. Even within the class of complexes with d^3 and d^6 configurations, much could be learned from studies of the luminescence from mixed-ligand materials, a topic that has received little attention but holds great promise for ascertaining the nature and extent of ligand–ligand interactions in complexes.[49]

Application of New Techniques. Although the methods outlined above for probing excited states have produced much valuable information, recent developments in instrumentation point to a host of feasible new measurements. The application of lasers, especially the tunable dye varieties, offers great promise for investigating such important phenomena as wavelength-dependent quantum yields, slow thermal relaxation steps, the incidence of magnetic field dependent relaxation rates, and many others. For nonluminescent materials lasers provide the opportunity to measure excited-state properties by viewing transient absorption spectra and monitoring depletion of the ground state.[50] For luminescent complexes such techniques as circularly polarized luminescence, phosphorescence microwave double resonance, infrared optical double resonance, infrared absorption spectroscopy of excited states, and emission polarization measurements have great potential for delineating excited-state properties.

Spectroscopy and Photochemistry. Perhaps the most exciting and explosive development involving excited states is the current effort to correlate photophysical properties with photochemical behavior.[51] The use of materials that act as energy donors or reducing agents when excited and *exhibit luminescence in solution* has opened up a host of possibilities for investigating photochemical mechanisms.[52] Coupled with the use of high power lasers and single-photon counting equipment such substances will certainly play key roles in unravelling inorganic photo-

chemical pathways. Yet to be exploited, however, is the use of photochemical results to clarify the nature of spectroscopically nonobserved excited states.

Spectroscopy and Electrochemistry. The observation of electrochemical luminescence (ecl) from inorganic complexes and its correlation with photoluminescence have joined the fields of inorganic emission spectroscopy and electrochemistry.[53] This bridge will undoubtedly facilitate the flow of information between the two fields, to the benefit of both. By a systematic correlation of the polarographic behavior with the spectroscopic properties, one has the real possibility of relating electronic structures to redox potentials, a necessary step toward tying spectroscopy to chemical thermodynamics.

Spectroscopy and Chemistry. Still to be found is a firm connection between the nature of excited states, as revealed by spectroscopic studies, and the chemical behaviors of inorganic complexes. Although many thermal reactions are not expected to go through excited-state intermediates, some may, and the spectroscopic probe should be a valuable tool for studying mechanisms. In the author's laboratory we have attempted to establish such connections for very limited classes of reactions, but the waters are still muddy. The quest continues.

Material Design

A long sought goal of this investigator has been to design complexes, especially solids, that will exhibit unusual electronic properties. The knowledge of excited states of complexes that has already accumulated can now be used to engineer potentially valuable materials. A combined effort, integrating synthesis and physical measurements guided by semiquantitative theoretical models, appears to be the kind of program required. Finding interesting substances to characterize spectroscopically is no problem whatsoever; identifying those that will elucidate fundamental principles or lead to valuable new materials is a far more difficult task, but the potential rewards certainly make the effort worthwhile.

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