metal complexes even at room temperature, e.g., in tris(dipyridyl)cobalt(III) perchlorate doped with $^{57}Co^{2+}$. This is a very intriguing observation, as the isotopic exchange involves high activation energies associated with breaking of strong coordination bonds. We proposed that the large activation barrier for exchange is surmounted by the electronic excitation of the dopant resulting from its combination with a free electron or hole. The highly electronically excited radiodopant interacts with a neighboring coordinated moiety, and the ligands are transferred onto the dopant. The material can have shallow electron donors (or acceptors) that can depopulate and trigger exchange at relatively low temperatures.

We have verified the basic feature of the proposed model by direct injection of electrons and holes into cobalt phthalocyanine doped with $^{57}Co^{2+}$. Both the injected electrons and holes lead to considerable exchange. These technqiues may be applied to labeling complex biomolecules like vitamin B_{12}. At present vitamin B_{12} is labeled biosynthetically and it involves tedious purification procedures.

Free electrons and holes can trigger fairly energetic reactions, and their role in biological systems, like the photosynthetic apparatus, can perhaps be evaluated via space-charge-limited injection of electrons and holes. These studies may also help in verifying some of the proposed steps in the primary process.

The radiodopant can also serve as a probe and provide useful information regardng the electronic behavior of the material. For instance, studies on $^{57}Co^{2+}$-doped cobalt phthalocyanine system indicate that the recombination centers in CoPc can be deactivated by interaction with holes. Subsequently, if both electrons and holes are injected simultaneously, then they seem to coexist for considerable lengths of time without recombinations and that the free electron or hole can interact with a dopant, $^{57}Co^{2+}$ ion, and induce isotopic exchange. It seems that the spatial distortion of $CoPc^+$ molecules (trapped holes) hinders the transfer of electron into the site and thereby reduce dramatically the rate of electron-hole recombination. Materials endowed with this unusual property are likely to find applications in photocatalysis and as electrode material in solar photoelectrochemical cells, where recombination of charge carriers often limits the efficiency.

Quantum Yield Variation over Narrow Spectral Regions in Coordination Photochemistry

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In the visible and near-UV region of the spectrum, most organic molecules offer a limited number of distinct excited states. To examine competition among a rich variety of organic photochemical pathways, it is necessary to work with far-UV sources. When this is done, significant reactivity differences over *narrow spectral regions* can be observed, although it is still called "unusual" wavelength dependence.[1] Transition-metal complexes,[2] on the other hand, commonly possess both ligand field and charge-transfer excited states in the visible and near-UV region of the spectrum and commonly several of both! For example, the lower energy spectrum of a simple chloropentaamminecobalt(III) complex ion displays chloride to metal charge transfer with both a singlet and triplet excited state, four ligand field levels derived from the strong field d^6 configuration each of which yields singlet and triplet states, and quite probably an accessible quintet state related to the weak field d^6 configuration. It should not be surprising that plausible evidence for the involvement of four distinct states in the photochemistry of this compound can now be adduced from wavelength dependence of yields.

However, it is not the point of this Account to complicate photochemistry with a taxonomy of exotic "photofauna". In nature two major photoreactions, photosynthesis and vision, seem to suggest a common lesson. Productive exploitation of photons can be based on a very rapid "irreversible" photochemical reaction that competes with facile relaxation to a lower, longer lived, excited state. This latter state seems less useful (perhaps because the system has already dissipated too much energy). I am thinking, of course, of the chlorophyll singlet vs. its triplet and the picosecond changes in the Raman spectra of visual pigments. To understand the strategy of such photon exploitation, it is necessary to discover the factors that govern competition among pathways in the short time domain. The simplest approach is to look for measurable variations of photochemical and photophysical yields *over narrow frequency domains*. Such experiments are quite practicable in the dye laser era, and transition-metal com-

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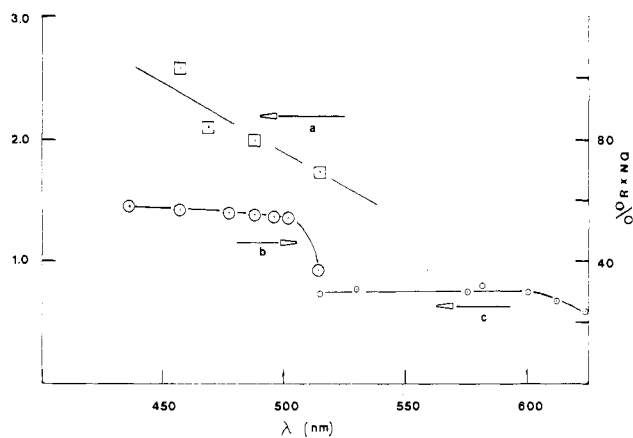
Figure 1. Three examples of the wavelength dependence found in the photochemistry of Cr(III) complexes associated with the "crossover" wavelength at which intersystem crossing to the doublet becomes less efficient. (a) Yield for photoisomerization of $Cu(phen)_3^{3+}$ with doublet quenched by CsI. Points refer to left ordinate with a scale of $10^3\Phi$ (quantum yield). (b) Quenchable fraction of quantum yield for photohydrolysis of $Cr(en)_3^{3+}$. Points refer to right-hand ordinates in units of percent. (c) Photoisomerization of $Cu(phen)OX_2^-$ without doublet quenching. Points refer to the left ordinate with units of $10^2\Phi$. (Note that uncertainty of these points is smaller than that for the other curves.)
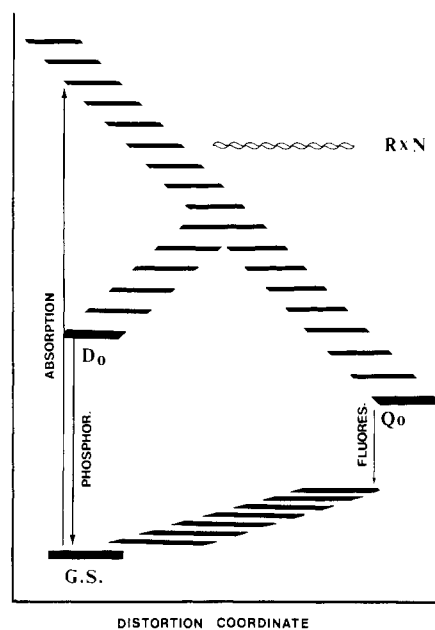

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Figure 2. The extended Jablowski diagram introduced by Adamson. Note that more dimensions are probably needed to include also crossing to the "reactive" surface.

plexes offer a special opportunity for this kind of work.

Intersystem Crossing in Cr(III) Complexes

In the "locally" octahedral complexes of Cr(III), reaction quantum yields following irradiation of spin-allowed quartet to quartet ligand field transitions of these high-spin d^3 systems are commonly greater than 0.1 and in some cases above 0.5. It has not proven to be an easy matter to assign unambiguous pathways to these reactions because of the complications that follow from consideration of intersystem crossing to the doublet state derived from the t_{2g}^3 configuration, but it has been possible to monitor enough distinct processes to conduct sophisticated examination of these reactions since Kane–Maguire and I reported in 1971 that phosphorescence remains observable, if weak, in fluids at and above room temperature.[3] In particular, quartet to doublet intersystem crossing in Cr(III) has attracted a great deal of attention. Kane–Maguire and his students were the first to report[4] an important example of wavelength dependence over a narrow spectral region.

In a study of tris(ethylenediamine)chromium(III), they found that the yield of phosphorescence decreased on the low-energy side of the lowest lying quartet band as did the fraction of reaction quenchable. The result is shown in Figure 1 accompanied by two related results that indicate the generality of the phenomenon.[5-7] It was suggested that the decline in intersystem-crossing yield at lower energy results from the quartet and doublet potential surfaces crossing above the 0–0 band of the quartet. Intersystem crossing following excitation beyond the crossing point is then an activated process. Of course, they also emphasized the implication that

above the crossing point intersystem crossing must occur *in competition with vibrational relaxation* within the quartet manifold. Subsequent mode locked laser flash work has verified their suggestion that intersystem crossing in Cr(III) is a picosecond process.[8,9]

This, by itself, would be interesting. But, at the time that intersystem crossing was being shown to compete with vibrational relaxation, evidence was already accumulating that ligand substitution reactions might also compete with intersystem crossing. The evidence came from study of the effect of doublet quenchers on yields of photochemical ligand substitution. Chen and Porter[10] observed that only 50% of the thiocyanate release yield for reineckate ion could be quenched by a quencher that quenched essentially 100% of the phosphorescence, i.e., $Cr(CN)_6^{3-}$. They argued that this implied that some photoreaction preceded intersystem crossing and, consequently, *occurred on a comparable time scale* to intersystem crossing. With the observation of luminescence in room-temperature fluids,[3] several similar results were obtained.[11,12] This combination of information leads toward the conclusion that some processes that *ultimately result in ligand substitution* also *compete with vibrational relaxation* to the lowest vibrational level of the quartet—Q(0).[13] We advance the proposition that three processes may compete in the picosecond domain: (1) vibrational relaxation, (2) intersystem crossing, and (3) the initial step of photoreaction.[13]

The phosphorescence of an octahedral Cr(III) complex is a sharp transition with a narrow bandwidth and

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is located at essentially the same wavelength where weak absorption from the $^4A_{2g}$ ground state to the spin-forbidden ^2E occurs. From this it is evident that there is a very great similarity in the equilibrium geometries and potential surfaces between the ground and doublet states. This is not unexpected since both are derived from the orbital configuration t_{2g}^3. The quartet excited states arise from the orbital configuration $t_{2g}^2 e_g^1$ and would be expected to have altered equilibrium geometry because of the occupied σ antibonding e_g level. This expectation is confirmed for the few Cr(III) complexes for which it has been possible to observe fluorescence. For example, a broad emission that mirrors the first quartet absorption band of Cr(urea)$_6^{3-}$ is found in the spectrum of this ion at 77 K Stokes shifted by more than 4000 cm^{-1}.[14]

This information about the geometry of the excited states can be used as a complement to the above information about the rapidity of intersystem crossing to construct a new and more ambitious type of Jablonski diagram for the excited states of metal complexes. Such diagrams were introduced by Adamson.[15] An Adamson type Jablonski diagram for a Cr(III) complex is shown in Figure 2. Here the vertical axis is energy and the horizontal axis represents a distortion coordinate leading from the initial geometry of the ground state $^4A_{2g}$ to the vibrationally equilibrated excited $^4T_{2g}$, which is labeled Q(0). The horizontal hash marks are intended to suggest vibrational levels and the branch point indicates the energy at which the efficiency of intersystem crossing falls, the crossover wavelength mentioned above. This diagram provides a framework for discussion of processes occurring in competition with vibrational relaxation. This is its advantage over the traditional Jablonski diagram from which it derives. Note that the diagram places fluorescence to the long-wavelength side of the phosphorescence, a circumstance that matches those cases for which fluorescence is known but is probably not general.

In the original Adamson diagram, that yield of photoreaction of the Cr(III) complex that is not quenched by doublet quenchers was assigned to the vibrationally equilibrated excited quartet, Q(0). It was suggested above that wavelength-dependence studies demand a more complicated picture. The critical test is as follows. If photochemical substitution reaction originates exclusively from the lowest lying quartet excited state, Q(0), then as the complex is excited at wavelengths longer than the critical wavelength for the branch point, the nonquenchable quantum yield should increase. This is because beyond the branch point, production of Q(0) becomes more efficient in comparison to intersystem crossing. Two studies of the wavelength dependence of nonquenchable rection have now been reported. The first was the study of photoracemization of tris(o-phenanthroline)chromium(III) as quenched by CsI reported by Langford and Sasseville[16] and the second was a study of aquation of tris(bipyridine)chromium(III) by Serpone et al.[17] In both cases, it was

found that the nonquenchable photoreaction yield *declined* slightly in the same wavelength region where intersystem crossing declines. These results imply another branch to be added to Figure 2, leading along a different coordinate to either the primary photoproduct or its unknown vibrationally equilibrated excited-state precursor. As suggested above, we must entertain the notion that the path leading to reaction is *separately* in competition with vibrational relaxation in the quartet manifold.

Wavelength, Isotope, and Temperature Effects in Ferrioxalate

For the larger goal of the Account, we will introduce four other cases of wavelength dependence over narrow spectral regions before returning to mechanistic discussions. The first is a case involving the long-popular chemical actinometer reaction, photolysis of tris(oxalato)ferrate(III) to give CO_2 and Fe(II). This reaction has been carefully examined by classical means, and its quantum yield was found to be wavelength independent throughout the UV with a primary yield just above 0.5.[18]

The first clue that something more subtle was occurring appeared in a fascinating paper by Betts and Buchannon.[19] They undertook a mass spectrometric study of $^{12}C/^{13}C$ isotope fractionation in the photochemical evolution of CO_2 by $Fe(C_2O_4)_3^{3-}$. Over the UV region they found that isotope fractionation was accurately zero; that is, no oxalate C vibrations were crucial to determination of the quantum yield. However, in the long-wavelength tail of the oxalate to iron charge-transfer absorption band near 500 nm, they found that isotope fractionation occurred in the photoreaction. At long wavelength, the oxalate C vibrations play a role in determining yield! Betts and Buchannon proposed that two states were involved in the reaction.

We undertook the study of this sytem with the wavelengths available between 488 and 514 nm, using an Ar ion laser.[20] Our first observation was that a "tailing off" of the quantum yield at 25 °C (which has been reported) is an artifact of traditional light sources with their poor resolution. In fact, the yield is essentially constant to 514 nm and drops quite precipitiously somewhat beyond that wavelength. However, the evidence for two modes of reaction persists. We found that the reaction in the UV is temperature independent, but that at 514 nm, the quantum yield has become significantly temperature dependent, changing by a factor of 2 between 12 and 40 °C. An MCD spectrum of the complex helped to reveal what would have been undiscoverable from the broad featureless envelope of the tail of the charge-transfer band in the ordinary absorption spectrum. A spin-forbidden ligand field transition is present near the region of changing photochemistry.

The primary product of this system has been assigned as an Fe(II) and an oxalate radical. To reach this, the initially octahedral coordination geometry around iron must relax to select one Fe–O bond as the oxidized O site of the radical. This *unsymmetrical* vibration of the

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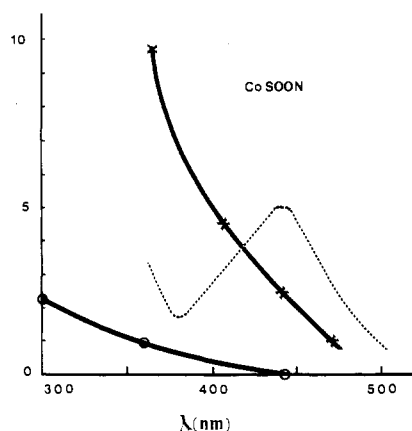(21) Langford, C. H.; Carey, J. H. *Can. J. Chem.* **1975**, *53*, 2430.

Figure 3. Wavelength dependence of quantum yield for (lower curve) reduction of $Co(NH_3)_5Br^{2+}$ and (upper curve) linkage isomerization of the Co(III) sulfinate complex. Compare the shape of the lowest lying absorption band of the sulfinate complex, which is indicated by the dashed curve.

Fe–O framework appears to proceed irreversibly and *without significant interactions with the oxalate C vibrations as long as enough energy is initially supplied*. However, *at low energy there is a branch to intersystem crossing* to the ligand field state whose reactions are slower, temperature dependent, and subject to isotope fractionation.

The mechanism suggested relates this case to the Cr(III) case. If we construct an extended Adamson type Jablonski diagram, we must indicate separate branching for the processes leading from the initial octahedral geometry of the charge-transfer state to either the ligand field state on the one hand or the distorted product geometry on the other.

Wavelength Dependence in the Photochemistry of Co(III) Complexes

In approximately octahedral Co(III) complexes the best studied example of wavelength dependence is the wavelength dependence of the photoreaction leading to Co(II) and oxidized ligands in complexes such as the chloropentaamminecobalt(III) ion.[22]   A significant quantum yield for this reaction is found only at energies larger than a threshold energy for electron transfer to produce Co(II) and a ligand radical (or atom) which can be calculated pseudothermodynamically. However, one specific aspect of this reaction is related to the wavelength dependencies that form our main subject. It is frequently found that the quantum yield for this photochemical electron transfer is not constant above the threshold wavelength but is a monotonic function of the excess energy available.[22] A recent example of behavior of this sort is shown in Figure 3 (lower curve).[23]

The monotonic decline of a yield for a reaction initiated by homolytic cleavage as wavelength increases was interpreted, from an early date, in terms of the kinetic energy of the primary radicals and the relative probability of separation and recombination. Phrasing such an explanation in terms of a non-hard-sphere model, rapid redistribution of energy into all vibrational modes of the complex favors recombination. Excess reaction at shorter wavelengths indicates some cage

escape prior to full vibrational relaxation. As Endicott has observed,[22] vibrational relaxation is coupled to solvent reorganization.

Even more complex patterns of wavelength dependence emerge in studies of Co(III) complexes at longer wavelengths where ligand substitution reactions become a significant part of the photochemistry. The yields for these reactions are much lower than those for their Cr(III) counterparts.   An Ar ion laser excites the "ammine and haloammine" complexes in the low-lying spin-allowed band-labeled $^1A_{1g}{}^1T_{2g}$, which involves states of the strong field d^6 configuration. It is certain that there is a triplet region at lower energy since very weak bands are seen in absorption and it is not at all improbable that the quintet state derived from a weak field d^6 configuration is also below the absorption position in energy. Consequently, it was interesting to compare the Ar results[24] to those obtained with a Kr ion laser, which excites directly the triplet region of the spectrum.[25]

All photosubstitution quantum yields for $Co(NH_3)_6{}^{3+}$ and $Co(NH_3)_5Cl^{2+}$ ions were found to be smaller at the Kr wavelengths of 647 nm than at the Ar wavelengths of 488 and 514 nm. Moreover, the chloropentaammine ion had a larger yield for NH_3 loss than chloride loss at 514 nm and the reverse at 647 nm. It is fairly clear that these complexes do not simply exhibit reaction from the vibrationally equilibrated triplet after moderately efficient intersystem crossing as their d^6 Rh(III) analogues appear to do.[26]

The full wavelength dependence of the yields of the chloropentaamminecobalt(III) ion was recently investigated with use of a tunable dye laser between 560 and 620 nm.[27] The decline of both NH_3 and chloride yields across the singlet manifold suggests an intersystem-crossing process competing with vibrational relaxation in the singlet. However, if this were simply crossing to the triplet, one would be forced to predict an equal or higher yield for direct irradiation of the triplet region. Since a smaller yield is observed at 647 nm, it seems likely that a third state, quite possibly the quintet, must be considered. Moreover, the reversal of the chloride and ammonia yields at longer wavelengths presents a major challenge to theory.

Recently, somewhat different reactions have been reported for some Co(III) complexes, which include S-donor ligands.[23] These complexes are spectroscopically complicated because their lowest lying spin-allowed transitions are somewhat more intense than typical ligand field bands and some charge-transfer character may be important. Commonly these complexes undergo photochemical redox reactions with a sharp threshold at the treshold of readily assignable charge-transfer absorption. In contrast, the sulfinato complex $Co(en)_2(SO_2CH_2CH_2NH_2)^{2+}$ undergoes photochemical linkage isomerization. The yield for this reaction varies across the first spin-allowed band from 9.6 $\times$ 10^{-2} at 366 nm to 9.9 $\times$ 10^{-3} at 458 nm (see Figure 3, upper curve and superimposed spectrum). The sharp threshold reported in the same paper for other com-

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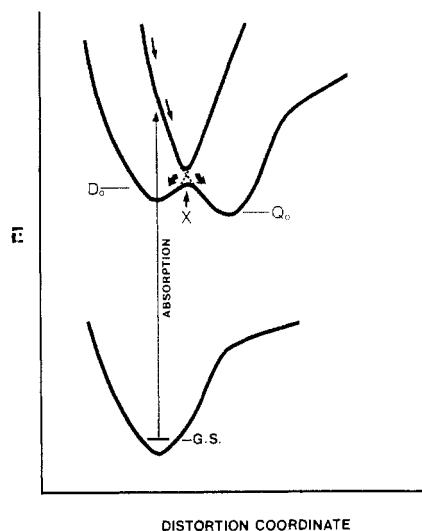
Figure 4. Potential surface diagrams to aid discussion of intersystem crossing in Cr(III).

Figure 5. Potential surface diagram for reactions of ferrioxalate.

pounds[23] confirms that this is another example of a process operating in competition with vibrational relaxation within a single electronic band envelope to determine the overall reaction yield.

Models for Interpretation of Wavelength Dependence

Having summarized the experiments that show that wavelength dependence of quantum yields is a general and common phenomenon in the photochemistry of transition-metal complexes, we must now discuss possible interpretative models for the phenomena. It is such models that may help to harness the fast processes implied by wavelength dependence over narrow spectral regions. We will begin with models derived from the approach to yields that has been the most fruitful in organic photochemistry, namely, the assumption that the system evolves along adiabatic Born–Oppenheimer potential surfaces to critical regions at which there is a suitable probability of jump from one such surface to another. For a general development of this approach, see Turro's valuable book.[28]

The problem of intersystem crossing from the quartet to the doublet in Cr(III) systems is represented in this approach by the potential surfaces in Figure 4. The upper surface is reached by vertical excitation in the lowest "spin-allowed" band; the system rapidly relaxes to the minimum on this upper surface, which arises because of a "weakly avoided" crossing. The system undergoes a "jump" between the upper and the lower surfaces with partitioning on the lower surface between the level D(0) of the vibrationally equilibrated doublet and Q(0) of the vibrationally equilibrated quartet. Classically, nuclear momentum would favor continuation to Q(0) as the system's representative point moves over the surface. This is the picture of the branch point of Adamson's extended Jablonski diagram.

To account for the wavelength dependence of intersystem crossing, we must excite to a point to the right of the minimum where quartet character, and hence allowed character, is associated with the lower surface and relaxation is preferentially to Q(0). After this, intersystem crossing is probably associated with passage
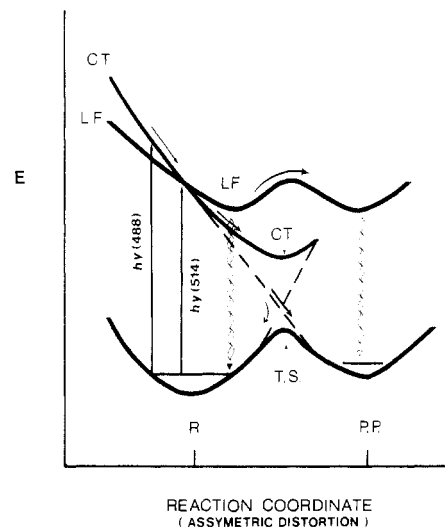
over the barrier at X and may be thermally activated. This picture has been thought to be favored by the evidence from picosecond spectroscopy[8,9] that assigns a grow in time of 20–100 ps to the formation of D(0). It is argued that this time is long enough compared to the relevant molecular vibration periods that vibrational relaxation should be complete and an adiabatic surface is relevant. There are two problems with this. First, it is clear that the wavelength dependence of the non-quenchable quartet reactivity is not so explained. At a minimum, we must bring a potential surface leading to product formation into the same region of nuclear coordinate space. Second, some of the physics is unsatisfactory. Spin–orbit coupling constants for Cr(III) complexes are only about 50 cm^{-1}.[29] There is some mystery as to why intersystem crossing is not slower. It is not clear how to describe the probability of the "jump" between surfaces. (An alternative approach can address this problem[2] vide infra.) For the moment, we leave this case with a remark on solvent effects. The most recent picosecond study[9] has revealed that the intersystem-crossing rate may or may not be a function of solvent depending on whether or not ligands in the first coordination sphere are of a type to interact strongly with second sphere solvent molecules. This indicates that solvent relaxation processes, which are not faster than the 20–100-ps time scale, may be involved in the "vibrational relaxation".

Let's turn next to the ferrioxalate results. To assimilate the results to the adiabatic potential surface models, we introduce the diagram in Figure 5. In the figure, a weakly avoided crossing is shown between the charge-transfer surface and the ligand field surface. To account for the wavelength dependence of intersystem crossing, we are required to introduce an idea that considerably weakens the separation of movement along an adiabatic surface from jumps between surfaces, which characterizes the approach as developed in Turro's book.[28] To account for the results, it is necessary to assume (putting the matter classically) that the jump from the charge-transfer surface to the ligand field surface is less probable when the initial energy is higher and the momentum of the representative point is greater as it nears the critical region. This is equiv-

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alent to discard of the Born–Oppenheimer approximation.

This brings us quite naturally to the beginning of the interesting problem posed by the Co(III) complexes. The homolytic cleavage reaction was discussed by Endicott.[22] The classic view is that additional kinetic energy increases the probability that the radicals escape from the primary solvent cage and must diffuse back together in order to recombine. This approach has assumed that the excited state is dissociative, but Endicott showed that the complexities of the observed solvent dependence indicate that the ligand to metal charge transfer state reached by vertical excitation of these complexes in the ultraviolet is a partially bound state, if only as a result of the requirements of solvent relaxation. Translating these comments into our terms, we see that relaxation to the vibrationally equilibrated charge-transfer state corresponding to the geminate radical pair is a process that competes with separation of the geminate pair. Separation of the geminate pair is commonly supposed to be a process in the time domain approaching nanoseconds. Thus, with all relevant solvent relaxation included, so must be the process of thermalizing the radical pair. The situation is reminiscent of the recent solvent-dependence results on intersystem crossing in Cr(III) complexes. *Coupling with the solvent is important to the overall time scale of thermalization.*

With the background of the results for the UV region, we can turn attention to effects in visible-region photochemistry. The low-energy absorption band of the sulfinato Co(III) complex has an extinction coefficient of several thousand and is a factor of 10 too intense to be a simple ligand field band. Thus, it was considered[23] to exhibit charge-transfer character. The linkage isomerization reaction observed was attributed to a radical pair.[23] If this state communicates with a lower lying ligand field state, a diagram similar to Figure 5 would describe the reaction. Whereas it took rather subtle experimentation to reveal the complexity of the ferrioxalate system and to demonstrate that nuclear and electronic motions could not be fully separated, the complexity is immediately apparent here. The higher the initial energy, the greater the probability of reaching the vibrationally equilibrated, thermalized, radical pair that is the precursor of linkage isomerization. Making the "jump" to the ligand field state is more probable if the system starts with lower nuclear momentum. In a situation where chelation prevents the radicals from separating, we see an effect exactly analogous to the change of geminate vs. secondary radical ratio, which has classically been used to account for wavelength dependence in cases of dissociative states.

These remarks lead to the substitution reactions of the chloropentaammine ion of Co(III). In this case, we will not have the radical pair to consider and the wavelength dependence involves more than the "crossover" wavelength phenomenon seen in Cr(III) photochemistry. Thus, it is probably the most revealing case so far.

In the case of $Co(NH_3)_5Cl^{2+}$, a diagram of the type used above provides very little in the way of an approach to understanding the observations. The lowest excited singlet and triplet ligand field potential surfaces are considered quite similar since the electron config-

uration is the same for these two excited states. These will be displaced relative to the ground state due to the occupancy of the σ antibonding e_g level in the configuration $t_{2g}^5 e_g^1$. These may cross a surface that may correspond either to the primary product or to the high-spin excited-state configuration, ^5T. A major problem is that the "distortion" coordinate relevant to this last state is probably different from that for ^1T, ^3T. If, for example, the final state is ^5T, it probably differs from the initial geometry by a symmetrical expansion (breathing mode), whereas ^1T, ^3T differ by a tetragonal distortion accommodating the single σ antibonding electron.

The yield for ammonia aquation that drops across the singlet band to near zero at 647 could be understood with the aid of the new final state mentioned. Singlet to "new state" intersystem crossing is wavelength dependent. We cannot, however, attribute the chloride aquation (which is distinguishable) to the triplet alone since yields are smaller on irradiation in the triplet band (647 nm). The various yields are determined by a competing crossover to a surface associated with the product (either the primary product or an intermediate excited state), the efficiency of which varies monotonically with irradiation wavelength. *We are clearly required to consider electronic and nuclear motions simultaneously to deal with such a result.* Solvent, T, and viscosity effects point again to a role for solvent.

We have arrived at the key point of this Account. We have shown increasingly well-defined requirements for the simultaneous consideration of electronic and nuclear motion, or as it has otherwise been called, competition between various "surface to surface jumps" and vibrational relaxation. Our focus has been conventional transition-metal complexes. At this point it may be useful to record in passing a related example. Recent picosecond studies by Bergkamp et al.[30] have indicated directly that electron transfer occurs "from an unrelaxed triplet biradical to the ground-state surface in competition with continued vibrational relaxation" in a porphyrin. Our final task will be to discuss a means to treat the nuclear and electronic processes conjointly, but we should not overlook the repeated evidence that solvent is important.

Theory of Fast Processes

To accommodate all of the possibilities, we need an approach to the theory of radiationless transitions that emphasizes overall state to state transitions so that electronic and nuclear factors are jointly accommodated. We begin from an equation discussed by Turro,[28] using an analogy to the expression for the intensity of a radiative transition:

$$\text{rate} = R(O) \times F(E) \times F(N) \times F(S) \qquad (1)$$

In this equation, the factor $R(O)$ is a term for a fully allowed process and each of the factors, F, represents "a prohibition factor" that approaches a maximum value of unity and is entirely analogous to oscillator strength in the theory of radiative transitions. The three factors in the equation, $F(E)$, $F(N)$, and $F(S)$, represent prohibition factors due to electronic, nuclear, and spin configurational changes, respectively. Each of the three may be rate limiting in a given situation.

(30) Bergkamp, M. A.; Dalton, J.; Netzel, T. L. *J. Am. Chem. Soc.* **1982**, *104*, 253.

Implicitly, this assumes that the excess electronic energy released by the radiationless transition is "accepted" somehow and that this is not rate determining. The acceptors may be modes of motion of the molecule undergoing transition or the medium, that is, we assume a "heat bath". The analogy to the radiation case is not merely formal. We do assume in our approach[2] that transition-moment operators must be specified just as they are in the radiative case.

The present objective is to report a precise quantum mechanical foundation for the partitioning expressed in eq 1 independent of the Born–Oppenheimer approximation that separates electronic and nuclear motion. The strategy is to formulate a description of the nonradiative event which is complete in the group theoretic sense that the basis vectors representing both obervable states (initial and final) and the transition-moment operators are given enough quantum mechanical characteristics to establish all orthonormality conditions and, thus, set the stage for selection rule formulation. The methodology is borrowed from ligand field theory.[31,32] In ligand field theory, it is often true that representations and component labels derived from the finite group of the molecule are inadequate to the complete description sought. The problem is resolved by appeal to generative groups of higher symmetry which may include infinite groups. Molecular operators and states are projected out of a sufficiently large generative group by a "subduction" technique.[33] It is familiar to derive electronic wave functions by subduction from those appropriate to the spherically symmetric "free ion" functions. The only novel feature of the procedure under discussion is that it treats the *vibrational part* of the problem *similarly*, using in the molecular case the basis set of functions for harmonic motion in three dimensions which span SU.[3] These are familiar in the discussion of nuclear mass excitation.[34]

The approach of ref 2 begins with eq 2, which uses the Dirac tensorial bracket evaluated, using the Wigner–Eckart theorem algebra in magnetic moment vector space. Here, T, Γ, and γ, are the labels of the infinite

$$\text{rate} = R(O) \sum_{T,\Gamma,\gamma} C \langle T'\Gamma_{T'}\gamma_{T'} | \hat{T}\hat{\Gamma}_{T}\hat{\gamma}_{T} | T\Gamma_{T}\gamma_{T} \rangle \quad (2)$$

group representation (e.g., labels from spherical symmetry), the finite group representation (e.g., the familiar Mulliken symbols of the molecular point groups), and the labels of the components along the axis of quantization for the finite group, respectively. The *primed* and *unprimed* symbols represent *initial* and *final* state basis function labels. The "hat" symbols represent transition operator labels. The three inhibition factors of eq 1 must be found in the bracket. The Dirac bracket form permits calculation of such selection rules by tensor algebra techniques. Applying the Wigner–Eckart theorem assumes complete separation of radial and angular terms and yields a product of four terms, which we call A, B, C, and D here. A is a phase factor, B is a partition coefficient whose value is available from tables,[32] C is a 3Γ symbol describing permitted cou-

plings of a vector component, and D is a radial reduced matrix element, which is the only part of the expression not calculable by tensor algebra.

We can now turn to the question of factoring such events into changes in coupled physical processes. We do not need to assume a *strength* of coupling (as in the Born–Oppenheimer approximation) using the complete basis and operators just described. The uncoupling procedure[2] involves a summation of the product functions over all contributing electronic and vibrational states at both finite and infinite group levels. The result of the uncoupling procedure[2] is to give initial- and final-state basis functions in eq 2 as *products* of *partition coefficients* times 3Γ *symbols* times *uncoupled scalar products* of electronic and vibrational basis sets. The operator partitions similarly, and when all the terms are combined, eq 2 may be written as the sum over the product of a series of partition coefficients times a series of 3Γ symbols (all available) times two scalars, which are *separated* electronic and vibrational matrix elements. If we go on to uncouple spin and orbital electronic terms, that is split J to $L + S$ as is conventional in ligand field theory, we complete a derivation of an equation of the type of eq 1. The purpose of the Born–Oppenheimer approximation is served without the physical approximation.

From the theory just sketched, a fearsome jungle of potential deductions could proceed. Hollebone has argued[2] that the simplest one that may be of use in our problem is an "octupole selection rule" arising from the first term in a multipole expansion of the operator that excites mass motion in conjunction with an Ungerade character for an exciting photon; that is, vibronic transitions occur only if $\hat{T} = 3$ (in SU(3)) or by subduction onto the O_h group, $\Gamma = T_{1u}$ for octahedral complexes.

Concluding Remarks

We conclude this Account with two preliminary indications of the fruitfulness of Hollebone's theory that touch the problems outlined above. First is the intersystem-crossing problem in Cr(III) complexes. Vibrational basis functions carry angular momentum labels in exactly the same way that electronic basis functions do in Hollebone's theory. This opens an overlooked aspect of the change of angular momentum (intersystem crossing) problem, namely, intersystem crossing by vibronic coupling. It explains why the process can be faster than spin–orbit coupling considerations have indicated and, especially, provided direct insight into the significant role for solvent[9,10] that cannot be related to heavy-atom (spin) effects.

Second, in two d^3 systems, $Cr(OH_2)_6^{3+}$ and MnF_6^{2-}, the vibronic structure of quartet and doublet absorption bands have been assigned. The vibronic selection rule in O_h for both requires that a t_{1u} vibration is involved. In the octahedron there are two modes that are not distinguished in O_h symmetry, an "asymmetric stretch" mode and a "buckle" mode. In spherical symmetry they do carry distinct lables. The asymmetric stretch basis function is $|1,0\rangle$, whereas the buckle is $|3,0\rangle$. Application of the octapole selection rule ($\Delta T = 3$) implies that the buckle mode should be associated to transitions to the quartet (from the quartet ground state); $\Delta L = 0$, $\Delta S = 0$, $\Delta V = 3$. Similarly, the asymmetric stretch is involved in the quartet to doublet transitions; $\Delta L = 1$,

(31) Donini, J. C.; Hollebone, B. R.; Lever, A. B. P. *Prog. Inorg. Chem.* 1977, *22*, 225.

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(34) Irvine, J. M. "Nuclear Structure Theory"; Oxford University Press: Oxford, 1972.

$\Delta S = 1$, $\Delta V = 1$. This difference *is* observed in the two cases. The spectral analysis can be extended to begin a theory of photoreactivity. It was shown above that reactions can occur promptly from quartets of Cr(III) complexes. Thus, we may look to the vibrations excited in the absorption process to suggest the coordinates for relaxation, i.e., the unspecified direction in the abscissa of Figure 4. If we do so, attention is drawn to the t_{1u} buckle, which is fruitful because it suggests stereochemical rearrangement that is, independently, a well-recognized feature of photosubstitution at Cr(III)

centers. This stereochemistry has been discussed effectively by Kirk.[35]

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Carbonylation of Zirconocene Complexes

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Organometallic carbonylation reactions sometimes follow complicated pathways. As a typical and important example for this often undesirable feature, transition-metal-mediated synthesis gas conversions of the Fischer–Tropsch type usually proceed unspecifically, yielding a broad spectrum of compounds ranging from complex hydrocarbon mixtures to oxygen-containing products alcohols, aldehydes, or ketones.[1] For future rational design of specific catalysts for carbon monoxide utilization,[2] a fundamental understanding of the complex possibilities of competing pathways is required. This understanding is now beginning to emerge from recent detailed mechanistic studies on well-defined molecular model systems.[3]

Bis(η-cyclopentadienyl) group 4 transition-metal systems have turned out to be interesting model substrate for CO conversion. Some of these systems have been shown to activate dihydrogen quite easily even in a high oxidation state of the metal.[4] Specific stoichiometric reduction and/or reductive coupling of carbon monoxide has been achieved starting from group 4 metallocene complexes. For example, methane is formed from $Cp_2Ti(CO)_2$ and H_2.[5] Similarly, methanol precursors are formed from various zirconocene hydrides,[6,7] some of which also induce coupling of CO units to form endiolates[7] or, promoted by aluminum alkyls, a mixture of precursors of linear alcohols.[8]

In some carbon–carbon bond-forming reactions of bis(η-cyclopentadienyl)zirconium complexes with carbon monoxide, the interplay of kinetic[7,10,11] and thermodynamic effects[12,13] has made it possible to trace major pathways leading to thermodynamically favored final products through a variety of isolated intermediates. As typical examples, carbonylation reactions of bis(η-cyclopentadienyl)zirconium alkyl, aryl, and hy-

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dride complexes are discussed in this Account.

The Problem of the Initial CO Coordination

In pseudotetrahedral bent metallocene complexes, Cp_2MR_2, eight out of the available nine metal valence orbitals are used for making metal-to-ligand bonds. For the remaining ninth orbital, which determines the chemical reactivity of such complexes to a considerable

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