Relative Ligand Labilization in Transition Metal Photochemistry. A Molecular Orbital Approach

Jeffrey I. Zink

Contribution No. 3251 from the Department of Chemistry, University of California, Los Angeles, California 90024. Received November 15, 1973

Abstract: A theoretical approach to the determination of the relative ligand photolabilizations in excited states of transition metal complexes is developed. The approach is based on the relative changes in metal–ligand overlap populations between the ground and the photoactive excited states. Two types of calculations were carried out. The first is a model problem where only the metal d and ligand donor orbitals along one axis are considered. The model problem gives physical insight into the metal and ligand properties which determine which ligand on the labilized axis gains the most antibonding character in the photoactive excited state. It is found that the larger the metal–ligand overlap or the smaller the ligand donor orbital ionization energy the greater the σ labilization. Secondly, the results of complete calculations on mixed ligand cobalt(III) and chromium(III) amine complexes are reported. The results are shown to completely agree with the model problem and with experiment. The applications of the molecular orbital approach to understanding photolabilization in cases where the spectroscopically determined deviations from octahedral symmetry are small are discussed.

In the past 2 years, ligand field theory (LFT) has been applied to the interpretation of transition metal photoreactions.[1-6] Specifically, LFT can be used to determine which axis of a six-coordinate transition metal complex will be photolabilized by identifying which of the metal orbitals are the predominant components of the photoactive excited state. For example, for d^3 and d^6 complexes in O_h symmetry, the lowest energy transition is $(t_{2g})^n \rightarrow (t_{2g})^{n-1}(e_g)^1$. The e_g orbitals are σ antibonding orbitals between the metal and the ligands. Therefore, a nondirectional bond weakening will occur which will weaken all of the metal ligand bonds equally because the excited e_g state contains equal admixtures of metal $d_{x^2-y^2}$ and d_{z^2} orbitals.[7] In C_{4v} and D_{4h} symmetries, the e_g orbitals split into a_1 (d_{z^2}) and b_1 ($d_{x^2-y^2}$). The lowest energy transition will involve selective population of a_1 or b_1 depending on the relative energies of these two orbitals.[1-3] Thus, in the lower symmetry complexes, a directionality of labilization is implied as has been verified by experiment.[8]

When the ligands in the labilized direction are different, different degrees of labilization are expected for each of them which will depend on the metal–ligand antibonding properties of each ligand in the excited state. However, the determination of the relative differences in σ labilization and the determination of the relative importance of the σ vs. the π bonding effects lies outside the realm of crystal field theory. It is the purpose of this paper to determine the relative importance of the various effects using simple molecular orbital (MO) theory and to develop the general principles on which the relative labilizations can be understood. The principles which are derived here are valuable not only to the determination of which ligand on the labilized axis is preferentially labilized but also to the understanding of which ligand will be lost when different ligands cause accidental degeneracy of the split components of the excited state. In these two situations, crystal field theory is inapplicable.

Two sets of results are reported in this paper. First, a simple model problem involving only the metal and ligand orbitals of the proper symmetry along one axis is examined. The relative effects on the bonding and antibonding character of the metal–ligand interactions in the excited state caused by varying specific metal and ligand properties are derived. Secondly, the results of full calculations of experimentally studied complexes of cobalt and chromium are reported. The trends derived in the simple model problem are also observed in the full calculations. The results are shown to be completely verified by experiment.

A Model Problem

All MO calculations were performed on an IBM 360/91 computer using an extended Hückel program developed as stated in the literature.[9] Off-diagonal matrix elements were calculated using the expression $H = (k/2)S_{ij}(H_{ii} + H_{jj})$, where $k = 1.75$.[10] The S_{ij} are overlap integrals between the ith and jth atomic orbitals and the H_{ii} are the valence orbital ionization potentials (VOIP's). A Mulliken population analysis was used in the charge iteration.[11] VOIP's and charge correction terms for all atoms including the metals were taken from the tables reported by Basch, Viste, and Gray.[12] Burn's orbitals[13] were used for all atoms because overlap integrals calculated using them have been shown to correspond best with SCF wave functions.[14,15]

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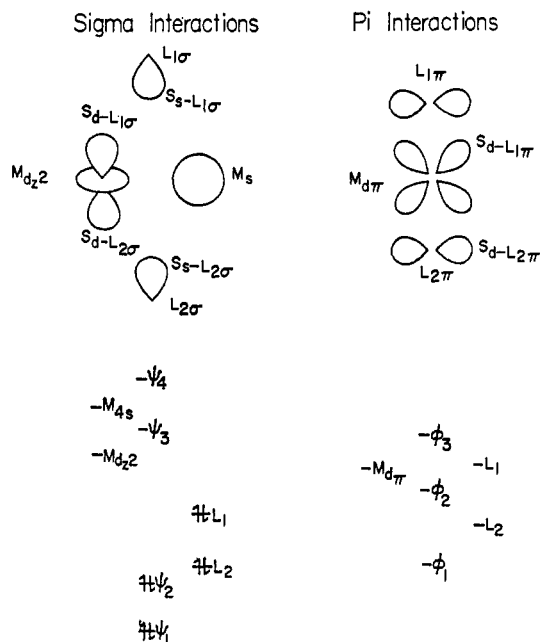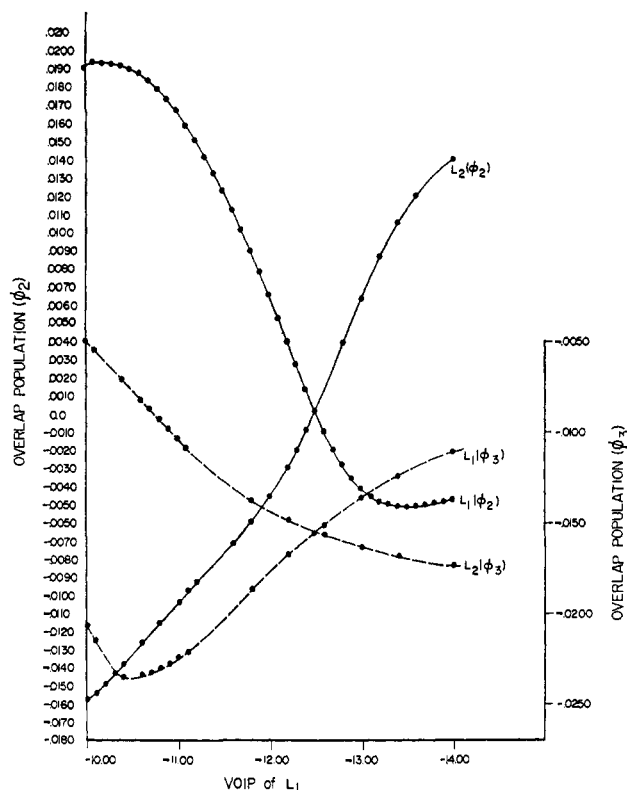
Figure 1. The atomic orbitals and the MO energy level diagrams for the three-center, four-orbital model problem (left) and for the three-center, three-orbital model problem (right). The symbol S_d-$L_{2\sigma}$ represents the overlap integral between a metal d orbital and a σ donor orbital on ligand 2.

The model problem calculation was performed using the extended Hückel method and parameters as described above. The program, written in our laboratory, varied individual metal or ligand properties holding all others constant. Mulliken overlap populations were calculated for the appropriate orbitals.

In a d^3 or d^6 transition metal complex having C_{4v} symmetry and weak field axial ligands, the lowest energy electronic transition is primarily d-$\pi \rightarrow$ d$_{z^2}$.[7,16,17] The changes in bonding which occur as a result of this transition thus occur from loss of an electron from a π orbital and gain of an electron in a σ antibonding orbital. As a simple model problem, we can treat the complex as a linear triatomic molecule. Because the complex contains a plane of symmetry under C_{4v} or D_{4h} symmetry, the σ and π systems are orthogonal and will be treated separately. To further simplify the model problem, only the orbitals of the atom on the ligand directly bound to the metal will be considered. Thus for ligands along the unique axis, the problem reduces to a three-center, three-orbital problem for the π interactions and a three-center, four-orbital problem for the σ interactions. The orbitals and the symbols used in the following discussion are shown in Figure 1.

In the model problem, the ψ_3 molecular orbital corresponds to the metal d_{z^2} orbital of crystal field theory. The ψ_3 orbital is populated by the lowest energy electronic transition and is thus responsible for the σ-bonding changes in the lowest energy excited state. In this transition, the electron is removed from one of the d orbitals of π symmetry. If the ligands L_1 and L_2 are both π acceptors or both π donors, the electron is removed from Φ_1 or Φ_3, respectively. If one is a π donor and the other a π acceptor, the transition occurs from

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Figure 2. The variation of the overlap population in the three-orbital model problem between a metal and ligands L_1 and L_2 as a function of the energy of the donor orbital of L_1. The energy of the metal d orbital was -11.000 eV and that of the donor orbital of L_2 was -12.500 eV. The value of the overlap integral was 0.05. The above values are similar to those of the π system for chromium(III) complexes.

Φ_2. In the following discussion, we shall focus attention on the molecular orbitals which change their electronic populations in the transition.

The quantity of importance to the interpretation of transition metal photochemical reactivity is the relative change in bonding or antibonding character acquired by each ligand in the excited state compared to the ground state. The distribution of the antibonding character between L_1 and L_2 in the ψ_3 orbital is not intuitively obvious when L_1 is different from L_2.

As a measure of the changes in bonding which occur during an electronic transition, we have chosen to use the difference, D, between the Mulliken overlap populations[11] of the atoms involved in the MO's which change their electronic populations (eq 1a, 1b) where

$$D = n(i) - n(j) \qquad (1a)$$

$$n(i) = \sum_{r_k, s_l} N_i c_{ir_k} c_{is_l} S_{r_k s_l} \qquad (1b)$$

$n(i)$ is the overlap population between atoms k and l. N_i is the number of electrons in the ith orbital, c_{ir_k} is the coefficient of the rth AO of atom k, and $s_{r_k s_l}$ is the overlap integral between the r and s AO's of atoms k and l.

The model problem is particularly useful for answering the following questions concerning the interpretation of the photochemical reactions in terms of bonding changes. First, in a complex which contains two different ligands on the labilized axis, what properties of the ligands determine the relative amount of labilization between the two? Second, in a series of
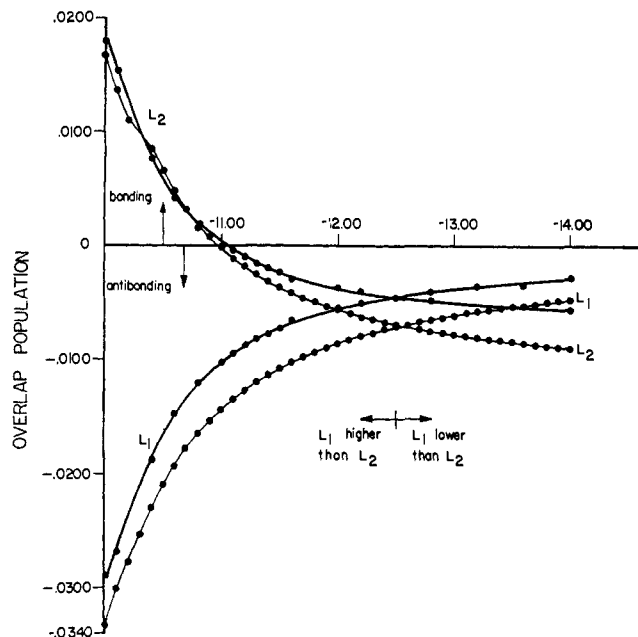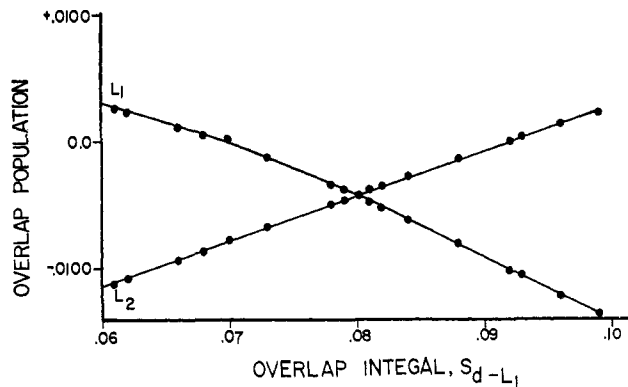
Figure 3. The variation of the overlap population in the four-orbital problem in the ψ_3 orbital as a function of the energy of the donor orbital of L_1. The orbital energies were: metal d, -11.000 eV; metal s, -9.000 eV; L_2, -12.500 eV. The values of the overlap integrals were 0.08 (heavy line) and 0.11 (light line).

Figure 4. The variation of the overlap population in the ψ_3 orbital of the four-orbital problem as a function of the overlap integral between the metal and L_1. The orbital energies were: metal d, -11.000 eV; metal s, -9.000 eV; donor orbital of L_1 and L_2, -13.000 eV. The metal L_2 overlap integral was 0.08. The above parameters are representative of the σ system of Cr(III) complexes.

complexes containing two different ligands on the labilized axis, one of which is varied (e.g., trans-Cr-(en)$_2$XY^{n+} where X is varied), how do the relative labilizations vary as a function of the properties of variable ligand X? Third, for complexes containing the same ligands but different metals (e.g., trans-M(NH$_3$)$_4$-XY^{n+}, M = Cr^{3+}, Co^{3+}, Ru^{2+}, Rh^{3+}) how do the relative labilizations of ligands X and Y vary as a function of the metal properties? Finally, what general rules to aid in interpreting the photochemical results can be deduced without resorting to detailed calculations of each individual complex? The ligand quantities which we have used as variables are the energies of the donor orbitals, i.e., the VOIP's, and the overlap with the metal orbitals. The metal properties which were varied are the VOIP's of the d and s orbitals and their overlap with the ligand donor orbitals.

The results of calculations on the simplest formulation of the problem, the three-center three-orbital system, conform to physical intuition as shown in Figure 2. In general, the ligand whose overlap with the metal is largest or whose donor orbital energy lies closest to the molecular orbital in question has the largest coefficient in that MO. For example, in the Φ_3 MO, the metal–ligand bond with the ligand having the smallest VOIP or largest overlap integral will be the most antibonding. Hence, loss (or gain) of an electron from Φ_3 will respectively preferentially strengthen (or weaken) that bond.

The three-center, three-orbital model can be explicitly used to treat the π-bonding changes. The overlap populations shown in Figure 2 were calculated using values for the constant parameters which are typical for π interactions between first-row transition metals and halide ligands. The three-orbital model can also be used to treat the σ system if the metal s orbital is neglected and appropriate values of the VOIP's and

overlap integrals are used. If the three-center, three-orbital model were used to treat the σ system, Φ_3 would correspond to the antibonding d_{z^2} orbital in ligand field theory.

Because it is not immediately obvious what the effects of mixing an additional orbital into the three-center, three-orbital σ system will be, it is useful to point out a simple correlation which can lead to an intuitive understanding of the three-center, four-orbital problem. The additional orbital will mix with the existing orbitals such that of the four new MO's formed, the lowest will be lower than Φ_1, the highest higher than Φ_3, and the middle two between Φ_1 and Φ_2 and Φ_2 and Φ_3, respectively.[1,18,19] If the additional orbital is a metal s orbital which only weakly mixes with the others, the lowest MO retains predominantly the character of Φ_1, the next highest that of Φ_2, etc. The highest will then be primarily metal s in character. This simple correlation, derived using the Hylleraas–Undheim theorem,[18,19] leads us to expect that the ψ_3 photoactive orbital of the four-orbital problem will have properties similar to Φ_3 of the three-orbital problem.

The effects of varying the ligand and the metal properties on the overlap populations of the σ system including the metal 4s orbital are shown in Figures 3–6. The general conclusion which can be drawn from these results and the above correlation rule is: the ligand with the largest overlap integral or the smallest VOIP will be the one with the largest antibonding overlap population with the metal in the photoactive ψ_3 orbital.

The details of the effect of varying only one of the ligand VOIP's on the metal–ligand overlap populations in the ψ_3 orbital are shown in Figure 3 for two values of the metal–ligand overlap integral. The other parameters have median values for the σ interactions of a first-row transition metal with amine or halide ligands. For a given difference in the ligand VOIP's, the difference in the overlap populations increases when both of the metal–ligand overlap integrals increase equally. Regardless of the value of the overlap integral (over the range 0.05–0.11), the ligand with the largest VOIP remains the least antibonding (e.g., L_2 in Figure 1). For the usual range VOIP's and overlap integrals for transi-

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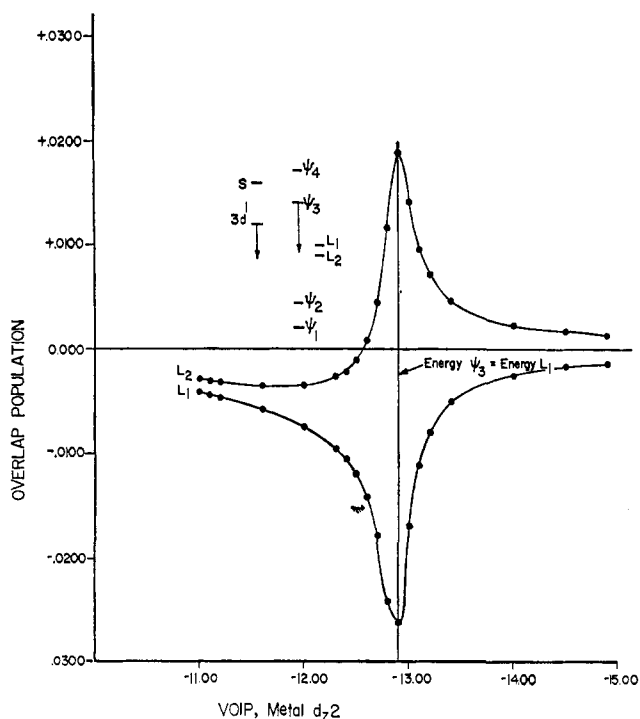
Figure 5. The variation of the overlap population in the ψ_3 orbital of the four orbital problem as a function of metal d orbital energy. The other energies were: metal s, -9.000 eV; L_1 -12.45 eV; L_2, -13.000 eV. The overlap integral between the metal d and ligand orbitals was 0.07.

Figure 6. A comparison of the relative importances of variations in the difference between the VOIP's (top scale) and overlap integrals (bottom scale) on the overlap population differences between the two ligands. The parameters are the same as those in Figures 3 and 4.

tion metal complexes, the above statement remains true even if one of the ligand VOIP's is smaller than that of the metal d orbital (*cf.* Figure 5 and discussion concerning it). This result was unexpected, particularly when the VOIP's of a ligand and the metal are accidentally degenerate. The origin of this result lies in the proof given in ref 1 that the ψ_3 orbital can never drop below that of the donor orbital of the ligand with the greatest VOIP. In terms of practical applications to the interpretation of photochemistry, the above result means that of the two ligands on the labilized axis the one with the smallest VOIP will gain the greatest antibonding character in the excited state. This result invalidates the earlier formulation of ref 1 which holds true in general only for the antibonding orbitals of the two-center, two-orbital problem and the ψ_2 orbital.

The effect of varying only a metal–ligand overlap integral on the antibonding overlap populations of the ligands is shown in Figure 4. The difference between the overlap populations for the two ligands varies in a roughly linear manner with the difference between the overlap integrals for the two ligands with the metal. As a general rule, *for two ligands with the same VOIP's, the ligand with the larger metal–ligand overlap integral will have the most σ antibonding character in the ψ_3 excited state.*

The major complication which could occur when applying the above results to the interpretation of photoreactions is the case of two ligands whose trends in VOIP's and overlap integrals oppose each other. Such cases are surprisingly rare in the transition metal complexes which have been studied to date, particularly when the VOIP's and not the ionization energies of the atoms are considered. It is worthwhile to consider the relative importance of the two effects. From Figures
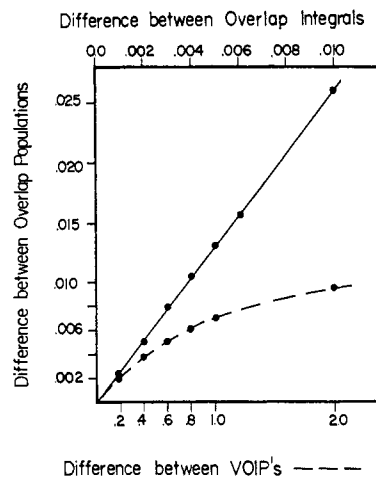
3 and 4, it can be seen that a difference of 1.3 eV in the VOIP's of the ligands gives rise to the same difference in overlap population as a difference of 0.01 or less in the overlap integrals. For comparison, the difference between the ionization energies of a nitrogen 2p and a chlorine 3p orbital is 0.50 eV while the difference between their overlap integrals with a chromium $3d_{z^2}$ orbital is 0.076. A more quantitative comparison is shown in Figure 5 where the difference in antibonding character is plotted as a function of VOIP and overlap integral differences using the parameters taken directly from a complete calculation of $Cr(NH_3)_5Cl^{2+}$ (*vide infra*). In order for the effect of the VOIP difference to counteract the difference in overlap integrals, the VOIP's would have to differ by more than 5 eV! In general, we conclude that *the antibonding character between the metal and the ligands in the excited state is much more sensitive to the overlap integrals than it is to the ligand VOIP's.*

The effect of varying the metal VOIP on the overlap populations of the metal–ligand bonds in the ψ_3 orbital is shown in Figure 6. This formulation of the model represents one aspect of the effect of varying the metal. The shape of the plot in Figure 6 is primarily a function of the energy of the ψ_3 orbital with respect to those of the ligand donor orbitals. As the VOIP of the metal increases, the energy of the ψ_3 orbital decreases. As ψ_3 approaches the energy of the L_1 donor orbital, the difference in the antibonding character rapidly increases. The maximum difference in the overlap populations occurs when the energy of the ψ_3 orbital equals that of the L_1 donor orbital. When ψ_3 lies between L_1 and L_2 in energy, the overlap population between the metal and the ligand with the smallest VOIP represents metal–ligand stability in the ψ_3 orbital. For most transition metal complexes, the energy of ψ_3 will never be lower than that of the ligand donor orbitals because this situation would tend to allow rapid redox reactions to occur. In general, the closer in energy the ψ_3 orbital lies to the ligand orbitals, the greater the difference in labilization between the ligands in the excited state. The relative energy of the ψ_3 orbital can be empirically determined from the spectrochemical series of the metals

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Table I. Results of EHMO Calculations

Complex	Orbital (atom)	VOIP (charge)	S	ψ_3 overlap pop	Total overlap pop	Predicted labilization	Obsd labilization[a]	Ref
$Cr(NH_3)_5Cl^{2+}$	3s (Cl)	−24.40 (−0.056)	0.0514	−0.0040				
	$3p_\sigma$ (Cl)	−12.96	0.0940	−0.0349				
	$3p_\pi$ (Cl)	−12.96	0.0414	−0.0171	−0.0218			
	2s (N)	−24.86 (−0.036)	0.0650	−0.0069				
	$2p_\sigma$ (N)	−12.60	0.1016	−0.0355	−0.0424	NH_3	NH_3	b
$Cr(NH_3)_5Br^{2+}$	4s (Br)	−24.11 (0.013)	0.0273	−0.0014				
	$4p_\sigma$ (Br)	−12.54	0.0825	−0.0329				
	$4p_\pi$ (Br)	−12.54	0.0368	−0.0153	−0.0190			
	2s (N)	−24.74 (−0.041)	0.0650	−0.0062				
	$2p_\sigma$ (N)	−12.51	0.1016	−0.0336	−0.0398	NH_3	NH_3	b
$Cr(NH_3)_5H_2O^{3+}$	2s (O)	−31.56 (−0.074)	0.0600	−0.0069				
	$2p_\sigma$ (O)	−14.45	0.0936	−0.0207				
	$2p_\pi$ (O)	−14.45	0.0353	−0.0111	−0.0165			
	2s (N)	−25.92 (0.017)	0.0650	−0.0084				
	2p (N)	−13.48	0.1016	−0.0432	−0.0516	NH_3	NH_3	c
$Cr(NH_3)_5FCl^+$	2s (F)	−31.18 (−0.368)	0.0661	−0.0045				
	$2p_\sigma$ (F)	−11.58	0.0967	−0.0316				
	$2p_\pi$ (F)	−11.58	0.0352	−0.0118	−0.0243			
	3s (Cl)	−23.00 (−0.147)	0.0514	−0.0040				
	$3p_\sigma$ (Cl)	−11.79	0.0940	−0.0397				
	$3p_\pi$ (Cl)	−11.79	0.0414	−0.0141	−0.0296	Cl	Cl	28
$Cr(NH_3)_5F^{2+}$	2s (F)	−33.44 (−0.270)	0.0661	−0.0051				
	$2p_\sigma$ (F)	−13.36	0.0967	−0.0298				
	$2p_\pi$ (F)	−13.36	0.0352	−0.0145	−0.0204			
	2s (N)	−25.41 (−0.008)	0.0650	−0.0079				
	$2p_\sigma$ (N)	−13.06	0.1016	−0.0412	−0.0491	NH_3	?	d
$Co(NH_3)_5F$	2s (F)	−31.80 (−0.341)	0.0358	−0.0016				
	$2p_\sigma$ (F)	−12.07	0.0608	−0.0224				
	$2p_\pi$ (F)	−12.07	0.0197	−0.0020	−0.0220			
	2s (N)	−25.72 (0.007)	0.0488	−0.0048				
	$2p_\sigma$ (N)	−13.31	0.0793	−0.0256	−0.0304	NH_3	NH_3	e
$Co(NH_3)_5Cl$	3s (Cl)	−23.79 (−0.095)	0.0236	−0.0011				
	$3p_\sigma$ (Cl)	−12.45	0.0507	−0.0183				
	$3p_\pi$ (Cl)	−12.45	0.0196	−0.0009	−0.0183			
	2s (N)	−25.32 (−0.012)	0.0488	−0.0042				
	$2p_\sigma$ (N)	−12.99	0.0793	−0.0226	−0.0268	NH_3	NH_3	f, g
$Co(NH_3)_5Br^{2+}$	4s (Br)	−23.89 (−0.019)	0.0133	−0.0004				
	$4p_\sigma$ (Br)	−12.43	0.0485	−0.0183				
	$4p_\pi$ (Br)	−12.43	0.0204	−0.0016	−0.0171			
	2s (N)	−24.89 (−0.035)	0.0488	−0.0037				
	$2p_\sigma$ (N)	−12.61	0.0793	−0.0200	−0.0237	NH_3	NH_3	f, g
$Co(NH_3)_4(NCS)Cl^+$	2s (N)	−22.75 (−0.144)	0.0277	−0.0022				
	$2p_\sigma$ (N)	−10.88	0.0510	−0.0125				
	$2p_\pi$ (N)	−10.88	0.0188	−0.0003	−0.0144			
	3s (Cl)	−22.40 (−0.186)	0.0236	−0.0009				
	$3p_\sigma$ (Cl)	−11.29	0.0507	−0.0163				
	$3p_\pi$ (Cl)	−11.29	0.0196	−0.0000	−0.0172	Cl	Cl^-, SCN^-	h
$Co(NH_3)_5N_3^{2+}$	2s (N_3^-)	−23.19 (−0.121)	0.0415	−0.0060				
	$2p_\sigma$ (N_3^-)	−11.24	0.0700	−0.0188				
	$2p_\pi$ (N_3^-)	−11.24	0.0297	−0.0013	−0.0248			
	2s (NH_3)	−25.40 (−0.008)	0.0488	−0.0047				
	$2p_\sigma$ (NH_3)	−13.05	0.0793	−0.0239	−0.0286	NH_3	NH_3	i

[a] Major photolabilization. In many cases, both ligands were photoaquated. [b] H. F. Wasgestian and H. L. Schläfer, *Z. Phys. Chem. (Frankfurt am Main)*, **62**, 127 (1968). [c] M. R. Edelson and R. A. Plane, *Inorg. Chem.*, **3**, 231 (1964). [d] Has not been studied. [e] A. W. Adamson, Abstracts, 14th International Conference on Coordination Chemistry, Toronto, 1972. [f] R. A. Pribush, C. K. Poon, C. M. Bruce, and A. W. Adamson, private communication. [g] A. W. Adamson, *Discuss. Faraday Soc.*, **29**, 163 (1960). [h] A. Vogler and A. W. Adamson, *J. Phys. Chem.*, **74**, 67 (1970). Both ligands were labilized with almost identical quantum yields. [i] J. F. Endicott, private communication.

for a constant amine ligand, $Pt^{4+} > Rh^{3+} > Co^{3+} > Cr^{3+}$.[20] The above considerations qualitatively explain the heretofore puzzling observation that for chromium(III) (low in the series, low ψ_3) the discrimination between the labilizations of the ligands on the z axis is large[1] whereas for cobalt(III) and rhodium(III) (high in the series, high energy ψ_3) the discrimination is much smaller.[3]

Complete Calculations of Co(III) and Cr(III) Complexes

The general principles enumerated in the discussion

(20) *Cf.* B. N. Figgis, "Introduction to Ligand Fields," Interscience, New York, N. Y., 1966, p 242.

of the model problem were more completely tested by carrying out full calculations including all atoms of complexes of cobalt(III) and chromium(III). Several factors might be expected to complicate the general trends expected from analysis of the model problem. The most important of these are the presence of the other ligands and the charge redistribution caused by varying the ligands. The presence of other atoms will in general cause the d_{z^2} orbital to participate in bonding in the XY plane as well as along the z axis.[7] These additional interactions, neglected in the model problem, result in smaller interactions along the z axis and thus tend to diminish the discrimination compared to that in

the model problem. The effect of the changing charge also tends to diminish the discrimination. As the variable ligand becomes more electronegative, the formal charge on the metal will tend to increase, thus increasing the metal d orbital VOIP and decreasing the discrimination. Furthermore, the VOIP of the electronegative ligand is decreased as the negative charge increases, further diminishing the discrimination. (The fluoride ion is an important example, *vide infra*.) Thus, while the expected general trends are observed, they are sometimes not as pronounced as expected from the model problem. The results for a variety of Cr(III) and Co(III) complexes are summarized in Table I.

Several interesting points emerge from these data. First, in Cr(III) complexes, the π-bonding changes in the excited state are 20–30% as important as σ-bonding changes whereas in Co(III) complexes they are generally less than 10% as important. This difference between the metals arises because of the larger π overlap integrals between chromium and a ligand compared to those with cobalt. Second, although in the MO interpretation of which ligand on the labilized axis is lost, the σ-bonding changes alone usually (but not always) give the correct results, the π effects reinforce the explanation. Both the σ and the π effects must be considered when applying the model. Third, the differences between the antibonding overlap populations of the two ligands are small. In monosubstituted chromium amine complexes the relative labilization between the two ligands, expressed as the ratio of antibonding overlap populations, ranges from 1.9 to 3.1 while in monosubstituted cobalt amine complexes it ranges from 1.1 to 1.5. The discrimination is smaller for cobalt than for chromium as expected from the model problem. (Recent experimental results verify this result, *vide infra*.) Fourth, the photochemistry of Co(III) complexes which are monochromatically irradiated in the LF bands is explained by the MO approach without the necessity of including mixing of LF and charge transfer states[3] (see Table I).

Comparison with Experiment

The changes in the overlap populations between a metal and its ligands in the excited state involving the metal d_{z^2} orbital are tabulated in Table I and compared with experimental results. In all cases, the MO approach correctly predicts which ligand will be labilized.

The relationship between our approach and Adamson's second rule[21] is clear. A spectroscopically "strong" ligand is usually one which is both a good σ donor and a poor π donor. It is exactly these factors which tend to increase the antibonding character in the excited state of the strong ligand compared to a weak one.

Spectroscopic properties can sometimes lead to incorrect interpretations of metal–ligand "bonding." For example, the ligands OH$^-$ and F$^-$ have been spectroscopically shown to raise the energy of the d_{z^2} orbital relative to the $d_{x^2-y^2}$ orbital in *trans*-bisethylenediaminechromium(III) complexes.[22–24] This result has

led to the interpretation that F$^-$, for example, is a "stronger" σ donor than an ammine nitrogen. The observed ordering of the one-electron orbitals is opposite to that expected from the overlap integrals and ligand VOIP's. Lever, *et al.*,[23] have suggested that the abnormally large π donor strength of F$^-$, calculated from a ligand field analysis of the electronic absorption spectrum, arises from electrostatic interactions. The same argument could be applied to the σ interactions. According to this interpretation, the small, highly charged fluoride, located closer to the chromium in the positively charged Cr(en)$_2$F$_2$$^+$ complex than the en nitrogens, raises the energy of the d_{z^2} orbital *via* electrostatic repulsions. Thus, the energy required to populate the excited state primarily d_{z^2} in character is larger than would be expected on the basis of the overlap integrals and VOIP considerations discussed previously. As a consequence, the tetragonal perturbation on the octahedral field is small and the metal d orbital character in the excited state calculated from crystal field theory approaches equal distribution along all three molecular axes.[25] However, when the excited state is populated, the bond weakenings and ligand labilizations will be dominated by the VOIP and overlap criteria. Thus, F$^-$ could perturb the metal d orbitals as if it were a "strong" σ donor and yet give relatively small amounts of antibonding character in the excited state. In light of the above interpretation, Adamson's second rule would be expected to fail in ionic complexes whenever the spectroscopically determined bonding effects (and the concomitantly calculated orbital orderings) are not caused by covalency but rather by electrostatic interactions. These situations would be expected to occur primarily with anionic ligands with electronegative donor atoms.

The recent incorrect applications of ligand field and MO theory to fluoride containing complexes[26,27] arose because of the misinterpretation of the spectroscopically determined crystal field σ parameters as being completely related to σ covalency. It is not necessary to selectively invoke a physically incorrect one-electron model to explain photochemistry of these compounds.

In summary, the MO interpretation of relative labilizations can be important in applying step 1 of our ligand field model.[5] Whenever the labilization caused by d_{z^2} antibonding character in the excited state approaches that caused by the $d_{x^2-y^2}$ orbital, the prediction of which ligands are lost must be based on considerations of the relative antibonding of all the ligands on all of the molecular axes. In other words, the antibonding between the metal and a ligand on the x or y axis having a very large overlap integral could override that for a ligand on the z axis with a smaller overlap integral even when the fractional composition of d_{z^2} in the excited state would lead to the expectation that the z axis would be more strongly labilized than the xy plane. This situation is common when the in-plane ligands are ethylenediamine, for example.[26–29] The above ex-

(21) A. W. Adamson, *J. Phys. Chem.*, 71, 798 (1967).
(22) L. Dubicki, M. A. Hitchman, and P. Day, *Inorg. Chem.*, 9, 188 (1970).
(23) M. Deeton, B. F. Chow, and A. B. P. Lever, *Can. J. Chem.*, 49, 192 (1971).
(24) D. A. Rowley, *Inorg. Chem.*, 10, 397 (1971).

(25) The symmetry orbital containing 75% d_{z^2} and 25% $d_{x^2-y^2}$ character represents equal spatial distribution between the x, y, and z axes. Deviation from these values represents directionality of the labilization. For a more complete discussion see ref 4 and 6.
(26) S. C. Pyke and R. G. Linck, *J. Amer. Chem. Soc.*, 93, 5281 (1971).
(27) G. Wirth and R. G. Linck, *J. Amer. Chem. Soc.*, 95, 5913 (1973).
(28) M. T. Gandolfi, M. F. Manfrin, L. Moggi, and V. Balzani, *J. Amer. Chem. Soc.*, 94, 7152 (1972).

planation shows why the quantum yields for ethylenediamine protonation are often large. Our initial ligand field prediction[1] that xy axis labilization can accompany z axis labilization is thus further justified.

It is of interest to note that the molecular orbital approach provides an *a posteriori* explanation for the stereochemical changes accompanying ligand aquation from chromium(III) complexes.[8c] In the excited state involving primarily a metal $d_{zz} \rightarrow d_{z^2}$ electronic transition, for example, the equatorial ligands will experience a repulsion from the axial belt of the d_{z^2} orbital. In addition, those in the xz plane will experience an attraction toward the lobes of the vacated d_{zz} orbital. The combination of repulsion from the xy plane and attraction toward the z direction could cause the observed rearrangements. The absence of such rearrangements in cobalt(III) complexes is explained by the single occupancy of the d_{zz} orbital which does not allow as strong an attraction.

The excellent correlation between the relative bond labilizations deduced from MO theory and the observed photoreactions suggests that those factors treated in the MO theory are primarily responsible for the photoactivity. However, several potential pitfalls must be considered. First, the relative labilizations were deduced for the complex in its ground state geometry. At least one school of thought considers the reactions to occur from a thermally equilibrated excited state[30,31] which may be distorted from the ground state geom-

etry. Two probable reasons why the initial labilization at the ground state geometry could govern the reactions from the excited state potential surface are (1) the ligand with the donor orbital having the greatest radial extent will "feel" the antibonding repulsion at larger distances as the distortion occurs and (2) its initial motion on the excited state potential surface will be larger. However, the full potential surface for the excited states must be known before the problem can be treated quantitatively. Closely related to the above problem is the case where L_1 gains more antibonding character than L_2 in the ψ_3 orbital but still has a larger bonding character when all the orbitals are considered. This case may be common among zero valent mixed ligand carbonyl complexes.[32] Again, the full potential surface must be known to completely treat the problem. Finally, the photoreactions in fluid solution can be affected by many competing factors such as solvation, etc. The relationship of the competing factors to our electronic approach has been discussed.[5]

The combined crystal field–MO approach offers a viable way of understanding and predicting excited state photoreactions. It unifies the spectroscopic and photochemical properties of transition metal complexes. In addition, it provides a means of assessing when the purely electronic factors are not dominant in determining the photoreactions. If reactions are found which do not correspond with those expected from the crystal field–MO analysis, other factors will be implicated which in turn will initiate progress toward a more complete model.

(29) These considerations apply to the photoreactions of *trans*-Cr(en)₂(OH)₂⁺: A. W. Adamson, *Advan. Chem. Ser.*, No. **49**, 237 (1965). The large fractional $d_{x^2-y^2}$ character in the lowest quartet state and the large Cr–N interactions would be expected to cause ethylenediamine labilization. However, at the high pH at which the reaction was carried out (pH 10.5), labilized ethylenediamine could not be trapped by protonation, and a very low quantum yield of product formation was observed.

(30) S. Chen and G. B. Porter, *Chem. Phys. Lett.*, **6**, 41 (1970).

(31) J. Marth and A. W. Adamson, *Theor. Chim. Acta*, **20**, 119 (1971).

(32) R. M. Dahlgren and J. I. Zink, unpublished observations.