On the Interpretation of the Optical Spectra of Hexahalogen Complexes of 4d and 5d Transition Metal Ions

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The electronic spectra of octahedral hexahalide complexes of 4d and 5d transition metal ions have been of interest for many years.[1] The interpretation of these spectra (and those of many similar compounds) has provided much of the impetus for the development of ligand-field theory and for the application of molecular orbital theory to extremely complex systems. These theories provide the framework for understanding bonding and assigning transitions in these complexes. Recent high-resolution spectra,[2-9] in which some line widths are less than 1 cm^{-1}, allow exceptionally stringent tests of the assignment schemes which have been proposed; this analysis will be the focus of this Account.

A large number of these complexes are known; their composition is MX^{m-}, where m may be 0, 1, 2, or 3. While not all such compounds have been observed, there appears to be only one restriction to species that can be synthesized. If we represent the electronic structure as $M^{6-m}(X^-)_6$, the outer electronic shell of the metal ion is composed of d electrons. No isolatable species exist with more than six d electrons in this shell. Neutral species other than hexafluorides are uncommon (WCl_6 is the only example), and few uninegative complexes are known.

The neutral species have been studied in gas phase and in solution at room temperature. The complex ions have been studied in numerous solvents at room temperature, in glasses, in various crystalline hosts at temperatures as low as 1.3 K, and as pure single crystals. The spectroscopic techniques that have been used include electron paramagnetic resonance, optical, infrared, Raman, and reflectance spectroscopy, magnetic circular dichroism measurements, and Zeeman studies. With such an arsenal of experimental tools it would appear that assignment of the electronic transitions should be relatively straightforward. Due to the experimental and theoretical complexity of this problem, such is not the case.

The electronic spectra of these species are superficially quite similar.[1b] At low energy there is a series of sharp, weak transitions having molar extinction coefficients, ϵ, of 100 or less (region I) in gas phase or HX solution at room temperature. At intermediate energies numerous broad intense transitions are found for which ϵ may be as large as 9000 (region II). In the far-uv region extremely intense, very broad structureless transitions are observed with $\epsilon \gtrsim 20,000$ (region III). For example, in $IrCl_6{}^{2-}$ region I extends to ~17,000 cm^{-1}, region II lies between ~17,000 and ~35,000 cm^{-1}, and region III is beyond ~35,000 cm^{-1}. The pattern is general, with details depending upon the individual complex. If the central metal ion has six d electrons, region I is absent and region II spectra are much less intense.

Interpretation of these spectra is based upon the ideas of ligand-field theory.[10] In its simplest form, this theory treats the complex as a central metal ion surrounded by six univalent halide ions. The outer d orbitals of the metal ion are perturbed by the ligand field of octahedral symmetry created by the halide ions. The degeneracy is partially removed, the orbitals being split into two groups which can be classified according to their transformation properties under the operations of the group O_h: the d_{xz}, d_{yz}, and d_{xy} orbitals form a set of t_{2g} orbitals and the d_{z^2} and $d_{x^2-y^2}$ orbitals form a set of e_g orbitals. In general the t_{2g} level is lower in energy.

The systems we consider correspond to strong ligand-field coupling, *i.e.*, the $t_{2g} \rightarrow e_g$ excitation energy is large. As the transition metal ions of interest have n (≤ 6) d electrons, only the t_{2g} subshell is occupied in the ground state, which is therefore $t_{2g}{}^n$. Electrostatic interaction and spin–orbit coupling split the states in this configuration. In the strong-field coupling limit these states are in 1:1 correspondence to those arising from the familiar p^{6-n} configuration.[11] Figure 1 gives a schematic correlation diagram for the $t_{2g}{}^4$ (p^2) system as a function of the spin–orbit coupling constant, ζ. When ζ is small, Russell–Saunders coupling is applicable; when it is large, j–j coupling is appropriate. We use Griffith's notation[12] in the two limiting cases and the Bethe notation[13] (Γ_i) in the intermediate region. The accidental degeneracy of Γ_3 and Γ_5 states, corresponding to atomic states with $J = 2$ ($^1D_2$ and $^3P_2$), arises be-

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(11) See ref 10, p 238 ff.

(12) See ref 10, p 226 ff; p 242; p 396 ff.

(13) G. F. Coster, *et al.*, "Properties of the Thirty-Two Point Groups," MIT Press, Cambridge, Mass., 1963.

Figure 1. Correlation diagram for states arising from the electronic configuration t_{2g}^4 as a function of spin-orbit coupling. The isomorphism with states arising from the p^2 configuration is indicated in each coupling region. Notation indicates the symmetry of the states.

Figure 2. Relative energy of spectroscopically significant molecular orbitals for MX_6^{2-} ions. The energies of ligand MO's are taken from ref 17 for $OsCl_6^{2-}$. The notation on the left denotes the symmetry of spatial orbitals; that on the right is for spin orbitals.

cause we limit consideration to the t_{2g}^4 configuration; it is removed in a more complete treatment. Using correlation diagrams such as this one it is possible to account for the region I spectra, as was first done by Van Vleck[14] and Tanabe and Sugano[15] for iron group complexes. The low intensity of these spectra is due to the fact that pure electronic transitions within these configurations are parity forbidden. In molecular systems they may be activated by coupling with an ungerade vibrational mode and are thus expected to be weak.

If one only considers the possibility of d-d transitions, there are serious difficulties in interpreting region II spectra. If we follow Moffitt's[16] suggestion and assume that these are due to $t_{2g} \rightarrow e_g$ excitations, they would be parity forbidden and could only be activated by vibronic coupling. Such a mechanism does not account for the large extinction coefficients observed in some of the transitions. Transitions of the type 5d → 6p (or 4d → 5p) are parity allowed but may be ruled out on energetic grounds; they are expected to occur in the vacuum ultraviolet.[17] A totally different viewpoint is needed; this was introduced by Jorgensen[18] who suggested that region II spectra arose *via* electron transfer from a ligand orbital to a metal t_{2g} orbital.

Of the outer orbitals of the halide ligands, only the p orbitals appear to be important in understanding the spectra.[17] They may be grouped into two sets: six σ orbitals directed along the metal–ligand axes and 12 π orbitals perpendicular to these axes. The octahedral field of the ligand ions interacts with these orbitals and splits their degeneracy just as it does that of the metal d orbitals. Figure 2 presents a molecular orbital energy level diagram (including both ligand p and metal d orbitals) based upon semiempirical calculations.[17] There is some disagreement as to the location of the σe_g orbital[19] and the πt_{2g} orbital,[6-9] but the ordering in Figure 2 remains

the most likely. Orbitals of the same symmetry interact so that the πt_{1u} orbital incorporates some σt_{1u} character, etc.

In addition to perturbations induced by the octahedral ligand field, the molecular orbitals are further perturbed by spin–orbit coupling. Just as an atomic p orbital is split into doublet ($j = \frac{1}{2}$) and quartet ($j = \frac{3}{2}$) states, a t_1 or t_2 orbital splits into doublet (e' or e'') and quartet (u') states. The magnitude of the splitting depends upon both atomic number and ionic charge, increasing with increasing atomic number and with increasing positive charge. A qualitative splitting pattern is also incorporated in Figure 2. It should be noted that spin–orbit coupling need not affect all the ligand molecular orbitals equally; the amount of the splitting depends greatly on the extent of mixing of orbitals of the same symmetry.

On the basis of the MO picture given in Figure 2, it is possible to account for the large extinctions seen in region II since many parity-allowed transitions are possible. These involve excitation of an electron from an ungerade ligand MO to the metal t_{2g} orbital, *i.e.*, an electron-transfer transition. However, with the quantity of high-resolution data now available, there are far more sensitive tests than extinction coefficients alone from which to infer reasonable assignments. Just as the $t_{2g} \rightarrow e_g$ hypothesis cannot account for all region II features, we shall see that the electron-transfer hypothesis is equally fallible. Arguments based mainly upon analogy or plausibility have a nasty habit of breaking down when subjected to critical tests. The central problem is determining selection rules to limit the possible assignments. In $OsCl_6^{2-}$ there are only six major bands in region II

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while 34 different $t_{2g} \rightarrow e_g$ transitions and 90 different electron-transfer transitions are possible.

Region III is attributed to electron transfer from a ligand orbital to the metal e_g orbital which is consistent with the enormous intensities of these bands. The high-resolution data required to make more precise assignments are presently unavailable.

Before proceeding, it is necessary to have a general feeling for the nature of the experimental data that are available. A great number of studies have been made at room temperature, but these do not provide the sort of information we need. Under such conditions only broad band absorptions are observed; details of the individual vibronic transitions which comprise the band are completely obscured. Only at low temperature is the vibronic structure resolved. The importance of this vibronic data cannot be overemphasized. Spectroscopic assignments can never be proved; instead, just as with the deduction of kinetic mechanisms, arguments are based upon negative inference. The process of assignment is rather like a trial—determination should be beyond reasonable doubt. The more evidence that is available, the fewer assignments that are tenable. While we shall not ignore other data, we shall mainly consider low-temperature spectra of various M(IV) ions in single cubic crystals for the following reasons: more studies have been carried out on these systems than on any others; at low temperature individual vibronic lines can be seen; the cubic environment ensures that stringent selection rules are in force.

The available data have been obtained by two different procedures, each with its own limitations. Photographic recording of spectra provides unsurpassed resolution.[2-4,20] There is a wealth of detail; the energy and line width of a transition can be determined with exceptional accuracy. Due to the peculiarities of photographic plates it is, however, extremely difficult to determine relative intensity in any but the most qualitative terms. Spectrophotometric recording on a double-slit instrument generally allows accurate measurement of extinction coefficients.[6-9] However, it is not possible to obtain anything like the resolution available photographically.

Both techniques have been used to study the magnetic field dependence of the transitions. The photographic approach is based upon Zeeman effect studies.[20] Not only does this yield information about the shift of the energy levels in a field but, by making absorbance measurements using polarized light, the possible assignments are greatly limited since there are generally extremely severe restrictions on selection rules. The experimental difficulty is that the energy shifts must be at least as large as the line widths or no effect can be observed.

The spectrophotometric method uses the phenomenon of magnetic circular dichroism (MCD),[6-9] that is, in a magnetic field all molecules become optically active. The magnitude of this induced optical activity depends upon three factors:[21] the magnetic moment of the ground state; the magnetic moment of the excited state; and the amount of magnetically induced mixing of ground and excited states with states with nonzero magnetic moments. It is this last contribution which ensures that *all* molecules are optically active in a magnetic field.

It is possible to distinguish these factors experimentally: The first leads to a temperature dependence (type C features in MCD), the difference between the first two leads to a dispersion line shape (type A), and the third leads to an absorption line shape (type B). The advantage of MCD is that the phenomenon is observable even for broad band transitions. The difficulty is that assignments based upon MCD are less constrained than ones based upon Zeeman studies. The problem is one of resolution: individual Zeeman features on a photographic plate coalesce to a single MCD feature if the instrument's slit width exceeds the splitting of the lines.

Magnetic data are commonly given in terms of g values. The shift in an energy level due to a magnetic field is defined as

$$\Delta E = |\beta_0| g H m_J \qquad (1)$$

where β_0 is the Bohr magneton, H is the field strength, and m_J is the azimuthal quantum number. For singlets m_J is 0; for doublets it is $\pm\frac{1}{2}$; for triplets it is 0, ± 1; and for quartets it is $\pm\frac{1}{2}$, $\pm\frac{3}{2}$.

In addition to the instrumental problems common to any spectroscopic analysis, there are difficulties particular to the study of doped crystals. As these are solid solutions the choice of host crystal is crucial. Only with the host crystals Cs_2ZrCl_6 and Cs_2ZrBr_6 is extensive vibronic structure found; presumably these show the least distortion from cubic symmetry.[22] The species for which good vibronic data are available are few: $RuCl_6^{2-}$,[4] $ReCl_6^{2-}$,[2] $OsCl_6^{2-}$,[3,7] $IrCl_6^{2-}$,[5,7,20] $OsBr_6^{2-}$,[9] and $IrBr_6^{2-}$.[6] Our discussion is limited to these systems, and we emphasize the spectra of Os(IV) in Cs_2ZrCl_6 for which the most extensive and best resolved data are available. Even with the "perfect host crystal" there remain problems in solid-state spectroscopy. Determination of molar extinction coefficients is only approximate, as one cannot run a doped crystal and a blank crystal of the same thickness, surface properties, and strain characteristics simultaneously.[23] Finally the vibrational spectrum is no longer that of an isolated MX_6^{2-} octahedron; the crystal lattice modifies both vibrational frequencies and vibronic selection rules.[24]

Analysis

A catalog of observed region II transitions and their most probable assignments is given in Table I. A band is described as very broad if it has no vibrational structure, as broad if the only vibrational feature appears to be a progression in the symmetric stretching frequency, $\nu_1(a_{1g})$, as sharp when individual vibronic features are seen, and as very sharp when there is an embarrassment of vibronic detail.

In this section we shall mainly discuss the spectra

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Table I
Catalog of Observed Region II Spectra (Data Are of Low Temperature Measurements on Doped Crystals of Cs_2ZrCl_6 or Cs_2ZrBr_6)

Species	Band	Energy, 10^3 cm^{-1}	Intensity[h]	Structure[h,i]	Probable assignment[i]	Bases for attribution[k]
$ReCl_6{}^{2-}$ [a]	A[g]	28.2	vw	br	$\pi t_{1g} \rightarrow u_g'$, V	E, I, S, A
	B	29.3	w	sh	$^4T_{2g}$, V (?)	E, S
	5	30.0	m	br	$\pi t_{1u} \rightarrow u_g'$	I, S, A
	6	31.5	m	sh	$^4T_{1g}$, V (?)	E, S
	8	33.7	vs	br	$\pi t_{1u} \rightarrow e_g''$; $\pi t_{2u} \rightarrow u_g'$	E, I, S, A
	9	35.7	vs	br	$\pi t_{2u} \rightarrow e_g''$	E, I, S, A
$OsCl_6{}^{2-}$ [b]	3	24.1	w	sh	$\Gamma_{4g} + \nu_4$	E, RI, S, MCD
					$\pi t_{1g} \rightarrow e_g''$, V	E, S, A
	4	25.5	s	br	$u_u'(\pi t_{1u}) \rightarrow e_g''$	E, I, MCD
	6	27.2	m	vsh	$\Gamma_{5g} + \nu_4(2)$	E, RI, MCD, g
	8	28.7	s	sh	$e_u''(\pi t_{2u}) \rightarrow e_g''$; $u_u'(\pi t_{2u}) \rightarrow e_g''$; $\pi t_{2u} \rightarrow e_g''$, V	E, I, MCD
	9	32.1	m	sh	$\Gamma_{5g} + \nu_4$	E, S, RI, MCD
					$(\pi t_{2u}, u_g') \rightarrow (e_g'')^2$ (?)	E
	10	35.7	m	br	$\sigma e_g \rightarrow e_g''$, V (?)	E
$RuCl_6{}^{2-}$ [c]	3	18.3	w	sh	$\pi t_{1g} \rightarrow e_g''$, V	E, S, A
	4	19.1	s	br	$u_u'(\pi t_{1u}) \rightarrow e_g''$	E, I, S, A
	5	20.4	m	br	$(u_u'(\pi t_{1u}), u_g') \rightarrow (e_g'')^2$	E, I, S
	6	21.9	m	br	$(u_u'(\pi t_{1u}), u_g') \rightarrow (e_g'')^2$ (?)	E, S
	7	22.8	s	sh	$\pi t_{2u} \rightarrow e_g''$ then $(\pi t_{2u}, u_g') \rightarrow (e_g'')^2$	E, I, S, A
$IrCl_6{}^{2-}$ [d]	D	17.9	w	vbr	$\pi t_{1g} \rightarrow e_g''$, V	E, S, MCD, A
	C	19.3	s	br	$\pi t_{1u} \rightarrow e_g''$	E, S, I, MCD
	B	20.8	m	vsh	d-d, V	S, MCD, g, Z, A; NI
	A	22.9	vs	vsh	$\pi t_{2u} \rightarrow e_g''$	E, I, MCD, A
					d-d, V	P, Z, S; NI
$OsBr_6$ [e]	1 + 2	17.5	w	vbr	$u_g'(\pi t_{1g}) \rightarrow e_g''$	E, S, A
	3	18.5	s	vbr	$u_u'(\pi t_{1u}) \rightarrow e_g''$	E, S, I, MCD
	4	20.0	m	vsh	d-d, V	S, MCD; NI
	5	22.2	s	sh, then	$e_u''(\pi t_{2u}) \rightarrow e_g''$	E, S, I, MCD
				br	$e_u'(\pi t_{1u}) \rightarrow e_g''$, V	E, MCD
	6	24.0	s	sh	$u_u'(\pi t_{2u}) \rightarrow e_g''$	E, S, I, MCD
$IrBr_6{}^{2-}$ [f]	1 + 2	11.8	w	vbr	$u_g'(\pi t_{1g}) \rightarrow e_g''$, V	E, S, MCD, A
	3 + 4	13.0	s	br	$u_u'(\pi t_{1u}) \rightarrow e_g''$	E, I, S, MCD
	5	14.5	w	sh	d-d, V (?)	S, MCD; NI
	6	17.1	s	vsh	$e_u''(\pi t_{2u}) \rightarrow e_g''$	E, I, S, MCD
	7	~17.6	s	br	$e_u'(\pi t_{1u}) \rightarrow e_g''$, V	E, MCD
	8	18.7	s	vsh	$u_u'(\pi t_{2u}) \rightarrow e_g''$	E, I, S, MCD

[a]–[f] Band nomenclature corresponds with the notation of ref 2–5, 9, and 6, respectively. [g] Bands A and B were not reported in ref 2. [h] m, medium; s, strong; w, weak; br, broad; sh, sharp; v, very. [i] See text for discussion of terminology. [j] Charge-transfer assignments are identified by subshells (see Figure 2). d–d transitions are noted by their most intense vibronic state (if such precision is warranted). Other vibronic transitions are indicated by V. Assignments marked (?) are tentative. [k] The bases are energy (E); intensity (I); relative intensity of vibronic states (RI); vibronic structure (S); MCD; g value (g); polarization (P); Zeeman studies (Z); and analogy with other systems (A). Where positive identification has not been possible, assignment is based on negative inference (NI).

of $OsCl_6{}^{2-}$ to indicate the way in which the data—frequency, intensity, relative intensity, MCD pattern, g value, polarization, and systematic trends—can be used to limit assignment possibilities. We choose this system because its spectra are the richest and best resolved and its ground state is singlet (see Figure 1), conditions which limit assignment possibilities. Our fundamental criterion for assessing a proposed assignment is consistency; the absence of an allowed transition is *prima facie* evidence against an interpretive scheme. Correlation of spectroscopic data with theoretical predictions can only be used to corroborate an assignment.

The most intense features in the $OsCl_6{}^{2-}$ spectra are bands 4 and 8 (see Table I). Because of their strength these transitions must be electric dipole allowed charge-transfer (CT) processes; the lowest lying of these transitions should then be $\pi_{1u} \rightarrow t_{2g}$ and $\pi t_{2u} \rightarrow t_{2g}$ CT excitations (see Figure 2). Since the ground state of $OsCl_6{}^{2-}$ is Γ_{1g}, the only electric dipole allowed transitions occur to Γ_{4u} states. In Figure 3 we present the energy level diagram for the possible Γ_{4u} states arising from the two low-lying CT

excitations. The orbitals are ordered according to MO calculations,[17] with orbital excitation energies chosen to fit the positions of bands 4 and 8. We assume that spin–orbit coupling is the dominant interaction and ignore effects such as metal–ligand electrostatic interactions.[25] The spin–orbit parameters used are $\zeta \sim 600$ cm^{-1} for chloride[6] and $\zeta \sim 2400$ cm^{-1} for Os(IV).[3] Since ζ_{Os} is large, j–j coupling is a good approximation, and the ground state would be $(u_g')^4$ (see Figure 1). The Γ_{4u} levels can then be classified according to the subshells involved in a particular transition, e.g., $u_u' \rightarrow e_g''$, $(e_u', u_g') \rightarrow (e_g'')^2$, etc. Note that two Γ_{4u} states arise from each $(u_u', u_g') \rightarrow (e_g'')^2$ transition. The relative intensity of transitions in each CT manifold and the g values of the excited states have been included in the diagram. Since the ground state of $OsCl_6{}^{2-}$ contains about 10% of the $(u_g')^2(e_g'')^2$ configuration,[3] the j–j coupling description is only approximate. The "two-electron" transitions are no longer forbidden but may have significant intensity.

(25) This is a serious limitation whose validity can only be assessed when more data are available.
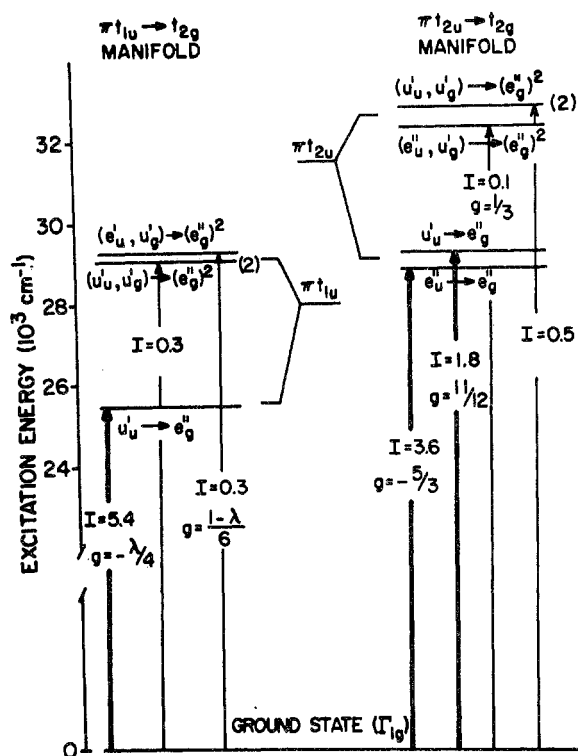
Figure 3. Energy level diagram for Γ_{4u} states arising from $\pi t_{1u} \rightarrow t_{2g}$ and $\pi t_{2u} \rightarrow t_{2g}$ charge-transfer excitations in $OsCl_6^{2-}$. Classification of levels is discussed in text. Intense transitions are noted by heavy arrows. Relative intensities and g values (where meaningful) are included. Total intensity in each manifold is arbitrarily set to 6. For reference, energies before and after including metal spin–orbit coupling are shown in the center. An orbital reduction factor of unity has been assumed.

Figure 3 has been calculated assuming a simple CT model. Neglect of electrostatic effects which would shift the energy levels and split the remaining degeneracies probably does not change any major qualitative features. However. the g values of the individual $(u_u', u_g') \rightarrow (e_g'')^2$ states depend on the size of such effects; for this reason no g values are given for these states. Finally, g values for states in the $\pi t_{1u} \rightarrow t_{2g}$ manifold are given in terms of a parameter λ which is a measure of $\sigma - \pi$ mixing of the two t_{1u} orbitals; it varies between $-1 \leq \lambda \leq 2$.[26]

The CT model predicts three very intense transitions. The low-energy band involves a single electronic state for which the probable g value suggests a $-A$ feature in MCD; this accords with the observed properties of band 4.[8] The upper band should be composed of two electronic transitions split by ~ 450 cm^{-1}; the lower of these transitions should be about twice as intense; the MCD should show a $-A$ feature followed by a $+A$ feature. These predictions are in good accord with the properties of band 8.[8] The actual splitting seems closer to ~ 1200 cm^{-1}; part of this difference may be accounted for when ligand–metal electrostatic interactions are considered.[27]

There is extensive structure associated with band 8 probably due in part to vibronically activated transitions involving other electronic states in this region

of the $\pi t_{2u} \rightarrow t_{2g}$ manifold.[8] From Figure 3 we see that the upper Γ_{4u} states in the $\pi t_{1u} \rightarrow t_{2g}$ manifold should occur in the vicinity of band 8. Since these are similar to the state which gives rise to band 4, they should be rather broad and quite weak in comparison to the intense $\pi t_{2u} \rightarrow t_{2g}$ features. While they are likely to be masked, they may account for some of the band 8 structure.

The only low-lying Γ_{4u} state in the $\pi t_{1u} \rightarrow t_{2g}$ manifold arises from the subshell excitation $u_u' \rightarrow e_g''$. However, a vibronically activated progression based upon the subshell excitation $e_u' \rightarrow e_g''$ is expected to commence between 25,250 and 26,600 cm^{-1}, depending upon the value of λ. As such features are found in most other systems[6,7,9] studied, it seems that this transition is masked by the excitation to the Γ_{4u} state; this indicates that λ is small, between 0 and 0.3 for this system.

Band 6 contains an unbelievable amount of fine structure; there are at least 14 separate vibronic progressions.[3] We consider only the most intense based upon lines at 27,080 (6-D) and 27,157 cm^{-1} (6-G).[3] Higher members of both progressions 6-D and 6-G are split,[3,28] 6-D into four lines. As individual electronic states in d^4 systems such as $OsCl_6^{2-}$ cannot be quartets, the feature 6-D must be a vibronic transition based upon degenerate electronic and vibrational states. Analysis of the splitting pattern of 6-D indicates that the activating vibration is $\nu_4(t_{1u})$.[3] Analysis of the d–d model showed that for $t_{2g} \rightarrow e_g$ transitions in d^4 systems there are certain approximate selection rules: vibronic transitions to Γ_{1g}, Γ_{2g}, and Γ_{3g} states are forbidden and those to Γ_{4g} states are much weaker than those to Γ_{5g} states.[29] On this basis the lines 6-D and 6-G were assigned as transitions to $\Gamma_{5g} + \nu_4(t_{1u})$ states with g values of $+0.12$ and -0.31, respectively. This agreed with the relative intensity of the transitions[29] and with the MCD pattern, a $-A$ feature followed by a $+A$ one.[8] The MCD may also be accounted for if band 6 arises from a $\pi t_{2g} \rightarrow t_{2g}$ CT excitation.[8] Then lines 6-D and 6-G would be transitions to $\Gamma_{4g} + \nu_4(t_{1u})$ vibronic states with $g = -1.67$ and $+0.92$, respectively. However recent measurements in fields as high as 70 kG show no magnetically induced splitting.[30] Using line widths as a guide, $|g| \lesssim 0.3$ for both states, which rules out the CT hypothesis. The surprising feature of this $t_{2g} \rightarrow e_g$ identification is that band 6 is a moderately intense, vibronically activated band which must borrow its intensity not from the nearby bands 4 or 8 but rather from the region III transitions some 15,000 cm^{-1} to the blue.[29]

Band 3 shows structure superposed upon a broad background. The intense resolved features are a progression of sharp lines beginning at 24,087 cm^{-1} (3-A) and a pair of broader lines beginning at 24,777 cm^{-1} (3-G).[3] As we expect the $\pi t_{1g} \rightarrow t_{2g}$ CT band to occur in this region (see Figure 2) we may compute the properties of the possible vibronic transition on the assumption that they are activated by vibronic mixing with the nearby Γ_{4u} state, band 4. The re-

(26) Previous authors introduced a bonding criterion to suggest that $\lambda > 1$ (see ref 22). Overlap was used as a basis for fixing the relative phases in the bonding and antibonding t_{1u} orbitals. This assumes that interactions with the core (one-electron effects) dominate, which need not be so. Electrostatic (two-electron) interactions are surely important in determining the extent of $\sigma - \pi$ mixing; if these dominate, λ may even become negative, though this is unlikely.

(27) P. C. Jordan, in preparation.

(28) P. B. Dorain, private communication.

(29) P. C. Jordan, H. H. Patterson, and P. B. Dorain, *J. Chem. Phys.*, **49**, 3858 (1968). When the parameters of the theory are reduced to their simplest forms, reasonable estimates of the reduced matrix elements which appear lead to W/V ratios between 20 and 500, this can qualitatively account for the low intensity of vibronic transitions to Γ_{4g} states.

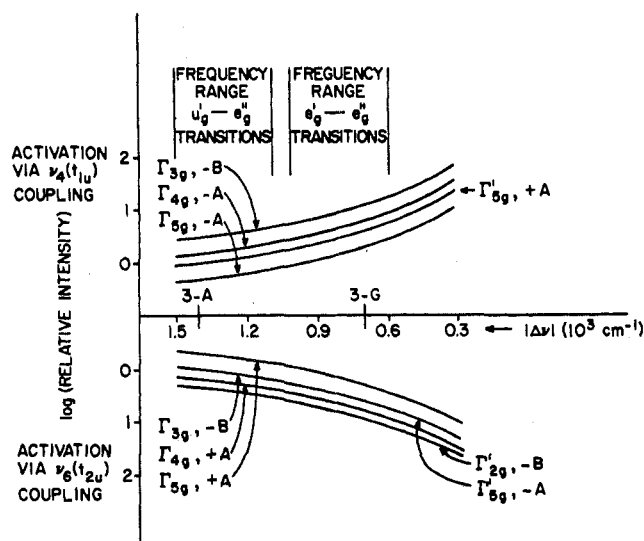(30) P. B. Dorain, private communication.

Figure 4. Relative intensities of transitions in the $\pi t_{1g} \rightarrow t_{2g}$ manifold assuming activation by vibronic mixing with the nearby $\pi t_{1u} \rightarrow t_{2g}$ Γ_{4u} state: $\Delta\nu$ is the separation of the vibronic state from the Γ_{4u} state. The nature of the MCD features predicted ($\pm A$, $\pm B$) is included. The frequency ranges shown refer to $OsCl_6^{2-}$, assuming electrostatic effects are small. For reference, the positions of lines 3-A and 3-G in $OsCl_6^{2-}$ are also indicated.

sults are given in Figure 4 for both $\nu_4(t_{1u})$ and $\nu_6(t_{2u})$ activation. The observed MCD shows +A features for both 3-A and 3-G.[8] The most obvious assignments based upon splitting and MCD, 3-A as $\Gamma_{4g} + \nu_6$ and 3-G as $\Gamma_{5g}' + \nu_4$, are inconsistent with the relative intensity pattern as there should then be intense $\Gamma_{5g}' + \nu_6$ and $\Gamma_{2g}' + \nu_6$ lines with −A and −B MCD features; none are found. Other assignment schemes lead to similar contradictions. The d–d hypothesis suggests only one state with a magnetic moment in this region,[3,29] the most intense of the $\Gamma_{4g} + \nu_4$ vibronic states with $g = +0.58$ which is consistent with the MCD of either state. We assign it to 3-A which is very sharp, reminiscent of the more intense $t_{2g} \rightarrow e_g$ transition of band 6. The broad background and some structure presumably does arise from the $\pi t_{1g} \rightarrow t_{2g}$ CT excitations. The broader resolved feature 3-G could be the $\Gamma_{5g}' + \nu_4(t_{1u})$ vibronic state as has been proposed.[8] The absence of resolved features corresponding to the $u_g' \rightarrow e_g''$ states is then puzzling but may be accounted for in two ways: if these are strongly overlapped, a broad absorption is likely; electrostatic mixing acts to increase the intensity of the $\Gamma_{5g}' + \nu_4$ state. The possibility of other CT excitations, $\pi t_{2g} \rightarrow t_{2g}$ and $\sigma e_g \rightarrow t_{2g}$, has also been considered. Such attributions lead to inconsistencies between MCD and relative intensity, run counter to trends in other MX_6^{2-} systems, and contradict the predictions of MO theory.[17]

Band 9 contains three major progressions commencing at 32,097 (9-A), 32,156 (9-B), and 32,208 cm^{-1} (9-C). The first is intense and shows a +B feature in MCD, the second is slightly more intense with a +A MCD, and the third is weak with a +A MCD. Higher members in the progression 9-B split into four components, indicative of vibronic excitation.[31] The data may be correlated on the basis of a $\sigma e_g \rightarrow t_{2g}$ CT assignment but there are three serious drawbacks.[8] Gross features of CT spectra for various
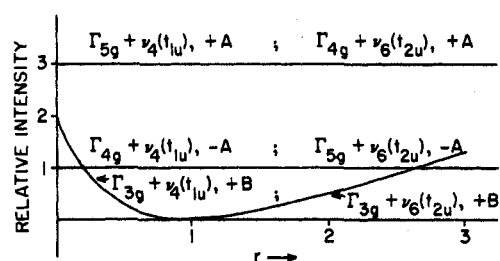

Figure 5. Relative intensities of transitions in the $\sigma e_g \rightarrow t_{2g}$ manifold assuming activation by vibronic mixing with the $\pi t_{2u} \rightarrow t_{2g}$ Γ_{4u} states; the parameter r is discussed in the text. The nature of the MCD features predicted is included. Intensities for ν_4 and ν_6 activated transitions are normalized separately.

MCl_6^{2-} compounds in the 5d transition metal series should be similar.[8,32] An analogous transition should be seen in $IrCl_6^{2-}$. None is found,[5,7,32] which suggests that this band is due to an effect specific to a d^4 system. MO calculations place the transition at higher energy (Figure 2).[17] Assuming the transition is activated by vibronic mixing with the Γ_{4u} states in band 8, we can characterize the possible vibronic transitions. The results are shown in Figure 5 in terms of a parameter, r, $r = (E - E_e)/(E - E_u)$. E is the energy of the vibronic line, and E_e and E_u are the frequencies of the no-phonon lines of the $e_u'' \rightarrow e_g''$ and $u_u' \rightarrow e_g''$ transitions in the $\pi t_{2u} \rightarrow t_{2g}$ manifold. Reasonable values for r are ~ 1.5. CT assignments consistent with the intensity and MCD of lines 9-B and 9-C require 9-A to be a weak transition and the occurrence of a fourth line of intermediate intensity with a −A feature in MCD. The d–d hypothesis predicts a moderately intense $\Gamma_{5g} + \nu_4$ state with $g = -0.82$;[3,29] this can account for the vibronic structure and MCD of line 9-B. If this is correct, the other two lines may correspond to two Γ_{4u} states of the upper levels of the $\pi t_{2u} \rightarrow t_{2g}$ manifold which are expected in this region (Figure 3). Under some circumstances electrostatic effects could account for the observed pattern of two lines, one with $g = 0$.

Little is known of band 10. It is a rather structureless transition of moderate intensity which is possibly a vibronically activated CT transition. As there is reason to believe the $\sigma t_{1u} \rightarrow t_{2g}$ transition occurs at 38,000 cm^{-1},[33] attribution of this band to a $\sigma e_g \rightarrow t_{2g}$ transition is suggested by MO calculations (Figure 2).[17]

The analysis we have given has correlated *all* features predicted to have moderate or large intensity with observed spectroscopic lines. Absent features (such as two of the $\Gamma_{5g} + \nu_4(t_{1u})$ d–d states) occur at energies where they are masked by very intense transitions.[3,29] The only tentative assignments are in bands 9 and 10. Transitions in other complexes have been assigned using similar arguments but with less assurance as the data do not limit attributions as strictly as in $OsCl_6^{2-}$. A few of these assignments warrant closer attention.

It has been proposed that bands 1 and 2 and band 4 in $OsBr_6^{2-}$ are $u_g' \rightarrow e_g''$ and $e_g' \rightarrow e_g''$ transitions, respectively, in the $\pi t_{1g} \rightarrow t_{2g}$ manifold.[9] While energetically reasonable, the vibronic structure of the bands is vastly different, which is unlikely for states arising from similar electronic configura-

(31) P. B. Dorain, private communication.

(32) B. D. Bird, P. Day, and E. A. Grant, *J. Chem. Soc. A*, 100 (1970).

(33) G. C. Allen, *et al.*, *Inorg. Chem.*, 11, 787 (1972).

tions. An analysis, similar to that made for band 3 in $OsCl_6^{2-}$, indicates that this CT assignment of band 4 cannot simultaneously account for the MCD and the relative intensities. The possibility of a d-d assignment should be considered even though this raises other questions. Why is there just one when four or five are expected? Can the large shift in $t_{2g} \rightarrow e_g$ excitation energy from that in $OsCl_6^{2-}$ be rationalized?

In $IrBr_6^{2-}$ bands 6 and 8 have been assigned to the two components of the $\pi t_{2u} \rightarrow t_{2g}$ transition.[6] The very different vibronic structure of these two bands can be understood if each is activated by coupling with the no-phonon line of that band. In the lower transition ($e_u'' \rightarrow e_g''$) only a_{1g} and t_{1g} lattice modes are active. This accounts for both the MCD and the vibronic spacing if $\nu_9(t_{1g})$ is ~ 40 cm^{-1}, which is reasonable.[9] In the upper transition ($u_u' \rightarrow e_g''$), all vibrations are active and a far different pattern is possible. The suggestion that band 5 is the upper spin-orbit component of the $\pi t_{1g} \rightarrow t_{2g}$ CT transition[6] is unlikely for reasons similar to those given in the discussion of $OsBr_6^{2-}$.

In $IrCl_6^{2-}$ the very intense band A is extraordinary. Its intensity and energy relative to band C suggest, by analogy with all other MX_6^{2-} systems considered, that it arises from a $\pi t_{2u} \rightarrow t_{2g}$ excitation.[7,22] Therefore one expects two well-separated spin-orbit components, the lower twice as intense, with a $-A$ feature followed by a $+A$ feature in MCD. Nothing like this is observed; instead there is a doublet, split by only 5 cm^{-1}, with the lower frequency component far more intense which exhibits the expected MCD pattern.[7] If an extremely strong Ham effect[34] were operative this might be rationalized with the proposed CT assignment.[7] However, high-resolution studies of the ν_1 progressions based upon this doublet show that the intense line contains at least three components and cannot be correlated

(34) F. Ham, *Phys. Rev.*, 138, A1727 (1965).

with a no-phonon state.[20] Furthermore, Zeeman studies indicate that neither feature obeys no-phonon selection rules.[20] If the $\pi t_{2u} \rightarrow t_{2g}$ CT states and some vibronic states arising from a $t_{2g} \rightarrow e_g$ transition were nearly degenerate, these anomalies might be accounted for. Band' B is also interesting. Hot band studies suggest a vibronic transition. Tentative assignment[7] to a $\pi t_{2g} \rightarrow t_{2g}$ CT transition is unlikely: the MCD would require inversion of the spin-orbit levels of the πt_{2g} orbital;[7] a similar suggestion for $OsCl_6^{2-}$ was shown to be untenable; Zeeman studies indicate some magnetic moments far too small for components of a $\pi t_{2g} \rightarrow t_{2g}$ CT state.[20] Douglas's suggestion[5] of a d-d transition seems more reasonable, although the low magnetic moments cannot be accounted for by his assignment to a $^4T_{1g}$ strong coupling state.

In summation, critical analysis of the structure of the region II spectra in MX_6^{2-} systems indicates that few assignments of intermediate intensity bands can be made with confidence. There are even unanswered questions about the gross features of some intense bands. While many assignments can be ruled out, positive identifications are often difficult to make.

Further MCD studies on $RuCl_6^{2-}$ and $ReCl_6^{2-}$ would provide tests of our proposed assignments. Zeeman studies on the sharp bands in $IrBr_6^{2-}$ and $OsBr_6^{2-}$ would help determine whether these are CT or d-d transitions. Advances in crystal growing methods could provide better host lattices and therefore even higher resolution spectra.

A detailed theoretical study of $IrCl_6^{2-}$ is surely needed. Analysis of metal–ligand electrostatic interactions would be most useful to corroborate assignments in d^4 systems. Finally, a more complete treatment of the vibronic coupling problem including the effects of the crystal lattice should be undertaken.