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Charge-Transfer Excited States of Ruthenium(II) Complexes. III. An Electron–Ion Coupling Model for $d\pi^*$ Configurations[1]

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Abstract: An electron–ion (parent) coupling model first proposed on experimental and group theoretical grounds (R. W. Harrigan and G. A. Crosby, *J. Chem. Phys.*, **59**, 3468 (1973)) for predicting the symmetries of $d\pi^*$ excited states has been mathematically developed. An energy level scheme for the lowest $d\pi^*(a_2)$ excited configuration of trigonal d^6 complexes has been developed in terms of a limited number of molecular parameters to be evaluated experimentally. The model satisfactorily rationalizes the experimental data on excited states of ruthenium(II) complexes of 2,2′-bipyridine and 1,10-phenanthroline obtained previously from decay time and quantum yield measurements and predicts a semiquantitative relationship between the g factors of excited states of a d^6 complex and the ground states of the corresponding d^5 species obtained by chemical oxidation. The extension of the coupling model to complexes of other ions and to ions with different symmetries is also discussed.

Extensive optical measurements on a series of ruthenium(II) complexes containing π-conjugated ligands have been reported previously.[2-5] A variety of experimental techniques was used. The main thrust of the research was to elucidate the nature of the low-lying charge-transfer (CT) excited states responsible for the unusual photoluminescence exhibited by these materials. The extensive experimental evidence led to a multiple-state model for the origin of the emission. Indeed, a combination of spectroscopic, transient decay, quantum yield, and magnetic measurements has produced a well-defined picture of the emitting manifold, including splittings, radiative and radiationless rate constants, and group theoretic symmetry labels. In addition a coupling model has emerged that offers a new view of the nature of CT excited states and provides a conceptual scheme for rationalizing their observed properties and for attaching symmetry labels.

In this paper we pursue the development of the coupling model for CT excited states mathematically. Our purpose is to place the intuitive group theoretical model induced from the experiments on a firm mathematical foundation. We show that the proposed model is not only subject to quantification in a straightforward way but also that it provides a basis for relating the experimental data thus far obtained to fundamental molecular parameters. It possesses the merits of relative simplicity and predictive capability. The mathematical extension offers valuable insight into the nature of CT excited states and provides a scheme for exploiting periodic table relationships among transition metal complexes for spectroscopic purposes.

Electron–Ion (Parent) Coupling Model for $d\pi^*$ Excited States

Following the discussion of Harrigan and Crosby[6] we visualize the low-lying charge-transfer excited configurations in these systems to be the result of the promotion of a d electron, initially localized on the metal ion, to a π^*-antibonding orbital delocalized over the ligand system. The states are viewed as arising from electrostatic coupling between the promoted (optical) electron and the $(n - 1)$ electrons remaining on the ion core. The core electrons are pictured to be strongly coupled both electrostatically and magnetically to produce well-defined core states. The final CT excited states of the d^n system are then visualized as arising from weak electrostatic coupling between the promoted (optical) electron on the ligand system and the strongly coupled core electrons on the central ion. The mathematical scheme adopted is first to couple one-electron spin orbitals on the $(n - 1)$ electron core and find eigenkets of the core Hamiltonian. Next, these core eigenkets are combined with the spin orbitals of the promoted electron to generate a product space for representing the full Hamiltonian. This Hamiltonian contains additional small electrostatic terms connecting the core electrons with the promoted electron residing on the ligand system. It is these terms that produce the final splittings into states for each $d\pi^*$ configuration. The type of coupling proposed here and the concept of ion parents are frequently employed to analyze complex atomic spectra. In this context the subject is discussed by Herzberg[7] and by Condon and Shortley.[8]

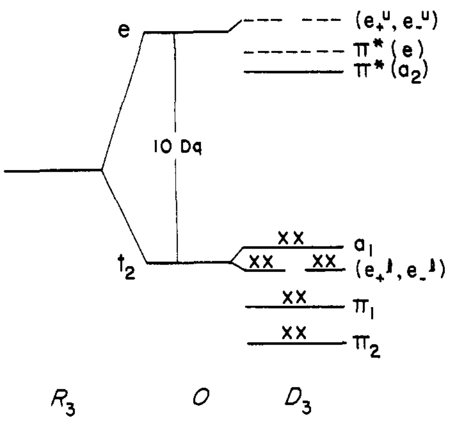

Figure 1. Proposed orbital scheme for trigonal ruthenium(II) complexes.

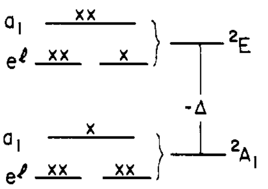

Figure 2. Lowest electronic configuration of a d^5 core with trigonal symmetry.

Since the experimental data on CT luminescence and the natures of the excited states have been generated for ruthenium(II) $(4d)^6$, osmium(II) $(5d)^6$, and iridium(III) $(5d)^6$ complexes, we have carried through the mathematical development of the model for metal ions with strong-field $(nd)^6$ configurations. We have also restricted our treatment to tris complexes possessing D_3 symmetry, since the most accurate and extensive data are available for systems possessing this geometry. Considerable simplification of the mathematics also obtains.

Description of the Model

We begin by establishing a one-electron orbital diagram for a $(nd)^6$ complex ion typified by $[Ru(bpy)_3]^{2+}$ (Figure 1). We envision the degeneracy of the five d orbitals of the free ion to be lifted, first by the octahedral crystal-field potential of the surrounding nitrogens to produce an e and t_2 set (in O) and then a further splitting of the t_2 set into a_1 and e (in D_3) generated by the smaller trigonal perturbations. Also indicated on the figure are both π (bonding) and π^* (antibonding) orbitals derived from the conjugated ligands. The π orbitals are conceived as symmetrized linear combinations of molecular orbitals from each of the attached ligands. The final symmetries of such orbitals belong to any one of the three irreducible representations of D_3. For the bonding π orbitals the symmetries, splittings, and relative energies are unknown, and they are left unassigned. What is important, however, is that they lie as indicated below the e, a_1 set derived from the metal t_2 orbitals.

The lowest vacant π^* orbital on the diagram is assumed to lie below the $e_+{}^u$, $e_-{}^u$ set, a location dictated by the assignment of the well-known luminescence to transitions originating from a $d\pi^*$ configuration.[9] The symmetry labels of the π^* orbitals on the figure are derived from an analysis of the electronic structures of the ligands themselves (vide infra).

Following Orgel[10] we assume the lowest unfilled π^* orbital on 2,2′-bipyridine (or *o*-phenanthroline) to be antisymmetric with respect to a C_2 axis perpendicular to the threefold principal axis of the complex. Properly symmetrized combinations can only be of a_2 or e symmetry in D_3. We have placed $\pi^*(a_2)$ lower than $\pi^*(e)$ in the figure, an ordering that is intuitively appealing but is also justified by the number of low-lying emitting levels observed experimentally for the complexes.[2,3] (We return to this point later.)

The relative ordering of the a_1 and e levels derived from the t_2 (O) set has been discussed qualitatively by Orgel for D_3 complexes with symmetrical bidentate ligands such as those discussed here. Although the trigonal splitting is estimated to be small for bi- or trivalent metals, such as iron, values as high as 3000 cm^{-1} have been proposed for osmium(III) in trigonal complexes.[11] Spin resonance studies on $[Ru(bpy)_3]^{3+}$ and $[Ru(phen)_3]^{3+}$ also point to the ordering given in Figure 1.[12]

The ground state configuration is portrayed in Figure 1. All spins are assumed paired to conform to the known diamagnetism of the complexes. Excited configurations are obtained by promoting an electron from the d^6 metal core to the $\pi^*(a_2)$ or $\pi^*(e)$ antibonding orbitals, respectively. In principle the core is left in one of several possible core states whose energies can be calculated to a fair degree of approximation by treating the system as a d^5 ligand-field problem of a complex that has been oxidized by one unit.

Once the positions and natures of these core states are calculated, the final CT states arising from the $d\pi^*$ configurations are computed by introducing terms into the Hamiltonian to account for the optical electron residing in one of the π^* symmetrized orbitals on the ligand system. Inclusion of the promotional energy and the additional electrostatic terms between the core and the excited electron produces final CT state functions and energies of the excited d^6 complex ion.

Mathematical Development

The Core States. In principle, the d^5 core states are found by solving the many particle Hamiltonian for all the electrons on the central-metal ion. Since we are interested only in the first-order splittings arising from the open d shell, we restrict the operator to those electrons that comprise the d^5 configuration.

$$H^c = \sum_i^5 h_i + V_{LF} + \sum_{i<j}^5 e^2/r_{ij} + \sum_i^5 \xi_{nd}(r)\mathrm{l}_i \cdot \mathbf{s}_i \qquad (1)$$

For our purposes, it is most convenient to write H^c as a sum of terms

$$H^c = H^0 + H^e + H^{SO} \qquad (2)$$

where $H^0 = \Sigma_i^5 h_i + V_{LF}$, $H^e = \Sigma_{i<j}^5 e^2/r_{ij}$, and $H^{SO} = \Sigma_i^5 \xi_{nd}(r)\mathrm{l}_i \cdot \mathbf{s}_i$.

It is well known that the one-electron orbitals that are eigenfunctions of $H_i{}^0$ transform according to the irreducible representations of D_3.[13] They comprise the set ($e_+{}^l$, $e_-{}^l$, a_1, $e_+{}^u$, $e_-{}^u$; where the superscript l is an "el" throughout) depicted in Figure 1.

If we place five electrons in the lowest three orbitals, we arrive at antisymmetrized five-electron functions, which must transform as the irreducible representations of the $D_3{}^*$ double group. They are $|1E'\alpha'\rangle$, $|1E'\beta'\rangle$ $[^2A_1]$ and $|\hat{\rho}_1\rangle$, $|\hat{\rho}_2\rangle$, $|2E'\alpha'\rangle$, $|2E'\beta'\rangle$ $[^2E]$ (see Figure 2). We note that $|\hat{\rho}_1\rangle$ and $|\hat{\rho}_2\rangle$ are members of a Kramers doublet and will remain degenerate under all time-even operators.

The effect of the interelectronic repulsion operator H^e is to change the spacing of the two sets of eigenstates of H^0, but no lifting of the accidental degeneracy or mixing of them will occur, since they may also be regarded as ^2E and $^2A_1$ states at this point and H^e transforms as A_1. Any modification of the kets due to interaction with higher excited configurations we ignore, since these are known to lie high-

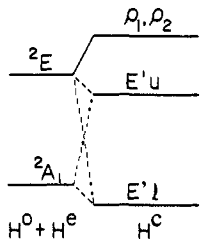

Figure 3. Lowest electronic states of a d^5 core with trigonal symmetry.

er than 15 kK, the approximate energy of the observed luminescence.

An energy diagram for the five-electron core including both H^0 and H^e in the Hamiltonian is given in Figure 2. Note the definition of Δ. We see that the first-order eigenkets of the core to this point are dependent upon the geometry of the ligands and the properties of the central ion but are independent of ligand "strength" to the extent that configuration interaction can be ignored and any covalency neglected. For ligands of similar "strength", we would expect Δ to be approximately constant for a single ion but to change with the identity of the ion.

At this point we are ready to complete the core Hamiltonian. Since the exact forms of our functions are needed, we list them here in the form of normalized Slater determinants.

$$|\hat{\rho}_1\rangle = |1e'\alpha'(1)\ 1e'\beta'(2)\ \rho_1(3)\ 2e'\alpha'(4)\ 2e'\beta'(5)| \quad (3a)$$

$$|\hat{\rho}_2\rangle = |1e'\alpha'(1)\ 1e'\beta'(2)\ \rho_2(3)\ 2e'\alpha'(4)\ 2e'\beta'(5)| \quad (3b)$$

$$|2E'\alpha'\rangle = |1e'\alpha'(1)\ \rho_1(2)\ \rho_2(3)\ 2e'\alpha'(4)\ 2e'\beta'(5)| \quad (3c)$$

$$|2E'\beta'\rangle = |1e'\beta'(1)\ \rho_1(2)\ \rho_2(3)\ 2e'\alpha'(4)\ 2e'\beta'(5)| \quad (3d)$$

$$|1E'\alpha'\rangle = |1e'\alpha'(1)\ 1e'\beta'(2)\ \rho_1(3)\ \rho_2(4)\ 2e'\alpha'(5)| \quad (3e)$$

$$|1E'\beta'\rangle = |1e'\alpha'(1)\ 1e'\beta'(2)\ \rho_1(3)\ \rho_2(4)\ 2e'\beta'(5)| \quad (3f)$$

In these expressions the following definitions have been employed

$$1e'\alpha' = e_+^{l}\beta,\ 1e'\beta' = e_-^{l}\alpha$$
$$\rho_1 = \frac{1}{\sqrt{2}}(e_+^{l}\alpha - e_-^{l}\beta),\ \rho_2 = \frac{1}{\sqrt{2}}(e_+^{l}\alpha + e_-^{l}\beta)$$
$$2e'\alpha' = a_1\alpha,\ 2e'\beta' = a_1\beta \quad (4)$$

H^{SO} lifts all the accidental degeneracy of the core and mixes the two sets of E′ functions. The resultant energy-level sequence is shown in Figure 3. The ground state of the five-electron core possesses E′ symmetry,[12] and in terms of our elementary functions the set of degenerate kets becomes

$$|E'\alpha'l\rangle = k_1|1E'\alpha'\rangle + k_2|2E'\alpha'\rangle \quad (5a)$$

$$|E'\beta'l\rangle = k_1|1E'\beta'\rangle + k_2|2E'\beta'\rangle \quad (5b)$$

(where |E′αl and E′βl define the lowest E′ eigenkets). To determine the coefficients k_1 and k_2 we need only solve the 2 × 2 matrix of H^c on the (|1E′α′⟩, |2E′α′⟩) basis. For calculating these matrix elements, as well as the others that follow, we make use of the overlap matrix technique developed by Löwdin[14] (see Appendix I).

In terms of our elementary functions we find (Appendix I)

$$\left\langle 1E'\alpha' \middle| \sum_i \xi_{nd}(r) l_i \cdot \mathbf{s}_i \middle| 1E'\alpha' \right\rangle = 0 \quad (6a)$$

$$\left\langle 2E'\alpha' \middle| \sum_i \xi_{nd}(r) l_i \cdot \mathbf{s}_i \middle| 2E'\alpha' \right\rangle = \frac{\zeta}{2}\langle e_+^{l}|l_z|e_+^{l}\rangle \quad (6b)$$

$$\left\langle 1E'\alpha' \middle| \sum_i \xi_{nd}(r) l_i \cdot \mathbf{s}_i \middle| 2E'\alpha' \right\rangle = \frac{-\zeta}{2}\langle e_-^{l}|l_-|a_1\rangle \quad (6c)$$

(where l_z and l_- are "els"). We may approximate these elementary integrals by considering the situation in which |Δ| ≪ |10*Dq*|. In this case $e_\pm^{l} \rightarrow e_\pm^{a}$ where $e_\pm^{a}$ are just the correct combinations of t_2 orbitals that transform according to $e_\pm = (-i/\sqrt{2})(e_x \pm ie_y)$. Similar functions are given by Tanabe and Sugano.[13] The *matrix* elements are:

$$\langle e_+^{l}|l_z|e_+^{l}\rangle \simeq \langle e_+^{a}|l_z|e_+^{a}\rangle = -1 \quad (7)$$

$$\langle e_-^{l}|l_-|a_1\rangle \simeq \langle e_-^{a}|l_-|a_1\rangle = +\sqrt{2} \quad (8)$$

For functions that are only specified by symmetry we define

$$\left\langle 2E'\alpha' \middle| \sum_i \xi_{nd}(r) l_i \cdot \mathbf{s}_i \middle| 2E'\alpha' \right\rangle = -\zeta A \quad (9a)$$

$$\left\langle 1E'\alpha' \middle| \sum_i \xi_{nd}(r) l_i \cdot \mathbf{s}_i \middle| 2E'\alpha' \right\rangle = +\zeta B \quad (9b)$$

where $A \approx +\frac{1}{2}$, $B \approx -1/\sqrt{2}$.

The complete core Hamiltonian on this 2 × 2 basis becomes

$$\begin{array}{c|cc} H^c & |1E'\alpha'\rangle & |2E'\alpha'\rangle \\ \hline \langle 1E'\alpha'| & 0 & \zeta B \\ \langle 2E'\alpha'| & \zeta B & -\Delta - \zeta A \end{array} \quad (10)$$

where we have chosen the energy of the |1E′α′⟩ state in the absence of spin–orbit coupling to be the zero of energy. Solutions of the secular equation are

$$W_\pm = -\frac{\Delta}{2}\{(1 + \alpha A) \pm \sqrt{(1 + \alpha A)^2 \pm 4\alpha^2 B^2}\} \quad (11)$$

where we have used the defining relation, $\zeta = \alpha\Delta$. The energy of the lowest state is given by W_-.

Application of the normalization condition ($k_1^2 + k_2^2 = 1$) leads to the relations

$$k_2^2 = \frac{W_-^2}{\zeta^2 B^2}k_1^2 = \frac{[(1 + \alpha A) - \sqrt{(1 + \alpha A)^2 + 4\alpha^2 B^2}]^2}{4\alpha^2 B^2}k_1^2 \quad (12)$$

A and *B* are "weak" functions of Δ for |Δ| ≪ |10*Dq*| and in this limit can be replaced by +½ and $-1/\sqrt{2}$, respectively. The ratio k_1/k_2 becomes a function of α only. Figure 4 is a plot of k_1^2 vs. α in this limit. If |Δ| ≈ |10*Dq*|, no such simple relation is possible.

The energies and the functional forms of the eigenkets for the complete set of core states arising from the configurations of Figure 2 are easily computed. The upper E′ eigenkets, orthogonal to the set |E′α′l⟩, |E′β′l⟩, are given by

$$|E'\alpha'u\rangle = k_1|2E'\alpha'\rangle - k_2|1E'\alpha'\rangle \quad (13a)$$

$$|E'\beta'u\rangle = k_1|2E'\beta'\rangle - k_2|1E'\beta'\rangle \quad (13b)$$

with energy W_+ (see eq 11). If interaction with higher configurations is neglected, $|\hat{\rho}_1\rangle$ and $|\hat{\rho}_2\rangle$ remain correct eigenfunctions of H^c. Their energy is computed from the diagonal element

$$\langle\hat{\rho}_1|H^c|\hat{\rho}_1\rangle = -\Delta(1 - \alpha A) \quad (14)$$

Equations 11 and 14 define the energies of the d^5 core states arising from the combined effects of electrostatic, spin-orbit, and ligand-field interactions. The corresponding eigenkets are given in eq 3a,b, 5a,b, and 13a,b.

We now proceed to the second phase of the calculation in which the core states obtained above are coupled with the molecular spin orbitals of the sixth electron delocalized over the ligand system in excited dπ* configurations.

Electron–Ion Coupling. The final charge-transfer-to-ligand (CTTL) states of the d^6 complex are obtained from diagonalizing the six-electron Hamiltonian

$$H = H^c + H_p{}^0 + O_6 \qquad (15)$$

where $H_p{}^0$ is the term that gives the promotional energy of the electron occupying a π^* orbital of the ligand system. We can write

$$H_p{}^0|i\rangle = \delta(i)|i\rangle \quad i = a_2 \text{ or } e \qquad (16)$$

Here $\delta(i)$ represents the energy of the excited "optical" electron occupying a molecular orbital on the ligand π system in the polarizing field of the central d^5 metal core. Thus, $\delta(i)$ includes not only the one-electron promotional energy but also those terms arising from the changes in electrostatic interactions that occur when the optical electron is taken from the core.

O_6 requires some discussion. It is a standard operator whose method of evaluation has been restricted. The matrix elements of O_6 are just those of $\Sigma_{i<j}e^2/r_{ij}$ *provided* that i or j labels an electron occupying a ligand orbital but zero otherwise. O_6 gives the electrostatic interaction of an electron in the occupied π^* orbital with the five remaining electrons coupled within the core.

As discussed previously[2,3] the experimental evidence strongly suggests that $\delta(a_2) < \delta(e)$ (see eq 16), i.e., that the lowest two CT excited configurations are $d\pi^*(a_2)$ and $d\pi^*(e)$, respectively. We proceed, therefore, to obtain first the eigenkets and energies of the lowest states arising from the $d\pi^*(a_2)$ configuration. In the context of our model, these eigenkets are the properly symmetrized (to D_3) products of $\{|E'\alpha'l\rangle, |E'\beta'l\rangle\}$ with $\{|a_2\alpha\rangle, |a_2\beta\rangle\}$. After antisymmetrization (S_6) one obtains the functions of interest

$$|A_1;E'la_2\rangle = |A_1\rangle = (k_1/\sqrt{2})\{|(1E'\alpha')a_2\beta(6)| + |(1E'\beta')a_2\alpha(6)|\} + (k_2/\sqrt{2})\{|(2E'\beta')a_2\alpha(6)| + |(2E'\alpha')a_2\beta(6)|\} \qquad (17a)$$

$$|E_+;E'la_2\rangle = |E_+\rangle = k_1|(1E'\alpha')a_2\alpha(6)| + k_2|(2E'\alpha')a_2\alpha(6)| \qquad (17b)$$

$$|A_2;E'la_2\rangle = |A_2\rangle = (k_1/\sqrt{2})\{|(1E'\beta')a_2\alpha(6)| - |(1E'\alpha')a_2\beta(6)|\} + (k_2/\sqrt{2})\{|(2E'\beta')a_2\alpha(6)| - |(2E'\alpha')a_2\beta(6)|\} \qquad (17c)$$

To ensure clarity of notation we write out (17b) in long form

$$|E_+\rangle = k_1|1e'\alpha'(1)1e'\beta'(2)\rho_1(3)\rho_2(4)2e'\alpha'(5)a_2\alpha(6)| + k_2|1e'\alpha'(1)\rho_1(2)\rho_2(3)2e'\alpha'(4)2e'\beta'(5)a_2\alpha(6)| \qquad (17b')$$

If we neglect O_6, these three lowest $d\pi^*(a_2)$ excited states are accidentally degenerate. The effect of O_6 is to lift all the accidental degeneracy (provided $k_1{}^2 \neq 1$ or 0) through exchange terms. The results (Appendix II) of the calculations are:

$$E_{A_1} = W_- + \delta(a_2) + J(e_+,a_2)[3 + k_1{}^2] + J(a_1,a_2)[2 - k_1{}^2] - 2K(e_+,a_2) - K(a_1,a_2) \qquad (18a)$$

$$E_{E_+} = E_{E_-} = W_- + \delta(a_2) + J(e_+,a_2)[3 + k_1{}^2] + J(a_1,a_2)[2 - k_1{}^2] - K(e_+,a_2)[1 + k_1{}^2] - K(a_1,a_2) \qquad (18b)$$

$$E_{A_2} = W_- + \delta(a_2) + J(e_+,a_2)[3 + k_1{}^2 + J(a_1,a_2)[2 - k_1{}^2] - 2K(e_+,a_2) + K(a_1,a_2)[2k_1{}^2 - 1] \qquad (18c)$$

These four states are the lowest excited states possible for the $d\pi^*(a_2)$ configuration. They arise from coupling of the optical electron with the ground state of the d^5 core. Thus, the ordering of the luminescing levels inferred from the experimental results[2,3] is corroborated by the ion-parent model. In particular, the A_1 level must be lowest.

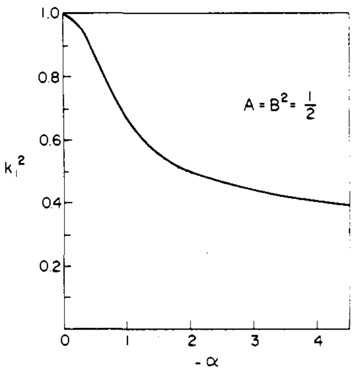

Figure 4. Dependence of configurational mixing parameter.

Higher excited states arise from this same $d\pi^*(a_2)$ configuration by coupling the optical electron with the excited core states. Coupling the Kramers pair $(\hat{\rho}_1, \hat{\rho}_2)$ with the a_2 ligand electron and applying O_6 we obtain as final states:

$$|E_+u;\hat{\rho}_1a_2, \hat{\rho}_2a_2\rangle = (1/\sqrt{2})\{|E_+;\hat{\rho}_1a_2\rangle + |E_+;\hat{\rho}_2a_2\rangle\}$$
$$|E_+l;\hat{\rho}_1a_2, \hat{\rho}_2a_2\rangle = (1/\sqrt{2})\{|E_+;\hat{\rho}_1a_2\rangle - |E_+;\hat{\rho}_2a_2\rangle\} \qquad (19)$$

where

$$|E_+;\hat{\rho}_ia_2\rangle = |1e'\alpha'(1)\, e'\beta'(2)\, \rho_i(3)2e'\alpha'(4)\, 2e'\beta'(5)\, a_2\beta(6)|$$

and $|E_+u;\hat{\rho}_1a_2,\hat{\rho}_2a_2\rangle$ is higher in energy by $K(e_+,a_2)$ than $|E_+l;\hat{\rho}_1a_2,\hat{\rho}_2a_2\rangle$. The E′u level couples with the a_2 electron to give another set of E, A_2, and A_1 states. The relevant splittings are

$$E_E - E_{A_1} = k_1{}^2K(e,a_2)$$
$$E_{A_2} - E_{A_1} = 2(1 - k_1{}^2)K(a_1,a_2) \qquad (20)$$

In principle we have now obtained all the energies and eigenkets for the lowest $d\pi^*(a_2)$ configuration. Similar calculations, albeit more tedious, could be carried out for the $d\pi^*(e)$ configuration. Such calculations have not been performed here, since insufficient experimental data are available to test the predictions, and configuration interaction may play a decisive role (vide infra).

Energy-Level Diagram for $d\pi^*$ Excited States (D_3 Symmetry). To put these results in perspective we particularize to the case of ruthenium(II) complexes containing three bipyridine or phenanthroline ligands for which spectroscopic and spin-resonance data are available. We emphasize, however, that the resultant energy-level scheme is semiquantitative only and rests on a mixture of experimental results and mathematical approximations. We choose $A = \frac{1}{2}$, $B = -1/\sqrt{2}$, and $k_1{}^2 = 0.84$. The latter parameter is an average value obtained from Figure 4 and the reported values of $\alpha = -1/1.91$ and $-1/1.74$ respectively for $[Ru(bpy)_3]^{3+}$ and $[Ru(phen)_3]^{3+}$ as obtained from electron spin resonance measurements.[15] We also choose $\Delta = -2000$ cm^{-1}, a compromise figure. Substitution into the energy expressions yields the approximate locations for the d^5 core states.

$$W(\rho) \sim -1.25\Delta \sim 2500 \text{ cm}^{-1}$$
$$W(E'u) \sim -0.89\Delta \sim 1800 \text{ cm}^{-1}$$
$$W(E'l) \sim +0.14\Delta \sim -280 \text{ cm}^{-1} \qquad (21)$$

Figure 5 summarizes the principal results of the application of the proposed model to the lowest $d\pi^*(a_2)$ configuration. Promotion of an electron from the metal core to the $\pi^*(a_2)$ orbital produces a cluster of eight levels (12 states) lying within 3000 cm^{-1} and located ~15000 cm^{-1} above the ground state. The center of gravity of the cluster is determined by the $\delta(a_2)$ promotional energy modulated by changes in electrostatic interactions that occur upon excitation. The eight energy levels fall into three groups; the separation between groups is dictated essentially by the electrostatic and spin-orbit interactions of the d^5 core. Each group is further split by exchange interactions between the promoted electron residing on the ligand and the five remaining electrons on the core. These latter splittings are small ($\sim$100 cm^{-1}) and are obtainable experimentally from a combination of spin-resonance results (on the oxidized complexes) and luminescence measurements on the parent (d^6) species. Quantitative values for the parameters have been obtained from experimental results on a number of ruthenium(II) complexes.[2,3] We wish to emphasize here, however, that only the ordering and splittings of the lowest group of levels have been thus far amenable to experimental measurement. Once its parameters have been found, however, the dispositions of the levels within the other two groups are, within the approximations of the model, completely determined.

In Figure 5 we have also indicated the symmetries and probable locations of states arising from the $d\pi^*(e)$ configuration. We defer discussions of these states until some additional consequences of the model have been explored.

Predictions

Although the separations of the groups of states in Figure 5 are semiquantitative at best, the splittings of the lowest set of levels arising from the $d\pi^*(a_2)$ configuration are relatively well defined. As discussed in parts I and II of this series, the parameters defining this set have been determined from optical and spin-resonance measurements for a number of trigonal ruthenium(II) complex ions, and both the ordering and symmetry labels appear to be secure. We now turn our attention to additional consequences of the model for both optical and magnetic properties of the complexes.

Magnetic Interactions. Reference to the D_3 group table shows that an external magnetic field aligned along the trigonal (z) axis should split the E level in first order and cause off-diagonal matrix elements to appear connecting the A_1 and A_2 levels. The E-level splitting is given by

$$\Delta E = g_{\parallel}\beta H_z = 2\left|\left\langle E_+ \middle| \sum_i \beta(l_{zi} + 2s_{zi}) \middle| E_+ \right\rangle H_z\right|$$

$$g_{\parallel} = 2\left|\left\langle E_+ \middle| \sum_i (l_{iz} + 2s_{iz}) \middle| E_+ \right\rangle\right|$$

$$g_{\parallel} = |4k_1^2 + 2k_2^2\{\langle e_+\beta|l_z + 2s_z|e_+\beta\rangle + \langle\rho_1|l_z + 2s_z|\rho_1\rangle + \langle\rho_2|l_z + 2s_z|\rho_2\rangle + \langle a_1\alpha|l_z + 2s_z|a_1\alpha\rangle + \langle a_1\beta|l_z + 2s_z|a_1\beta\rangle + \langle a_2\alpha|l_z + 2s_z|a_2\alpha\rangle\}|$$

The second and third terms as well as the fourth and fifth in the coefficient of k_2^2 add to zero. The final results are

$$g_{\parallel} = |4k_1^2 + 2k_2^2\{\langle e_+|l_z|e_+\rangle\}| = 4[-A + k_1^2(1 + A)]$$

In the limit of $|\Delta| \ll |10Dq|$ this becomes

$$g_{\parallel}^{+2} \simeq -2 + 6k_1^2 = 2 + g_{\parallel}^{+3} \qquad (22)$$

In this final expression $g_{\parallel}^{+2}$ is the g factor for the splitting of the lowest excited E state arising from the $d\pi^*(a_2)$ CT configuration of a ruthenium(II) complex. The parameter $g_{\parallel}^{+3}$ is the $g_{\parallel}$ for the ground term of the ruthenium(III) complex that is obtained by a one-electron oxidation. This is measurable by EPR. The result is intuitively reasonable, since the electron residing in the ligand a_2 orbital contributes the additional spin value of 2.

The mixing of the A_1 and A_2 levels that is caused by the z-field is easily computed. The Hamiltonian matrix becomes

$$\begin{array}{c|cc} H & |A_1\rangle & |A_2\rangle \\ \hline \langle A_1| & 0 & M\beta H \\ \langle A_2| & M\beta H & \epsilon_{A_2}^{0} \end{array}$$

where we have chosen $E_{A_1} \equiv 0$ and $E_{A_2} - E_{A_1} = \epsilon_{A_2}^{0}$. In this matrix $M = 1 - \frac{1}{2}g_{\parallel}^{+3} = (1 - k_1^2)(1 + A)^2$. Diagonalization yields the roots

$$W_{\pm}(H) = \frac{\epsilon_{A_2}^{0}}{2}\{1 \pm \sqrt{1 + 4M^2\beta^2H^2/(\epsilon_{A_2}^{0})^2}\}$$

Thus the behavior of the lowest set of CT levels arising from a magnetic field impressed along the trigonal axis is predicted. Since this lowest set of levels is responsible for the visible luminescence whose behavior can be studied in magnetic fields, the above equations are subject to experimental check. Qualitative verification has already been achieved.[16]

We direct special attention to the equations $g_{\parallel}^{+2} = 2 + g_{\parallel}^{+3}$ and $M = 1 - \frac{1}{2}g_{\parallel}^{+3}$. *Within the context of the model the magnetic behavior of the lowest CT levels of a ruthenium(II) species under the influence of a z-field is determined by a knowledge of the ground state $g_{\parallel}$ of the ruthenium(III) species obtained by a one-electron oxidation.*

Intensities. The transition dipoles are easily calculated. They are

$$\left|\left\langle A_1;gs \middle| \sum_i r_i \middle| A_1;E'la_2 \right\rangle\right|^2 = 0$$

$$\left|\left\langle A_1;gs \middle| \sum_i r_i \middle| E_+;E'la_2 \right\rangle\right|^2 = k_2^2|\langle e_-|x - iy|a_2\rangle|^2$$

$$\left|\left\langle A_1;gs \middle| \sum_i r_i \middle| A_2;E'la_2 \right\rangle\right|^2 = 2k_1^2|\langle a_1|z|a_2\rangle|^2$$

$$\left|\left\langle A_1;gs \middle| \sum_i r_i \middle| A_1;E'ua_2 \right\rangle\right|^2 = 0$$

$$\left|\left\langle A_1;gs \middle| \sum_i r_i \middle| E_+;E'ua_2 \right\rangle\right|^2 = k_1^2|\langle e_-|x - iy|a_2\rangle|^2$$

$$\left|\left\langle A_1;gs \middle| \sum_i r_i \middle| A_2;E'ua_2 \right\rangle\right|^2 = 2k_2^2|\langle a_1|z|a_2\rangle|^2$$

$$\left|\left\langle A_1;gs \middle| \sum_i r_i \middle| E_+u;\hat{\rho}_1a_2,\hat{\rho}_2a_2 \right\rangle\right|^2 = 0$$

$$\left|\left\langle A_1;gs \middle| \sum_i r_i \middle| E_+u;\hat{\rho}_1a_2,\hat{\rho}_2a_2 \right\rangle\right|^2 = |\langle e_-|x - iy|a_2\rangle|^2$$

where

$$|A_i;gs\rangle = |1e'\alpha'(1)1e'\beta'(2)\rho_1(3)\rho_2(4)2e'\alpha'(5)2e'\beta'(6)|$$

The two nonvanishing matrix elements appearing in these expressions can be evaluated empirically. Employing the experimental values for τ_{ir} listed in Table II of ref 3 for the lowest E and A_2 levels and using 0.84 for k_1^2, one can calculate the required quantities. The oscillator strengths of all the higher E and A_2 states arising from the $d\pi^*(a_2)$ configuration calculated in this way lie in the range $0.01 \geq f \geq 0.001$, indicative of extremely weak transitions.

As seen in parts I and II, for all the molecules studied to date intense CT absorption bands dominate the visible region of the spectrum. They fall within the range of the two upper groups of levels predicted to arise from the $d\pi^*(a_2)$ configuration (Figure 5). The calculated intensities of these latter levels are far too weak, however, to account for the observed spectra. We conclude that the intense absorption band(s) that produces the colors of these molecules does not arise from the $d\pi^*(a_2)$ configuration. The most likely assignment is $d\pi^*(e)$, and we have included in Figure 5 the clusters of states derived from this configuration that are

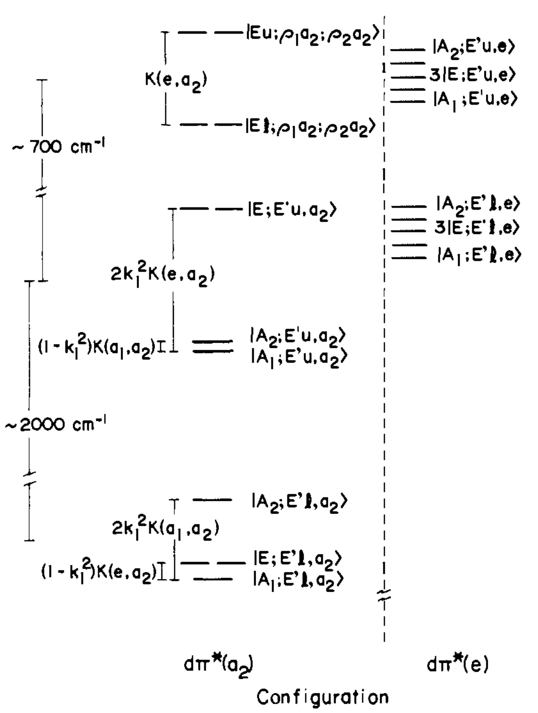

Figure 5. Proposed energy level scheme for the lowest two dπ* configurations of ruthenium(II) complexes.

expected to fall in this region. From the figure we conclude that the intense visible CT absorptions of the complexes are superpositions of a host of transitions arising from both the dπ*(a_2) and dπ*(e) configurations strongly mixed by configuration interaction. Some dd states, not included in the figure, could also lie in the same region.

The numerous electronic states predicted to fall within 3000 cm^{-1} of the lowest emitting group of levels would provide efficient paths for the degradation of excitation energy. Their probable existence is in consonance with the experimental observation that no emitted light has yet been detected emanating from levels that are not accessible thermally from the lowest excited state of any of the D_3 complexes reported in parts I and II.

If one accepts the identification of the strong visible absorption primarily as dπ*(e) excitation, then a crude estimate of the magnitude of ligand-ligand interaction can be obtained; it is approximated by the difference between the observed highest energy emission peak and the maximum of the lowest energy prevalent absorption band. For the molecules of parts I and II, this is in the range of 1200-1500 cm^{-1}. In our view this is the splitting of the a_2 and e set that arises from the interaction of the lowest π* vacant orbitals of bipyridine (phenanthroline) across the metal ion in the complex.

Conclusion

Although the model derived here applies strictly to CTTL excited states of complex ions with trigonal symmetry and π-conjugated ligands, there is no conceptual difficulty using it to describe excited CT states of complex ions with lower symmetry. Loss of the threefold axis lifts all degeneracies in the systems, however, and thus much of the appealing simplicity dictated by D_3 geometry is gone. There is also no compelling reason to limit one's view to ruthenium(II) complexes. Osmium(II) and iridium(III) (d^6) complex ions also display luminescence of CT origin, and the model can be applied to them also.[17] Qualitatively one expects, and obtains, experimental energy-level patterns resembling those of Figure 5 for osmium(II) complexes but with substantially different splittings and decay parameters than those found for ruthenium(II) species. Since we have been successful in obtaining only bis complexes of iridium(III) with bipyridine and phenanthroline ligands,[18] the D_3 scheme must be modified to conform to the lower symmetry (C_2). Nonetheless, the qualitative prediction of the model for the optical properties of the lowest CT states of these systems appears to be borne out by experiment. In short, the experimental evidence to date supports the appropriateness of the proposed coupling model for these types of CT excited states for complexes of both $(4d)^6$ and $(5d)^6$ ions that contain π-conjugated ligands. It may also be appropriate for describing CTTL states of first-row transition metal complexes in spite of the lower values of the spin-orbit coupling parameters.

A particularly important facet of this view of CT excited states is the semiquantitative relationship connecting the excited state properties of a given d^6 complex with the ground and low-lying excited state properties of the related (oxidized) d^5 molecule. Since both substances can be generated and studied separately, one has the machinery for relating experimental results from two entirely different chemical species; EPR data from a d^5 complex ion can be correlated with optical data from a d^6 species. Employing knowledge of relative values of spin-orbit coupling and ligand-field parameters one has, for example, the additional possibility of comparing the excited CT state properties of an iridium(III) complex ion with the ground state properties of a ruthenium(III) species. In short, one has the real prospect of exploiting the periodic table.

An important feature of the proposed model for CT excited states is the dominance of spin-orbit coupling. Indeed the final electrostatic splitting of a group of states is on the order of 100 cm^{-1}; whereas the contribution of the spin-orbit terms to the Hamiltonian of the d^6 system is an order of magnitude larger, even for ruthenium(II) species. For osmium(II) and iridium(III) complexes the disparity is even greater. Thus, in contradistinction to usual chemical thinking, attaching of a singlet or triplet label to these final states has no clear meaning in the context of the model. This point is elaborated elsewhere.[19]

A final conclusion stemming from this view of CT excited states in complexes of this type is that certain experimental methods do not appear to be well suited to explore further the higher lying excited states. In particular, a detailed evaluation of polarization data would appear to be complicated by the high density of predicted states.

Appendix I

Following Löwdin,[14] let

$$\mu = |\mu_1(1)\,\mu_2(2)\,\ldots\,\mu_n(n)|$$

$$\nu = |\nu_1(1)\,\nu_2(2)\,\ldots\,\nu_n(n)|$$

and generate the overlap matrix

$$[D\mu\nu]_{ij} = \langle \mu_i | \nu_j \rangle$$

Then

$$\left\langle \mu \middle| \sum_i \hat{O}_i \middle| \nu \right\rangle = \sum_{i<j} \langle \mu_i | \hat{O} | \nu_j \rangle D\mu\nu(i|j)$$

and

$$\left\langle \mu \middle| \sum_{i<j} \hat{g}_{ij} \middle| \nu \right\rangle = \sum_{i<j} \sum_{l<m} \langle \mu_i\mu_j | g | \nu_l\nu_m \rangle - \langle \mu_i\mu_j | g | \nu_m\nu_l \rangle D\mu\nu(ij|lm)$$

where

$D\mu\nu(i|j) = (-1)^{i+j}$ × determinant of D after removing the ith row and jth column, and $D\mu\nu(ij|lm) = (-1)^{i+j+l+m}$ × determinant of D after removing the ith and jth columns and the lth and mth rows.

For a diagonal element $D\mu\mu(i|j) = \delta(i|j)$, thus

$$\left\langle 1\mathrm{E}'\alpha' \middle| \xi_{\mathrm{nd}}(r) \sum_i \mathrm{l}_i \cdot \mathbf{s}_i \middle| 1\mathrm{E}'\alpha' \right\rangle = \zeta\{\langle 1\mathrm{e}'\alpha'|\mathbf{l}\cdot\mathbf{s}|1\mathrm{e}'\alpha'\rangle + \langle 1\mathrm{e}'\beta'|\mathrm{l}\cdot\mathbf{s}|1\mathrm{e}'\beta'\rangle + \langle\rho_1|\mathbf{l}\cdot\mathbf{s}|\rho_1\rangle + \langle\rho_2|\mathrm{l}\cdot\mathbf{s}|\rho_2\rangle + \langle\mathrm{a}_1\alpha|\mathrm{l}\cdot\mathbf{s}|\mathrm{a}_1\alpha\rangle\}$$

where $\langle 1\mathrm{e}'\alpha'|\mathbf{l}\cdot\mathbf{s}|1\mathrm{e}'\alpha'\rangle = \langle 1\mathrm{e}'\beta'|\mathrm{l}\cdot\mathbf{s}|1\mathrm{e}'\beta'\rangle$ and $\langle\rho_1|\mathrm{l}\cdot\mathbf{s}|\rho_1\rangle = \langle\rho_2|\mathbf{l}\cdot\mathbf{s}|\rho_2\rangle$ by group theory. Direct evaluation shows $\langle\mathrm{a}_1\alpha|\mathrm{l}\cdot\mathbf{s}|\mathrm{a}_1\alpha\rangle = \frac{1}{2}\langle\mathrm{a}_1|\mathrm{l}_z|\mathrm{a}_1\rangle = 0$.

Substitution of the defining relations (text eq 4) and evaluation of the spin contributions yields

$$\left\langle 1\mathrm{E}'\alpha' \middle| \sum_i \xi_{\mathrm{nd}}(r)\mathbf{l}_i \cdot \mathbf{s}_i \middle| 1\mathrm{E}'\alpha' \right\rangle = 2\zeta\{\langle 1\mathrm{e}'\alpha'|\mathrm{l}\cdot\mathbf{s}|1\mathrm{e}'\alpha'\rangle + \langle\rho_1|\mathbf{l}\cdot\mathbf{s}|\rho_1\rangle\} = 2\zeta\{-\tfrac{1}{2}\langle\mathrm{e}_+^{1}|\mathrm{l}_z|\mathrm{e}_+^{1}\rangle + \tfrac{1}{2}\{\tfrac{1}{2}\langle\mathrm{e}_+^{1}|\mathrm{l}_z|\mathrm{e}_+^{1}\rangle - \tfrac{1}{2}\langle\mathrm{e}_-^{1}|\mathrm{l}_z|\mathrm{e}_-^{1}\rangle - \langle\mathrm{e}_-^{1}\beta|\mathbf{l}\cdot\mathbf{s}|\mathrm{e}_+^{1}\alpha\rangle - \langle\mathrm{e}_+^{1}\alpha|\mathrm{l}\cdot\mathbf{s}|\mathrm{e}_-^{1}\beta\rangle\}\} = -\zeta\{\langle\mathrm{e}_-^{1}|\mathrm{l}_+/2|\mathrm{e}_+^{1}\rangle + \langle\mathrm{e}_+^{1}|\mathrm{l}_-/2|\mathrm{e}_-^{1}\rangle\}$$

since $\langle\mathrm{e}_+^{1}|\mathrm{l}_z|\mathrm{e}_+^{1}\rangle = -\langle\mathrm{e}_-^{1}|\mathrm{l}_z|\mathrm{e}_-^{1}\rangle$ by group theory.

By time reversal $\langle\mathrm{e}_-^{1}|\mathrm{l}_+|\mathrm{e}_+^{1}\rangle = \langle\mathrm{e}_+^{1}|\mathrm{l}_-|\mathrm{e}_-^{1}\rangle = 0$, and thus

$$\left\langle 1\mathrm{E}'\alpha' \middle| \xi_{\mathrm{nd}}(r) \sum_i \mathbf{l}_i \cdot \mathbf{s}_i \middle| 1\mathrm{E}'\alpha' \right\rangle = 0 \qquad (6a)$$

Similarly,

$$\left\langle 2\mathrm{E}'\alpha' \middle| \xi_{\mathrm{nd}}(r) \sum_i \mathrm{l}_i \cdot \mathbf{s}_i \middle| 2\mathrm{E}'\alpha' \right\rangle = \zeta\{\langle 1\mathrm{e}'\alpha'|\mathrm{l}\cdot\mathbf{s}|1\mathrm{e}'\alpha'\rangle + 2\langle\rho_1|\mathbf{l}\cdot\mathbf{s}|\rho_1\rangle\} = \zeta\{-\tfrac{1}{2}\langle\mathrm{e}_+^{1}|\mathrm{l}_z|\mathrm{e}_+^{1}\rangle + \langle\mathrm{e}_+^{1}|\mathrm{l}_z|\mathrm{e}_+^{1}\rangle\} = \zeta/2\langle\mathrm{e}_+^{1}|\mathrm{l}_z|\mathrm{e}_+^{1}\rangle \qquad (6b)$$

For an off-diagonal element, all $D\mu\nu(i|j) = 0$ except for $D\mu\nu(2|5) = -1$. Thus

$$\left\langle 1\mathrm{E}'\alpha' \middle| \sum_i \xi_{\mathrm{nd}}(r)\mathbf{l}_i \cdot \mathbf{s}_i \middle| 2\mathrm{E}'\alpha' \right\rangle = -\zeta\langle\mathrm{e}_-^{1}\alpha|\mathbf{l}\cdot\mathbf{s}|\mathrm{a}_1\beta\rangle = -\frac{\zeta}{2}\langle\mathrm{e}_-^{1}|\mathrm{l}_-|\mathrm{a}_1\rangle \qquad (6c)$$

Appendix II

To calculate the final state energies we employ the techniques detailed in Appendix I.

$$\langle\mathrm{E}_+|O_6|\mathrm{E}_+\rangle = k_1^2\langle(1\mathrm{E}'\alpha')\mathrm{a}_2\alpha(6)|O_6|(1\mathrm{E}'\alpha')\mathrm{a}_2\alpha(6)\rangle + k_2^2\langle(2\mathrm{E}'\alpha')\mathrm{a}_2\alpha(6)|O_6|(2\mathrm{E}'\alpha')\mathrm{a}_2\alpha(6)\rangle + 2k_1k_2\mathrm{Re}\langle(1\mathrm{E}'\alpha')\mathrm{a}_2\alpha(6)|O_6|(2\mathrm{E}'\alpha')\mathrm{a}_2\alpha(6)\rangle$$

The last term vanishes.

$$\langle(1\mathrm{E}'\alpha')\mathrm{a}_2\alpha(6)|O_6|(1\mathrm{E}'\alpha')\mathrm{a}_2\alpha(6)\rangle = \sum_{i=1}^{5}[\langle\phi_i\mathrm{a}_2\alpha|e^2/r_{12}|\phi_i\mathrm{a}_2\alpha\rangle - \langle\phi_i\mathrm{a}_2\alpha|e^2/r_{12}|\mathrm{a}_2\alpha\phi_i\rangle]$$

where i runs over the orbitals listed in eq 3e of the text.

We find

$$\langle(1\mathrm{E}'\alpha')\mathrm{a}_2\alpha(6)|O_6|(1\mathrm{E}'\alpha')\mathrm{a}_2\alpha(6)\rangle = 4J(\mathrm{e}_+,\mathrm{a}_2) - 2K(\mathrm{e}_+,\mathrm{a}_2) + J(\mathrm{a}_1,\mathrm{a}_2) - K(\mathrm{a}_1,\mathrm{a}_2)$$

Likewise,

$$\langle(2\mathrm{E}'\alpha')\mathrm{a}_2\alpha(6)|O_6|(2\mathrm{E}'\alpha')\mathrm{a}_2\alpha(6)\rangle = \sum_{i=1}^{5}[J(\phi_i,\mathrm{a}_2) - K(\phi_i,\mathrm{a}_2)]$$

where i runs over the orbitals listed in eq 3c of the text. The result is

$$\langle(2\mathrm{E}'\alpha')\mathrm{a}_2\alpha(6)|O_6|(2\mathrm{E}'\alpha')\mathrm{a}_2\alpha(6)\rangle = 3J(\mathrm{e}_+,\mathrm{a}_2) - K(\mathrm{e}_+,\mathrm{a}_2) + 2J(\mathrm{a}_1,\mathrm{a}_2) - K(\mathrm{a}_1,\mathrm{a}_2)$$

Substitution of these results into the expression for $\langle\mathrm{E}_+|O_6|\mathrm{E}_+\rangle$ given above yields eq 18b of the text. Analogous computations lead to the results listed in eq 18a,c.

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