Franck-Condon Analysis of Transition-Metal Complexes

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Abstract: The vibronic structure in the single crystal polarized luminescence spectra of $K_2[PtCl_4]$, $K_2[PtBr_4]$, and $K_3[Co(CN)_6]\cdot 3H_2O$ is analyzed by Franck-Condon calculations. The various degrees of approximation in the Franck-Condon calculations are described. The differences in the calculated vibronic intensities and in the calculated excited state distortions resulting from the approximations are discussed. The interpretation of the changes in individual metal-ligand bond lengths is described and photochemical implications are suggested.

Introduction

Changes in metal-ligand bond lengths between the ground electronic state and excited electronic states are important in the spectroscopy and photochemistry of transition-metal complexes. The spectral bandwidths of ligand field transitions are related to the distortions of the excited states relative to the ground state.[2] The photoreactivities of metal systems are interpreted in terms of the changes of the metal-ligand bonding between the ground and excited states.[3] In spite of the importance of such changes, detailed knowledge has been hindered by the general lack of high-resolution vibrational structure in emission and absorption spectra.

The change in molecular geometry which accompanies an electronic transition can be calculated from the distribution of vibrational intensity using the Franck-Condon (FC) principle.[4] The simplest calculation of vibronic intensity, which assumes that the vibrational frequencies in the ground and excited electronic states are equal, has been carried out for polyatomic aromatic compounds[5] and transition-metal complexes.[6-14] A more exact calculation which takes into account the changed vibrational frequencies in excited states has been developed[15] and applied to metal systems.[16] In the reported FC analyses of metal systems, inconsistencies in both the calculation and the interpretation exist.

In this paper, the excited-state distortions of $K_2[PtCl_4]$, $K_2[PtBr_4]$, and $K_3[Co(CN)_6]\cdot 3H_2O$ are calculated from the well-resolved vibrational progressions in the single crystal polarized emission spectra. The various approximations in the FC analyses are compared. The interpretation of the calculated distortions in terms of individual metal-ligand bond distances is discussed. The relevance of the calculated distortions to the photochemical reactions is suggested.

Theory

1. Vibronic Intensities in Emission and Absorption. The theory of electronic transitions has been well developed in standard textbooks.[4] Recursion relationships for the necessary vibrational overlap integrals have been published.[15] In this section, only an outline of the development will be presented in order to establish the notation and to show the origin of the factors which have been omitted in recent analyses.

The emission and absorption intensities are given respectively by

$$I_{\mathrm{em}}{}^{v'v''} = \frac{64}{3}\frac{\pi^4 c}{h^4} N_{v'} E_{v'v''}{}^4 \overline{R}_{\mathrm{e}}{}^2 [\textstyle\int \psi_{v'} \psi_{v''}\, \mathrm{d}\tau]^2 \quad \text{(emission)} \tag{1a}$$

$$I_{\mathrm{abs}}{}^{v'v''} = \frac{8}{3}\frac{\pi^3}{h^2 c} I_0 \Delta x N_{v''} E_{v'v''} \overline{R}_{\mathrm{e}}{}^2 [\textstyle\int \psi_{v'} \psi_{v''}\, \mathrm{d}\tau]^2 \quad \text{(absorption)} \tag{1b}$$

where $E_{v'v''}$ is the energy of the electronic transition between the electronic excited state with the vibrational quantum number v' and the ground state with the vibrational quantum number v'', $\overline{R}_{\mathrm{e}}$ is the average value of the electronic transition dipole moment, the integrals are the vibrational overlap integrals hereafter called $R_{v'v''}$, I_0 is the intensity of the incident radiation, Δx is the thickness of the layer, and N is the number of molecules in the initial state.[4] In practice, the relative vibronic intensities given in eq 2a and 2b are desired.

$$\frac{I_{\mathrm{em}}{}^{0,n}}{I_{\mathrm{em}}{}^{0,0}} = \left(\frac{E_{0,n}}{E_{0,0}}\right)^4 \left(\frac{R_{0,n}}{R_{0,0}}\right)^2 \quad \text{(emission)} \tag{2a}$$

$$\frac{I_{\mathrm{abs}}{}^{m,0}}{I_{\mathrm{abs}}{}^{0,0}} = \left(\frac{E_{m,0}}{E_{0,0}}\right)^1 \left(\frac{R_{m,0}}{R_{0,0}}\right)^2 \quad \text{(absorption)} \tag{2b}$$

The frequency dependences for emission and absorption are explicitly given by

$$\left(\frac{E_{0,n}}{E_{0,0}}\right)^4 = \frac{(E_{0,0} - nh\nu_0'')^4}{E_{0,0}{}^4} \quad \text{(emission)} \tag{3a}$$

$$\left(\frac{E_{m,0}}{E_{0,0}}\right)^4 = \frac{E_{0,0} + mh\nu_0'}{E_{0,0}} \quad \text{(absorption)} \tag{3b}$$

where $E_{0,0}$ is the energy of the electronic transition between the $v' = v'' = 0$ vibrational levels and ν_0'' and ν_0' are the eigenfrequencies of the oscillator in the electronic ground and excited states. The vibrational overlap integrals have been evaluated for harmonic oscillator wave functions.[15] The most useful relations are given by

$$R_{0,0} = [2\delta/(1 + \delta^2)^{1/2}] \exp\left(-\frac{1}{2}\rho^2\right) \tag{4a}$$

$$R_{n+1,0} = \frac{-2\delta D R_{n,0} - (2n)^{1/2}(\delta^2 - 1)R_{n-1,0}}{(\delta^2 + 1)[2(n + 1)]^{1/2}} \tag{4b}$$

where $\delta = (\nu_0'/\nu_0'')^{1/2}$, $D = C\sqrt{m\nu_0''}\Delta S$, and $\rho = D/(1 + \delta^2)^{1/2}$. ($D$ is defined for emission. For absorption ν_0'' should be replaced by ν_0'.) When the displacement ΔS of the minimum of the potential surface of the excited electronic state along the stretching normal coordinate S is expressed in Å, the vibrational energy in cm^{-1}, and the masses from the G matrix in amu's, the constant takes the value $C = 0.1217$.

The standard procedure for calculating ΔS involves choosing an initial value of ΔS, calculating the transition intensities using eq 2-4, comparing the calculated intensities with the observed spectrum, and varying ΔS until the calculated intensities most closely resemble those in the experimental spectrum.

2. Relationships between Internal and Normal Coordinates. The distortions calculated from the Franck-Condon analysis are distortions in the normal coordinate whose vibrations comprise the progression in the emission or absorption. The quantity desired in photochemical and spectroscopic interpretations is the change in the individual metal-ligand bonds, i.e., in the internal coordinates. Although the relationships

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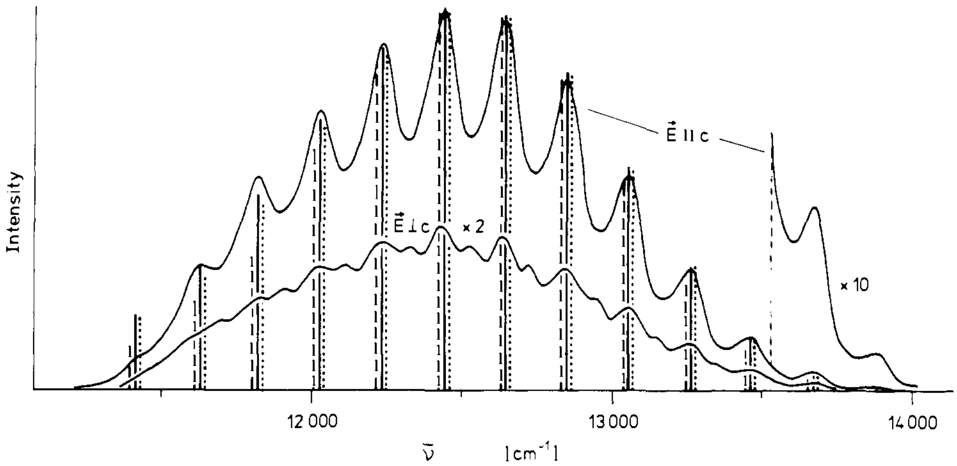

Figure 1. Single crystal polarized luminescence spectrum of $K_2[PtBr_4]$ at 5 K. The spectrum obtained with $\bar{E}$ parallel to the crystallographic axis is more intense than with $\bar{E}$ perpendicular to the axis. The normalized vibronic intensity ratios were calculated using the following parameters: (a) (solid lines) $[E_{0,n}/E_{0,0}]^1$, $\nu_0'/\nu_0'' = 1.0$, $\Delta S = 0.17$ Å; (b) (dotted lines) $[E_{0,n}/E_{0,0}]^4$, $\nu_0'/\nu_0'' = 1.0$, $\Delta S = 0.175$ Å; (c) (dashed lines) $[E_{0,n}/E_{0,0}]^4$, $\nu_0'/\nu_0'' = 0.83$, $\Delta S = 0.190$ Å. In all cases, $E_{0,0} = 13\,900$ cm^{-1}, $\mu = 79.9$ amu, $\bar{\nu}_0'' = 205$ cm^{-1}.

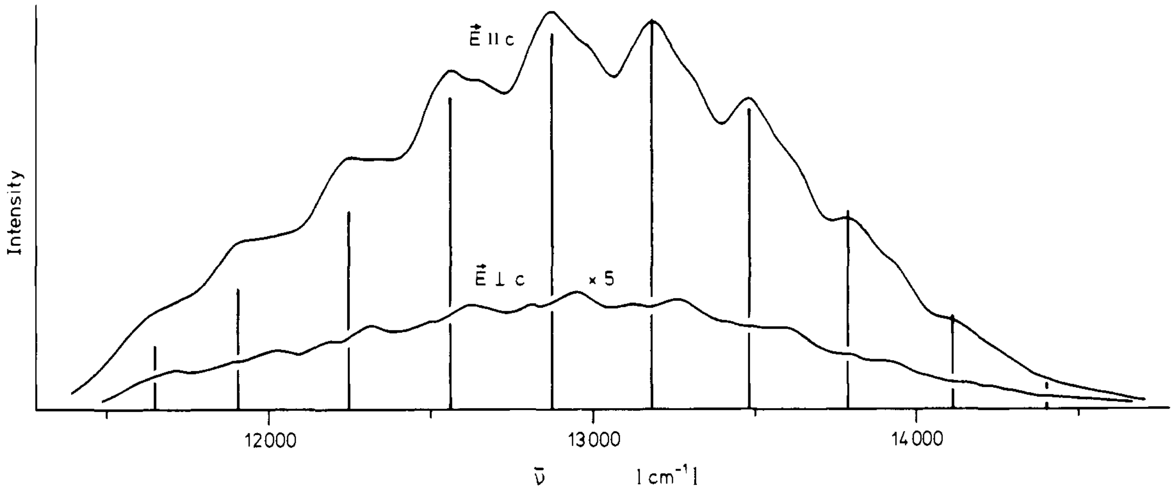

Figure 2. Single crystal polarized luminescence spectrum of $K_2[PtCl_4]$ at 5 K. The more intense spectrum was obtained with $\bar{E}\|c$. The calculated vibronic intensities, shown by vertical lines, were calculated using $\bar{\nu}_0'' = 329$ cm^{-1}, $\bar{\nu}_0' = 290$ cm^{-1}, $E_{0,0} = 16\,300$ cm^{-1}, $\mu = 35.5$ amu, and $\Delta S = 0.20$ Å.

between normal and internal coordinates are well established,[17] they have not been consistently applied in published FC calculations.

In the specific case of a D_{4h} square planar metal complex, the four internal stretching coordinates s_i lead to the four symmetry coordinates S (a_{1g}, b_{1g}, and e_u). For the totally symmetric stretch, the change in an individual metal-ligand bond, Δs, is related to the change in the symmetry coordinate ΔS by eq 5.[18] Thus, in the case of a square plane, the change in each metal-ligand bond length is *half* the change in the symmetry coordinate calculated using eq 2-4.

$$\Delta s_1 = \Delta s_2 = \Delta s_3 = \Delta s_4 = \frac{1}{\sqrt{4}}\Delta S_{a_{1g}} \qquad (5)$$

The mass which must be used in the expression for D in eq 4a and 4b is the appropriate term in the G matrix for the normal mode observed in the vibrational progression. In the case of the totally symmetric metal-ligand stretch in the square-planar complexes to be considered in this paper, $G = g_{rr}{}^2 + g'_{rr'}$ = (mass of a ligand)$^{-1}$.[17] The use of this value for the mass and the vibrational frequency measured from the spectrum defines the value of the force constant for the mode. This force constant is a combination of the individual metal-ligand stretch force constants and the interaction constants between the cis and trans ligands. For high-symmetry metal complexes, it is most convenient to use the mass derived from the G matrix and thus define the force constant. For lower symmetry organic molecules, it may often be more convenient to use known or assumed force constants for specific bond stretches and thus define the mass.[5]

The above considerations can readily be generalized for the commonly observed totally symmetric normal modes of six-coordinate complexes of O_h and D_{4h} symmetry. In these cases, the individual bond-length changes will be $\Delta S/\sqrt{6}$ for O_h symmetry, $\Delta S/\sqrt{4}$ for the equatorial ligands for D_{4h} symmetry, and $\Delta S/\sqrt{2}$ for the axial ligands for D_{4h} symmetry. In all of these cases, the mass to be used in eq 4a and 4b is the mass of the ligand involved in the motion.

Experimental Section

The compounds were prepared according to known methods.[19] The purity of the products was verified by elemental analyses and measurements of the solution spectra.

The crystals were grown by slow evaporation of saturated solutions at room temperature in the dark. The solution of the tetrahalo complexes contained an excess of the halogen ions. The crystals always presented a crystal face containing the crystallographic c axis.

The emission spectrometer is an apparatus particularly developed for investigations of small single crystals with polarized light.[20,21] A helium evaporation cryostat was used to cool the crystals to ca. 5 K.[20]

Table I. Energies (cm^{-1}) of the Progressions in the Emission Spectra

	$K_2[PtCl_4]$				$K_2[PtBr_4]$				$K_3[Co(CN)_6]\cdot 3H_2O$	
	$E_{0,n}$ $\pi(\vec{E}\parallel c)$	$\bar{\nu}_0''$[a]	$E_{0,n}$ $\sigma(\vec{E}\perp c)$	$\bar{\nu}_0''$[a]	$E_{0,n}$ $\pi(\vec{E}\parallel c)$	$\bar{\nu}_0''$[a]	$E_{0,n}$ $\sigma(\vec{E}\perp c)$	$\bar{\nu}_0''$[a]	$E_{0,n}$	$\bar{\nu}_0''$[a]
	11 640		11 700		11 410		11 625		14 166	
	11 760 sh		11 870 sh		11 620	210	11 725 sh		14 267	
	11 940	300	12 010	310	11 820	200	11 825	200	14 398	
	12 070 sh		12 180 sh		12 025	205	11 925 sh		14 573	407
	12 250	310	12 320	310	12 230	205	12 025	200	14 660	393
	12 380 sh		12 510 sh		12 440	210	12 125 sh		14 781	383
	12 570	320	12 640	320	12 640	200	12 225	200	14 956	383
	12 690 sh		12 800 sh		12 850	210	12 330 sh		15 048	388
	12 870	300	12 950	310	13 050	200	12 430	205	15 183	402
	13 000 sh		13 120 sh		13 260	210	12 525 sh		15 328	372
	13 175	305	13 260	310	13 470	210	12 630	200	15 439	391
	13 310 sh		13 430 sh		13 675	205	12 730 sh		15 573	390
	13 480	305	13 580	320	13 875	200	12 840	210	15 733	405
	13 620 sh		13 760 sh				12 930 sh		15 857	418
	13 780	300	13 890	310			13 050	210	15 976	403
	13 930 sh		14 075 sh				13 150 sh		16 121	388
	14 075	295	14 220	330			13 250	200	16 244	387
	14 240 sh						13 350 sh		16 361	385
	14 380	305					13 460	210	16 528	407
							13 560 sh		16 650	406
							13 660	200	16 780	419
$\bar{\nu}_0''$(av)		304		315		205		203		395
a_{1g}			329[b]				205[c]		406[e]	
$e_u(1)$			321[c]				225[d]			
$e_u(2)$			191[c]				112[d]			
ΔS, Å			0.20				0.19		0.30	

[a] $\bar{\nu}_0'' = E_{0,n} - E_{0,n\pm1}$. [b] Reference 7. [c] Reference 22. [d] Goggin, P. L.; Mink, J. *J. Chem. Soc., Dalton Trans.* **1974,** 1479. [e] Nakagawa, I.; Shimanouchi, T. *Spectrochim. Acta* **1962,** *18,* 101.

Results

1. **Spectra.** The results of the emission measurements are shown in Figures 1-3. $\vec{E}\parallel c$ yields the π spectra and $\vec{E}\perp c$ the σ spectra, with c being the crystallographic axis. The energies of the vibronic peaks are given in Table I.

2. **Franck-Condon Calculations.** Emission intensities calculated using the three methods found in the literature are compared in Figure 4. The parameters used in the calculations are those suitable for the $K_2[PtBr_4]$ emission spectrum to be discussed in detail below, viz., μ = 80 amu, ΔS = 0.17 Å, $\bar{\nu}_0''$ = 205 cm^{-1},[22] $\bar{\nu}_0'$ = 170 cm^{-1},[23] and $E_{0,0}$ = 13 900 cm^{-1}. All of the calculated intensities are displayed as the ratio $I_{em}^{0,n}/I_{em}^{0,0}$. Note that the inclusion of the fourth-power frequency dependence causes changes in the calculated intensities of the middle members of the series of the order of 50% and that the inclusion of the different vibrational frequencies in the ground and excited electronic states causes changes in the order of 70%.

The results of fitting the observed spectrum of $K_2[PtBr_4]$ using each of the three methods is shown in Figure 1. The best values of ΔS for each method are given in the caption of Figure 1. The calculation using the simplest method which ignores both the difference in the vibrational frequencies between the ground and excited states and the fourth-power dependence of the intensities of the transition energy underestimates the distortion by only 0.020 Å relative to that calculated using the more exact expression. The calculation including the fourth-power frequency dependence with $\nu_0' = \nu_0''$ underestimates the distortion by only 0.015 Å. The differences between the ΔS are larger than the uncertainties in ΔS produced by the formal fitting procedure for a given spectrum (±0.003 Å). The error in the calculated ΔS is smaller than the error in the relative intensities because only small changes in ΔS are necessary to fit the calculated intensities from Figure 4 to the observed spectrum as shown in Figure 1.

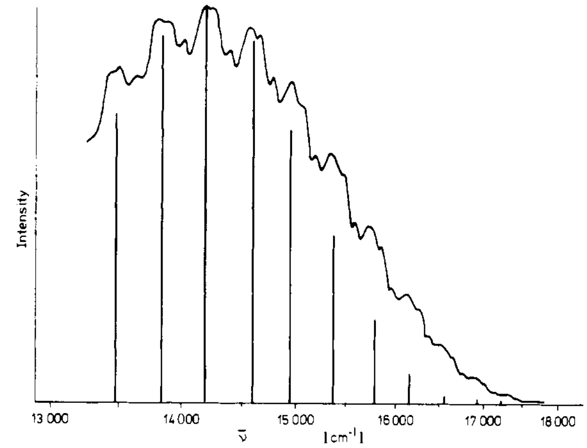

Figure 3. Single crystal emission spectrum of $K_3[Co(CN)_6]\cdot 3H_2O$ at 5 K. The vibronic intensities were calculated using $[E_{0,n}/E_{0,0}]^4$, ν_0'/ν_0'' = 0.65, ΔS = 0.295 Å, $E_{0,0}$ = 17 020 cm^{-1}, μ = 26 amu, and $\bar{\nu}_0''$ = 406 cm^{-1}.

The calculated emission intensities of $K_2[PtCl_4]$ and $K_3[Co(CN)_6]\cdot 3H_2O$ are compared to the experimental single crystal emission spectra in Figures 2 and 3. The spectra were fit using the fourth-power dependence of the intensity. The excited state totally symmetric vibrational frequency for $PtCl_4^{2-}$ was taken from the data of Patterson et al.[7] and for $Co(CN)_6^{3-}$ from the data of Crosby et al.[16]

Discussion

1. **Origin of the Transitions.** In the ground state of the tetrahalo compounds the highest filled orbitals are $a_{1g}(d_{z^2})$, $b_{2g}(d_{xy})$, and $e_g(d_{xz}, d_{yz})$; the lowest unfilled orbital is the antibonding $b^*_{1g}(d_{x^2-y^2})$.[7,8,11,24-31] The emission is assigned to a triplet-singlet transition from b^*_{1g} to the hole in the ground-state configuration and corresponds to the lowest absorption band, with a Stokes shift in the order of 4000 cm^{-1}.[31]

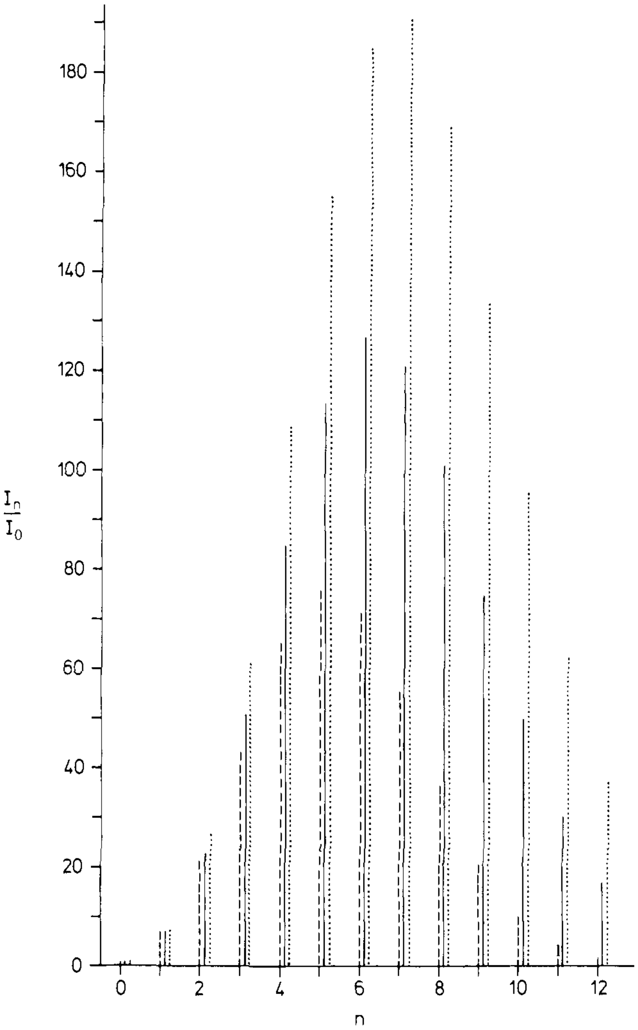

Figure 4. Calculated vibronic emission intensities using the three methods discussed in the text and the parameters given in the caption to Figure 1, with the exception that $\Delta S = 0.17$ Å in all cases: dashed lines, $[E_{0,n}/E_{0,0}]^4$, $\nu_0'/\nu_0'' = 0.83$; solid lines, $[E_{0,n}/E_{0,0}]^4$, $\nu_0'/\nu_0'' = 1.0$; dotted lines, $[E_{0,n}/E_{0,0}]^1$, $\nu_0'/\nu_0'' = 1.0$.

The emitting state is probably Γ_5^+ (D'_{4h} double group notation). As the selection rules show,[25] a dipole-allowed π transition to the ground state Γ_1^+ is possible from Γ_1^+ (with an a_{2u} vibration), Γ_3^+ (with a b_{2u} vibration), and Γ_5^+ (with an e_u vibration). The oscillator strength generally will be larger by coupling with a stretching vibration. Among the odd vibrations mentioned above only e_u has this property. Therefore the transition $\Gamma_1^+ \times e_u \leftarrow \Gamma_5^+$ should be the most intense in π polarization in accordance with our measurements (Figures 1 and 2). The fine structure in the emission bands is due to the totally symmetric ground-state vibration a_{1g} ($K_2[PtCl_4]$, 329 cm^{-1}; $K_2[PtBr_4]$, 205 cm^{-1}) based on the two different e_u promoting modes.[7,22]

With $K_3[Co(CN)_6]\cdot 3H_2O$, the emission is assigned to the transition $^1A_{1g} \leftarrow {}^3T_{1g}$. The fine structure of the band arises from the a_{1g} progression coupled to at least three different ungerade vibrations.[32] Thus the agreement between the calculated and observed intensities is not expected to be as good.

2. Comparisons of the Calculation Procedures. All of the calculations discussed in this paper and currently in use in the literature assume that the normal mode is a harmonic oscillator. This approximation is good for the transition-metal complexes studied in this paper for two reasons. First, no anharmonicity was observed in the vibrational progressions within the experimental error of our measurements. If anharmonicity were important, its effects would be most pronounced in the highly excited bands, contrary to our observations. Second, a rough estimation of the energies suggests that even the $v'' = 12$ vibrational level is well within the bottom of the potential surface. The individual metal-ligand bond energies are on the order of 10^2 kcal/mol or 35×10^3 cm^{-1}. For the a_{1g} normal mode of the PtX_4^{2-} complexes, the total dissociation energy would be on the order of 140×10^3 cm^{-1}.[33] For the usual metal-ligand frequency of 0.3×10^3 cm^{-1}, the system with $v'' = 12$ is only on the order of 4×10^3 cm^{-1} above the minimum, well within the nearly harmonic part of the surface. Other factors such as coupling with other normal modes can affect the validity of the harmonic oscillator approximation. In the square-planar systems only one mode of a_{1g} symmetry is present.

The simplest of the Franck-Condon calculations contains the assumption that the vibrational frequencies in the ground and excited electronic states are equal. For transition-metal systems, this assumption is not good. The ratio of the frequencies in the excited state to ground electronic state for metal system is often in the range of 0.8-0.9. (Specific values found in the recent literature include $PdBr_4^{2-}$, 0.83;[11] PtF_6^{2-}, 0.85;[13] $Cr(NH_3)_6^{3+}$, 0.87;[34] $PdCl_4^{2-}$, 0.88;[8] MnO_4^-, 0.89;[6] $PtCl_4^{2-}$, 0.91.[7]) The neglect of this change in the vibrational frequencies can cause errors of over 70% in the calculated intensities as seen in Figure 4. Fortunately, the error introduced into the calculated change in the metal-ligand bond lengths is only on the order of 10%.

The term used most inconsistently in published Franck-Condon calculations is the frequency dependence of the transition intensity given in eq 3. For example, in $PtBr_4^{2-}$ using the values given in the Results, the value of the fourth-power term, eq 3a, is 0.64 at the peak maximum. Neglecting this term results in a calculated intensity which is a factor of 1.6 too large. In the case of $Co(CN)_6^{3-}$ the calculated intensity without using this term is a factor of 2.4 too large at the peak maximum. However, the error in the calculated change in the metal-ligand bond lengths caused by neglecting the fourth-power energy term is much smaller (ca. 10%).

In the above discussion, the uncertainty in ΔS obtained from fitting a given spectrum is on the order of ± 0.003 Å. The absolute uncertainty in the calculated ΔS will be larger because of instrumental uncertainties (including that introduced in correcting the spectra for instrumental response), individual molecular properties (including anharmonicities, Jahn-Teller distortions, coupling between electronic states, underlying phonon intensity, etc.), and the assumptions inherent in the calculation. In a closely related series of similar compounds whose spectra are measured on the same instrument, the relative distortions may be meaningfully compared within the error limit given above. However, based on our experience, we estimate that the absolute uncertainty in any given measurements is on the order of at least ±5%.

3. Photochemical Implications. There are close connections between excited-state distortions and photochemical reactivity.[2] Both of these phenomena are related to the increase in the metal-ligand antibonding in the excited state relative to that in the ground state. The relative magnitudes of antibonding in a homologous series can be assessed from the contributions of individual d orbitals and from the metal-ligand overlap integrals.

In the case of the platinum(II) complexes reported here, the relationship between the spectrochemical parameters and the calculated distortion is readily demonstrated. The relative platinum-ligand antibonding is related to the platinum-ligand overlap integrals.[2] These integrals in turn are related to the ligand field parameters. The most readily interpretable parameters are the angular overlap parameters which are proportional to the square of the overlap integrals.[35] The σ angular overlap parameters for Cl^- ($l_\sigma^{Cl^-} = 11\,514$ cm^{-1}) and Br^- ($l_\sigma^{Br^-} = 10\,485$ cm^{-1}) can be calculated from the reported ligand-field analysis.[31] Because the Pt–Cl σ overlap is larger than that for the Pt–Br, the excited-state distortions should be larger in the chloride complex than in the bromide complex as is observed ($\Delta S_{Cl} = 0.20$ Å, $\Delta S_{Br} = 0.19$ Å). In fluid solutions where the labilized ligand can escape the primary coordination sphere, square-planar platinum complexes are photoactive.[36]

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References and Notes

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Electronic Structures and Photoelectron Spectra of the Metal Atom Cluster Species Re_3Cl_9, Re_3Br_9, and $[Re_3Cl_{12}]^{3-}$

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Abstract: The photoelectron spectra of gaseous Re_3Cl_9 and Re_3Br_9 have been measured using both He(I) and He(II) resonance lines for excitation. These have been assigned with the assistance of SCF-Xα-SW and Fenske-Hall molecular orbital calculations. For Re_3Cl_9, it is found that the first two ionizations are out of metal-metal π-bonding orbitals engaged in strong covalent interaction with the bridging and, to a lesser degree, the terminal chlorine atoms. The extent of Re-Cl interaction predicted by the calculations agrees well with the observed changes in intensity upon use of higher energy He(II) ionization source, and is consistent with a greater degree of covalency in the Re-Cl bonding in Re_3Cl_9 than in $[Re_2Cl_8]^{2-}$. The correlation of intensity changes for Re_3Br_9 is not as consistent as that in the nonachloride compound, although the calculations may be used as a guide in conjunction with the photoelectron spectra to construct a comprehensive picture of the bonding in these trinuclear metal atom clusters that is consistent with the basic idea that there are double bonds between each pair of metal atoms. Finally, the electronic transitions for Re_3Cl_9 are calculated and the optical absorption spectra for the general class of $Re_3Cl_9 \cdot 3L$ trimers are discussed and assigned.

Introduction

Interest in metal atom cluster compounds of the noncarbonyl type has increased steadily in recent years. A great deal of experimental study, both basic and applied, has established the breadth and variety of the field, but, because of the complexity of the problems and the presence of atoms with very high atomic numbers, descriptions of the bonding in metal atom cluster compounds have remained essentially qualitative.

It was recognized about 15 years ago that the crucial contribution to the electronic structures of these systems, as well as the quadruply bonded dinuclear ones, is the participation of metal atom d orbitals in the formation of molecular orbitals whose primary role is to bind the metal atoms together.[2] By treating only the metal-metal d-orbital overlaps, useful

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