

Environmentally Hindered Radiationless Transitions between States of Different Orbital Parentage in Iridium(III) Complexes. Application of Rigid-Matrix Induced Perturbations of the Pseudo-Jahn-Teller Potential to the Rigidochromic Effect in d^6 Metal Complexes

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Abstract: The emission spectroscopy of carefully purified samples of $\text{IrCl}_2(\text{phen})_2^+$ and $\text{IrCl}_2(5,6\text{-mephen})_2^+$ has been studied in DMF over the temperature range 77–352 K. Both complexes display intense blue-green emissions from either charge-transfer [$\text{IrCl}_2(\text{phen})_2^+$] or ligand-localized [$\text{IrCl}_2(5,6\text{-mephen})_2^+$] states in crystalline DMF. In fluid DMF a second emission is observed in the near-infrared region at ~ 740 nm from both complexes. Lifetime measurements and measurements of the relative intensities of the blue-green and red emissions as a function of temperature indicate that the emitting states are thermally equilibrated in fluid DMF. Combined considerations of direct spectroscopic measurements, spectroscopic measurements of analogous Rh(III) and Ir(III) complexes, and photochemical quantum yields of analogous Rh(III) and Ir(III) complexes all indicate that the lowest excited state of $\text{IrCl}_2(\text{phen})_2^+$ is a crystal field (d-d) state and that it is this state which is responsible for the near-infrared emission. Similar reasoning suggests that the crystal field state of $\text{IrCl}_2(5,6\text{-mephen})_2^+$ is nearly degenerate with the ligand-localized state. An interpretation of the spectroscopic effects observed in these complexes as well as in complexes of Re(I) displaying luminescence rigidochromism is presented. This interpretation stresses the role of orbital parentage in the application of rigid matrix perturbations to a pseudo-Jahn-Teller potential. An alternative interpretation based upon rigid matrix perturbations of a double-minima potential characteristic of transient photoisomerization is also presented. Effects arising from microenvironmental heterogeneity are divided between those in which the effects may be ascribed primarily to terms in the solute Hamiltonian and those in which large terms in the Hamiltonian for the solute-solvent interaction, such as hydrogen bonding, dominate. The effects observed for $\text{IrCl}_2(\text{phen})_2^+$ in this study fall into the former category.

I. Introduction

The photophysical¹⁻⁹ and photochemical¹⁰⁻¹⁵ properties of complexes of Ir(III) with 1,10-phenanthroline (phen) and its derivatives have been the subject of a number of recent studies. The series of complexes $\text{IrCl}_4(\text{phen})^-$, $\text{IrCl}_2(\text{phen})_2^+$, and $\text{IrCl}_2(5,6\text{-mephen})_2^+$ are particularly interesting since all three are luminescent at 77 K from states of different orbital parentage.¹⁶ Crystal field (d-d) emission is observed from [$\text{IrCl}_4(\text{phen})^-$], charge transfer (d- π^*) emission from [$\text{IrCl}_2(\text{phen})_2^+$], and ligand-localized emission from [$\text{IrCl}_2(5,6\text{-mephen})_2^+$]. This change in the character of the emission induced by the composition of the coordination sphere has been termed "tuning",¹⁶ and has been attributed to properties of the lowest excited state (les).¹⁷ Photochemical studies indicate that all three undergo photoaquation with loss of chloride in aqueous solutions.¹⁰⁻¹³ Hence, the photoluminescent tuning evidenced at 77 K is not generally reflective of the photochemical reactions prevalent near room temperature.

It is generally agreed that crystal field excited states give rise to the observed photosubstitution processes, but the location of these states relative to the luminescent states at 77 K in the cases of $\text{IrCl}_2(\text{phen})_2^+$ and $\text{IrCl}_2(5,6\text{-mephen})_2^+$ has been disputed.^{9,13} This disagreement hinges upon the relative efficiency of radiationless transitions between excited states at 77 K and near 295 K. On the one hand it has been argued that efficient energy conversion to the les occurs at 77 K; hence, the luminescent state identifies the les.¹⁷ This interpretation indicates that the crystal field states lie above the les, and photochemistry is attributed to thermal population of these levels from the lower energy d- π^* or π - π^* levels.¹³ On the other hand, it has been argued that thermal and viscoelastic barriers prevent efficient radiationless relaxation to the les at 77 K, resulting in emissions at 77 K which do not reflect the nature of the les.⁹ This interpretation maintains that the crystal field levels, which are populated by efficient radiationless

processes in fluid media near room temperature, constitute the les.⁹

Central to a resolution of this disputation are observations of photophysical properties of the complex ions in fluid solutions near room temperature. Reports of exciplex emission¹⁴ in the presence of naphthalene in DMF and crystal field emissions⁹ in glycerol have recently been attributed to impurities.⁵ Emission spectra of the purified complexes in DMF near room temperature have been reported to show only d- π^* or π - π^* excited states, as seen at 77 K.⁵ Naphthalene has been found to quench the emission of purified samples in DMF, but no new emission attributable to exciplex formation is observed.⁵ The purified samples have been reported to show no emission near room temperature in glycerol.⁵

In this paper we report further photophysical studies of carefully purified samples of $\text{IrCl}_2(\text{phen})_2^+$ and $\text{IrCl}_2(5,6\text{-mephen})_2^+$ in fluid solutions. These studies provide additional evidence in support of identification of the les of these complexes as crystal field states.

II. Experimental Section

Preparation and Purification of Complexes. *cis*-Dichlorobis(1,10-phenanthroline)iridium(III) chloride trihydrate, [$\text{IrCl}_2(\text{phen})_2$]Cl·3H₂O, was prepared by the method of Bromhead and Grumley¹⁰ by refluxing (phen)H[$\text{IrCl}_4(\text{phen})$] in glycerol for 1 min. Purification was carried out by repeated recrystallization from dilute HCl as described previously⁹ followed by repeated recrystallization from methanol as described more recently.⁵ In agreement with the recent report that recrystallization from methanol leads to improved purification, progressive changes in the emission spectrum in fluid DMF were observed following the first five recrystallizations. In particular, each successive crystalline crop showed an increase in the I_{max}/I_{580} ratio (where I_{max} and I_{580} are the emission intensities at the band maximum and at 580 nm, respectively) as previously reported. No substantial changes in the I_{max}/I_{740} ratio were observed during the purification procedure. Emission spectra of the first four crystalline crops were different from those of the mother liquor from

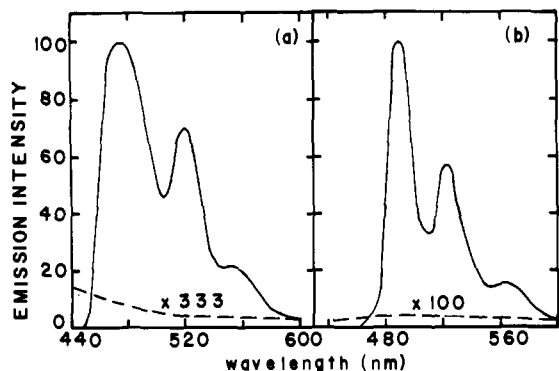


Figure 1. Uncorrected emission spectra of IrCl₂(phen)₂⁺ (a) and IrCl₂(5,6-Mephen)₂⁺ (b) in glycerol at 77 (—) and 295 K (---) monitored with the Perkin-Elmer MPF-3.

which they were taken. In each case the mother liquors showed a smaller I_{\max}/I_{580} ratio than the crystalline crop. After the first five recrystallizations no further changes occurred in the I_{\max}/I_{580} ratios (three additional recrystallizations were performed). No differences in the emission spectra of the mother liquor and crystalline fractions could be detected following the fifth through eighth recrystallizations.

cis-Dichlorobis(5,6-dimethyl-1,10-phenanthroline)iridium(III) chloride trihydrate, [IrCl₂(5,6-Mephen)₂]Cl·3H₂O, was prepared and initially purified in an analogous manner to that described above. Final purification was accomplished by repeated recrystallization from water-methanol mixtures owing to the excessive solubility of the complex in methanol. The purity of successive crystalline crops was followed by monitoring emission spectra in DMF as described above. No changes were observed after five recrystallizations on samples recrystallized a maximum of eight times.

Excitation spectra of both samples were measured at emission wavelengths of 480 and 680 nm. In each case the excitation spectrum at the shorter wavelength was found to be identical with that at the longer wavelength over the excitation range of 300–450 nm. This provides further confirmation of the purity of the samples used in the study.

Apparatus and Solvents. Both corrected and uncorrected emission spectra were determined on two spectrophotofluorimeters: (1) a Perkin-Elmer Hitachi MPF-3 equipped with a Hamamatsu R-446 multi-alkali photomultiplier tube and an automatic emission spectrum corrector (this apparatus was used for emission measurements in the region 400–700 nm); (2) a specially constructed red-sensitive apparatus employing an RCA7102 dry ice cooled photomultiplier tube and lock-in amplification (this apparatus, which has been described in detail previously,¹⁸ was used for emission measurements in the region 450–1100 nm). Excitation spectra used to confirm sample purity were all recorded with the former apparatus. Emission lifetimes were measured by excitation at 337 nm with an Avco C950 pulsed nitrogen laser. The laser pulse was filtered by two Corning 5840 glass filters and a 3-cm CuSO₄ filter to remove red light from the nitrogen discharge. Emitted light centered around 497 nm was isolated with a Balzers 497-nm narrow band-pass filter and three Corning 3387 glass filters. Emitted light centered around 703 nm was isolated with a Balzers 703-nm narrow band-pass filter and a combination of Corning 2403, 2408, and 2412 glass filters. Emission intensity as a function of time was detected with a dry ice cooled Amperex 56TVP photomultiplier and monitored with a Tektronix type 549 oscilloscope.

Selected temperatures between 77 and 273 K were maintained with low-temperature baths prepared from dry ice-ethanol (201 K), dry ice-acetonitrile (231 K), or dry ice-carbon tetrachloride (250 K). Temperatures between 273 and 373 K were maintained with a Haake FK thermostated circulating bath. All solvents were either reagent or spectroquality grade and were used without further purification. In order to establish the absence of effects attributable to water or other impurities in the Mallinckrodt reagent grade DMF used in the study, this solvent was dried over Linde Type 4A Molecular Sieve and vacuum distilled twice. The middle of three fractions was retained in each distillation for subsequent redistillation or final checks of impurity effects. Emission spectra of both of the Ir(III) complexes measured in the dry, purified DMF at room temperature were found

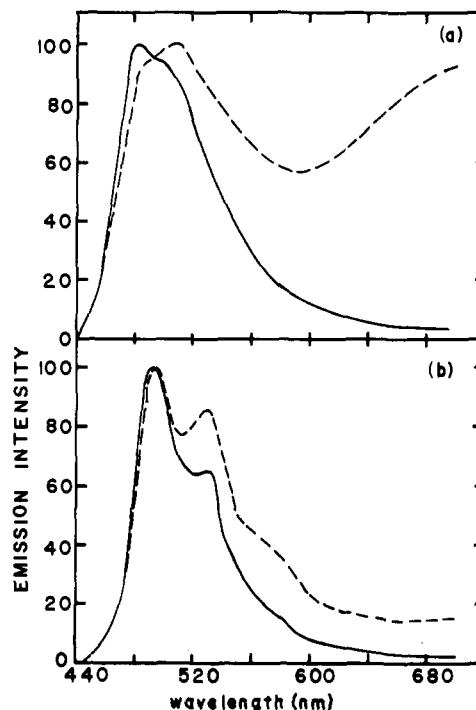


Figure 2. Uncorrected emission spectra (—) and corrected emission spectra (---) of IrCl₂(phen)₂⁺ (a) and IrCl₂(5,6-Mephen)₂⁺ (b) in DMF at 295 K monitored with the Perkin-Elmer MPF-3.

to be identical with those measured in reagent grade DMF with both sets of emission apparatus described above. Furthermore, DMF solvent blanks showed no detectable emission under equivalent excitation and attenuation conditions as used in the measurement of the complex emissions with either the Hitachi (400–700 nm) or the red-sensitive apparatus (450–1100 nm).

III. Results

A. Uncorrected Emission Spectra. Figure 1 shows uncorrected emission spectra of the two complex ions in glycerol at 77 and 295 K as measured with the Perkin-Elmer Hitachi MPF-3 spectrophotofluorimeter. Uncorrected emission spectra in deaerated DMF solutions at 295 K are shown in Figure 2. These results are in good agreement with the emission spectra of Ballardini et al. for highly purified samples of the complex ions (samples B).⁵ Small variations between the two sets of results are probably due to the additional red sensitivity of the R-446 photomultiplier tube used in this study compared to the R-106 photomultiplier tube used by Ballardini et al. Addition of 0.5 M naphthalene to DMF solutions of the complexes resulted in substantial quenching but no change in the structure of the emission in agreement with previous results (samples B).⁵

B. Corrected Emission Spectra. (1) Fluid DMF. Figure 2 shows corrected emission spectra of the two complexes in deaerated DMF solutions at 295 K as measured with the Perkin-Elmer Hitachi MPF-3. The spectrum of IrCl₂(phen)₂⁺ clearly suggests an emission band which maximizes at wavelengths beyond the range of the instrument (>700 nm). Some evidence of this is also found in the corrected emission of IrCl₂(5,6-Mephen)₂⁺, though the long-wavelength emission is somewhat less intense than in the former complex.

The corrected emission spectra in DMF at 231, 295, and 352 K measured with the S-1 photomultiplier tube using lock-in amplification are shown in Figure 3. In measurements with this instrumentation the red emission intensity appears far greater than the green intensity in the uncorrected spectra due to the enhanced red response of the S-1 photomultiplier. This further illustrates the dependence of the appearance of raw emission

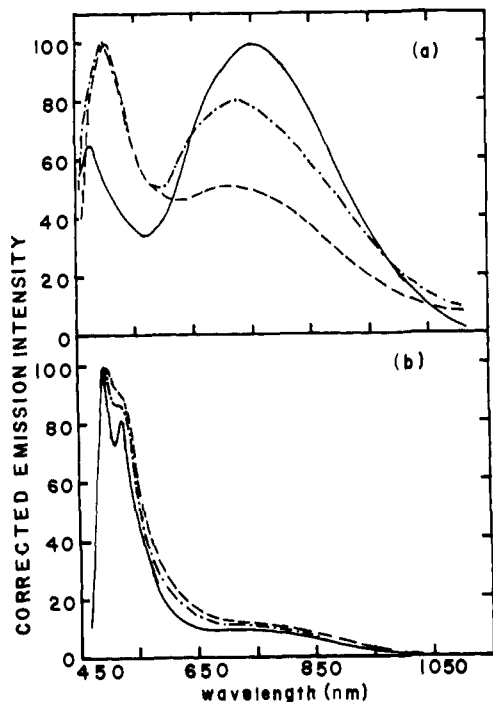


Figure 3. Corrected emission spectra of IrCl₂(phen)₂⁺ (a) and IrCl₂(5,6-Mephen)₂⁺ (b) in DMF at 231 (—), 295 (---), and 352 K (- · - ·) monitored with the red-sensitive apparatus.

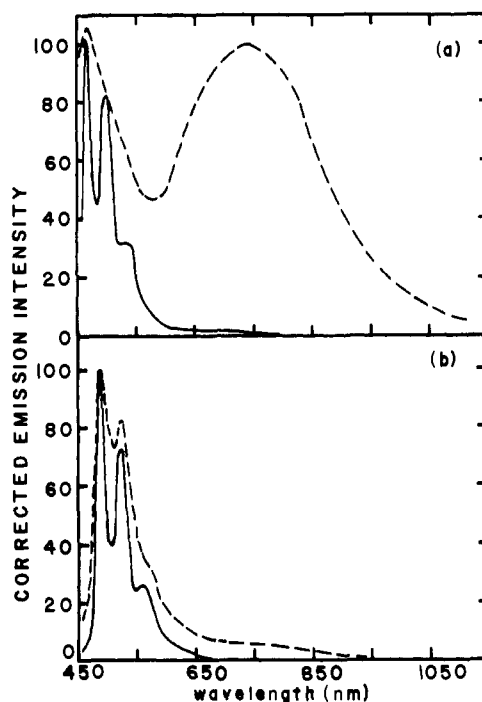


Figure 4. Corrected emission spectra of IrCl₂(phen)₂⁺ (a) and IrCl₂(5,6-Mephen)₂⁺ (b) in crystalline DMF at 77 (—) and 201 K (---) monitored with the red-sensitive apparatus.

data on instrumentation. The corrected spectra illustrate that a broad red emission is observed in both complexes with a maximum in the region of 730–740 nm. This emission is more intense relative to the green emission in IrCl₂(phen)₂⁺ than is the case in IrCl₂(5,6-Mephen)₂⁺ over the temperature range 231–352 K; furthermore, the ratio of the green to red emission intensity, I_g/I_r , displays a different functional relationship on temperature for the two complexes. The ratio increases substantially with increasing temperature in the former while a small decrease occurs in the latter complex.

In order to check for possible photodimerization or acid-base equilibria in the excited state, corrected emission spectra of IrCl₂(phen)₂⁺ were recorded at several different concentrations and with added HCl in DMF. The shape of the emission spectrum and the I_g/I_r ratio in DMF at 295 K were found to be independent of concentration over the range 10⁻³–10⁻⁴ M and independent of added HCl over the range 0–1.0 M at a complex concentration of 10⁻⁴ M.

(2) **Crystalline DMF.** Emission spectra of the two complexes in crystalline DMF at 201 and 77 K are illustrated in Figure 4. A reversal in the temperature dependence of I_g/I_r relative to that observed in fluid DMF is evident for IrCl₂(phen)₂⁺; I_g/I_r increases to 1.06 at 201 K in crystalline DMF relative to 0.65 at 231 K in fluid DMF and becomes nearly 100 at 77 K. In the case of IrCl₂(5,6-Mephen)₂⁺, I_g/I_r increases with decreasing temperature in both crystalline and fluid DMF. However, the increase is much more rapid in crystalline DMF than is the case in fluid DMF.

(3) **Glycerol.** Although the samples used in this study showed no detectable emission at 295 K when the Perkin-Elmer Hitachi MPF-3 was used with the amplification factors indicated by Ballardini⁵ et al. (vide supra), emission spectra in glycerol at 295 K could be readily detected with the red-sensitive apparatus. An amplification of about 5000× that used for measurements at 77 K was used in these measurements. Both complexes were found to be photoactive in glycerol at 295 K as evidenced by an increase in emission intensity in the 550–600-nm region when wide slits (10 mm) were used on the excitation monochromator. The spectra in Figure 5 were

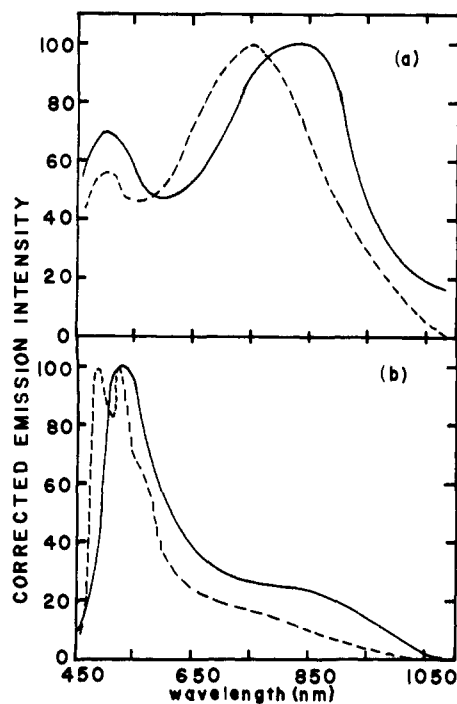


Figure 5. Corrected emission spectra of IrCl₂(phen)₂⁺ (a) and IrCl₂(5,6-Mephen)₂⁺ (b) in glycerol at 250 (---) and 295 K (—) monitored with the red-sensitive apparatus.

monitored using 3-mm excitation slits as well as two 3-cm CuSO₄ filters and one Corning 5840 glass filter. Under these excitation conditions consecutive emission spectra of the same samples were found to be identical, indicating no detectable photolysis. At temperatures above 295 K (~350 K) both complexes were found to be too photoactive to monitor reliable emission data. At lower temperatures an increase in the I_g/I_r ratio was evident for IrCl₂(5,6-Mephen)₂⁺ while I_g/I_r de-

creased for $\text{IrCl}_2(\text{phen})_2^+$. This is illustrated in Figure 5 by spectra monitored at 250 K.

C. Luminescence Decay Measurements. Decay curves for the green and red emissions of both complexes were monitored in deaerated DMF solutions at 295 K. In each instance the luminescence decay times were found to be identical within experimental error for the two emissions. Luminescence lifetimes of 324 ± 15 ns for $\text{IrCl}_2(\text{phen})_2$ and 840 ± 35 ns for $\text{IrCl}_2(5,6\text{-Mephen})_2$ determined in this study are in good agreement with the values of 310 and 860 ns reported by Baldardini⁵ et al.

Luminescence lifetimes were found to increase with decreasing temperature in fluid DMF over the temperature range 231–295 K. The green and red emissions of each complex were found to have identical lifetimes over this entire temperature range. At 231 K the lifetime of $\text{IrCl}_2(\text{phen})_2^+$ was found to be 534 ± 20 ns and that of $\text{IrCl}_2(5,6\text{-Mephen})_2^+$ was 1470 ± 65 ns.

In crystalline DMF the luminescence decay kinetics of both complexes was found to be far more complicated than in fluid solutions. The green and red emissions of each complex were characterized by different lifetimes in DMF at 201 K. In both cases the red emission was found to decay more rapidly than the green emission and the decay curves for each emission were clearly nonexponential. Limiting lifetimes taken from the tail of the decay curves were about $3.2 \mu\text{s}$ for the green and $0.78 \mu\text{s}$ for the red emission of $\text{IrCl}_2(\text{phen})_2^+$ and $3.2 \mu\text{s}$ for the green and $1.5 \mu\text{s}$ for the red emission of $\text{IrCl}_2(5,6\text{-Mephen})_2^+$.

At 77 K no red emission was observable from $\text{IrCl}_2(5,6\text{-Mephen})_2^+$ and the green emission displayed a nonexponential decay curve with a limiting lifetime of about $140 \mu\text{s}$. Both green and red emissions were observable from $\text{IrCl}_2(\text{phen})_2^+$ at 77 K. The green emission decayed nonexponentially with a limiting lifetime of $7.8 \mu\text{s}$. The limiting lifetime of the red emission was about the same as that of the green emission at this temperature. It is interesting to note that the initial segment of the decay curve for the green emission was characterized by a more rapid decay than observed in the tail whereas the initial segment of the decay curve for the red emission clearly showed a rise time. A typical intensity vs. time profile for the red emission is illustrated in Figure 6. Plots of log intensity vs. time indicate that the red emission intensity departs from exponential behavior for about the first $3 \mu\text{s}$ following excitation, after which a nearly exponential decay occurs. Similar intensity-time profiles were observed in glycerol at 77 K where a definite rise time followed by an exponential decay was observed for the red emission. In this solvent the limiting lifetimes for the red and green emissions were slightly different; lifetimes of about $7.6 \mu\text{s}$ for the green and $5.9 \mu\text{s}$ for the red emissions were observed.

IV. Discussion

A. Location of the Lowest Energy Crystal Field States of $\text{IrCl}_2(\text{phen})_2^+$ and $\text{IrCl}_2(5,6\text{-Mephen})_2^+$. The energies of d^6 metal complexes have generally been determined directly by measurements of emission spectra. In cases where the emissions originate from crystal field states, corrections for large Stokes shifts are required to locate zero-zero energies of the highly distorted excited states.¹⁹ Owing to the complicated nature of the emissions of $\text{IrCl}_2(\text{phen})_2^+$ and $\text{IrCl}_2(5,6\text{-Mephen})_2^+$ it is apparent that all possible sources of relevant information should be brought to bear on the location and identification of the les. Therefore the following three sources of information will be considered in this discussion: (1) direct observations by emission spectroscopy; (2) comparison with observation of energies of crystal field excited states in analogous complexes; (3) comparison of photoaquation quantum yields of these and analogous complexes.

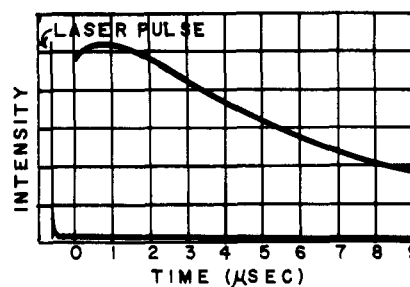


Figure 6. Intensity vs. time profile for the rise and fall of the red emission of $\text{IrCl}_2(\text{phen})_2^+$ in crystalline DMF at 77 K.

Table I. Crystal Field Emission Maxima and Estimated Zero-Zero Energies (μm^{-1}) of Analogous Rh(III) and Ir(III) Complex Ions

complex ion	M = Rh(III)		M = Ir(III)	
	E_{max}	E_{0-0}^a	E_{max}	E_{0-0}^a
<i>trans</i> - $\text{MCl}_2(\text{en})_2^+$	1.45 ^b	1.72	1.45 ^b	
<i>cis</i> - $\text{MCl}_4(\text{phen})_2^-$	1.17 ^c	1.60	1.11 ^c	1.51
<i>cis</i> - $\text{MCl}_4(5,6\text{-Mephen})_2^-$	1.15 ^c	1.53	1.05 ^c	1.47
$\text{M}(\text{acac})_3$	1.18 ^d		1.13 ^d	
$\text{M}(\text{en})_3^{3+}$	1.70 ^b	2.09	1.68 ^b	2.09

^a Estimated from half-widths, $E_{1/2}$. See ref 20. ^b See ref 1. ^c See ref 22. ^d G. A. Crosby, R. J. Watts, and S. J. Westlake, *J. Chem. Phys.*, **55**, 4663 (1971).

(1) **Direct Observations by Emission Spectroscopy.** It is clear that repeated recrystallizations of these complexes lead to removal of a small amount of impurity which emits strongly in fluid solutions in the region of 580 nm. The emission in the region of 740 nm is not affected by this purification process. Observation of these broad, red emissions is strongly dependent upon the use of detectors which are sensitive in the region 700–1100 nm. The previous failure to observe these emissions⁵ appears to be due to a lack of adequate instrumentation.

The broad, red emissions of these complexes are believed to arise from crystal field states. The present study shows that the red emissions lie at lower energies than indicated by the previous study.⁹ From the band maximum for the red emission of $\text{IrCl}_2(\text{phen})_2^+$ in DMF at 231 K ($1.35 \mu\text{m}^{-1}$, Figure 3) and the half-width of the emission band ($0.53 \mu\text{m}^{-1}$), the zero-zero energy of the crystal field state is estimated^{20,21} to be $2.03 \mu\text{m}^{-1}$; a similar estimate is made for $\text{IrCl}_2(5,6\text{-Mephen})_2^+$. The energy of the charge-transfer state of $\text{IrCl}_2(\text{phen})_2^+$ is estimated⁶ to be $2.14 \mu\text{m}^{-1}$ and the $\pi\pi^*$ state of $\text{IrCl}_2(5,6\text{-Mephen})_2^+$ lies at $2.05 \mu\text{m}^{-1}$.⁷ Hence, the data taken directly from the band positions and bandwidths suggest that the crystal field state lies 1100 cm^{-1} below the charge-transfer states of $\text{IrCl}_2(\text{phen})_2^+$ and 200 cm^{-1} below the $\pi\pi^*$ levels of $\text{IrCl}_2(5,6\text{-Mephen})_2^+$.

Since the lifetimes for the green and red emissions are identical in fluid DMF, the states from which these emissions originate are in thermal equilibrium under these conditions. Plots of $\log I_g/I_r$ vs. $1/T$ yield good straight lines for both complexes over the range 231–355 K in DMF. From these plots the crystal field levels are estimated to lie 500 cm^{-1} below the charge-transfer state of $\text{IrCl}_2(\text{phen})_2^+$ and 100 cm^{-1} above the $\pi\pi^*$ state of $\text{IrCl}_2(5,6\text{-Mephen})_2^+$.

(2) **Estimation of the Energies of the Crystal Field States by Comparison to Analogous Complexes.** There are presently a sufficient number of results published in the literature to make reasonable estimates of crystal field emission energies of Ir(III) complexes by comparison with analogous Rh(III) complexes. A listing of emission data for several such analogous pairs is presented in Table I. For each pair both the Ir(III) and Rh(III)

emission has been assigned to a crystal field transition. On the basis of this table it appears that an appropriate rule of thumb is that the crystal field emission maxima of Ir(III) complexes lie at about the same energy or slightly lower than those of analogous Rh(III) complexes. In cases where emission bandwidths are available, zero-zero energies have also been listed in Table I. The same rule of thumb apparently applies to zero-zero energies of analogous Ir(III) and Rh(III) complexes.

The band maximum for the red emission of $\text{IrCl}_2(\text{phen})_2^+$ lies at $1.35 \mu\text{m}^{-1}$ in excellent agreement with the value of $1.37 \mu\text{m}^{-1}$ for $\text{RhCl}_2(\text{phen})_2^+$.^{1,21} Measurements of the emission of $\text{RhCl}_4(5,6\text{-Mephen})_2^-$ indicate that the methyl ligand substituents have little effect on the crystal field emission.²² Hence, the emission band maximum of $\text{IrCl}_2(5,6\text{-Mephen})_2^+$ should lie close to $\text{IrCl}_2(\text{phen})_2^+$ as observed. From the published zero-zero energy of $\text{RhCl}_2(\text{phen})_2^+$ of $1.68 \mu\text{m}^{-1}$, the zero-zero energy for the lowest crystal field state of $\text{IrCl}_2(\text{phen})_2^+$ is estimated to be slightly less than $1.68 \mu\text{m}^{-1}$. Hence, the value of $2.03\text{--}2.09 \mu\text{m}^{-1}$, extracted from direct emission measurements, is much higher than comparison to analogous Rh(III) complexes would suggest. This is due to the much larger Stokes shift parameter used for $\text{IrCl}_2(\text{phen})_2^+$ ($0.68 \mu\text{m}^{-1}$) than for $\text{RhCl}_2(\text{phen})_2^+$ ($0.31 \mu\text{m}^{-1}$).

In summary, it appears that the red emission band maxima of these Ir(III) complexes lie exactly where crystal field band maxima would be expected by analogy with other Rh(III) and Ir(III) complexes. Comparison with emission data of analogous complexes suggests that it is not at all surprising that the zero-zero energies of these levels lie close to or below the charge-transfer and $\pi\pi^*$ levels; rather, it is surprising that they lie as high in energy as the direct emission measurements suggest.

(3) Considerations of Photoaquation Quantum Yields in the Estimation of the Energy of the Crystal Field Levels. Previous studies indicate that both $\text{IrCl}_2(\text{phen})_2^+$ and $\text{IrCl}_2(5,6\text{-Mephen})_2^+$ undergo photoaquation in aqueous solutions with loss of Cl^- ¹⁰⁻¹³ due to population of crystal field levels. The central question relevant to the location of these levels relates to the intrinsic reactivity they might be expected to have. A tabulation of pertinent photoaquation data is presented in Table II.

When compared with other Ir(III) complexes with crystal field levels and with the analogous $\text{RhCl}_2(\text{phen})_2^+$ complex, there appears to be nothing at all unusual about $\text{IrCl}_2(\text{phen})_2^+$.

If the reactive crystal field levels of this complex were above the charge transfer state, the relative population of these levels would be limited in accordance with the Boltzmann distribution. This would lead to very low photoaquation quantum yields unless the intrinsic reactivity of the crystal field levels was very high. However, there is nothing in Table I which suggests that the photoreactivity of crystal field levels in similar Ir(III) complexes is particularly high. Hence, the photoaquation data support the assignment of the levels of $\text{IrCl}_2(\text{phen})_2^+$ as a crystal field state.

B. Application of Rigid Matrix Perturbations of Molecular Potentials to an Interpretation of the Luminescence Rigido-chromic Effect. It is apparent that the photophysical properties of several d^6 metal complexes, including $\text{IrCl}_2(\text{phen})_2^+$ and $\text{IrCl}_2(5,6\text{-Mephen})_2^+$, are strongly dependent upon viscoelastic parameters of the solvent medium. A large amount of work in this area has been done by Wrighton and co-workers, who have coined the term "rigido-chromic effect" to describe a large change in color of an emission with a change in the rigidity (viscoelasticity) of the solvent medium.²³ Complexes of the type $\text{ClRe}(\text{CO})_3\text{X}$ (X = phen or substituted phen) were first put forth as examples displaying the rigido-chromic effect, and both the rigid and nonrigid emissions are believed to arise from charge-transfer transitions.²³ Similar effects are observed in

Table II. Photoaquation Quantum Yields of Analogous Rh(III) and Ir(III) Complexes

complex ion	M = Rh	M = Ir
<i>trans</i> - $\text{MCl}_2(\text{en})_2$	0.086 ± 0.04^a	$0.089\text{--}0.16^b$
<i>trans</i> - $\text{MCl}_2(\text{py})_4$	0.024 ± 0.012^a	$0.036\text{--}0.065^b$
$\text{MCl}_2(\text{bpy})_2$	0.03 ± 0.015^a	$0.027\text{--}0.049^b$
$\text{MCl}_2(\text{phen})_2$	0.02 ± 0.01^a	0.05^c
$\text{M}(\text{NH}_3)_5\text{Cl}$	0.16^d	0.13^e

^a M. M. Muir and W. L. Henry, *Inorg. Chem.*, **12**, 1831 (1973).

^b See ref 12. ^c See ref 13. ^d T. L. Kelly and J. F. Endicott, *J. Phys. Chem.*, **76**, 1937 (1972). ^e A. W. Zanella, M. Talebinasab-Sarvari, and P. C. Ford, *Inorg. Chem.*, **15**, 1980 (1976).

$\text{Ir}(\text{OH})_2(\text{bpy})_2^+$ and in $\text{IrCl}(\text{OH})(\text{bpy})_2^+$ where large red shifts in the emissions accompany transitions from rigid to nonrigid media, and both the rigid and nonrigid emissions are attributed to charge-transfer states.⁸

Recent reports²⁴ indicate that *fac*- $\text{ClRe}(\text{CO})_3\text{L}_2$ (L = 4-phenylpyridine) emits from a $\pi\pi^*$ state at 77 K and from a charge-transfer state at 298 K, suggesting that both temperature and viscoelasticity may affect the nature of the emission. Still more recent studies²⁵ of *fac*- $\text{XRe}(\text{CO})_3(3\text{-benzoylpyridine})_2$ complexes (X = Cl, Br) indicate that charge-transfer emission is observed at 298 K while both $n\text{-}\pi^*$ intraligand and charge-transfer emissions are observed at 77 K. The results presented in this study indicate that $\text{IrCl}_2(\text{phen})_2^+$ and $\text{IrCl}_2(5,6\text{-Mephen})_2^+$ emit primarily from charge-transfer or $\pi\pi^*$ states at low temperatures (rigid media) while enhanced crystal field emissions are observed at higher temperatures (fluid media).

The similarity between various examples of the rigido-chromic effect displayed by Re(I) and Ir(III) complexes is striking. The examples cited above suggest that the orbital parentage of the rigid and nonrigid emissions provides a convenient basis for discussing the origin of the effect. On the one hand the parentage of the two emissions may be the same [e.g., $\text{ClRe}(\text{CO})_3(\text{phen})$ or $\text{Ir}(\text{OH})_2(\text{bpy})_2^+$] or on the other hand they may be different [e.g., *fac*- $\text{ClRe}(\text{CO})_3(4\text{-phenylpyridine})_2$ or $\text{IrCl}_2(\text{phen})_2^+$].

A general discussion of the phenomenology of solvent matrix spectroscopic effects has been presented by Dellinger and Kasha.²⁶ An application of their discussion to interpretation of the rigido-chromic effect, with emphasis on the present study, will now be given.

(1) The Pseudo-Jahn-Teller Potential. The pseudo-Jahn-Teller potential, illustrated in Figure 7, has been used previously²⁷⁻²⁹ to describe vibronic interactions which lead to a splitting of quasi-degenerate states. The pseudo-Jahn-Teller potential is particularly useful in describing the rigido-chromic effect in those cases where emissions in rigid and nonrigid media are ascribed to states of different orbital parentage. This derives from the fact that differences in geometry are likely to be associated with differences in orbital parentage—hence the concept of orbital parentage generally provides a simple qualitative measure of the geometric distortion along Q requisite to the application of this potential.

With regard to the present study, the excited state, E, is identified with the charge-transfer state of $\text{IrCl}_2(\text{phen})_2^+$ or the $\pi\pi^*$ state of $\text{IrCl}_2(5,6\text{-Mephen})_2^+$, while E' is identified as the crystal field state in each case. Under the influence of a rigid matrix perturbation the additional barrier (dotted line) indicated in Figure 7 is presumed to be present, and thermal equilibration between E and E' over the range 77-241 K does not occur in DMF. Above the melting point of DMF the rigid matrix perturbation of the pseudo-Jahn-Teller potential is removed, and sufficient thermal energy is available to surmount the intrinsic molecular potential for conversion of E to

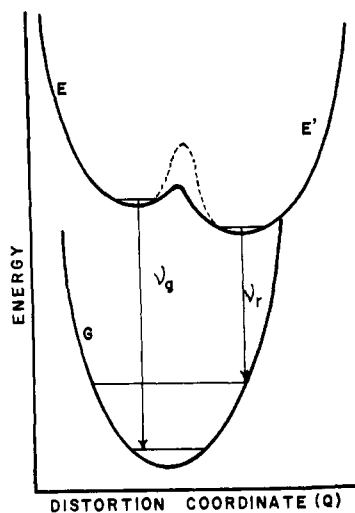


Figure 7. The pseudo-Jahn-Teller potential.

E' . The equivalent lifetimes for the green and red emissions under these circumstances indicate that the rate constants for interconversion of E and E' greatly exceed the rate constants for their return to the ground state.

The feasibility of application of a rigid matrix perturbation to the pseudo-Jahn-Teller potential is dependent upon the nature of the nuclear motions which take E to E' along Q . Implicit in the application is the assumption that the macroscopic viscosity or elasticity is a measure of this perturbation. While this is appropriate for large skeletal configuration changes, small amplitude motions by individual nuclei are unlikely to be affected by rigid matrix perturbations. Recent treatments of photosolvation processes in d^6 metal complexes³⁰ suggest that crystal field excitation of a species with symmetry of $\text{IrCl}_2(\text{phen})_2^+$ should lead to distortion in the weak field plane described by the two chlorides and the nitrogen atoms trans to them owing to population of the σ^* orbital in this plane. In this case, additional distortion of the metal ligand framework would arise from loss of π bonding to the portions of the two phenanthroline ligands lying close to the weak field plane. As a result, substantial movement of the phenanthroline ligands is anticipated to be required to reach the equilibrium nuclear configuration of the crystal field state from the charge-transfer state. Viscoelastic barriers to motions of this type are believed to give rise to the rigid-matrix perturbation depicted in Figure 7.

(2) The Double-Minimum Potential. Rigid matrix perturbations of a double minima potential²⁶ (Figure 8) have been used to describe spectroscopic phenomena associated with hydrogen bonding in the biprotonic photoautomerism of 7-azaindole.^{31,32} This potential is generally applicable to a description of the rigidochromic effect in situations where distinct chemical isomers are possible in both the ground and excited states.

Little is known with regard to possible isomerization processes in $\text{IrCl}_2(\text{phen})_2^+$, and there is no evidence for isomerization in the ground state. As depicted in Figure 8, an isomer which is unstable in the ground state may become the more stable of two isomers in the excited state. Whether or not isomerization to the more stable excited state isomer could occur would depend on the magnitude of the barrier introduced to the potential by a rigid matrix perturbation.

The application of this model to the rigidochromic effect in $\text{IrCl}_2(\text{phen})_2^+$ hinges upon a presumed reversible photoisomerization in the excited state. While no such process is known, one may conceive of a process similar to the covalent hydration equilibria used by Gillard³³ to explain a number of

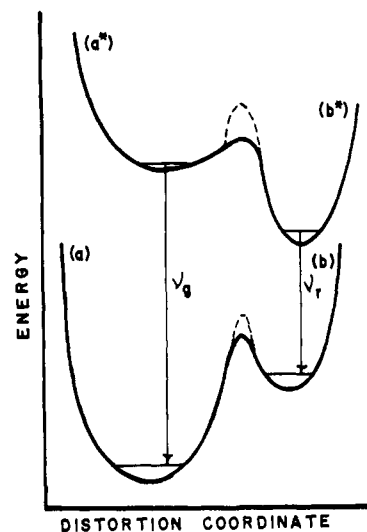
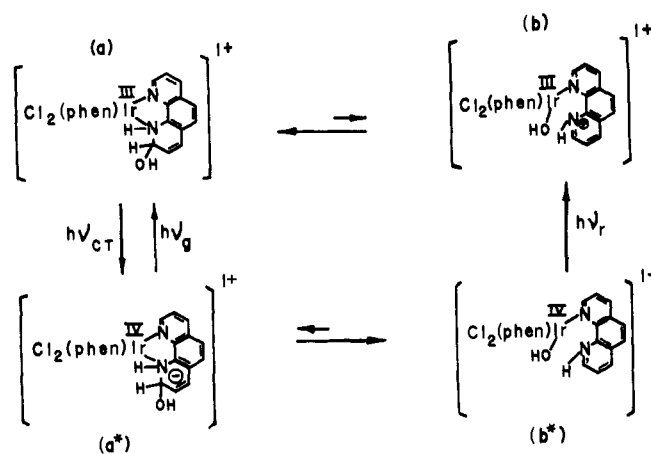


Figure 8. The double minima potential.

Figure 9. Hypothetical photoisomerization of the covalent hydrate of $\text{IrCl}_2(\text{phen})_2^+$.

anomalous properties of 2,2'-bipyridine metal complexes. Assume that ground-state $\text{IrCl}_2(\text{phen})_2^+$ exists primarily in the form of the covalent hydrate indicated by structure "a" in Figure 9. Formation of the charge-transfer excited state may be formally described as oxidation of Ir(III) to Ir(IV) and reduction of phen to phen⁻. On the basis of simple electrostatics it is apparent that structure "b" would be stabilized in this excited state. The green emission would be assigned to a charge-transfer transition between the "a" isomers while the red emission would arise from a charge-transfer transition between the "b" isomers. Since formation of the "b" isomer in the ground state would be followed by rapid equilibration to give the "a" isomer, no net photoisomerization would occur even though transient photoisomerization might occur with a high yield.

While the phenomenological basis for the application of the pseudo-Jahn-Teller potential and the double-minima potential finds common ground in the rigidochromic effect, it is apparent that distinctions exist in the conceptual basis for these two models. In particular, *transient photophysical* processes whose rates are dependent upon rigid-matrix perturbations characterize the former while rigid matrix-dependent *transient photochemical* processes are associated with the latter. The present study indicates that no concentration effect on I_g/I_r occurs over the range 10^{-3} – 10^{-4} M in DMF and that I_g/I_r is the same in neat DMF at 298 K and in DMF with added 1.0 M HCl at 298 K. It is difficult to conceive of an equilibrium

process associated with covalent hydration which would show no pH effect under the conditions studied. Equally relevant are considerations of the lack of any rigidochromic effect in similar complexes of Ir(III). For example, the $\text{Ir}(\text{bpy})_3^{3+}$ and $\text{Ir}(\text{bpy})_2(\text{H}_2\text{O})(\text{bpy})^{3+}$ complex ions have very similar emissions in rigid media at 77 K and in fluid solutions at 298 K.⁸ This suggests that the effect is related to physical features of the excited states rather than chemical features of both the ground and excited states.

(3) Microenvironmental Heterogeneity and Its Relationship to the Luminescence Rigidochromic Effect. The term microenvironmental heterogeneity has been used to describe situations in which a spectroscopic property, generally emission wavelength or lifetime, displays a range of values for a given solute in a polar solvent owing to inhomogeneous solute-solvent interactions.^{34,35} Generally, solvent reorientation in rigid media is slow relative to excited state lifetimes and microenvironmental heterogeneity gives rise to observable effects; in fluid media these effects generally disappear owing to rapid solvent reorientation, although solvent reorientation times in excess of 0.1 μs in fluid glycerol-water solutions at room temperature have recently been proposed.³⁶

The relationship between microenvironmental heterogeneity and luminescence rigidochromism may be conveniently divided into two categories: (1) situations where the rigidochromic effect is associated with a large change in molecular geometry as dictated either by orbital parentage changes (pseudo-Jahn-Teller potential) or transient photoisomerization (double minima potential); (2) situations where no large geometry changes are dictated by the solute.

Consider first the function of microenvironmental heterogeneity in cases where large changes in molecular geometry are associated with the luminescence rigidochromic effect, as in $\text{IrCl}_2(\text{phen})_2^+$, $\text{IrCl}_2(5,6\text{-Mephen})_2^+$, and $\text{fac-ClRe}(\text{CO})_3\text{L}_2$. It is evident that large differences in the dimensions and composition of the primary solvation sphere are likely to characterize the two emitting states or species. In this case the major terms dictating the origin of the different emissions in rigid and nonrigid media originate in the free solute. The importance of microenvironmental heterogeneity terms arises primarily from considerations of additional potential barriers (dotted lines in Figures 7 and 8), which may have a dominant influence on the rate of conversion from one state or species to another, but which are not responsible for the basic energy differences of the two emissions.

Now consider category 2 in which no large geometry changes in the rigid and nonrigid emissions are dictated by intramolecular terms. Examples of molecules in this classification displaying the rigidochromic effect are $\text{ClRe}(\text{CO})_3(\text{phen})$, $\text{Ir}(\text{OH})_2(\text{bpy})_2^+$, and $\text{Ir}(\text{OH})(\text{Cl})(\text{bpy})_2^+$, in which both the rigid and nonrigid emissions arise from charge-transfer states. The change in emission energy in these cases is due to large solute-solvent interactions such as those associated with hydrogen bonding. It is interesting to note that both $\text{Ir}(\text{OH})_2(\text{bpy})_2^+$ and $\text{IrCl}(\text{OH})(\text{bpy})_2^+$ show nonexponential luminescence decays in rigid media as well as rigidochromic effects. In both cases this has been attributed to hydrogen-bonding interactions of coordinated hydroxide with the polar solvent environment.

C. Energy Transfer in $\text{IrCl}_2(\text{phen})_2^+$ and $\text{IrCl}_2(5,6\text{-Mephen})_2^+$ —the Molasses Will Not Pour on a Cold Day. Remember when you were a kid and you got up one cold winter morning to find you could not pour the molasses on your pancakes because it was in the refrigerator all night? Well, spectroscopists, including this one, have kept metal complexes in the refrigerator for a lot of nights. It appears that sometimes energy, like molasses, will not flow when it is cold, and we have been eating our pancakes without molasses.

Previous studies of radiationless transitions in complexes

of $\text{Rh}(\text{III})^{37-39}$ and $\text{Ir}(\text{III})^{40-42}$ have indicated that energy transfer between excited states may be slow under certain combined conditions. These conditions may be divided broadly into intramolecular considerations and environmental considerations.

(1) Intramolecular Factors in the Decay of $\text{IrCl}_2(\text{phen})_2^+$ and $\text{IrCl}_2(5,6\text{-Mephen})_2^+$. Previous studies of complexes of $\text{Rh}(\text{III})$ and $\text{Ir}(\text{III})$ indicate that a necessary but not sufficient condition for slow energy transfer between excited states is that they have different orbital parentage. For example, show radiationless processes in $[\text{IrCl}_2(\text{phen})(5,6\text{-Mephen})]^+$ are associated with charge-transfer and $\pi-\pi^*$ states⁴¹ while dual emissions from $\pi\pi^*$ orbitals localized on bpy and phen are seen³⁷⁻³⁹ in $\text{Rh}(\text{bpy})_n(\text{phen})_{3-n}^{3+}$ ($n = 1$ or 2). It is relevant that the nonequilibrated states were found to be separated by small energy gaps of 100–300 cm^{-1} . While the exact magnitude of the energy gap necessary for slow radiationless transitions is likely to vary, it appears that small energy gaps are likely to be a second necessary but not sufficient intramolecular condition. In this context, $\pi\pi^*$ states localized on bpy and 5,6-Mephen in $\text{Rh}(\text{bpy})_n(5,6\text{-mephen})_{3-n}^{3+}$, which are separated by a $\sim 1600\text{-cm}^{-1}$ energy gap, have been found to undergo rapid interconversion.³⁹ From direct measurements of the emission properties of $\text{IrCl}_2(\text{phen})_2^+$ and $\text{IrCl}_2(5,6\text{-Mephen})_2^+$, the relevant energy gaps are 500–1100 cm^{-1} in the former and 0–200 cm^{-1} in the latter case. Hence, it appears that the slow radiationless rates encountered in rigid media are again associated with rather small energy gaps.

(2) Consideration of Environmental Factors in the Luminescence Decay. It is tempting to interpret the rising portion of the decay curve for the red emission of $\text{IrCl}_2(\text{phen})_2^+$ (Figure 6) in terms of conversion of the green-emitting charge-transfer state to the crystal field state. However, the rise time for the red emission is much shorter than the initial decay time for the green emission, indicating that another pathway must be largely responsible for population of the crystal field levels.

The conditions under which the experiment was performed suggest several possibilities. Firstly, excitation at 337 nm does not directly populate the green-emitting levels, but rather leads to formation of higher energy charge-transfer or $\pi\pi^*$ states. The rise time could, in part, reflect direct population of the crystal field state from these higher levels. This interpretation is complicated by the fact that no rise time is observed for the green emission. Thus, the levels feeding the green emission cannot be identical with those feeding the red emission. In fact, there must be at least two independent pathways for energy dissipation following excitation, one of which leads to the charge transfer state and the other to the crystal field state.

One possible explanation for the rise time of the red emission and the nonexponential decay of both the red and green emission is apparent. It is quite likely that the excited state species, whether they be in charge-transfer, $\pi-\pi^*$, or crystal field states, are subject to microenvironmental heterogeneity. Consider the effects of excitation of an ensemble of such molecules at a wavelength where the absorption is dominated, say, by charge-transfer character. Some of the molecules in the ensemble are likely to be in solvent environments which present high barriers to the geometric distortions (vide supra) required for radiationless formation of crystal field states, and are limited to processes which lead to formation of states of similar geometry. Other molecules in the microheterogeneous medium may encounter only small barriers for the geometric distortions required for nonradiative conversion to crystal field states and, perhaps, similar barriers for conversion to lower charge-transfer or $\pi-\pi^*$ states. These may account for formation of crystal field states at a rate given by the rise time for the red emission. The absence of a measurable rise time for the green emission could be accounted for in terms of the small

contribution which these molecules make to the total population of green-emitting species.

In terms of the rigid matrix perturbation of a pseudo-Jahn-Teller potential depicted in Figure 7, this explanation suggests that all molecules in the ensemble are described by the same intramolecular potential (solid line) but that the perturbation (dotted line) varies according to the particular site occupied by a given solute molecule. Solute species experiencing a large rigid matrix perturbation populate green-emitting levels only, while those experiencing a small perturbation may populate red-emitting levels. Thus, modification of the model for the rigidochromic effect based on a pseudo-Jahn-Teller potential by introduction of a variable rigid matrix induced potential is capable of accounting for the decay phenomena encountered in this study.

Acknowledgment is made to the Committee on Research of the University of California, Santa Barbara, for support of this research.

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Structures of Two Spiroarsoranones and Their Dynamic Implications

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Abstract: The crystal and molecular structures of two spiroarsoranones have been determined by single-crystal x-ray diffraction analyses. The compound 2,2,3,3,7,7,8,8-octamethyl-5-phenyl-1,4,6,9-tetraoxa-5-arsaspiro[4.4]nonane (I) crystallizes in the monoclinic space group $P2_1/c$ with cell constants $a = 9.150$ (5), $b = 12.699$ (8), $c = 17.386$ (7) Å; $\beta = 103.73$ (5)°; $Z = 4$. The geometry about arsenic lies on the Berry coordinate between rectangular pyramidal and trigonal bipyramidal. The compound 5-hydroxy-1,4,6,9-tetraoxa-5-arsaspiro[4.4]nonane (II) crystallizes in the monoclinic space group $P2_1/c$, with cell constants $a = 9.415$ (4), $b = 6.791$ (2), $c = 12.426$ (5) Å; $\beta = 119.11$ (6)°; $Z = 4$. It too has a geometry about arsenic that lies on the Berry coordinate between rectangular pyramidal and trigonal bipyramidal. These structures lead to a reassessment of dynamic nuclear magnetic resonance spectra of these and allied compounds and also show the close parallels between the structures of related arsenic and phosphorus systems.

Introduction

There has been a continuing evolution of our understanding of the geometries and dynamics of five-coordinate compounds of main-group elements. Phosphorus chemistry provides the principal domain of this evolution. Early ideas of an invariable trigonal bipyramidal arrangement gave way to a recognition

that distortions toward rectangular pyramidal might occur in some systems. It now appears that there is a whole range of possible structures for five-coordinate phosphorus compounds corresponding to points along the Berry coordinates for intramolecular exchange.¹

The present work was undertaken to explore whether a similar structural range might exist for five-coordinate arsenic