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Laser Studies of Radiationless Decay Mechanisms
in Os^{2+/3+} Polypyridine Complexes

1. Introduction

The lowest energy excited states in Os(II) polypyridine complexes are of a metal-to-ligand charge transfer (MLCT) type and live for 10-40 μ s at 4.2 K.¹ The long wavelength absorptions in the visible region of the spectrum in Os(III) polypyridine complexes arise from ligand-to-metal charge transfer (LMCT) transitions and do not produce detectable luminescence. This suggests that these LMCT states are very short lived. We report here the results of picosecond absorption studies on the lifetimes the LMCT states in OsL₃³⁺ complexes [L = 2,2'-bipyridine(bpy) or 1,10-phenanthroline(phen)] as functions of temperature and isotopic substitution. The LMCT lifetimes at low temperature are then contrasted with the low temperature lifetimes of the MLCT states of OsL₃²⁺ complexes and both are examined from the perspective of a coarse-grained radiationless decay theory developed by Englman and Jortner.² In particular we seek to understand which molecular factors are responsible for the experimentally observed lifetimes.

2. Results

For picosecond kinetic measurements of change-in-absorbance ($\Delta\Delta$) spectra, the samples were degassed in 2 mm path length cells and held at constant temperature in a flowing-helium cryostat. The samples were excited at 527 nm with 6 ps laser pulses and the $\Delta\Delta$ spectra of the excited states were measured with 8 ps white³ probe pulses. The laser system has been described elsewhere. The observed $\Delta\Delta$ signals are consistent with the known MLCT spectra of ground state OsL₃²⁺ complexes and support our assignment of the observed optical transients in OsL₃³⁺ complexes to the production of LMCT states.

Table I lists the excited state lifetimes for Os(phen)₃³⁺ at three temperatures. The striking result is the lack of any significant change in the LMCT state's lifetime on going from 295 to 10 K. Table I also presents data on the effects of deuteration on the charge transfer state lifetimes of Os(bpy)₃^{2+/3+} complexes. The lifetimes are lengthened, but only by factors of 2 and 2.5 respectively, for Os(bpy)₃³⁺ and Os(bpy)₃²⁺.

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Table 1. Charge Transfer Excited State Lifetimes^a

<u>Compound</u>	<u>Temperature</u> (K)	<u>Lifetime</u> (ps)
$\text{Os}(\text{phen})_3^{3+}$, ^b	295	≤ 9
	80	20 ± 3
	10	19 ± 2
$\text{Os}(\text{bpy})_3^{3+}$, ^b	5	62 ± 4 ^c
$\text{Os}(\text{dg-bpy})_3^{3+}$, ^d	10	120 ± 10
$\text{Os}(\text{phen})_3^{2+}$	4	$32 \mu\text{s}$ ^e
$\text{Os}(\text{bpy})_3^{2+}$, ^d	10	$1.05 \pm 0.04 \mu\text{s}$ ^f
$\text{Os}(\text{dg-bpy})_3^{2+}$, ^d	10	$2.5 \pm 0.2 \mu\text{s}$ ^f

^a The following abbreviations are used in this table:

phen = 1,10-phenanthroline and bpy = 2,2'-bipyridine.

^b In H_2O with 9 M H_2SO_4 .

^c The lifetime in H_2O with 9 M D_2SO_4 is 64 ± 4 ps.

^d In D_2O with 9 M D_2SO_4 .

^e From ref. 1.

^f Determined in this work by measurement of emission decay.

While the lifetimes of the OsL_3^{2+} and OsL_3^{3+} charge transfer states differ by a factor of 10^5 - 10^6 , the energy gaps between their ground and charge transfer states are similar, $2+$ 14.5×10^3 and $16.0 \times 10^3 \text{ cm}^{-1}$, respectively. However, OsL_3^{2+} complexes have IR bands that OsL_3^{3+} complexes don't have. Our observation of these absorptions agrees with a recent report by Kober and Meyer of IR absorptions in $[\text{Os}(\text{bpy})_3](\text{PF}_6)_3$ at 5090 and 4580 cm^{-1} .⁴ These transitions arise because spin-orbit coupling interactions in the trigonal field split the t_{2g} levels of O_h symmetry.

3. Discussion

We expect the charge transfer excited states of OsL_3^{2+} / $3+$ complexes to have much the same equilibrium nuclear configurations as their corresponding ground states and thus to fall into the weak electron-vibration coupling limit of Englman and Jortner's radiationless decay theory.² The small temperature dependence of the lifetime of the LMCT state in OsL_3^{3+} complexes suggests that its nonradiative decay rate (knr) has little activated component even at room temperature. Thus low frequency ($\leq 500 \text{ cm}^{-1}$) molecular modes are not critical to its decay mechanism. Similarly the small increase in charge transfer state lifetime upon deuteration implies that high frequency C-H stretching modes are not critical to the radiationless decay process in OsL_3^{2+} / $3+$ complexes. The above considerations imply that mid-frequency

(1000-2000 cm^{-1}) skeletal stretching modes are likely to be the key energy accepting channels in these molecules. Consistent with this is the 1300 cm^{-1} vibrational progression observed in the emission spectrum of OsL_3^{2+} complexes.¹

Equation 1 describes the radiationless decay rate for a single-frequency model with weak electron-vibration coupling in the low temperature limit as derived by Englman and Jortner.²

$$k_{nr} = \kappa_{el} \cdot \nu_M \cdot F_M \quad (1)$$

where κ_{el} is a dimensionless electronic coupling factor which should be near unity for the charge transfer states of $\text{OsL}_3^{2+/3+}$ complexes; ν_M is the frequency ($\sim 4 \times 10^{13} \text{ s}^{-1}$) of the critical vibration governing the decay process; and F_M is a Frank-Condon factor describing the vibrational overlap of the initial and final states.

$$F_M = \exp(-\gamma \cdot \Delta E / h\nu_M) \quad (2)$$

where

$$\gamma = \log_e [(2 \cdot \Delta E) / (d \cdot h\nu_M \cdot \Delta_M^2)] - 1 \quad (3)$$

In the above equations, ΔE is the electronic energy gap; d is the number of degenerate (or nearly degenerate) modes of frequency ν_M whose reduced displacement Δ_M is non-zero. ($d = 13$ and 16, respectively, for $\text{Os}(\text{bpy})_3^{2+/3+}$ and $\text{Os}(\text{phen})_3^{2+/3+}$.)

As a preliminary test of equations 1-3, we calculated the values of Δ_M required to explain the observed nonradiative deactivation rates for $\text{Os}(\text{phen})_3^{2+}$ and $\text{Os}(\text{bpy})_3^{2+}$ at 4.2 K.¹ The resulting values, respectively, 0.29 and 0.33 are in good agreement with the value of 0.29 calculated by Byrne *et al.*⁵ for skeletal stretching modes in large aromatic molecules.

A more stringent test of the formalism would be to explain the much shorter lifetimes of the LMCT states of $\text{Os}(\text{phen})_3^{3+}$ and $\text{Os}(\text{bpy})_3^{3+}$. Since OsL_3^{3+} complexes do not emit in the visible, the energy of the 0-0 level of the lowest LMCT state is not known. If one takes ΔE from the onset of absorption in the visible and uses $h\nu_M = 1300 \text{ cm}^{-1}$ and Δ_M and d as specified above, the calculated values of k_{nr} are seven orders of magnitude too small relative to the observed nonradiative decay rates. In fact the observation of IR transitions for $\text{Os}(\text{bpy})_3^{3+}$ shows that ΔE for this complex can be no larger than $11 \times 10^3 \text{ cm}^{-1}$. With this energy gap, the calculated value of k_{nr} can be brought into exact agreement with the observed decay rate if both the accepting mode frequency and displacement are increased slightly to 1600 cm^{-1} and 0.35, respectively.

4. Conclusions

The above agreement between experiment and theory suggests the following: 1) Englman and Jortner's theory of radiationless decay is useful for inorganic as well as organic systems, 2) mid-frequency ($1300\text{-}1600\text{ cm}^{-1}$) vibrations are the important energy accepting modes for radiationless decay of the charge transfer excited states of $\text{OsL}_3^{2+/\text{3}+}$ complexes, and 3) the $10^5\text{-}10^6$ difference in lifetimes between the MLCT states of OsL_3^{2+} complexes and the LMCT states of OsL_3^{3+} complexes is largely due to the difference in their energy gaps.

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