

Review

Charge transfer-excited state emission spectra of mono- and bi-metallic coordination complexes: Band shapes, reorganizational energies and lifetimes

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Received 20 March 2006; accepted 21 July 2006

Available online 18 August 2006

Contents

1. Introduction	329
2. Summary of the contributions to charge transfer emission band shapes	331
2.1. Emission intensity	331
2.2. Emission energy: $E^{0'0}$ and the “fundamental” component	331
2.3. Intrinsic bandwidth of the emission	333
2.4. Emission band shapes	333
3. Evaluation of the molecular parameters contributing to emission band shapes, and rR-based modeling of observed emission spectra	334
3.1. Evaluation of the fundamental	334
3.1.1. Based on the observed spectra	334
3.1.2. Based on electrochemical measurements	334
3.2. The basis for evaluating the relative intensity contributions of the distortion modes	335
3.3. Variations in vibrational reorganizational energies: reorganizational energy profiles (emreps) [32]	335
3.3.1. The basis for constructing emreps from the observed spectra	335
3.3.2. Uses and significance of emreps	336
3.4. Other considerations	336
3.4.1. Selection rule issues	336
3.4.2. Experimental artifacts	336
4. Effects of configurational mixing	336
4.1. General	336
4.2. Excited state–ground state mixing	336
4.2.1. Transition energies	336
4.2.2. Effect on force constants and vibrational frequencies	336
4.2.3. Vibronic sideband intensities	337
4.3. Band shape variations implicating configurational mixing among excited states	337
4.3.1. Possible ³ MLCT mixing ³ LF excited states	337
4.3.2. Possible mixing between different MLCT excited states	338
5. Applications to the 77 K emission spectra of [Ru(L) ₄ bpy] ²⁺ complexes	339
5.1. Pertinent rR observations	339
5.2. Vibronic attenuation in frozen solutions and the evaluation of the extent of configurational mixing	340
5.3. Evaluation of the contributions of the high frequency C–H and N–H stretching modes to MLCT excited state distortions	341
5.4. Effects of the “spectator” ligands on the emission properties of the Ru–bpy chromophore	342
5.5. Summary and overview of observations on monometallic complexes	344
6. The use of emreps to explore CT excited state properties in bi- and tri-metallic complexes	345
6.1. General considerations	345

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6.2.	Excited state–excited state electronic coupling in bis-Ru(II) complexes with mixed valence excited states	345
6.3.	Studies of transition metal–transition metal electron transfer excited states: cyanide-bridged Cr(III)–Ru(II) complexes	346
7.	Some implications for inverted region electron transfer rate constants	347
8.	Conclusions	348
8.1.	General	348
8.2.	MLCT excited state properties for some mono- and multi-metallic complexes inferred from emissionband shape variations	348
8.2.1.	[Ru(L) ₄ bpy] ²⁺ complexes	348
8.3.	Variations in vibronic sideband intensities of the CT emission spectra of bimetallic and trimetallic transition metal complexes	349
	Acknowledgement	349
	References	349
	Glossary	350

Abstract

The low energy sidebands of an emission spectrum contain information about the difference between the ground and the excited state molecular structures. The structural information that can be extracted from the sideband intensities and structure decreases as the component bandwidths increase, but there is significant structural information in the sidebands of the charge transfer emission spectra of even the relatively broad ($\Delta\nu_{1/2} \sim 1000 \text{ cm}^{-1}$) charge transfer (CT) emission spectra of transition metal complexes in frozen solutions. A Gaussian band shape model for the contributions of vibronic components is described and applied to the analysis of transition metal CT emission band shapes in frozen solution. The uncertainties of this approach are examined with respect to the emission spectra calculated from reported resonance-Raman (rR) parameters; such calculated spectra reproduce the frozen solution emission spectra of [Ru(bpy)₃]²⁺ and [Ru(NH₃)₄bpy]²⁺ very well. Patterns of excited state distortions can be expressed in terms of variations in the vibrational reorganizational energies, λ_k (proportional to the squared displacements), of the normal modes that correlate with the differences in excited and ground state geometries. The excited state distortions usually correspond to displacements in a large number of ground state molecular vibrational modes (more than 11 for the Ru–bpy complexes), and the bandwidths characteristic of CT spectra in frozen solutions preclude their resolution in frozen solution spectra. Thus, the convolution of the overlapping spectral contributions of these individual distortion modes results in a vibronic sideband that is broad and sometimes weakly structured, and the variations of the sideband amplitude provides information about variations in molecular structure for a series of closely related complexes. The emission sidebands can readily be converted into a reorganizational energy profile (emrep) in which the variations in amplitude are more readily interpreted in terms of molecular distortions and in which the contributions from the distortions in the highest frequency vibrational modes are more evident. This approach has been used to analyze the patterns of variations of the vibronic sideband structure of the frozen solution CT emission spectra of [Ru(L)₄bpy]²⁺, [Ru(bpy)₂PP]²⁺, [(bpy)₂Ru]₂PP⁴⁺ (bpy, 2,2'-bipyridine; PP, a tetraazapolypyridyl bridging ligand) and cyanide-bridged Cr(III)/Ru(II) complexes. The observed emission energies of the bpy complexes span a range of about 8000 cm⁻¹ and the vibronic sideband amplitudes tend to decrease appreciably (over about a two-fold range for the [Ru(L)₄bpy]²⁺ complexes) and systematically with decreasing emission energy in each class of these complexes. This attenuation of the vibronic sideband intensities is ascribed to the increases in ground state–excited state configurational mixing with decreasing energy differences between the states and to the large electronic matrix elements. The variations in emreps also suggest that there is a great deal of excited state–excited state configurational mixing (probably ligand field/metal to ligand CT) in most, but not all, [Ru(L)₄bpy]²⁺ complexes and relatively little such configurational mixing between the different MLCT valence isomer excited states of the [(bpy)₂Ru]₂PP⁴⁺ complexes. The comparison of the emreps of NH/ND isotopomers of the [Ru(L)₄bpy]²⁺ and of the cyanide-bridged Cr(III)/Ru(II) complexes has permitted the resolution of the very weak contributions of distortions of the C–H (in the former) and N–H (in the latter) stretching vibrational modes, and it appears that decay pathways that involve only nuclear tunneling in the C–H modes cannot account for the decay behavior of the [Ru(L)₄bpy]²⁺ complexes while such pathways in the N–H modes may account for that of the Cr(III)/Ru(II) complexes.

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Keywords: Zero point energy; MLCT; Resonance-Raman rR spectra; Emission spectral band shapes; MMCT; Reorganizational energy profiles; Transition metal complexes; Effects of configurational mixing

1. Introduction

The manipulation of chemical reactivity, the design reagents for specific purposes, etc., depends on knowledge of how the properties of molecules contribute to their reactivity. The simplest class of chemical reactions are those in which a single electron is transferred between donor and acceptor, key electron transfer parameters are often evaluated by means of spectroscopic measurements since it is well known that the same general molecular properties govern thermal electron transfer reactivity of donor–acceptor (D/A) complexes and the absorption of light in the formation of or the emission of light

in the relaxation of charge transfer (CT) excited states [1–14]. However, the characterization of the properties CT excited states and of evaluation of key electron transfer parameters is generally difficult at least in part because: (a) transition metal complexes typically have many electronic states that are relatively close in energy and configurational mixing between these states can make the characterization of reactivity patterns difficult; (b) the evaluation of key parameters tends to be model dependent. We have found that emission band shapes can provide useful experimental probes of the variations in key electron transfer properties of related coordination complexes.

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