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Coordination Chemistry Reviews 251 (2007) 328–350

COORDINATION CHEMISTRY REVIEWS

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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

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doi:10.1016/j.ccr.2006.07.021

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 ($\Delta\nu_{1/2} \sim 1000\,cm^{-1}$) 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 $[Ru(NH_3)_4bpy]^{2+}$ 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 $[Ru(L)_4bpy]^{2+}$, $[Ru(bpy)_2PP]^{2+}$, $[\{(bpy)_2Ru\}_2PP]^{4+}$ (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 $[\{(bpy)_2Ru\}_2PP]^{4+}$ 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.

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.