Effect of Jahn-Teller Distortions on Relaxation Dynamics

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Characterization of excited-state behavior of inorganic complexes will limit the set of dyes for the optimal dye-sensitized solar cell. This study goaled to elucidate Jahn-Teller distortions as manifestations of infinite nonadiabatic coupling added to adiabatic potential energy surfaces in conical intersections. Hence, relaxation dynamics of [IrBr6]2- compared to [Ir(bpy)Br4] have been studied. Matveev et al., 2015 identified a conical intersection in [CuCl4]2- and not [IrBr6]2-; however, the 2000nm pump pulse excited the metal-centered transition in both samples. Since energy decayed from the Jahn-Teller state in [CuCl4]2- but not in [IrBr6]2-, the study failed to investigate the effect of the distortion in [IrBr6]2-. In the presented study, [IrBr6]2- and [Ir(bpy)Br4] were synthesized and analyzed by UV-Vis spectrophotometry. Fluorescence spectrometry and transient absorption spectroscopy with an in-house femtosecond laser were used to determine relaxation pathways. [Ir(bpy)Br4] displayed a favorable metal-to-ligand fluorescence of 2x106 counts. Hence, the relaxation mechanism has been identified as fluorescence. [IrBr6]2- lacked fluorescence. Femtosecond laser analysis displayed a favorable, sub-picosecond lifetime mechanism. In combination, sufficient evidence was provided to identify an accessible conical intersection in [IrBr6]2-. Comparing the complexes, evidence suggests Jahn-Teller distortions are results of conical intersections. Future moieties to investigate include trans[Ir(CN)2Br4]2- to preserve D4h symmetry of distorted [IrBr6]2- but remove the Jahn-Teller Distortion; [Ir(ppy)Br4] and trans[Ir(Pph3)Br4] to use in dye-sensitized solar cells, and chlorine versions of aforementioned complexes to effectively eliminate ligand spin-orbit coupling.

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