

# 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 goal to elucidate Jahn-Teller distortions as manifestations of infinite nonadiabatic coupling added to adiabatic potential energy surfaces in conical intersections. Hence, relaxation dynamics of  $[\text{IrBr}_6]^{2-}$  compared to  $[\text{Ir}(\text{bpy})\text{Br}_4]$  have been studied. Matveev et al., 2015 identified a conical intersection in  $[\text{CuCl}_4]^{2-}$  and not  $[\text{IrBr}_6]^{2-}$ ; however, the 2000nm pump pulse excited the metal-centered transition in both samples. Since energy decayed from the Jahn-Teller state in  $[\text{CuCl}_4]^{2-}$  but not in  $[\text{IrBr}_6]^{2-}$ , the study failed to investigate the effect of the distortion in  $[\text{IrBr}_6]^{2-}$ . In the presented study,  $[\text{IrBr}_6]^{2-}$  and  $[\text{Ir}(\text{bpy})\text{Br}_4]$  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.  $[\text{Ir}(\text{bpy})\text{Br}_4]$  displayed a favorable metal-to-ligand fluorescence of  $2 \times 10^6$  counts. Hence, the relaxation mechanism has been identified as fluorescence.  $[\text{IrBr}_6]^{2-}$  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  $[\text{IrBr}_6]^{2-}$ . Comparing the complexes, evidence suggests Jahn-Teller distortions are results of conical intersections. Future moieties to investigate include  $\text{trans}[\text{Ir}(\text{CN})_2\text{Br}_4]^{2-}$  to preserve  $D_{4h}$  symmetry of distorted  $[\text{IrBr}_6]^{2-}$  but remove the Jahn-Teller Distortion;  $[\text{Ir}(\text{ppy})\text{Br}_4]$  and  $\text{trans}[\text{Ir}(\text{Pph}_3)\text{Br}_4]$  to use in dye-sensitized solar cells, and chlorine versions of aforementioned complexes to effectively eliminate ligand spin-orbit coupling.

## Awards Won:

First Award of \$5,000