EVOLUTION OF THE MLCT BAND FOLLOWING CHANGES IN OXIDATION STATE FOR HIGHLY COUPLED MIXED VALENCE COMPLEXES

BENJAMIN J. LEAR and MALCOLM H. CHISHOLM, *The Ohio State University, Department of Chemistry, Columbus, Ohio 43210*.

The MLCT band for a series of dimers composed of pairs of quadruply bonded metal-metal units ($[MM(CH_3CO_2)_3]_2$-μ_2-oxalate; where M=Mo or W) is examined in both the neutral and +1 (mixed valence) states. The MLCT band for the neutral state of these complexes exhibits clear vibronic features that are greatly reduced in intensity upon generation of the mixed valence state. Utilizing the time dependent theory of spectroscopy as developed by Eric Heller, these results (together with Raman spectra and TD-DFT calculations) are used in order to draw conclusions concerning the potential energy surfaces involved in the MLCT transition for these complexes. In particular, we are concerned with changes to the offset of the ground and excited state potential energy surfaces that occur along the coordinates involved in the vibronic coupling and which accompany changes in oxidation state. The insight thus gained is used in order to understand the degree of electronic coupling present in mixed valence species and to comment on the classification of mixed valence complexes.