Investigation of Iron-thiolate Interactions in $CpFe(CO)_2(SR)$ using Gas-Phase Photoelectron Spectroscopy and Density Functional Theory.

Matthew A. Cranswick, Kristie R. Winfield, Nadine E. Gruhn, Dennis L. Lichtenberger, John H. Enemark.

Department of Chemistry, The University of Arizona.

Iron-thiolate bonds are found throughout nature in various biological systems. For example, iron-thiolate bonds are found in FeS clusters, nitrogenase, cytochrome P_{450}, and hydrogenases. We are investigating the fundamentals of iron-thiolate interactions by gas-phase photoelectron spectroscopy (PES) and density functional theory (DFT), using compounds of the type $CpFe(CO)_2SR$ (where Cp is cyclopentadienyl, and SR is an alkyl thiolate). For $CpFe(CO)_2SCH_3$, DFT and PES indicate that the sulfur p orbital of the thiolate is less stable than the primary d orbitals of the $[CpFe(CO)_2]^+$ fragment. Consequently, the d -p filled-filled interaction of $CpFe(CO)_2SR$ results in high sulfur 3p character in the highest occupied molecular orbital (HOMO). Previous studies by Ashby et al.[1], have shown that by altering the electron donating or withdrawing ability of the para-substituent in $CpFe(CO)_2(p\text{-}C_6H_4\text{-}X)$, (where X is OCH_3, H, Cl, CF_3, and NO_2) the HOMO ionization energy can be stabilized or destabilized with the nature of the substituent. A study will be presented of the metal-thiolate interactions in a series of $CpFe(CO)_2SR$ compounds where the alkyl thiolates vary in both sterics and expected relative donor abilities.

1. Ashby, M. T.; Enemark, J. H.; Lichtenberger, D. L. *Inorg. Chem.* **1988**, *27*, 191-197