

METAL-LIGANDS AND METAL-METAL INTERACTIONS: SPECTROSCOPY AND KINETICS

BENOIT SIMARD, *Molecular Spectroscopy Program, Steacie Institute for Molecular Sciences, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, K1A 0R6.*

The first part of the talk will focus on complexations and oxydative addition reactions at metal centers. Three examples will be reviewed and discussed: $Y + NH_3$, $Al + NH_3$, and $Zr + O(CH_3)_2$. The reaction of yttrium with ammonia proceeds without the formation of a stable adduct. The N-H bond is readily activated and the reaction proceeds with the elimination of molecular hydrogen to produce yttrium imide, $YNH(D)$. We have studied the visible spectrum of yttrium imide at medium and high resolution using laser induced fluorescence (LIF). Following a brief survey of the visible spectrum, the presentation will focus on the origin band of the $\tilde{B}^2\Sigma^+ - \tilde{X}^2\Sigma^+$ system for which rotational, fine and nuclear magnetic hyperfine structure has been recently analyzed in detail. The reaction of aluminum with ammonia proceeds with the formation of a stable adduct, $Al(NH_3)$, which we have recently studied using photoionization spectroscopy. Resonant two-photon ionization (R2PI) yielded a vibronically resolved spectrum in the 18000-21000 cm^{-1} , which is believed to be due to four electronic band systems. Photoionization efficiency (PIE) spectroscopy yielded Rydberg spectra whose limits provided information on the ground state of the cation. All of these observations will be summarized in the presentation. The reaction of zirconium with dimethylether also leads to the formation of an adduct. We have studied the adduct using a combination of pulsed field ionization-zero electron kinetic energy (PFI-ZEKE) photoelectron spectra, density functional calculations and kinetic measurements. The latter yielded a binding energy of 16 kcal/mol. Detail of these measurements and calculations will be provided. A novel apparatus for the rapid acquisition of absorption spectra for metal-containing complexes will be introduced. The apparatus consists of a fast-flow reactor coupled to a multipass absorption cell and a Fourier transform spectrometer.

The second part of the presentation will focus on the structures of small ligated yttrium and niobium clusters. The structures of these species have been determined using a combination of PFI-ZEKE measurements and density-functional calculations. Detail of these experiments and calculations will be given.