

# Abstract

Molecular spectroscopy is an invaluable tool to probe the electronic structure and dynamics in atoms, molecules, and clusters. The presence of electron-electron correlation, coupling of nuclear and electronic degrees of freedom, and coupling of spin and orbital motion of electrons make interpretation of molecular spectra a challenging task. In this thesis, ab initio electronic structure calculations have been performed to investigate the photoelectron spectroscopy and photoionization dynamics of three different molecular systems. The computational techniques employed in this work are outlined in **Chapter 2** of the thesis. In **Chapter 3**, an interpretation of the experimental photoelectron spectra of  $\text{MnX}_2$ ,  $X = \text{Cl, Br, and I}$ , is presented by obtaining accurate treatment of electron correlation and spin-orbit coupling for these high-spin, open-shell transition metal dihalides, for which the Dyson orbitals are used to explain the photoelectron band intensity. The analysis of the spectra provides a detailed account of the contribution of one- and two-electron transitions in the experimental photoelectron spectra of the manganese dihalides. In **Chapter 4**, the challenging problem of the photoelectron spectroscopy of ICN has been undertaken, for which a conclusive interpretation, in particular, of the complex spin-vibronic structures of the  $\tilde{\text{B}}^2\Pi$  state, has remained elusive. The complicated vibronic structure of ICN has been explained by analyzing the Dyson orbitals corresponding to the ionized electrons for a range of conformations sampled by Wigner sampling as well as exciting the molecule along normal modes of vibration. This approach reproduces the complex vibronic structures of the four observed photoelectron bands. Additionally, the photoionization cross-section and asymmetry parameter for these ionization channels have been calculated that explain the experimentally observed shape-resonances. In **Chapter 5**, the valence shell photoelectron spectroscopy of  $\text{OsO}_4$  is studied by considering electron correlation in the wave functions of the ejected photoelectrons as well as the resulting cation in its lowest five electronic states. The computational results are compared with those from synchrotron measurements. The kinetic energy dependence of the photoionization dynamical parameters for each of the photoionization channels are analysed in terms of the complex interplay of multiple partial waves that define the wave function of the ejected electron at different photon energy. It is expected that the work presented in this thesis will inspire further experimental and theoretical investigations of high-resolution spectroscopy of complex molecules with heavy atoms.

**Keywords:** Photoelectron Spectroscopy; Photoionization Cross-section; Angular Distribution; Shape Resonance; Dyson Orbitals; Multi-reference Electronic Structure Methods.