SUMMARY OF Ph.D. DISSERTATION

School	Student Identification Number	SURNAME, First name
Fundamental Science and Technology		TAKEGAMI Ryuta

Title

Theoretical Analysis and Modeling of Molecular Spectroscopy on Oxygen Molecule and One-Dimensional Lanthanide-Cyclooctatetraene Clusters

Abstract

One of the viewpoints for understanding molecular chemistry is to focus on electron motion in molecules. Molecular spectroscopy and electronic structure theory are the experimental and theoretical methods to analyze the electron and nuclear motions. In this thesis, I will perform theoretical analysis on the oxygen molecule and one-dimensional lanthanide-cyclooctatetraene clusters, and develop theoretical models to provide necessary and sufficient explanations for experimental spectroscopy.

In Chapter 1, I discuss the role of theoretical chemistry in the present science realm, and summarize the basic theory of my thesis.

In Chapter 2, I give the analysis on the vibration and rotation spectra of the Herzberg I band system of O_2. I develop three different level of theoretical models to consider the spin-orbit interaction (SO) and L-uncoupling (RO) as perturbations. The first model calculates the SO interaction variationally, and uses the first-order perturbation theory for the RO interaction (SOCI). The second one employs the first-order perturbation theory for both the SO and RO interactions (Pert(Full)). The last one is a limited version of Pert(Full), in that the first-order wave functions are represented by only two dominant bases (Pert(England)). In comparison of each result, I find that the Pert(England) model is not adequate for calculating the rotational line strengths, because the model cannot consider the complicated configuration interactions with highly excited states induced by the perturbations which have been believed as small in the past.

In Chapters 3 and 4, I describe the theoretical studies on the photoelectron spectra of Ln-COT clusters which have one-dimensional multiple-decker structures based on the strong ionic bonding. Especially, in the case of one-end open sandwich clusters with Ln=Eu, their photoelectron spectra show significant size dependence : (i) the first peak shift to the higher energy side as increasing n, (ii) the second peak is independent of n. From the calculation results, I notice that these size dependences are due to the characteristic intra-cluster electrostatic field induced by the one-dimensional structure with the strong ionic bonding. Then, I develop simple "point charge models" reflecting the above characteristic bonding, which can reproduce the qualitative behavior of the spectra. This model can also give qualitative explanation for the unique behavior of their ionization energies.

In Chapters 5, I summarize my results and discuss the generality of my models to other molecules.