The Effect of Sequential Oxidation and Composition on the Structural and Electronic Properties of Gas-Phase Transition-Lanthanide Bimetallic Clusters

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Statement of Originality

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Alexander S. Gentleman

May, 2014.

Abstract

This thesis presents experimental and theoretical work performed on various rhodium-holmium (Rh-Ho) and gold-praseodymium (Au-Pr) bimetallic clusters and their oxide counterparts. More specifically, structural and/or electronic properties for these clusters are ascertained from investigating how their adiabatic ionisation energies (IEs) are affected by: (a) the sequential addition of oxygen atoms onto the base bimetallic cluster within each series, or (b) the composition of the bimetallic clusters i.e. the transition:lanthanide metal atom ratio within each cluster.

The clusters were experimentally generated via dual laser ablation and detected using time-of-flight mass spectrometry (TOF-MS) coupled with threshold laser ionisation. Upon successful formation and detection, the experimental adiabatic IEs of these clusters were determined using Photoionisation Efficiency (PIE) spectroscopy. In regards to aspect (a) of this thesis listed above, it was observed that the sequential addition of individual oxygen atoms onto bare Rh-Ho and Au-Pr clusters either caused: (i) a significant change in or (ii) had little-to-no effect on the experimental adiabatic IE. For clusters that displayed the former behaviour, the addition of the first oxygen atom was observed to significantly decrease the adiabatic IE relative to that of the bare bimetallic cluster within that series. The addition of a second oxygen atom onto the monoxide counterpart was observed to significantly increase the adiabatic IE back to a value similar to that of the bare bimetallic cluster. In regards to aspect (b) of this thesis listed above, it was observed that: (i) the substitution of a transition metal atom for a lanthanide metal atom generally lowers the experimental adiabatic IE of each cluster, and (ii) the sequential addition of transition metal atoms onto a cluster generally increases the experimental adiabatic IE of each cluster.

In order to gain more insight into the nature of the observed experimental adiabatic IE trends mentioned above, Density Functional Theory (DFT) Investigations were performed on the neutral and cationic species for the $RhHo_2O_n$ (n = 0-2), $Rh_2Ho_2O_m$ (m = 0-2) and the $Au_{3-k}Pr_k$ (k = 0-3) clusters. From these, the lowest energy

neutral and cationic geometries (in addition to other properties such as atomic charges and normal modes of vibration) were determined and subsequently, the theoretical adiabatic IEs of each cluster were calculated. When compared within each series, the experimental and theoretical adiabatic IE trends as a function of: (i) sequential addition of oxygen atoms in the $RhHo_2O_n$ (n = 0-2) and $Rh_2Ho_2O_m$ (m = 0-2) cluster series, and (ii) substitution of a gold atom for a praseodymium atom in the $Au_{3-k}Pr_k$ (k = 0-3) cluster series, both displayed similar behaviour. From this, specific ionisation transitions between neutral and cationic structures were able to be assigned and thus, structural and electronic information about each cluster was able to be inferred.

In addition to the DFT investigations, Franck-Condon Factor (FCF) calculations were performed in order to simulate the Zero Electron Kinetic Energy (ZEKE) and PIE spectra for each cluster in the $RhHo_2O_n$ (n = 0-2), $Rh_2Ho_2O_m$ (m = 0-2) and $Au_{3-k}Pr_k$ (k = 0-3) series. The purposes of these additional calculations were to: (i) identify the most likely transition from two or more competing candidates that occurs upon ionisation for each cluster, and (ii) apply slight corrections to the experimental adiabatic IEs obtained from the PIE spectra in order to account for thermal tailing resulting from vibrational hot band transitions at 300 K.

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Publications

The following publication contains some of the work presented in this thesis:

Photoionisation Efficiency Spectroscopy and Density Functional Theory Investigations of $RhHo_2O_n$ (n = 0-2) Clusters.
A. S. Gentleman; M.A. Addicoat; V. Dryza; J. R. Gascooke; M. A. Buntine; G.F. Metha, Journal of Chemical Physics, 130, 164311 (2009).

The following publications are currently in preparation and will each contain some of the work presented in this thesis:

Structural and Electronic properties of Gas-Phase Neutral and Cationic $Rh_2Ho_2O_m$ (m = 0-2) Clusters Determined using Photoionisation Efficiency Spectroscopy, Density Functional Theory and Franck-Condon Factor Calculations.
A. S. Gentleman; M. A. Buntine; G.F. Metha (in preparation).

Photoionisation Efficiency Spectroscopy, Density Functional Theory Investigations and Franck-Condon Factor Calculations of Gas-Phase $Au_{3-k}Pr_k$ (k = 0-2) Clusters: How composition affects their structural and electronic properties.
A. S. Gentleman; M. A. Buntine; G.F. Metha (in preparation)

Elucidation of the Structural and Electronic Properties of the Gas-Phase $AuPr_2O_x$ (x = 0-2), $Au_2Pr_2O_m$ (m = 0-1) and $Au_3Pr_2O_n$ (n = 0-2) Bimetallic Clusters using Photoionisation Efficiency Spectroscopy, Density Functional Theory and Franck-Condon Factor Calculations.
A. S. Gentleman; M. A. Buntine; G.F. Metha (in preparation)

Abbreviations

AE	Appearance Energy
AO	Atomic Orbital
CGF	Contracted Gaussian Function
DFT	Density Functional Theory
ECP	Effective Core Potential
eV	Electron Volt
FC	Franck-Condon
FCF	Franck-Condon Factor
GTO	Gaussian-Type Orbital
HOMO	Highest Occupied Molecular Orbital
IE	Ionisation Energy
MO	Molecular Orbital
MP	Model Potential
PES	Potential Energy Surface
PIE	Photoionisation Efficiency
PFI-ZEKE	Pulsed Field Ionisation Zero-Electron Kinetic Energy
PGF	Primitive Gaussian Function
PP	Pseudopotential
SPI	Single Photon Ionisation
TMO	Transition Metal Oxide(s)
TOF	Time-of-Flight
TOF-MS	Time-of-Flight Mass Spectrometry
UPS	Ultra-violet Photoelectron Spectroscopy
ZEKE	Zero-Electron Kinetic Energy
ZPE	Zero-Point Energy

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