“Electronic Structure of Transition Metal Clusters, and Actinide Complexes, and Their Reactivities” October 2006

K. Balasubramanian

Dept of Mathematics, computer science and physics, California State University East Bay, Hayward CA; Chemistry and Material Science Directorate, Lawrence Livermore National Laboratory, University of California, Livermore, California 94550; Glenn T. Seaborg Center, Lawrence Berkeley National Laboratory, Berkeley, California 94720;

balu@csueastbay.edu

Program Scope

We work on two major areas: (1) computational chemistry and computational spectroscopy of transition metal clusters, carbides and complexes, (2) computational actinide chemistry of complexes of relevance to environmental management of high-level nuclear wastes. Many of our studies in transition metal area are driven by experimental works on gas-phase spectroscopy of transition metal compounds. Computational actinide chemistry has been an important area of interest for (1) interface with ongoing experimental works at LBNL, ORNL, (2) Educational outreach efforts in computational actinide chemistry as there is dearth of young actinide chemists. Computations of actinide complexes are also important to understanding of the complexes found in geochemical and biochemical environment and are thus critical to management of high-level nuclear wastes. Our studies are focused on the geometrical and electronic properties such as ionization potentials, electron affinities, and binding energies of transition metal species. Especially third and second row transition metal clusters transition metal carbides have been considered. Actinide complexes such as uranyl and plutonyl complexes are being studied in solution. These studies are made with relativistic complete active space multi-configuration self-consistent-field (CASSCF) followed by large-scale CI computations and relativistic CI (RCI) computations up to 60 million configurations.

Recent Progress

Results of our computational studies and comparison with experiment have been described extensively in publications1-16, which contain details such as tables and figures. We have outlined here only the major highlights, in each of the categories. For this purpose, we have two major categories as described below.

Spectroscopic Properties of Transition Metal Species.

We have carried out systematic studies on the potential energy curves and spectroscopic constants of a number of second-row transition metal carbides such as MoC13, NbC10, ZrC14 and RuC1. In addition in collaboration with experimental work, we have studied the gold dihydride2, molecule. All of the second-row transition metal carbides are challenging due to the open-shell nature of the metal resulting in a number of low-lying electronic states for this molecule. We have carried out state-of-the-art complete active space multi-configuration self-consistent-field (CASSCF) followed by multireference configuration interaction methods in conjunction with relativistic effects. For MoC our computed transition energies to the 1^3Δ and 4^1Δ states are 3430 and 8048 cm\(^{-1}\) respectively, in fair agreement with the results obtained by Morse and coworkers [JCP 114, 2938, (2001)] namely, 4003 and 7834 cm\(^{-1}\) respectively. The three band systems located at 18611, 20700 and 22520 cm\(^{-1}\), observed by Morse et al. [JCP 109, 7851,(1998)] were attributed to the excited 1^1Σ\(^{−}\), 1^4Π, and 1^5Π states of MoC. Table I summarizes dipole moment trends.
We have determined that the ground state of ZrC as $^3\Sigma^+$ although there are two low-lying $^1\Sigma^+$ states (below 5000 cm$^{-1}$) which strongly interact resulting in avoided crossings. The lowest $^1\Sigma^+$ state corresponds to a combination of $1\sigma^2x\sigma^21\pi^4$ configurations whereas the second is an open shell singlet $1\sigma^22\sigma^13\sigma^11\pi^4$. Several avoided crossings were observed, for $^1\Pi$, $^3\Pi$, $^1\Delta$, $^3\Sigma^+$, and $^3\Delta$ states. We have identified $^3\Pi$ and $^1\Pi$ lying at 4367 and 5797 cm$^{-1}$ respectively. The results are in good agreement with experimental findings of Rixon, Chowdhury and Merer [J. Mol. Spectrosc. 228, 554, (2004)], and indicate that the $^3\Pi$-$^3\Sigma^+$, and $^1\Pi$-$^1\Sigma^+$ bands located between 16000-19000 cm$^{-1}$ are extremely complex due to near degeneracy of several $^1\Pi$ and $^3\Pi$.

Prof Lester Andrews carried out the matrix-isolation spectroscopy of AuH$_2$ molecule formed in solid hydrogen by reactions of excited gold atoms from laser ablation and irradiation after thermal evaporation. The X$^2\Pi_2$ ground state of the AuH$_2$ molecule is separated by a 53 kcal/mol barrier from the Au($^2\Pi$) + H$_2$ decomposition products and it is 27 kcal/mole more stable than Au($^2\Pi$) + H$_2$. The bending modes of AuH$_2$, AuHD, and AuD$_2$ have been observed at 638.1, 570.6, and 457.0 cm$^{-1}$. These frequencies and the lack of infrared intensity in the stretching modes are in agreement with the results of our calculations.

**Electronic Structure of Actinide Complexes.**

Our computational studies on actinide complexes were motivated by ongoing EXAFS studies of speciated complexes in geo and biochemical environments carried out by Prof Heino Nitsche’s group at Berkeley, Dr. David Clark at Los Alamos and Dr. Gibson’s work on small actinide molecules at ORNL. The hydrolysis reactions of uranyl, neptunyl and plutonyl complexes have received considerable attention due to their geochemical and biochemical importance but the results of free energies in solution and the mechanism of deprotonation have been topic of considerable uncertainty. We have computed deprotonating and migration of one water molecule from the first solvation shell to the second shell in UO$_2$(H$_2$O)$_2^{2+}$, UO$_2$(H$_2$O)$_3^{2+}$NpO$_2$(H$_2$O)$_6^{2+}$, and PuO$_2$(H$_2$O)$_2^{2+}$ complexes. Our computed Gibbs free energy(7.27 kcal/m) in solution for the first time agrees with the experiment (7.1 kcal/m) while previous computations produced results in strong disagreement. Fig 1 below shows the mechanism of proton migration and hydroxide formation.

**Transition state for the reaction**

$$\text{UO}_2(\text{H}_2\text{O})_2^{2+} + \text{H}_2\text{O} \rightarrow \text{UO}_2(\text{H}_2\text{O})_4^{2+} + \text{H}_3\text{O}^+$$
We have studied the electronic and spectroscopic properties of plutonyl carbonate complexes of the types PuO$_2$CO$_3$.nH$_2$O, (n=1,2) and PuO$_2$(CO$_3$)$_2$Ca$_3$. Our computed equilibrium geometries and vibrational spectra of these species agree quite well with the EXAFS and Raman data available on related complexes. We have reported the results of ab initio quantum chemical computations on the plutonyl carbonate complex and its hydrated forms, viz., PuO$_2$CO$_3$, PuO$_2$CO$_3$.H$_2$O and PuO$_2$CO$_3$.2H$_2$O. The results of our computations show that the computed geometries and vibrational frequencies are in reasonable agreement among these theoretical levels. Our computed geometries for the various interatomic distances at both MP2 and DFT levels agree quite well with the experimental EXAFS results of Clark et al. at Los Alamos in solution for the limiting Pu(VI)O$_2$-carbonate complex. Our predicted equatorial carbonate vibrational mode frequency of 754 cm$^{-1}$ at the MP2 level is consistent with the observed Raman band at 755 cm$^{-1}$ in solution form of plutonyl carbonate complex.

Our computations on uranyl silicate complexes explained the observed contrasting pattern in the EXAFS spectra of Prof Nitsche and coworkers at Berkeley which showed two types of structures. With theoretical computations we were able to assign the origin of two different spectra to a bridge and atop type of complexes. We also studied the characteristics of UO$_2$(CO$_3$)$_2^{2-}$ and M$_2$UO$_2$(CO$_3$)$_2$ (M= Li$^+$, and Na$^+$) b in solution using coupled cluster doubles (CCD). The uranyl carbonato complexes are known to form water-soluble metal salts. In order to understand the nature of metal binding with carbonato complexes, we have studied here the structure and bonding of UO$_2$(CO$_3$)$_2^{2-}$ and M$_2$UO$_2$(CO$_3$)$_2$ (M= Li$^+$, and Na$^+$). The gas-phase structure UO$_2$(CO$_3$)$_2^{2-}$ is a D$_{2h}$ structure with the carbonates in the equatorial position and the uranyl forming the axial linear bonds.

**Future Plan**

We are studying the spectroscopic properties and potential energy curves of YC and YN. We have also been considering actinyl complexes of experimental importance in collaboration with Prof Nitsche. There are mind boggling questions concerning the nature of these species and the role of 5f versus 6d orbitals in bonding and how relativistic effects influence the structures of these species. There are many challenges as we attempt to study these species. Both relativistic effects including spin-orbit effects and electron correlation effects must be considered accurately. We have also been investigating actinide complexes of environmental importance and their salvation phenomena. We have been looking at methods to consider aqueous actinide complexes.

**References to Publications of DOE-sponsored work in 2004-2006**


3. K. Balasubramanian, “Relativity and the Periodic Table”, (D. Rouvary & R. B. King, editors), Periodic Table into the 21st Century, 2004


16. K. Balasubramanian and Z. Cao, “Fluxional Motions and internal rotational barriers of Water molecules bound to UO₂²⁺, NpO₂⁺, and PuO₂²⁺”, Chemical Physics Letettrs , to be submitted