Proposal ID number: 1391a
Title of the Proposal: Probing the Electronic Structure of Metal Clusters
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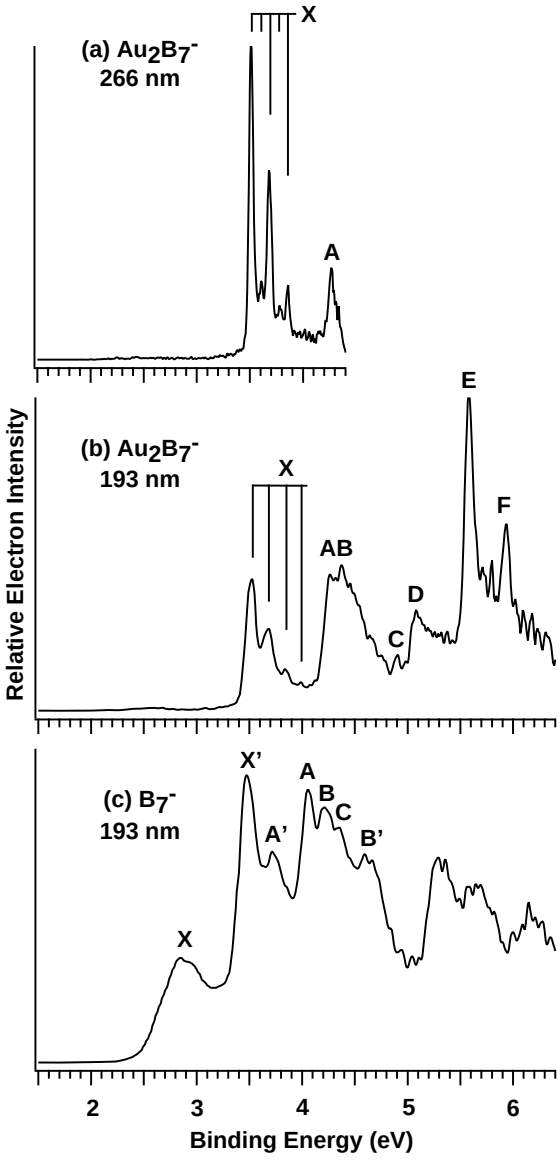
The goal of the project is to understand interaction between gold and boron atoms in gold-boron clusters in order facilitate rational design of gold-boron nanoparticles for nanotechnology and catalysis.

Gold is capable to form strong covalent bonds with silicon atoms as it was recently demonstrated by Wang and co-workers [1,2]. In such compounds gold atoms mimics hydrogen atoms adopting valence 1. In the current project we studied a possibility that gold may mimic hydrogen in gold-boron clusters too, because boron is close in electronegativity to silicon and thus has a potential to form strong covalent bond with gold atoms.

The project is a joint experimental and theoretical study. Experimental study includes generating negatively charged gold-boron clusters in molecular beam and recording the photoelectron spectra of such species using laser photodetachment technique at several photon energies. Theoretical study is based on quantum chemical search for the most stable structure for experimentally studied species and computational calculations of theoretical photoelectron spectra. Good agreement between experimental and theoretical spectra guarantee reliable assignment of the most stable structure for studied clusters. We than analyze electronic structure of studied clusters in order to develop a chemical bonding model capable to explain and predict structure of other gold-boron clusters.

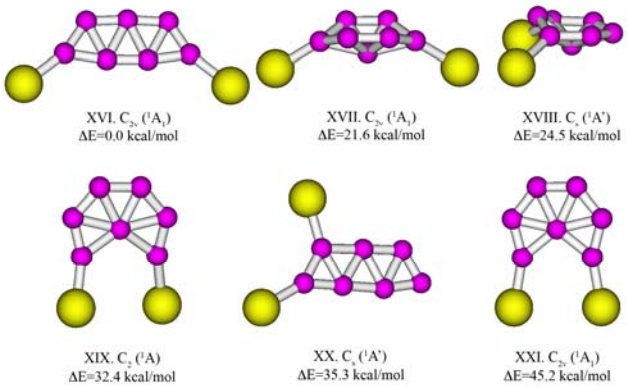
In the current project we selected a set of clusters B_7^-, $H_2B_7^-$ and $Au_2B_7^-$ for our joint experiment and theory study. In our previous work [3] we have shown that three isomers contributing to photoelectron spectrum of B_7^- (Figure 1c) making it complicated and congested. In the current project we demonstrated theoretically using our newly developed gradient embedded genetic algorithm that addition of two hydrogen atoms to B_7^- cluster resulted in great stabilization of only one isomer of $H_2B_7^-$. If our conjecture is correct we should expect much simpler spectrum for $Au_2B_7^-$. In order to test that, we generated $Au_2B_7^-$ anions in molecular beams and recorded its photoelectron spectra at 266 and 193 nm photon energies (Figure 1a and 1b). Indeed, the

Figure 1. Photoelectron Spectra of $Au_2B_7^-$ (a) at 266 nm and (b) at 193 nm and B_7^- (c) at 193 nm.



photoelectron spectra of $B_7Au_2^-$ are substantially simpler and better resolved than that of B_7^- despite its large size. Most surprisingly, despite the addition of two heavy atoms, the ground state transition (X) of $B_7Au_2^-$ is completely vibrationally resolved with the excitation of two vibrational modes, a low frequency mode of 790 ± 40 cm^{-1} and a high frequency mode of 1,380 ± 40 cm^{-1}. We also theoretically performed the search for the most stable structure of $Au_2B_7^-$ using our theoretical results on $H_2B_7^-$ by substituting H by Au. The global minimum structure (Figure 2) was found to be the same as in $H_2B_7^-$, thus confirming that Au could indeed mimic H in gold-boron clusters.

Figure 2. Alternative Local Minimum Structures Identified in Theoretical Calculations for $Au_2B_7^-$



Theoretically calculated photoelectron spectrum for $Au_2B_7^-$ was found to be in excellent agreement with experimental one confirming theoretical assignment of the most stable structure of the anion (Table 1). We shown that multiple aromaticity, multiple antiaromaticity and conflicting aromaticity concepts can be powerful tools in rationalizing chemical bonding in gold-boron clusters. We plan to test further the hypothesis that gold mimics hydrogen in other gold-boron clusters and use our chemical bonding model for designing gold-boron nanopaticles.

Table 1. Experimental vertical detachment energies (VDEs) of $B_7Au_2^-$ from the photoelectron spectra, compared with theoretical calucaltions

Feature	VDE (expt), eV[a]	MO	VDE (theor), eV[b]
X[c,d]	3.52 (2)	$3a_2$	3.46
A	4.27 (2)	$9a_1$	4.21
B	4.38 (3)	$8a_1$	4.36
C	4.90 (2)	$7b_2$	4.92
D	5.08 (3)	$6b_2$	5.19
E	5.58 (2)	$7a_1$	5.31
F	5.93 (2)	$3b_1$	5.75

a) Experimental vertical detachment energies (VDEs) of $B_7Au_2^-$ from the photoelectron spectra, compared with theoretical calucaltions.
b) At TD-B3LYP/B/aug-cc-pvTZ/Au Stuttgart_rsc_1997_ecp level of theory.

Results of our gold-boron project have been summarized in two articles submitted in press [4,5]. We did not use most of the allocated computer time for this project during our first two years, because we also used computer cluster at USU, which is now almost out of business.

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[2] B. Kiran, X. Li, H.-J. Zhai, L.-F. Cui, L. S. Wang, Angew. Chem. Int. Ed. 2004, 43, 2125.
[3] A. N. Alexandrova, A. I. Boldyrev, H/-J. Zhai, L. S. Wang, J. Phys. Chem. A, 2004, 108, 3509.
[4] A. N. Alexandrova, E. Koyle, A. I. Boldyrev, J. Mol. Mod. 2005, in press.
[5] H.-J. Zhai, L. S. Wang, D. Yu. Zubarev, A. I. Boldyrev, J. Phys. Chem. A, 2005, submitted for publication.