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# Department of Chemistry

## Student Seminar Series

9:45 a.m. Thursday, November 3, 2011 • 331 Smith Hall

Assistant Professor

### Christine Aikens

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#### *Unraveling Nanoparticle Properties Using Density Functional Theory*

Website:

<http://www.k-state.edu/chem/people/faculty/aikens.html>

#### Abstract

Theoretical investigations of monolayer-protected noble metal nanoparticles play an important role in determining the origins of the unique chemical and physical properties of these systems that lead to applications in photonics, sensing, catalysis, etc. In contrast to the strong plasmon resonance peak of larger nanoparticles, the optical absorption spectra of small (< 2 nm) nanoparticles display multiple peaks. Time-dependent density functional theory (TDDFT) is employed to examine the spectrum of the  $\text{Au}_{25}(\text{SR})_{18}$  nanoparticle, and it is determined that delocalized orbitals in the 13-atom nanoparticle core are primarily responsible for the excited state transitions. The ligand field arising from the surrounding gold-thiolate oligomers is responsible for the splitting of the intraband transition.

In the past decade, several gold and silver nanoparticles have been determined to be chiral. Density functional theory calculations on the  $\text{Au}_{11}(\text{BINAP})_4\text{Cl}_2^+$  system provide important information regarding ligand effects on core structure and the resulting circular dichroism spectra. The low energy peaks of  $\text{Au}_{11}\text{L}_4\text{X}_2^+$  arise mainly from transitions between delocalized metal superatom orbitals. Bidentate phosphine ligands have both a structural and electronic effect on the system. Whereas monodentate phosphine ligands lead to a  $C_1$  geometry, the lowest energy structure of  $\text{Au}_{11}\text{L}_4\text{X}_2^+$  has a chiral  $C_2$  structure. The chiral core of  $\text{Au}_{11}\text{L}_4\text{X}_2^+$  is not sufficient to explain the strong Cotton effects, and the intensity of the CD spectrum is increased by the presence of the bidentate phosphine ligands.

Using a combination of electronic structure calculations, XRD, and optical and chiroptical spectra, the "magic"  $\text{Au}_{38}(\text{SR})_{24}$  nanocluster is shown to be chiral with  $D_3$  symmetry.  $\text{Au}_{38}(\text{SR})_{24}$  is found to have an elongated, prolate structure; the electronic structure of this prolate "nanorod" is similar to that previously determined for silver nanorods. As for  $\text{Au}_{25}(\text{SR})_{18}$ , delocalized superatom-like orbitals are responsible for its properties.



Assistant Professor Christine Aikens graduated with a bachelor's degree from the University of Oklahoma. She did a summer internship at the Minnesota Supercomputing Institute under the tutelage of Chemistry Professor Donald Truhlar. She earned her doctorate at Iowa State University, and was a postdoctoral research fellow at Northwestern University.

Two of the major research aims in the Aikens group involve developing a theoretical understanding of the relationship between structure and properties of nanomaterials. Those research areas include the structure and spectroscopic properties of gold and silver nanoparticles and nanoparticle arrays, and the reactivity of nanostructured metal oxide particles.

Aikens is an award-winning scientist, honored with the HP Junior Faculty Award from the American Chemical Society Division of Computers in Chemistry; the Camille-Dreyfus Teacher-Scholar Award; Sloan Research Fellowship; and National Science Foundation CAREER Grant.

Host:

Makenzie Provorse