Lichang Wang
Assistant Professor
Department of Chemistry & Biochemistry
Carbondale, IL 62901-4409
Phone: 618-453-6476; FAX: 618-453-6408
E-Mail: lwang@chem.siu.edu
http://www.science.siu.edu/chemistry/lwang

Theoretical and Computational Chemistry – Method Development and Computation of Phenomena at Nanoscales

Research Progress

August 2006

Page No.

Research Perspective 2

Research Team 3

A. Method Development 4

B. Transition Metal Nanoparticles 8

C. Hydrogen Bonding Network in SAMs 17

D. Fluorescence Sensors 19

Publications and Presentations 20

Support 24

Research Perspective

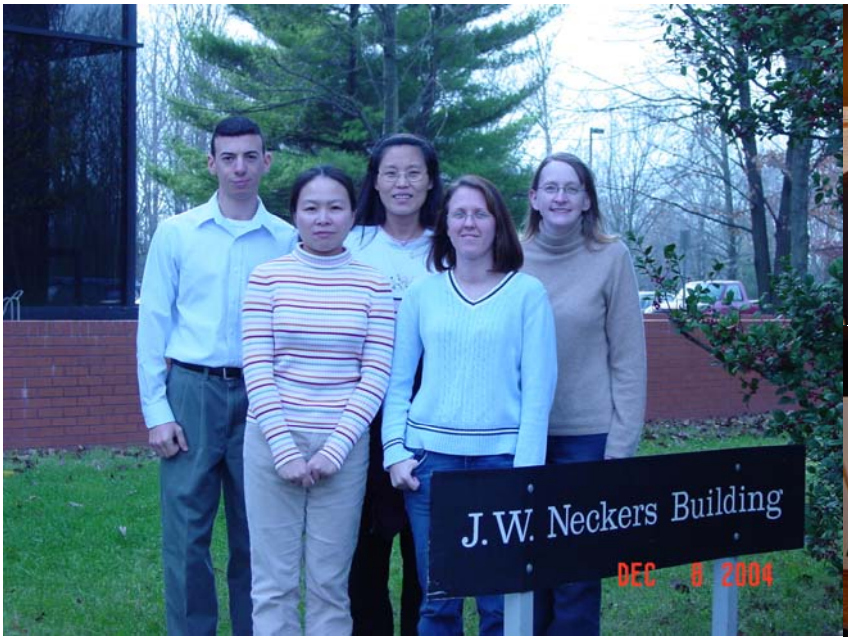
Research in Professor Wang's group at the *Department of Chemistry and Biochemistry, Southern Illinois University Carbondale* has been centered on the development of theoretical methods and computation of thermodynamics, dynamics, and kinetics of chemical processes that take place in materials science and biological systems.

On the research of method development, our interests focus on developing advanced theories for dynamics simulations that are used to deal with large and complex systems. Particular efforts include finding methods to better describe dynamics of large systems with significant quantum effects and constructing potential energy surfaces (PESs) to describe accurately the interactions among atoms. During the past five years, we have been developing methods to provide a measurement on the accuracy of the mixed quantum/classical dynamics theory in the calculation of critical properties, such as reaction probabilities, for large systems that have a strong quantum character but a full quantum treatment is not feasible. We are also in the process of developing and implementing a Nuclear Density Functional Theory (NDFT) to treat the dynamics of large systems full quantum mechanically. In the research of constructing PESs for transition metal nanoparticles, we have particularly examined the accuracy of the Sutton-Chen PES for Ir_n, Pt_n, Au_n, and Ag_n clusters through comparisons with our density functional theory (DFT) results. As a result, new Sutton-Chen parameters were obtained for these metals.

Our research in materials science focuses on two areas. The first area is the study of transition metal nanoparticles, Fe, Co, Ni, Cu, Ru, Rh, Pd, Ag, Os, Ir, Pt, Au, Mo, as well as their alloys, as potential nanoscale information storage materials and as catalysts for oxygen reduction and for methane activation. The second focus is to understand the intermolecular interactions in self-assembled monolayers and multilayers (SAM), particularly the formation of hydrogen bonding network. This understanding is important to better control the supramolecular organization. Both electronic structure calculations and dynamics simulations have been employed in these studies.

The objective of our research in developing fluorescence sensors based on the photoinduced electron transfer mechanism is to advancing sensing systems that are capable of sensitive and selective detection of small molecules of biological significance, such as glucose metabolites. We have performed electronic structure calculations to select fluorophores and receptors that are suitable for the target molecules as well as kinetic calculations to determine the electron transfer rates.

Research Team



Current group members

Left Picture (from left): **Mark Sadek** (URS–Undergraduate Research Student),
Li Xiao (Ph.D. student), **Lichang Wang,**
Jennifer Yukna (Ph.D. student), **Tiffany Pawluk** (Ph.D. student).

Right Pictures (from top): **Kasi Spivey** (M.Sc. student), **Joe Williams** (URS).

Not shown in the pictures: **Chasity Love** (URS), **Brian Stachowiak** (URS).

Past group members

Prof. Ju Xin (Visiting Professor), **Prof. Wenqin Zhang** (Visiting Professor), **Chunrong Song** (Research Student), **Hongmei Tang** (Visiting Scholar), **Bethany Tollberg** (Summer URS), **Xianqui Hu** (Research Student), **Yanping Cao** (Graduate, M.Sc.), **Yasuhiro Hirata** (URS), **Ron Jenkins** (URS), **Aaron Logan** (URS), **Naga Jyothi Lavu** (Computer Assistant).

Project A. Method Development

In the research of method development, we have been working on developing accurate dynamics theories for large and complex systems, constructing potential energy surfaces (PESs) for systems including transition metal nanoparticles, and conducting comparative studies of various functionals in density functional theory (DFT) calculations.

For any given system, if the potential energy surface (PES) of the system is known, many interesting properties of the system can be obtained by solving nuclear equations of motion, i.e. the Schrödinger or the Newton equation. The most accurate description of dynamics for a system is the Schrödinger equation, but this can be done only for small systems, i.e. systems consisting of 4 or less atoms. For a system consisting of more than 4 atoms, the current practice is to describe its dynamics using either a pure classical method or an approximate method.

With many applications in the past, however, two of the most important issues need to be addressed in the field of dynamics theories if one wants to obtain various properties for large systems accurately. One issue is that we don't yet have any measure of the accuracy of an approximate method when it is used to describe dynamics of a large system that shows a significant quantum character. The second issue is the need of a capable full quantum dynamics theory that can describe dynamics of large systems. Over the past five years, our research efforts have been directed at providing solutions to these issues.

An accurate PES is another important factor to ensure accurate dynamics results. Although there is a possibility of using direct dynamics simulations, or ab initio molecular dynamics simulations, to study dynamics of various systems, it is unlikely feasible to the systems of our interest due to at least the following reason. The systems that we are interested in contain transition metal elements. Our extensive electronic structure calculations have shown that many electronic states are close to each other energetically. In ab initio dynamics simulations, one may use different electronic states and consequently results in wrong dynamics information. Therefore, we put a lot of efforts in constructing accurate PESs for transition metal nanoparticles.

A key to construct accurate PESs is to obtain as many accurate points from electronic structure calculations as possible. Density functional theory calculations are used in our work and none of the functionals can guarantee to generate accurate results. We therefore have conducted comparative studies of functionals usined in DFT calculations for transition metal nanoparticles.

Some of our results are summarized below with the abstracts of our publications attached at the end of this section.

(i) Predicting the accuracy of Q/CTDSCF theory for describing large systems.[A2]

Our effort to address the accuracy issue started from the investigation on the accuracy of the mixed quantum/classical time-dependent self-consistent field (Q/CTDSCF) theory when it is applied to describe dynamics of large systems.

In a Q/CTDSCF MD simulation, one first divides a system of interest into two subsystems with one being represented quantum mechanically and the other classically. A primitive Q/CTDSCF MD simulation involves solving equations of motion for these two subsystems self-consistently:

$$i\hbar\frac{\partial\varphi(\boldsymbol{r},\boldsymbol{t})}{\partial\boldsymbol{t}}=[\hat{\boldsymbol{H}}_0+\boldsymbol{V}(\boldsymbol{r},\boldsymbol{R}(\boldsymbol{t}))]\varphi(\boldsymbol{r},\boldsymbol{t}),\quad(1)$$

$$\dot{\boldsymbol{P}}_R(\boldsymbol{t}) = -\frac{\partial}{\partial \boldsymbol{R}} < \varphi \,|\, \boldsymbol{V}(\boldsymbol{r}, \boldsymbol{R}) \,|\, \varphi >|_{R=R(t)}, \quad (2)$$

$$\dot{\boldsymbol{R}} = \boldsymbol{P}_{\boldsymbol{R}}(\boldsymbol{t}) / \boldsymbol{m}, \quad (3)$$

where Eq.(1) is for the quantum subsystem and Eq.(2) and Eq.(3) for the classical subsystem. We use R and r to represent the classical and quantum coordinates, respectively, and $\varphi(\boldsymbol{r},\boldsymbol{t})$ is the wavefunction of the quantum subsystem. Eqs. (1)—(3) consist of the simplest version of the Q/CTDSCF methods.

Examples have shown that the Q/CTDSCF simulations often provide more accurate results than a classical MD simulation when quantum effects are important. However, the accuracy of this approximate treatment to an arbitrary large system is unknown. For instance, studies of different benchmark systems have shown that the Q/CTDSCF treatments work in some cases but not always. These studies revealed that the accuracy depends sensitively on the system that is being investigated and the PES that is used for the study. Furthermore, these benchmark studies cannot provide answers as to how the accuracy of this method extrapolates to larger systems in which full quantum calculations cannot be performed.

Our strategy to predict the accuracy of Q/CTDSCF results is based on the hypothesis: If the accuracy of the Q/CTDSCF results from a few reduced dimensional studies of a large system does not change, we can then use the accuracy of the carefully-chosen reduced-dimensional systems as the accuracy of the Q/CTDSCF treatment for the large system.

In order to test whether the above strategy works, we used the $O(^3P)$ + HCl reaction as the first benchmark study. In this case, we consider the collinear case as a reduced system of the entire system (three-dimensional). When the Q/CTDSCF treatment failed in describing the reduced system, i.e. the linear case, we predict that it will also fail in describing the entire system, i.e. the three-dimensional case. The comparison shown in Fig.1 between the Q/CTDSCF results (short dashed line) and the full quantum results (solid line) illustrates that it is indeed the case. This hypothesis is being further tested using other reactions.

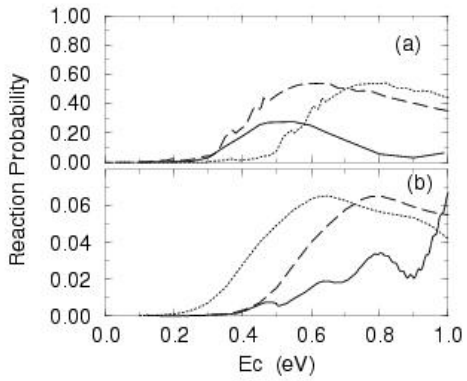


Figure 1. Thereaction probability as a function of collision energy (Ec) for the collinear (a) and the J=0 (b) O + HCl reaction obtained from a full quantum (solid), mixed quantum/classical (short dashed line), and a simple shifted quantum/classical (long dashed line).

(ii) Developing a full quantum MD theory that can deal with large systems with significant quantum effects.

The current full quantum treatment by solving Schrödinger equation does not allow us to study dynamics of large systems, such as CH_4 dissociation on nanoparticles at high coverage, where quantum effects are expected to be significant. Over the past five years, we have devoted our efforts in developing and implementing a new full quantum dynamics theory, i.e. Nuclear Density Functional Theory (NDFT).

Quite similar to the electronic DFT, the NDFT involves, in principle, solving the Kohn-Sham type equations for the nuclei in a homonuclear system:

$$[-\frac{1}{2\boldsymbol{M}}\nabla^2 + \boldsymbol{V}(\boldsymbol{R}) + \mu_c(\boldsymbol{R})]\psi_i(\boldsymbol{R}) - \int \frac{\rho(\boldsymbol{R},\boldsymbol{R}')}{|\boldsymbol{R}-\boldsymbol{R}'|}\psi_i(\boldsymbol{R}')d\boldsymbol{R}' = \varepsilon_i\psi_i(\boldsymbol{R}), \quad (4)$$

$$\mu_c(\boldsymbol{R}) = \boldsymbol{d}(\rho\varepsilon_c)/\boldsymbol{d}\rho \quad \text{and} \quad \rho(\boldsymbol{R},\boldsymbol{R}') = \sum_{j=1}^{N}\psi_j(\boldsymbol{R})\psi_j^*(\boldsymbol{R}'), \quad (5)$$

where these equations are the same as the electronic Kohn-Sham equations except for the variables V and R in the above equations representing the PES and the nuclear coordinates, respectively.

Despite the similarities in spirit between the electronic DFT and NDFT, there are many theoretical challenges which need to be addressed before NDFT becomes a practical theory. For instance, the systems in the electronic DFT consist of only electrons. In contrast, NDFT will have to deal with systems with more than one type of nuclei. Therefore, a strategy has to be developed in NDFT to deal with systems consisting of different types of nuclei. One advantage of NDFT over the electronic DFT is that one can easily obtain accurate exchange-correlation energy. Preliminary framework of NDFT was developed, but many of the theoretical issues are being studied.

The implementation of the NDFT theory for systems consisting of the same type of atoms, i.e. uniatomic systems, is very similar to those of electronic DFT. However, for the systems consisting of more than one type of nuclei, different implementations will have to be employed. We are implementing the NDFT and using the dissociation of H_3^+ as our first benchmark system to test various perspective of the NDFT theory.

(iii) Constructing potential energy surfaces for describing interactions among atoms in transition metal nanoparticles. [A1]

There are four types of PESs, i.e. the Finnis-Sinclair potentials, the embedded atom potentials, the tight binding potentials, and the Murrell-Mottram potentials, which have been widely used for describing interactions among transition metal atoms. Using DFT results of Ir_n, Pt_n, Au_n, Ag_n, we have examined the accuracy of the Sutton-Chen potential, which is a modified Finnis-Sinclair potential:

$$V = \varepsilon\left[\frac{1}{2}\sum_{ij} v(r_{ij}) - c\sum_i \sqrt{\rho_i}\right], \quad (6)$$

where the pair potential is given by

$$v(r_{ij}) = \left(\frac{a}{r_{ij}}\right)^n, \quad (7)$$

and the local electron density is given by

$$\rho_i = \sum_j \left(\frac{a}{r_{ij}}\right)^m. \quad (8)$$

In Eqs. (6)-(8), r_{ij} is the distance between two atoms and ε, a, c, m, and n are parameters, which are constant for each metal but vary for different metals.

The parameters used in the Sutton-Chen potential were optimized by fitting to the bulk properties of each metal. Therefore, it is necessary to investigate whether the Sutton-Chen potential can be used to accurately describe the interactions among transition metal atoms in small systems. As our extensive results obtained for transition metal clusters from DFT calculations have just become available, it is possible to investigate the accuracy of the PESs.

Our study shows that the original Sutton-Chen potential was not accurate for describing small metal clusters. We optimized these parameters to our DFT results for the small clusters and constructed a new PES for Ir_n, Pt_n, Au_n, Ag_n clusters.

(iv) Comparative studies of various functionals in DFT calculations.

One of our goals in the method development is to assess the accuracy of various functionals that are widely used in the studies associated with transition metal nanoparticles. Comparative studies have been carried out for transition metal clusters. Our current focus is to compare the results of PW91, PBE, B3LYP, and M05 functionals when they are used to describe CH_4-Pt_n and O_2-PtVFe systems. Future work will include extend the comparative studies to other systems that we have studied.

Abstracts:

[A1] **The impact of PES on MD results of the coalescence of M_2 + M with M = Ir, Pt, Au, Ag**

Tiffany Pawluk, Li Xiao, Jennifer Yukna, and Lichang Wang, *J. Chem. Theo. Comput.* (submitted).

The accuracy of the Sutton-Chen potential energy surface (PES) for describing atomic interactions in small metal clusters was investigated by comparison with density functional theory (DFT) calculation results. The binding energies calculated using the Sutton-Chen PES for the dimers, trimers, 8-, and 13-atom clusters of four transition metals, Ir, Pt, Au, and Ag differ from those obtained with DFT calculations. As the DFT results agree well with the available experimental data, the above disagreement indicates that the original Sutton-Chen PES cannot accurately describe the interactions among atoms in the cluster for these metals. The parameters of the Sutton-Chen potential were therefore optimized to the DFT results for each of the metals. Molecular dynamics (MD) simulations were carried out on the coalescence of a dimer with a single atom for these metals. Both the original bulk and the cluster optimized Sutton-Chen PESs were tested with various incident angles and initial kinetic energies. The MD results show that the coalescence is highly dependent on the PES. This demonstrates that use of an accurate PES is critical, particularly at low energy regime. The kinetic energy, incident angle, and choice of metal were examined for their role in the outcome of the coalescence process.

[A2] **The accuracy of the quantum/classical time-dependent self-consistent field treatment to reaction dynamics of large systems**

Lichang Wang, *Chem. Phys. Lett.* 383(2004)62-66.

A method is proposed to predict the accuracy of the quantum/classical time-dependent self-consistent field (Q/C TDSCF) treatment in the calculation of reaction probabilities. This method was derived based on comparisons of calculated reaction probabilities between the collinear and the three dimensional results for the benchmark $O(^3P)$ + HCl reaction, which show that the accuracy of the Q/C TDSCF reaction probabilities does not change from the collinear to the three dimensional dynamics. In addition, an energy shift correction is introduced to improve the accuracy of the Q/C TDSCF results. The results from studies of the $O(^3P)$ + HCl reaction indicate that the inclusion of this simple shift in the Q/C TDSCF treatments allows us to obtain accurate reaction probabilities within the energy range of chemical and biological interest. Our analysis indicates that this shift is related to the symmetry of the potential energy surface between the reactant and product channels in the transition state region.

Project B. Transition Metal Nanoparticles

A major goal of our research in the studies of transition metal nanoparticles is to provide fundamental understanding of their catalytic activities as well as to establish the correlation between the catalytic activities and the intrinsic properties of these nanomaterials. Our research activities have focused on studies of the size and structure effects on the energetic and electromagnetic properties of the transition metal nanoparticles, Fe, Co, Ni, Cu, Ru, Rh, Pd, Ag, Os, Ir, Pt, Au, V, Mo, and their alloys, PtAu and PtVFe. Three reactions, CO adsorption, CH_4 activation, and O_2 reduction, have also been investigated with transition metal clusters as model catalysts.

(i) Bare transition metal clusters [B4–B18]

The most fundamental questions in the study of bare transition metal clusters are: what are the most stable structures? Are there any novel structures? And how do various electromagnetic properties correlate with the cluster size and structure? Our research aims to provide answers to these questions.

Simple cubic structures. It had been general believed that the most stable structures of small transition metal clusters may be different from their corresponding bulk structures when the clusters consist of less than 10 atoms. In the search for the most stable structure of small clusters, however, we found that simple cubic structure is the most stable structure among Ru, Ir, and Rh clusters consisting of more than 10 atoms. Our work also shows that a transition from the simple cubic to the corresponding bulk structure occurs at different cluster size depending on the element that it is made of.[B15, B16]

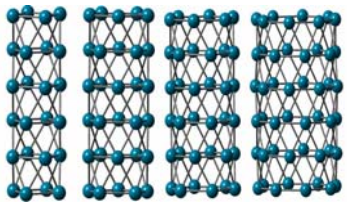


Figure 2. Single-wall transition metal nanotubes.

Planar structures of Au clusters. It had been believed that the most stable small gold clusters are planar with the clusters consisting of less than 7 atoms. The prediction from our DFT calculation shows that the transition from a more stable planar structure to a more stable three-dimensional structure for Au clusters occurs around the size of 13. The inclusion of spin-orbit coupling does not change the prediction.[B14] On the other hand, the structures of ligand protected undecagold clusters, Au_{11}, were shown experimentally to be three-dimensional. We carried out DFT calculations using SCH_3 as ligands to explore the effect of ligands on the structure of Au_{11} clusters. The results show that the structures of small gold clusters are altered substantially in the presence of ligands. In the case of Au_{11} clusters, the most stable structure is three-dimensional in the presence of SCH_3 ligands.[B4]

Novel structures. Our DFT calculations predicted the existence of single-wall Pd and Pt nanotunes [B6] with interesting electromagnetic properties, as shown in Fig. 2. Single-wall Ir nanotubes were also predicted from our DFT calculations.[B11] So far, only single-wall Pt nanotubes were detected experimentally. The second class of novel structures predicted from our DFT calculations is transition metal fullerenes. Currently, we are performing frequency calculations to ensure that these fullerene structures are energy minima.

Definition of structure factor. It is well known that structure is an important factor that affects cluster properties. However, there is no single quantity that can be used to distinguish one structure from another. This makes it difficult to predict the electromagnetic properties for a given sized cluster in response to a change in structure. Furthermore, the lack of structure characterization makes it more difficult to compare clusters made of different elements. As such, we defined a structure factor, S_f, through analysis of a collection of clusters that we

investigated: $S_f = g_s\ g_d\ N_c$, where N_c is the coordination number per atom of the cluster and g_s and g_d are the factors to account for symmetry and the dimensionality of the structure, respectively. This definition is made based on the fact that the strongest characteristic of a structure is determined by the coordination numbers of each atom.

This structure factor allows us to uniquely and conveniently correlate a structure among isomers with its properties and make direct comparisons of their properties among different types of clusters, such as those shown in Fig. 3. Analysis shows that the contour plots, such as in Fig.3, can be used as the fingerprint for the nanoparticles of different elements. Moreover, if the electromagnetic properties and the binding energy are measured experimentally, the structure of the nanoparticle can be predicted by mapping these properties onto the contour plots.[B13,B15,B17]

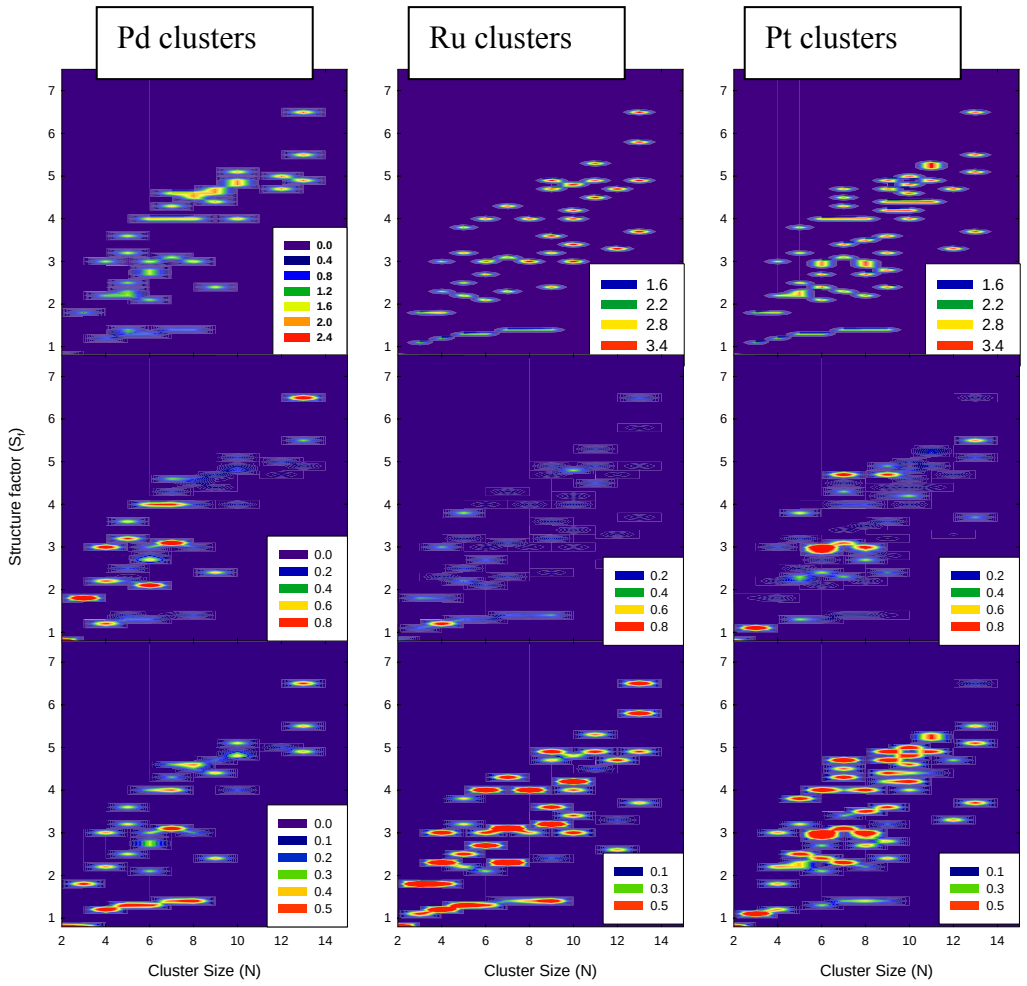


Figure 3. Contour plots of the binding energy(in eV/atom, top), the HOMO-LUMO energy gap (in eV, middle), and the magnetic moment (in μ_B/atom, bottom) as a function of cluster size (N) and structure factor (S_f) for Pd clusters (left), Ru clusters (middle), and Pt clusters (right).

The current definition of structure factor allows us to correlate the properties of small clusters with their structures. Its usefulness for describing larger clusters is being further examined. Furthermore, we are also exploring whether the use of this definition can allow us to predict some new physics and chemistry of transition metal nanoparticles.

(ii) Carbon monoxide adsorption

In order to explore the effect of size, structure, adsorption site, and composition of transition metal nanoparticles on the catalytic activities, we chose to carry out DFT calculations for CO adsorption on PtAu clusters. The results show that CO stretching frequencies can be used as a sensitive tool to probe the adsorption site and cluster composition. [B2,B9,B10]

(iii) Methane activation

Methane activation on Pt surfaces and clusters has been studied extensively both experimentally and computationally due to the practical applications. However, to fully understand methane activation on transition metal nanoparticles, further investigation in both experiments and computation is needed. For instance, theoretical studies of CH_4 activation on Pt clusters were done only for systems consisting of 1-2 Pt atoms. We carried out DFT studies of CH_4 activation on one Pt atom and Pt_4 cluster. Both B3LYP and PW91 were used in our study. New lower energy reaction pathway was obtained for CH_4 activation in the presence of one Pt atom. Reaction pathways were also obtained for the first time for CH_4 activation in the presence of a 4-atom Pt cluster. Furthermore, our study shows that the most discrepancies between the B3LYP and PW91 results are in the calculation of reaction barrier height.[B3]

(iv) Oxygen reduction

An important issue in the design of hydrogen fuel cell is the lack of efficient cathode catalysts for oxygen reduction that can operate at room temperatures. Common cathode catalysts are platinum or platinum based alloys. It has been shown experimentally that bimetallic or ternary platinum alloys are more efficient catalysts. Theoretical studies of alloy catalysts will be helpful in understanding of their catalytic activities and consequently be helpful in the practical design. In addition, platinum is expensive and its replacement will be useful economically. The purpose of our research in the study of oxygen reduction is, therefore, two folds. One is to understand why platinum alloys have better catalytic activities. The second is to explore what is the minimum Pt composition such that the alloys still maintain high catalytic activities. Towards that end, DFT calculations were performed for O_2 chemisorptions, molecular and dissociative, in the presence of PtVFe, Pt_3, and $PtFe_2$. It has been found that PtVFe is a better catalyst in O_2 chemisorption due to higher charge transfer to O_2, direct dissociative pathways, and narrower barrier widths. Two O_2 reaction pathways are shown in Fig.4. [B1]

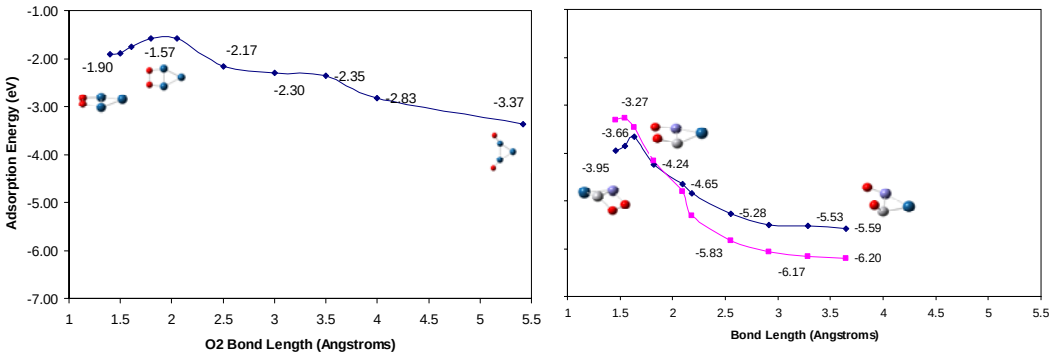


Figure 4. O_2 dissociation pathways on a Pt_3 cluster (left) and on a PtVFe cluster (right). Three structures starting from left in each picture are the reactant, transition state, and product, respectively. Red, blue, gray, and purple balls represent O, Pt, V, and Fe atoms, respectively. Blue and pink curves represent DFT results obtained for different spin states.

Abstracts:

[B1] **Density functional theory studies of O_2 chemisorptions on model ternary PtVFe catalysts**

Joseph I. Williams and Lichang Wang, *J. Am. Chem. Soc.* (submitted).

We report the first theoretical studies of O_2 molecular and dissociative chemisorptions on the model ternary PtVFe catalysts. In order to choose model catalysts we studied bare dimer and trimer PtVFe clusters with all possible compositions. Among three adsorption structures being studied, Pauling, Griffith, and bridge structures, the O_2 bond is weakened the most in the bridge structure, then the Griffth structure, and then the Pauling structure. The alloyed clusters are most effective in transferring electrons to O_2 species and weakening O_2 bond when the O atoms are attached to non-Pt atoms. Our results suggest that the presence of any Pt skin would decrease the overall effectiveness of the cluster with respect to oxygen reduction. A linear correlation can be found between the frequency and the O_2 bond distance up to 1.4Å. Finally, our calculations suggest that the effectiveness of PtVFe nanoparticles in the oxygen reduction is due to a narrower activation energy width, and due to the presence of a greater number of direct O_2 dissociation pathways.

[B2] **Effect of adsorption site, size, and composition of Pt/Au bimetallic clusters on the CO frequency: A density functional theory study**

Mark M. Sadek and Lichang Wang, *J. Phys. Chem. B* (submitted).

Density functional theory (DFT) calculations were performed to investigating the C–O stretching frequency changes when CO molecule was adsorbed to the Pt/Au clusters of 2-4 atoms. Our calculations show that the adsorption site is the most sensitive quantity to the C–O stretching frequency shifts. All the bridge site adsorptions yield a CO frequency band of 1737–1927 cm^{-1} with the CO bond distance of 1.167–1.204 Å regardless cluster composition and size, and all the atop site adsorptions yield a CO frequency band of 2000–2091 cm^{-1} with the CO bond distance of 1.151–1.167 Å. More detailed analysis of the two frequency bands shows that each band may consist of two emerging subbands with the lower frequencies corresponding to the CO adsorption to Pt atoms and the higher frequencies to the CO adsorption to Au atoms. Furthermore, the CO frequency decreases with increasing Pt composition in the bimetallic clusters. Our results indicate that the Fourier transform infrared spectroscopy measurement may be used as a sensitive tool to identify adsorption sites and perhaps surface composition of the Pt /Au nanoparticles using CO adsorption as the probe.

[B3] **Methane activation on Pt and Pt_4: A density functional theory study**

Li Xiao and Lichang Wang, *J. Phys. Chem. B* (submitted).

The activation mechanisms of a methane molecule on a Pt atom (CH_4-Pt) and on a Pt tetramer (CH_4-Pt_4) were investigated using density functional theory (B3LYP and PW91). A new lower energy pathway was identified for the CH_4 activation on a Pt atom. In the new pathway, the Pt atom forms a complex with carbene and two hydrogen atoms below the reactant asymptote. Subsequently, a hydrogen molecule was formed and desorbed from the CH_4-Pt system by a small amount of energy. We report here the first theoretical study of methane activation on a Pt_4 cluster. The DFT studies show that the cleavage of the C-H bond occurs initially on one Pt atom rather than on a surface of the tetrahedral structure then the H atom migrates to a neighboring Pt atom undergoing a small energy barrier. The results also indicate that the reaction rate of the CH_4-Pt system is smaller than that of CH_4-Pt_2/Pt_3/Pt_4 system due to

the electronic state crossing taking place at the early stage. Compared with both CH_4-Pt_2 and CH_4-Pt_3 systems, CH_4-Pt_4 exhibits a slightly larger reaction rate.

[B4] **Structures of undecagold clusters: Ligand effect**
Kasi Spivey, Joseph I. Williams, and Lichang Wang, *Chem. Phys. Lett.* (submitted).

The most stable structure of undecagold, or Au_{11}, clusters was predicted from our DFT calculations to be planar [Chem. Phys. Lett. 392 (2004) 452; J. Chem. Phys. 124 (2005) 114309]. The structures of ligand protected undecagold clusters were shown to be three-dimensional experimentally. In this work, we used DFT calculations to study the ligand effect on the structures of Au_{11} clusters. Our results show that the most stable structure of Au_{11} is in fact three-dimensional when SCH_3 ligands are attached. This indicates that the structures of small gold clusters are altered substantially in the presence of ligands.

[B5] **Theoretical studies of silver clusters**
Jennifer Yukna, Hongmei Tang, and Lichang Wang, *J. Chem. Phys.* (submitted).

Silver clusters consisting of 2-16 atoms were investigated using spin polarized density functional theory calculations with PW91 functional and a plane wave basis set. Linear clusters were found to undergo Peierls bond distortion and the most stable planar clusters have high coordination numbers. The results show that planar silver clusters up to six atoms are more stable than their three-dimensional isomers. The linear trimer is just as stable as the planar trimer. New global minima were found for clusters of 9, 10, and 13–16 atoms. The most stable even numbered clusters are singlet and odd-numbered clusters are doublet. The Sutton-Chen potential was also used to calculate the relative stability of selected clusters; however, the results overestimate the binding energy of these clusters. This suggests that a modification has to be made in order to use it in the search of global minima for larger silver clusters or in the study of coalescence of silver clusters. In this work, the Sutton-Chen potential was modified by fitting the Sutton-Chen parameters to the selected DFT results. The modified Sutton-Chen potential agreed well with the DFT results.

[B6] **Density functional theory study of single-wall platinum nanotubes**
Li Xiao and Lichang Wang, *Chem. Phys. Lett.* (submitted).

Single-wall platinum nanotubes (SWPtN) were studied using spin-polarized density functional theory calculations. These nanotubes consist of 5-, 6-, and 8- Pt atoms coiling around the tubular axis forming 3.54 – 4.73 Å in diameter and 0.7 – 1.4 nm and infinite in length. Two types of wall structures, square and triangular, were investigated. The results show that triangular nanotubes are more stable. Our results suggest that it is also feasible to synthesize the 5- and 8-atom triangular nanotubes as the 6-atom Pt nanotubes were found experimentally. These SWPtN may provide a new dimension in the catalytic applications of platinum.

[B7] **The impact of PES on MD results of the coalescence of M_2 + M with M = Ir, Pt, Au, Ag**
Tiffany Pawluk, Li Xiao, Jennifer Yukna, and Lichang Wang, *J. Chem. Theo. Comput.* (submitted).

The accuracy of the Sutton-Chen potential energy surface (PES) for describing atomic interactions in small metal clusters was investigated by comparison with density functional theory (DFT) calculation results. The binding energies calculated using the Sutton-Chen PES for the dimers, trimers, 8-, and 13-atom clusters of four transition metals, Ir, Pt, Au, and Ag

differ from those obtained with DFT calculations. As the DFT results agree well with the available experimental data, the above disagreement indicates that the original Sutton-Chen PES cannot accurately describe the interactions among atoms in the cluster for these metals. The parameters of the Sutton-Chen potential were therefore optimized to the DFT results for each of the metals. Molecular dynamics (MD) simulations were carried out on the coalescence of a dimer with a single atom for these metals. Both the original bulk and the cluster optimized Sutton-Chen PESs were tested with various incident angles and initial kinetic energies. The MD results show that the coalescence is highly dependent on the PES. This demonstrates that use of an accurate PES is critical, particularly at low energy regime. The kinetic energy, incident angle, and choice of metal were examined for their role in the outcome of the coalescence process.

[B8] **Structural study of gold clusters**

L. Xiao, B. Tollberg, X. Hu, and L. Wang, *J. Chem. Phys.*124 (2006)114309-1—114309-10.

Density Functional Theory (DFT) calculations were carried out to study gold clusters of up to 55 atoms. Between the linear and zigzag monoatomic Au nanowires, the zigzag nanowires were found to be more stable. Furthermore, the linear Au nanowires of up to 2 nm are formed by slightly stretched Au dimers. These suggest that a substantial Peierls distortion exists in those structures. Planar geometries of Au clusters were found to be the global minima till the cluster size of 13. A quantitative correlation is provided between various properties of Au clusters and the structure and size. The relative stability of selected clusters was also estimated by the Sutton-Chen potential, and the result disagrees with that obtained from the DFT calculations. This suggests that a modification of the Sutton-Chen potential has to be made, such as obtaining new parameters, in order to use it to search the global minima for bigger Au clusters.

[B9] **A density functional theory study of CO adsorption on Pt-Au nanoparticles**

Q. Ge, C. Song, and L. Wang, *Comp. Mater. Sci.* 35(2006)247-253.

Structures and energetics of bimetallic Pt-Au clusters upto 13 atoms with different Pt/Au ratios have been studied using the density functional theory approach. Our results indicate that Pt and Au tend to segregate in the nanoparticles. Furthermore, CO adsorption on these nanoparticles was calculated and compared with that on the surface of bulk PtAu alloy. The results showed that both Pt and Au sites of the particles exhibit significant binding toward CO. Among all the sites explored, CO prefers Pt site that is adjacent to Au. These results were compared with CO adsorption on pure metal clusters as well as surfaces of bulk metals.

[B10] **DFT studies of Pt/Au bimetallic clusters and their interactions with the CO molecule**

Chunrong Song, Qingfeng Ge, and Lichang Wang, *J. Phys. Chem. B* 109(2005)22341-22350.

Density functional theory (DFT) calculations were performed to study Pt/Au clusters of different size, structure, and composition as well as their interactions with a CO molecule. Among the Pt/Au isomers studied here, the planar structure is the most stable structure in many Pt compositions, although three-dimensional structures become more stable with increasing Pt composition. Furthermore, structures with the Pt atoms surrounded by Au atoms are more stable among homotops. However, these conclusions will be altered if ligands are attached to the Pt/Au bimetallic clusters, as evidenced from the results of CO adsorption. When both Au

and Pt sites are exposed, CO adsorption at the Pt site is stronger. If only Au site is available for CO adsorption, the strongest adsorption occurs at ~25% Pt composition, which may correlate with the experimentally observed reactivity of the core-shell structured Pt/Au nanoparticles.

[B11] **Studies of iridium nanoparticles using density functional theory calculations**
Tiffany Pawluk, Yasuhiro Hirata, and Lichang Wang, *J. Phys. Chem. B* 109(2005)20817-20823.

The energetics and the electronic and magnetic properties of iridium nanoparticles in the range of 2-64 atoms were investigated using density functional theory calculations. A variety of different geometric configurations were studied, including planar, three-dimensional, nanowires, and single-walled nanotubes. The binding energy per atom increases with size and dimensionality from 2.53 eV/atom for the iridium dimer to 6.09 eV/atom for the 64-atom cluster. The most stable geometry is planar until 4 atoms and three-dimensional thereafter. The simple cubic structure is the most stable geometric building block until a strikingly large 48-atom cluster, when the most stable geometry transitions to face-centered cubic, as found in the bulk metal. The strong preference for cubic structure among small clusters demonstrates their rigidity. This result indicates that iridium nanoparticles intrinsically do not favor the coalescence process. Nanowires formed from linear atomic chains of up to 4-atom rings were studied, and the wires formed from 4-atom rings were extremely stable. Single-walled nanotubes were also studied. These nanotubes were formed by stacking 5- and 6-atom rings to form a tube. The ring stacking with each atom directly above the previous atom is more stable than if the alternate rings are rotated.

[B12] **The nonmetallicity of molybdenum clusters**
Wenqin Zhang, Xiaorong Ran, Haitao Zhao, and Lichang Wang, *J. Chem. Phys.* 121(2004)7717-7724.

Molybdenum clusters consisting of 2-55 atoms were investigated using density functional theory calculations with a plane wave basis set. The results show that the linear and planar molybdenum clusters have a strong tendency to form dimers. This tendency results in the formation of alternate short and long bonds within a linear cluster, in which the strength of these short bonds is covalent. Therefore, the linear and planar Mo clusters exhibit significant non-metallic characteristics. Furthermore, the linear and planar Mo clusters show a strong even-odd effect in binding energy with the even-numbered clusters being more stable than their neighboring odd-numbered clusters. On the other hand, the even-odd effect in the energy gap between the highest occupied and the lowest unoccupied molecular orbitals, i.e. the HOMO-LUMO energy gap, for the linear and the planar clusters is different. The odd-numbered linear clusters and even-numbered planar clusters have larger HOMO-LUMO energy gaps than their corresponding neighboring clusters.

[B13] **Structure of platinum clusters: planar or spherical?**
Li Xiao and Lichang Wang, *J. Phys. Chem. A* 108(2004)8605-8614

Platinum clusters of up to 55 atoms were studied using density functional theory with a plane wave basis set. The results show that the planar platinum clusters of up to 9 atoms are as stable as their three-dimensional isomers and the 6-atom planar cluster is, surprisingly, more stable than its three-dimensional isomers. Among the three-dimensional platinum clusters investigated in this work, the layered clusters are found to be as stable as their spherical close-packed isomers. The high stability of planar and layered clusters suggests that it is easy to grow

platinum monolayer or multilayer. The existence of many energetically possible isomers shows a fluxional structural characteristic of platinum clusters. The effect of the spin-orbit coupling was investigated and the results show that the relative stability of the Pt clusters is not affected although the binding energy of the cluster increases if the spin-orbit coupling is included in the calculation. Most of the platinum clusters studied here show good conductivity and ferromagnetism, which make them potentially useful as high density magnetic data storage materials. A quantitative correlation is provided between various properties of platinum clusters and the structure and size.

[B14] **From planar to three-dimensional structural transition in gold clusters and the spin-orbit coupling effect**

Li Xiao and Lichang Wang, *Chem. Phys. Lett.* 392(2004)452-455.

The transition from the planar to three-dimensional structures in Au clusters occurs at the cluster consisting of 14 Au atoms, which is predicted based on the first-principles density functional theory (DFT) calculations including the spin-orbital coupling. The results show that the spin-orbit coupling does not alter the relative stability of Au clusters but increases the binding energy of the cluster by about 0.08 eV/atom for all the clusters studied here. The energy gap between the highest occupied and the lowest unoccupied orbitals, on the other hand, decreases when the spin-orbit coupling is included.

[B15] **The simple cubic structure of ruthenium clusters**

Wenqin Zhang, Haitao Zhao, and Lichang Wang, *J. Phys. Chem. B* 108(2004)2140-2147.

Ruthenium clusters of up to 64 atoms were studied using density functional theory with a plane wave basis set. The simple cubic structure was found to be the most stable structure in the formation of small ruthenium clusters. A strong trend of trimer formation was also observed in the linear ruthenium clusters. All the ruthenium clusters investigated in this work are ferromagnetic with large magnetic moment and have small energy gaps between the highest occupied and the lowest unoccupied molecular orbitals. A quantitative correlation was established between the energetic, electronic, and magnetic properties of ruthenium clusters and the cluster size and structure. Our analysis showed that the atoms of similar bonding environments have similar binding energies. Based on this analysis, estimations were made on the binding energy for certain planar and simple cubic ruthenium clusters. The estimated binding energies are in good agreement with those from the density functional theory calculations.

[B16] **The simple cubic structure of Ir clusters and the element effect on cluster structures**

Wenqin Zhang, Li Xiao, Yasuhiro Hirata, Tiffany Pawluk, and Lichang Wang, *Chem. Phys. Lett.* 383(2004)67-71.

The simple cubic was found to be the most stable structure for Ir clusters in the subnanometer range from our density functional theory calculations. We further examined various structures of group 8-10 precious metal clusters. The tendency to form the simple cubic structure becomes stronger from right to left across a period and from top to bottom in the group, while the trend is opposite for the formation of icosahedrons or cubo-octahedrons.

[B17] **Structure effects on the energetic, electronic, and magnetic properties of palladium nanoparticles**

Wenqin Zhang, Qingfeng Ge, and Lichang Wang, *J. Chem. Phys.* 118(2003)5793-801.

A systematic investigation of palladium nanoparticles of up to 55 atoms (1.4 nm) has been conducted using density functional theory with a plane wave basis set. The stability of these nanoparticles increases with cluster size and dimensionality. It also depends strongly on the cluster structures through two factors, the coordination numbers of atoms and the strength of the single bonds. Both the energy gap between the highest occupied and the lowest unoccupied molecular orbitals and the magnetic moment change oscillatorily with cluster size. Furthermore, highly magnetic clusters tend to have large energy gaps. Analysis of the atom-resolved magnetic moment reveals that the local magnetism of a cluster depends mainly on the atomic bonding environments. A simple approach is proposed to predict relative stabilities of various structures for larger clusters. In addition, a structure factor is defined to correlate quantitatively various properties of the Pd clusters with their structures.

[B18] **Studies of rhodium nanoparticles using the first principles density functional theory calculations**

Lichang Wang and Qingfeng Ge, *Chem. Phys. Lett.* 366(2002)368-76.

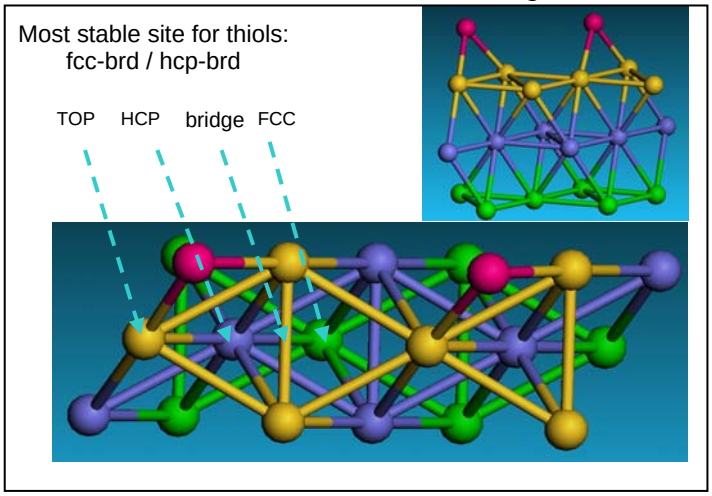
Rhodium nanoparticles in the range of 2-55 atoms were investigated using density functional theory calculations. The binding energy increases from 1.74 eV/atom for the dimer to 4.57 eV/atom for the 55-atom cluster. The stability of these nanoparticles increases in the order of linear, planar, and high-density close-packed configurations. The magnetic moments of the clusters depend strongly on the structure but not on the size. The results have shown that highly symmetric clusters have small HOMO-LUMO band gaps as well as small magnetic moments.

Project C. Hydrogen Bonding Network in SAMs

Fabrication of organic films based on self-assembly processes to make devices, such as electro-optical modulators and high-speed switching devices, has attracted great attention over the past decade. Although many efforts have been made to understand self-assembly processes, the current understanding does not allow us to perform "controlled" synthesis of large supramolecular assemblies with a well-defined structure. For instance, to synthesize liquid crystal polymer based on hydrogen bonding network, one needs to create working conditions so that an interlayer hydrogen bonding network can be formed while the intralayer hydrogen bonding network is prohibited. In order to achieve this goal, we need to have a better understanding of the adsorption process of organic molecules on the Au surface as well as the formation of hydrogen bonding network among these organics molecules.

In this project, we studied the steric effect of alkylthiolate self-assembled monolayers and multilayers (SAMs) and explored how the hydrogen bonding network is formed among the carboxylic acid terminated thiolates. Density functional theory calculations were performed and the results were compared directly with the experiments in Professor Dan Dyer's group at SIUC.

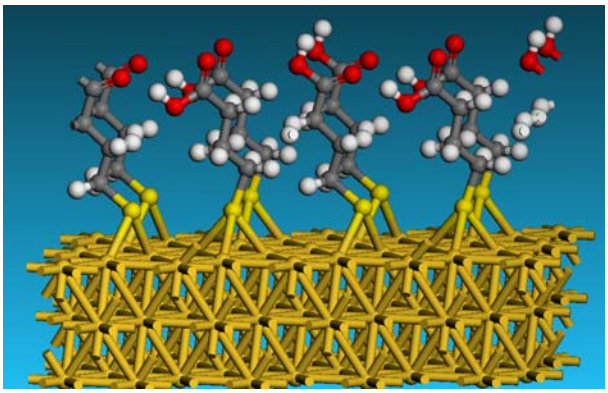
One of the important contributions from our work is the study of interaction of alkylthiolates consisting of more than one C atoms. We presented the first results on how the chain length, which is critical in the formations of SAMs, can influence the adsorption sites and the formation of hydrogen bonding network.



(i) The most stable adsorption site

Density functional theory calculations were performed for alkylthiolates of different chain length on an Au surface of 1/3ML coverage. Our DFT results show that there are two energetically favorable adsorption sites. One lies in between the face-centerd cubic (fcc) and the bridge (brd) site. The second is in between the hexagonal close-packed (hcp) and bridge site. (see the sites in the picture at right). [C1]

(ii) Formation of directional hydrogen bonding network



Two carboxylic acid terminated organic thiolates with 2, 3, and 4 carbon atoms were studied using DFT calculations. In the figure at left, a lateral hydrogen bonding network is found to be formed from our DFT calculations. Both our calculations and the experiments performed in Prof. Dyer's group show that a strong even-odd effect exists in the formation of hydrogen bonding network.

Abstracts:

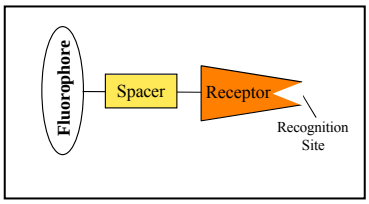
[C1] **Steric effects on the adsorption of alkylthiolate self-assembled monolayers on Au(111)**

Yanping Cao, Qingfeng Ge, Daniel J. Dyer, and Lichang Wang, *J. Phys. Chem. B* 107(2003)3803-07.

Steric effects on the adsorption of self-assembled monolayers (SAMs) formed by alkylthiolates on the Au(111) surface were investigated using density functional theory. Based on the ($\sqrt{3}\times\sqrt{3}$) R30° structure, the current results on methylthiolate (CH_3S) show that the adsorption prefers the face-centered cubic-bridge and hexagonal close-packed-bridge sites. Furthermore, the adsorption energy decreases slightly compared to the CH_3S adsorption on the p(2x2) structure due to lateral interactions. Comparison between the results on CH_3S and 1-propylthiolate (C_3H_7S) illustrates that the adsorption energy increases with chain length. Strong steric effects were found due to the chain length of the alkylthiolates and the hydrogen atoms in the CH_2 unit adjacent to the S atom (α hydrogens). The energetically favored tilt angle is 20^o for C_3H_7S. The preferred geometry for both CH_3S and C_3H_7S adsorptions has the two α hydrogens pointing towards the bridge Au atoms of the surface. The results suggest a flat potential energy surface, which correlates well with the dynamic nature of alkylthiolate SAMs observed experimentally.

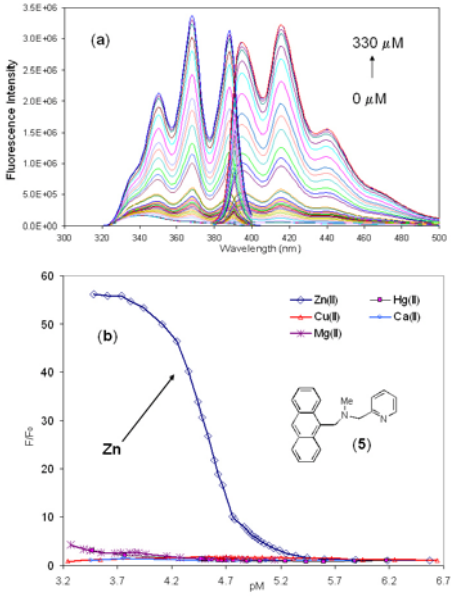
Project D. Fluorescence Sensors

The goal of this research project is to guide the design of fluorescence sensors with satisfactory sensitivity and selectivity using various theoretical tools. The transduction mechanism of our fluorescence sensors is based on Photoinduced Electron Transfer (PET) through molecular recognition events. A typical fluorescence sensor (see the flow chart below) consists of three components, i.e. a fluorophore, a spacer, and a receptor with a recognition site or binding site to bind analytes.



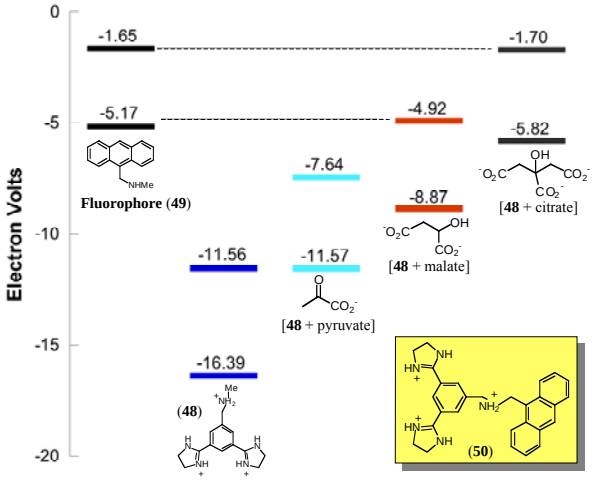
The "On-Off" or "Off-On" response from a fluorescence sensor upon binding-without binding an analyte makes it attractive sensing technique with a potential to achieve high selectivity and a detection limit of extremely low concentrations or even single molecule level.

We have performed calculations for designing fluorescence sensors to detect metabolites that are related to diabetes and associated problems during pregnancy. With the collaborations with Professor Dyer's organic synthetic group and Professor McCarroll's analytic group at SIUC, we have also successfully developed a sensor for detecting Zn caitons that may play important roles in many physiological processes such as cellular metabolism, gene expression, apoptosis, DNA repair, Alzemeimer's disease, diabetes, and cancer. The "Off-On" signal upon binding the zinc(II) is shown in the middle figure on the right.



In the design of fluorescence sensors, a two-step computational effort was made. For a given target molecule, we first find a receptor that binds favorably with the target among candidates of receptors using molecular dynamics simulations and electronic structure calculations. Meanwhile, the absolute HOMO and LUMO energy levels are obtained for the unbound receptor and bound receptor, i.e. target-receptor. Then, we select a fluorophore by calculating its HOMO and LUMO energy levels and match the receptors. The second step is to calculate electron transfer rate using the Marcus equation and the Rehm-Weller equation.

Our current computational efforts are directed at the theoretical selection of proper fluorophore and receptor pairs that allow us to detect citrate, malate, and pyruvate using both DFT and kinetics calculations. In the bottom figure on the right are the calculated HOMO-LUMO energy levels of one sensor candidate.



Research Publications and Presentations Since August 2001

Publications:

1. J. I. Williams and L. Wang, *J. Am. Chem. Soc.* (submitted): "Density functional theory studies of O_2 chemisorption on model ternary PtVFe catalysts".
2. M. M. Sadek and L. Wang, *J. Phys. Chem. B*(submitted): "Effect of adsorption site, size, and composition of Pt/Au bimetallic clusters on the CO frequency: A density functional theory study".
3. L. Xiao and L. Wang, *J. Phys. Chem. B* (submitted): "Methane activation on Pt and Pt_4: A density functional theory study".
4. K. Spivey, J. I. Williams, and L. Wang, *Chem. Phys. Lett.*(submitted): "Structures of undercagold clusters: Ligand effect".
5. J. Yukna, H. Tang, and L. Wang, *J. Chem. Phys.*(submitted): "Theoretical studies of silver clusters".
6. L. Xiao and L. Wang, *Chem. Phys. Lett.*(submitted): "Density functional theory study of single-wall platinum nanotubes".
7. T. Pawluk, L. Xiao, J. Yukna, and L. Wang, J. *Chem. Theor. Comput.*(submitted): "The impact of PES on MD results of the coalescence of M_2 + M with M = Ir, Pt, Au, Ag".
8. Q. Ge, C. Song, and L. Wang, *Comp. Mater. Sci.* 35(2006)247-253: "A density functional theory study of CO adsorption on Pt-Au nanoparticles".
9. L. Xiao, B. Tollberg, X. Hu, and L. Wang, *J. Chem. Phys.* 124(2006)114309-1—114309-10 : "Structural study of gold clusters ".
10. Song, Q. Ge, and L. Wang, *J. Phys. Chem. B* 109(2005)22341-22350: "DFT studies of Pt/Au bimetallic clusters and their interactions with the CO molecule".
11. T. Pawluk, Y. Hirata, and L. Wang, *J. Phys. Chem. B* 109(2005)20817-20823: "Studies of iridium nanoparticles using density functional theory calculations".
12. L. Wang, *Chem. Phys. Lett.* 383(2004)62-66: "The accuracy of the quantum/classical time-dependent self-consistent field treatment to reaction dynamics of large systems".
13. W. Zhang, X. Ran, H. Zhao, and L. Wang, *J. Chem. Phys.* 121(2004)7717-7724: "The nonmetallicity of molybdenum clusters".
14. L. Xiao and L. Wang, *J. Phys. Chem. A* 108(2004)8605-8614: "Structure of platinum clusters: planar or spherical?".
15. L. Xiao and L. Wang, *Chem. Phys. Lett.* 392(2004)452-455: "From planar to three-dimensional structural transition in gold clusters and the spin-orbit coupling effect".
16. W. Zhang, H. Zhao, and L. Wang, *J. Phys. Chem. B* 108(2004)2140-2147: "The simple cubic structure of ruthenium clusters".
17. W. Zhang, L. Xiao, Y. Hirata, T. Pawluk, and L. Wang, *Chem. Phys. Lett.* 383(2004)67-71: "The simple cubic structure of Ir clusters and the element effect on cluster structures".
18. Y. Cao, Q. Ge, D. J. Dyer, and L. Wang, *J. Phys. Chem. B* 107(2003)3803-07: "Steric effects on the adsorption of alkylthiolate self-assembled monolayers on Au(111)".
19. W. Zhang, Q. Ge, and L. Wang, *J. Chem. Phys.* 118(2003)5793-801: "Structure effects on the energetic, electronic, and magnetic properties of palladium nanoparticles".
20. L. Wang and Q. Ge, *Chem. Phys. Lett.* 366(2002)368-76: "Studies of rhodium nanoparticles using the first principles density functional theory calculations".

Presentations:

I. Conference presentations

1. L. Wang, M. Sadek, C. Song, Q. Ge, "Composition effect of bimetallic PtAu clusters on the adsorbed CO vibrational frequencies" (Oral) at *The 61th International Symposium on Molecular Spectroscopy*, June 19-23, 2006, The Ohio State University.
2. J. I. William and L. Wang, "DFT studies of PtVFe nanoparticles" (Poster) at *The 38th Midwest theoretical chemistry conference*, June 15-17, 2006, The Ohio State University.
3. K. Spivey, J. I. Williams, and L. Wang, "Structures of Au_{11} clusters: Ligand effect" (Poster) at *The 38th Midwest theoretical chemistry conference*, June 15-17, 2006, The Ohio State University.
4. B. A. Stachowiak, C. B. Love, and L. Wang, "DFT studies of small Cu clusters" (Poster) at *The 38th Midwest theoretical chemistry conference*, June 15-17, 2006, The Ohio State University.
5. L. Wang, R. Xu, J. Xin, I. Kimaru, C. Cook, D. J. Dyer, and M. E. McCarrol, "Fluorescent sensors for the recognition of citric, malic, and pyruvic acids" (poster) at the *Gordon Research Conference on Bioanalytical Sensors*, February 26-March 3, 2006, Ventura, California.
6. R. Xu, I. Kimaru, C. Cook, L. Wang, M. E. McCarrol, and D. J. Dyer, "A synergistic approach to sensor design based on PET" (poster) at the *Gordon Research Conference on Bioanalytical Sensors*, February 26-March 3, 2006, Ventura, California.
7. D. J. Dyer, R. Xu, S. Puli, C. Cook, M. McCarroll, I. Kimaru, Y. Shi, L. Wang, " Design of biomolecular sensors based on photoinduced electron transfer (PET) and molecular recognition" (Oral) at *230th National Meeting of the American Chemical Society*, August 28-September 1, 2005, Washington, DC.
8. L. Xiao and L. Wang, "The structure effect of Au and Pt clusters on the vibrational spectra of adsorbed methane molecules" (Oral) at *The 60th International Symposium on Molecular Spectroscopy*, June 20-24, 2005, The Ohio State University.
9. M. M. Sadek and L. Wang, "Studies of rhodium nanoparticles using first principles density functional theory" (Poster) at *The 37th Midwest theoretical chemistry conference*, June 16-18, 2005, University of Missouri-Columbia.
10. J. Yukna, H. Tang, and L. Wang, "Structures of silver clusters predicted from density functional theory calculations" (Poster) at *The 37th Midwest theoretical chemistry conference*, June 16-18, 2005, University of Missouri-Columbia.
11. L. Xiao and L. Wang, "Structural effect of Pt clusters on methane adsorption" (Poster) at *The 37th Midwest theoretical chemistry conference*, June 16-18, 2005, University of Missouri-Columbia.
12. L. Wang, Y. Cao, Q. Ge, and D. J. Dyer, "DFT studies of hydrogen-bond formation in the carboxylic acid terminated thiolate monolayer on Au surface" (Poster) at *Molecular quantum mechanics: The no nonsense path to progress*, July 24-29, 2004, Cambridge, U.K.
13. M. McCarroll, R. Xu, S. Puli, I. Kiragu, Y. Shi, L. Wang, and D. J. Dyer, "Design and synthesis of PET based fluorescent biosensors" (Poster) at *The Gordon research conference on bioanalytical sensors*, July 4-9, 2004, Oxford, U.K.
14. L. Wang, Y. Cao, Q. Ge, and D. J. Dyer: "FT-RAIRS and DFT studies of hydrogen bonding formation in the carboxylic acid terminated thiolate monolayers on Au surface" (Oral) at *The 59th International Symposium on Molecular Spectroscopy*, June 21-25, 2004, The Ohio State University.

15. T. Pawluk, Y. Hirata, and L. Wang, "Studies of iridium nanoparticles using density functional theory calculations" (Oral) at *The 36th Midwest theoretical chemistry conference*, June 17-19, 2004, Michigan State University.
16. L. Xiao and L. Wang, "Structural transition from planar to three dimension in gold clusters and the spin-orbit coupling effect" (Poster) at *The 36th Midwest theoretical chemistry conference*, June 17-19, 2004, Michigan State University.
17. J. Yukna, H. Tang, and L. Wang, "Studies of silver nanoparticles using density-functional theory calculations" (Poster) at *The 36th Midwest theoretical chemistry conference*, June 17-19, 2004, Michigan State University.
18. C. Song, L. Wang, and Q. Ge, "DFT study of PtAu alloy nanoparticles and its CO adsorption" (Poster) at *The 36th Midwest theoretical chemistry conference*, June 17-19, 2004, Michigan State University.
19. Q. Ge, C. Song, L. Wang, "A DFT study of CO adsorption on Pt/Au nanoparticles" (Poster) at *Theory of Atomic and Molecular Clusters, TAMC4*, Apr. 24-28, 2004 Toulouse, France.
20. L. Wang, "Dynamics density functional theory: a tool for studies of coalescence of nanoparticles" (Oral) at *227th ACS national meeting*, Mar. 28-Apr. 1, 2004, Anaheim, Carlifornia.
21. L. Wang: "Dynamics density functional theory (DDFT): Applications to homonuclear systems" (Oral) at *Theory and applications of computational chemistry*, Feb. 15-20, 2004, Gyeongju, Korea.
22. B. D. Tollberg, X. Hu, and L. Wang, "Structure of gold clusters: two to fourteen atoms and twenty atoms" (Oral) at *the fourteenth annual Argonne symposium for undergraduates in Science, Engineering and Mathematics & the central states universities, incorporated (CSUI)*, Oct. 24-25, 2003, Argonne National Lab.
23. L. Wang, "Transition Metal Nanoparticles: Novel structures and their catalytic behaviors" (Oral) at *Symposium in memory of Professor Gert Due Billing*, Aug. 11-13, 2003, Copenhagen, Denmark.
24. L. Xiao and L. Wang, "Density Functional Studies of Platinum Clusters" (Oral) at *The 35th Midwest theoretical chemistry conference*, June 12-14, 2003, Iowa State University.
25. W. Zhang, Q. Ge, and L. Wang: "Palladium nanostructures: ring, ball, and tube" (Poster) at *The International Symposium on Frontiers in Molecular Science 2002*, July 15-18, 2002, Qingdao, China.
26. W. Zhang, Q. Ge, and L. Wang: "Energetics, electronic structure, and magnetic property of palladium nanoparticles" (Poster) at *The International Symposium on Frontiers in Molecular Science 2002*, July 15-18, 2002, Qingdao, China.
27. Y. Cao, D. J. Dyer, L. Wang, and Q. Ge: "FT-RAIRS studies of hydrogen-bonding in self-assembled monolayers and multilayers on gold substrates" (Oral) at *The 57th International Symposium on Molecular Spectroscopy*, June 17-21, 2002, The Ohio State University.
28. W. Zhang, Q. Ge, and L. Wang: "Energetic and magnetic properties of palladium clusters" (Poster) at the *Annual APS March Meeting 2002*, March 18-22, 2002, Indianapolis, IN.
29. L. Wang: "Theoretical studies of NO dissociation dynamics on Rh nanoparticles" (Poster) at *the 34th Midwest Theoretical Chemistry Conference*, October 5-6, 2001, The University of Minnesota.
30. L. Wang: "The quantum/classical multi-configuration method for describing reaction dynamics of large systems" (Poster) at *The 14th Canadian Symposium on Theoretical Chemistry*, August 4-9, 2001, Carleton University, Ottawa, Ontario, Canada.

II. Departmental seminars

1. L. Wang, "Transition metal nanoparticles – Novel structures & unique properties", Departmental seminar at Department of Chemistry, State University of New York at Binghamton, February 17, 2006.
2. L. Wang, "Scrutinizing transition metal clusters", Departmental seminar at Department of Chemistry and Biochemistry, University of Arkansas, October 10, 2005.

Support

We are grateful for the financial support from:

1) Petroleum Research Fund (41572-G5; 7/1/04–8/31/07).
2) Pacific Northwest National Lab computing resources (Emsl16321, 11/05–10/06).
3) NPACI computing resources (Che020006S, 7/02–6/03).
4) NCSA computing resources (Che020033N; 4/02–4/03).
5) NPACI computing resources (Che020006, 1/02–12/02).
6) Seed grant from the Materials Technology Center (MTC) at SIUC (7/1/03–6/30/05).
7) Seed grant from the Graduate School at SIUC (1/1/02–12/31/03).
8) SIUC Start-up (8/15//01– 6/30/03).