

Computational Chemistry

Research:

Frank Hagelberg - Jackson State University

Self-assembled monolayers (SAMs) are molecular films that form spontaneously on solid surfaces. These systems have been the subject of intense research in recent years, both experimental and computational. This level of interest is related to their importance in wetting phenomena, tribology, chemical and biological sensing, optics and nanotechnology. Among the many varieties of SAMs, alkanethiol molecules on the Au(111) surface have been given special attention because of the relative simplicity of their structure, their highly stable and ordered SAM patterns, and the ease of preparing the Au(111) surface. Despite the apparent simplicity of this system, its observation in various experiments has led to controversial results. Among the much-debated key issues are two related questions:

- (1) Does S-H bond dissociation occur upon deposition of an alkanethiol molecule on the gold surface?
- (2) Do the alkanethiol adsorbates dimerize on the Au(111) surface?

Recent density functional computations performed in my group have addressed these problems and arrived at a new unified model of alkanethiol SAM formation on gold's surface that is consistent with all experimental observations.

Specifically, we found for the first time that the S-H bond of the adsorbate remains intact when the methanethiol molecules are adsorbed on the regular Au(111) surface. It breaks, however, when admission is made for surface defects. This finding leads to the expectation of different dimerization patterns of thiols on gold substrates, depending on whether or not they have undergone S-H bond scission, turning into thiolates. We demonstrated that methanethiol adsorbates on the Au(111) surface form Van der Waals dimers. For methylthiolate, it was shown that dimerization exists below a certain coverage threshold and is absent at high coverage levels, in full agreement with experimental data.

Do methanethiol adsorbates on the Au(111) surface dissociate? J.-G. Zhou, F.Hagelberg, *Phys.Rev.Lett.* 97, 45505 (2006), selected for inclusion in the *Virtual Journal of Nanoscale Science & Technology*, August 7 2006.

Tigran Shahbazyan - Jackson State University

We performed studies of surface-enhanced Raman scattering (SERS) from molecules adsorbed on noble-metal nanoparticles. In small silver nanoparticles, the electromagnetic enhancement of the Raman signal is strongly affected by the quantum-size and many-body effects originating from the different effect that the confining potential has on s-band and d-band electrons. Namely, the spillover of delocalized s-electrons beyond the

classical nanoparticle boundary results in an incomplete embedding of sp-electron distribution in the background of localized d-electrons whose density profile follows more closely the classical shape. The resulting underscreening of the s-electron local fields results in an enhancement of the surface plasmon local electric field that determines the enhancement of Raman scattering. We developed a microscopic theory of SERS based on quantum two-region model that incorporated the screening effects in nanometer-sized particles and performed numerical calculations of SERS based on time-dependent local-density approximation (TDLDA) for nanoparticle sizes in the range 1.4-4.5 nm (see Figure 1).

We investigated coherent oscillations of vibrational modes in metal nanoshells - metal particles with dielectric core that have recently been manufactured. These nanostructures possess unique optical properties related to the tunability of their electronic excitation spectrum. By varying the shell thickness during the manufacturing process, the energy spectrum of the surface plasmon resonance, that dominates the optical properties of nanoshells, can be varied in a wide range. We addressed the spectrum of acoustic vibrational modes in nanoshells that can be observed using ultrafast optical spectroscopy. The lowest mode corresponding to radial contractions (breathing mode) has been widely observed in solid nanoparticles as oscillations in time of the surface plasmon peak position. We developed a theory of the vibrational modes in gold nanoshells in dielectric media that predicted a number of significant differences with solid nanoparticles.

We published a work on the intersubband absorption of light in semiconductor quantum wells at low doping. In these structures, the optical properties are dominated by the intersubband plasmon corresponding to collective excitation between size-quantization subbands. We have predicted a new many-body phenomenon - an excitation of two intersubband excitations (single-particle or collective) by a single photon (see Fig. 2). This process is caused by electron-electron interactions and can take place only if the quantum well is subjected to a finite bias. We developed a nonperturbative theory of the light absorption in asymmetric quantum wells that incorporates those electron interaction effects.

Figure 1. Calculated SERS enhancement factor for several nanoparticle sizes with and without surface layer effect.

Figure 2. Calculated two-electron intersubband absorption spectra in quantum well.

John D. Watts - Jackson State University

Quantum chemical calculations have been performed on CuNO_2 , CuNO , and anions of these systems. Knowledge of such species may be useful in the development of catalysts for the transformation of NO_x species. While the aforementioned neutral species have been previously studied in some detail, to the best of our knowledge there have not been any prior calculations on the anions. Such calculations are timely in view of an experimental report of the photoelectron spectra of species with the formulae CuNO_2^- and

CuNO⁻ (F. Misaizu et al., Eur. Phys. J. D 9, 297-301 (1999)). Three isomers of CuNO₂ have been investigated, all of which can be regarded to a first approximation as complexes between Cu⁺ and NO₂⁻. These structures are: a C_{2v} structure in which the Cu⁺ is coordinated to the two oxygen atoms; a C_{2v} structure in which the Cu⁺ is coordinated to the nitrogen atom; and a "trans" C_s structure in which the Cu⁺ is coordinated to one of the oxygen atoms. Anions of these three structures were then studied, the ground states of which are ²A₁ (for C_{2v} species) and ²A' (for the C_s species). For CuNO, structures in which the Cu is coordinated to either the N or the O of nitric oxide were considered, as well as a structure in which the Cu is bonded to both the N and O. Studies of anions of these species were then made. Both coupled-cluster (CC) and density functional theory calculations have been performed. The CC calculations employed the CCSD(T) method, while the DFT calculations used the B3LYP functional. CCSD(T) and B3LYP geometry optimizations and vibrational frequency calculations used the LANL2DZ basis set on Cu and the 6-31+G(d) basis set on N and O. Single-point calculations with larger basis sets were performed, the main goal of which was to obtain refined electron detachment energies.

The photoelectron spectrum of CuNO₂⁻ up to 3 eV was reported by Misaizu et al. It consists of one broad band with a maximum at about 1.6 eV and other features up to about 2.1 eV. It was mentioned that the spectrum does not correspond to either Cu⁻ or NO₂⁻. Our results do provide some support for the assignment. The AEA's and VEDE's of the CuONO/CuONO⁻ and CuNO₂/CuNO₂⁻ systems fit the observed energies very well. Interestingly, however, there is no apparent role for the CuO₂N/CuO₂N⁻ system: the largest calculated AEA is 1.052 eV, while the largest VEDE is 1.205 eV. Even allowing for some effects of basis set incompleteness, these numbers cannot be reconciled with the reported spectrum. These results suggest either that the experiments observed an isomer that is not the lowest-energy species, or that the observed spectrum may need re-examination.

This work is being prepared for publication.

Ming-Ju Huang - Jackson State University

Since each of ¹-THC and ⁶-THC has two chiral centers, there are four possible stereoisomers for each of them. The structures of these eight stereoisomers are ¹-THC-RR, ¹-THC-RS, ¹-THC-SR, ¹-THC-SS, ⁶-THC-RR, ⁶-THC-RS, ⁶-THC-SR, and ⁶-THC-SS. The orientation of these different substituted-phenols inside the 2-hydroxypropyl- β -cyclodextrin and 6-hydroxypropyl- β -cyclodextrin can be either "tail-first" or "head-first", there are a total of 32 inclusion complexes.

We have performed semi-empirical quantum mechanical (PM3) calculations on all the 32 inclusion complexes by using Gaussian software. Since these complexes include 270 atoms, it is very time consuming to get the optimization done. So far we have finished 32 complexes with full PM3 optimization. We will analyze very carefully each of the optimized geometries and heats of formation to compare the stabilization energies of each inclusion complex.

Robert J. Doerksen - University of Mississippi

My paper with researchers from University of Massachusetts Amherst and University of Pennsylvania, entitled "Biomimetic facially amphiphilic antibacterial oligomers with conformationally stiff backbones" published in Chemistry & Biology was featured in Royal Society of Chemistry's Chemistry World. To quote from the 'significance' section of that paper, "Novel nonnatural sequences have been designed with intramolecular interactions that lead to an extended conformation and place polar and nonpolar groups on opposite faces of the structure." The overriding hypothesis was that stiffening the conformation of the backbone would generate more active and more selective compounds. Although a direct measurement connecting backbone stiffness to antibacterial potency remains elusive, the newly designed oligomer, 10, is more active and more selective than [previously published, flexible] 11. By tuning the oligomer length and intramolecular interactions, improved selectivity for bacterial cells versus RBCs was generated for 10. The activity and selectivity of 10 was improved compared to 11; however, the optimal charge density, hydrophobic moment, and spatial arrangement of charge remain important unanswered questions to be pursued. Computational methods were used to guide molecular design and accurately predicted overall conformation as well as NMR chemical shifts. The conformation of [uncharged analog of 11] 5 appears to be stabilized by the presence of intramolecular interactions. These novel sequences combine conformational design with biological properties. This backbone represents a robust platform to build shape-specific oligomers, and the potent activity of the short oligomer 10 is encouraging for the generation of new therapeutic agents to combat the emerging resistance to traditional antibiotics.

Jerzy Lezczynski - Jackson State University

The evaluation of structure and activity of nucleic acid bases, base pairs and model systems was the main objective of the work. Our research was focused on both the ground and excited state of molecular systems. We specifically studied the excited state geometries, spectral origins and ionization potentials of all guanine tautomers, proton transfer in hypoxanthine and its hydrated form in the ground and excited state, interaction of metal cations with different tautomers of adenine, structural and hydrogen bonding properties of guanine-cytosine and guanine-guanine base pairs in the ground and singlet excited states, interaction of aqua-copper cation with guanine, structure of medium hydrated guanine in the ground and excited state, ground and excited state proton transfer in the guanine in the isolated and hydrated form, structure of antioxidants and their interaction with alkali and alkaline earth metal cations, vibrational analysis of DNA base pairs at the post Hartree-Fock level, structural properties of crystals of pyrrole-2-carboxamide (PyCa), aromaticity of substituted benzene, structural properties and interaction of atomic clusters, effect of shellvation, etc. We have used generally high level molecular orbital methods in these investigations.

It was revealed that stable tautomers of guanine generally have similar ionization potential and the keto-N7H tautomer will have the highest value. An important outcome

of our investigation on excited states of all guanine tautomer was the prediction of the spectral origin of the keto-N9H and keto-N7H tautomer in between the spectral origins of the keto-N7H-IMINO-cis and enol-N9H-trans tautomers. This may help experimentalists to assign keto-N9H and keto-N7H tautomers in the R2PI experiment on guanine. Our investigation also revealed that electronic excitations may not facilitate the keto-enol proton transfer reaction in guanine and hypoxanthine. It was found that the out-of-plane deformability is a more universal and sensitive aromaticity index than the known structural and magnetic indices. The value of ring deformation energy demonstrated linear correlation with the substituent that is constant for electron donation and electron withdrawing substituents. Our activities included the training of minority students, active participation in conferences and symposia, invited presentations, organizing conferences, and the summer institute.

Recruiting and Hiring of New Faculty: An advertisement for a position at the University of Southern Mississippi has been sent to Chemical and Engineering News, posted on the University of Southern Mississippi departmental website, and sent to several prominent computational chemists around the country. The university had a recruiting booth at the Current Trends in Computational Chemistry meeting in Jackson, Mississippi.

After a search, Jackson State University has located a post-doctoral researcher (Dr. Sridhar Vaddadi, University of North Texas) who is scheduled to join their research efforts in January 2007.

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Curriculum Development and Enhancement:

A computational medicinal chemistry component was added to University of Mississippi courses MEDC416/501, Fall 2006:

MEDC 416. Medicinal Chemistry of Therapeutic Agents I. An introduction to the chemical and physical properties of medicinal agents. Discussion of relationships of structural properties of drugs to pharmacological properties, absorption, distribution and metabolism profiles, chemical stability, mechanism of action and clinically significant drug interactions.

MEDC 501. Advanced Medicinal Chemistry I. Advanced study of organic medicinal agents with emphasis on names, synthesis, chemical properties, and pharmacological properties. Readings in the current literature required.