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The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

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RPPR Final Report
as of 17-Nov-2017

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INVESTIGATOR(S):

Name: Jerzy Leszczynski
Email: jerzy@icnanotox.org
Phone Number: 6019793723
Principal: Y

Organization: **Jackson State University**
Address: 1400 John R. Lynch Street, Jackson, MS 392170002
Country: USA
DUNS Number: 044507085 EIN: 646000507
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Submitted By: Jerzy Leszczynski Email: jerzy@icnanotox.org
Phone: (601) 979-3723
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STEM Degrees: 0 **STEM Participants:** 43

Major Goals: Major Goals are provided in the Dissemination and Upload section of this report to maintain consistency.

Accomplishments: This year, the ICN, in partnership with Jackson State, the US Army Corps of Engineers, and with support from the Army Research Office, hosted the 24th International Conference on Current Trends in Computational Chemistry. The Conference was held in Jackson, Mississippi, on November 11–12, 2016, and hosted over 120 participants from 8 countries including Russia, Poland, Ukraine, Czech Republic, Italy, Germany, Iraq, and Poland.

The format of the 24th CCTCC consisted of 6 sessions of (invited) plenary lectures and over 45 poster presentations covering applications as well as theory. Over 40 of the poster presentations were given by students. A total of 9 prizes ranging from first place to honorable mention were awarded for best high school, undergraduate and graduate poster presentations. The full conference proceeding is provided in the Upload section for complete reference.

Training Opportunities: Please see the Upload section of this report.

Results Dissemination: Please see the Upload section of this report.

Honors and Awards: Nothing to Report

Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: PD/PI
Participant: Jerzy Leszczynski
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:

National Academy Member: N
Other Collaborators:

24th CCTCC

CONFERENCE ON CURRENT TRENDS IN COMPUTATIONAL CHEMISTRY

November 11-12, 2016
Jackson, MS

Department of Defense
US Army Corps of Engineers
JSU Jackson State University
Springer
National Science Foundation

Organizing Committee

Shonda Allen	Jackson State University
Delbert Bagwell	U.S. Army Corps of Engineers
Jaroslav Burda	Charles University in Prague
Cary F. Chabalowski	Michigan Technological University
Glake Hill	Jackson State University
Olexandr Isayev	University of North Carolina, Chapel Hill
William A. Lester, Jr.	University of California at Berkeley
Jerzy Leszczynski (Chairman)	Jackson State University
David Magers	Mississippi College
W. Andrzej Sokalski	Wroclaw University of Technology

Staff

Cathy B. Head	U.S. Army Corps of Engineers
Galina Lobodina	Jackson State University

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Springer
US Army Corps of Engineers
Army Research Office

Schedule of Events

Friday, November 11, 2016

8:00A – 12:00P	Registration	
8:00A – 9:00A	Coffee and morning snacks	
9:00A - 9:10A	Opening Remarks	
9:10A - 10:35A	**1st Session** *Chairperson: Peter Pulay*	**Rodney J. Bartlett** “The Transition to the Dark Side: Making Kohn-Sham DFT Give the Right Answer for the Right Reason” **Tigran Shahbazyan** “Universal Local Density of States for Nanoplasmonics: From Energy Transfer to Strong Coupling to Loss Compensation and Spasing”
10:35A–11:00A	Coffee Break / Pictures	
11:00A–12:30P	**2nd Session** *Chairperson: Szczepan Roszak*	**Paola Gramatica** “ From Chemical Structure to Environmental Hazard: Exploiting QSAR for Screening, Prioritization and Safer Alternatives’ Design” **Jane Murray & Peter Politzer** “ ‘Impenetrable’ Molecular Volumes In Noncovalent Interactions”
12:30P -2:00P	Lunch	
2:00P -3:30P	**3rd Session** *Chairperson: Bidisha Sengupta*	**Andrzej Sobolewski** “ New Paradigms in the Photophysics of Hydrogen-Bonded Molecular Systems” **Jiri Sponer** “Advanced Computational Studies of Nucleic Acids. Advantages and Limitations”
3:30P -3:50P	Coffee Break	
3:50P – 6:00P	First Poster Session (P1)	
6:00P	Dinner	

Saturday, November 12, 2016

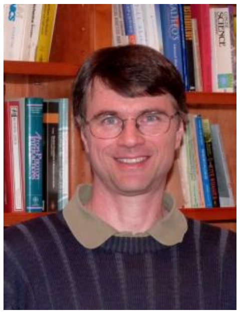
8:00A – 9:00A	Coffee and morning snacks	
8:30A – 11:00A	Registration	
9:00A – 10:30A	**4th Session** *Chairperson: Andrzej Wierzbicki*	**Martin Head-Gordon** "Some New Developments in Density Functional Theory for Calculating and Analyzing Intermolecular Interactions" **Henry Pinto** "Challenges in Modeling Atomic Scale Surfaces and Interfaces"
10:30A -10:50A	Coffee Break	
10:50A-12:20P	**5th Session** *Chairperson: Pradip Biswas*	**Tore Brinck** "Computational Design of New Enzyme Activities" **Tim Clark** "Approaching Reality"
12:20P – 2:00P	Lunch	
2:00P – 4:15P	**6th Session** *Chairperson: Frank Hagelberg*	**Larry Fried** "Challenges in the Prediction of Energetic Material Performance and Safety" **Manoj Shukla** "Computational Chemistry Investigation of Fate and Effects of Some Munition Compounds" **Piotr Paneth** "New Developments in Theoretical Assessments of Isotope Effects"
4:15P- 4:40P	Coffee Break	
4:40P- 6:30P	**2nd Poster Session** (P2)	
6:30P – 9:00P	Dinner Speaker	

1st Session

Rodney J. Bartlett

"The Transition to the Dark Side: Making Kohn-Sham DFT Give the Right Answer for the Right Reason"

Martin Head-Gordon



"Some New Developments in Density Functional Theory for Calculating and Analyzing Intermolecular Interactions"

2nd Session

Paola Gramatica

"From Chemical Structure to Environmental Hazard: Exploiting QSAR for Screening, Prioritization and Safer Alternatives' Design"

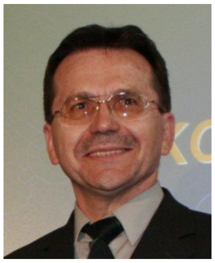
Peter Politzer & Jane Murray

" 'Impenetrable' Molecular Volumes

In Noncovalent Interactions"

3rd Session

Andrzej Sobolewski



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"Universal Local Density of States for Nanoplasmonics: From Energy Transfer to Strong Coupling to Loss Compensation and Spasing"

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5th Session

Tore Brinck

"Computational Design of New Enzyme Activities"

Tim Clark

"Approaching Reality"

Dinner Speaker

Melinda Z. Kalainoff

6th Session

Larry Fried

“Challenges in the Prediction of Energetic Material Performance and Safety”

Manoj Shukla

“Computational Chemistry Investigation of Fate and Effects of Some Munition Compounds”

Piotr Paneth

“New Developments in Theoretical Assessments of Isotope Effects”

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Obie Allen IV, Glake Hill, Wojciech Kolodziejczyk

P1 **Twisting Motions in $[Fe(bpy)_3]^{2+}$ are Intimately Connected to Spin State, Sterics, and Fe−N Bond Strength**
Daniel C. Ashley and Elena Jakubikova

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P2 **Molecular docking combined with classification-and regression-based QSTR models of the endocrine-disrupting activity of poly- and perfluoroalkyl substances**
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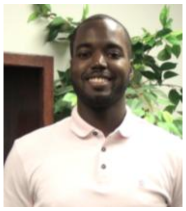
List of Participants

Hassan Hadi Abdullah
Salahaddin University
Department of Chemistry
Erbil, Iraq
E-mail: hassan.abdullah@su.edu.krd



Obie Allen
Jackson State University
Interdisciplinary Center for Nanotoxicity
Department of Chemistry and Biochemistry
1400 J.R. Lynch Street
Jackson, MS 39217
E-mail: alleniv.obie@yahoo.com

Shonda Allen
Jackson State University
Interdisciplinary Center for Nanotoxicity
Department of Chemistry and Biochemistry
Jackson, MS 39217 U.S.A.
Tel: 6019793723
E-mail: shonda@icnanotox.org

Richard Alo
Dean
College of Science, Engineering & Technology
Jackson State University
Jackson, MS 39217
Tel: 601-979-2153
E-mail: richard.a.alo@jsums.edu

Eyram Asempa
Mississippi State University
Chemistry, Box 9573, Mississippi State, MS 39762
E-mail: ea599@msstate.edu

Daniel C. Ashley
North Carolina State University
Department of Chemistry
Raleigh, NC 27695
E-mail: dcashley@ncsu.edu

Zikri Arslan
Jackson State University
Department of Chemistry and Biochemistry
1400 J.R. Lynch Street
Jackson, MS 39217
E-mail: zikri.arslan@jsums.edu

Nataliia Atamas
National Taras Shevchenko University of Kyiv
Department of Physics
2 Glushkov Ave.
Kyiv 03124, Ukraine
E-mail: atamasphys@univ.kiev.ua

Del Bagwell
US Army Corps of Engineers, ACE-IT
3909 Halls Ferry Road
Vicksburg, MS 39180-6199
Tel: 601-634-2860
Fax: 601-634-2236
Email:Delbert.L.Bagwell@usace.army.mil

Dajah Barnes
Murrah High School
1400 Murrah Drive
Jackson, MS 39202
E-mail: Dbtinkerbell24@gmail.com

Rodney J. Bartlett
Quantum Theory Project
2338 New Physics Building
PO Box 118435
University of Florida
Gainesville, FL 32611
Email: bartlett@qtp.ufl.edu

Ja'Nautica Bee
Tougaloo College
500 W. County Line Rd.
Tougaloo, MS 39174
Email: jjnbee@gmail.com

Salma Begum
Jackson State University
Department of Chemistry and
Biochemistry
Jackson, MS 39217 U.S.A.
E-mail: salmaalamgir@gmail.com

Pradip Biswas
Tougaloo College
Physics/Laboratory of
Computational Biophysics &
Bioengineering
500 West County Line Rd
Tougaloo, MS 39174
E-mail: pbiswas@tougaloo.edu

Jerrano Bowleg
Mississippi State University
Chemistry, Box 9573, Mississippi State,
MS 39762
E-mail: jlb1692@msstate.edu

Tore Brinck
KTH Royal Institute of Technology
Applied Physical Chemistry
SE 100 44 Stockholm
Sweden
Email: tore@physchem.kth.se

Tiffany Bryant
Lanier High School
833 West Maple Street
Jackson, MS 39203
E-mail: tiffanydanya601@gmail.com

Thomas Calhoun
Associate Vice President
for Academic & Student Affairs
Jackson State University
Jackson, MS 39217

Tyeashia Carson
Jim Hill High School
2185 Coach Fred Harris Street
Jackson, MS 39204
E-mail:
Carson.tyeashia1999@gmail.com

Hao Cheng
Mississippi State University
Chemistry, Box 9573, Mississippi State,
MS 39762
E-mail: hc741@msstate.edu

Timothy Clark
Computer-Chemistry-Center
Friedrich-Alexander-Universitaet
Erlangen-Nuernberg,
Naegelsbachstrasse 25,
91052 Erlangen, Germany
Email:tim.clark@fau.de

Christopher Copeland
Jackson State University
Interdisciplinary Center for Nanotoxicity
Department of Chemistry and
Biochemistry
1400 J. R. Lynch Street
P.O. Box 17910
Jackson, MS 39217-0510
E-mail: ccopeland@icnanotox.org

Dalia Daggag
Clark Atlanta University
Department of Chemistry
223 James P. Brawley Drive, S.W.
Atlanta, GA 30314
E-mail: dalia.daggag@students.cau.edu

Alva Devon Dillon
Jackson State University
Interdisciplinary Center for Nanotoxicity
Department of Chemistry and
Biochemistry
1400 J. R. Lynch Street
P.O. Box 17910
Jackson, MS 39217-0510
E-mail: devondillion333@gmail.com

THEORETICAL STUDY FOR THE ACIDITY OF CYANOOLYYNES $HC_{2N+1}N$ (N= 0-5) IN GAS AND AQUEOUS PHASES

Hassan H. Abdullah

Chemistry Department, College of Education, Salahaddin University, Erbil, Iraq
Computational nanotechnology research Lab., CNRL, Salahaddin University, Erbil, Iraq.
Email: hassan.abdullah@su.edu.krd

Theoretical calculations are carried out to predict gas and aqueous phase acidities of a series of cyanopolyynes acids. Two levels of theory were used in this study, with the combination of DFT and MP2 methods with Pople's 6-311++g(d,p) basis set and Dunning's aug-cc-pVTZ basis set. The calculations of these molecules reveal pK_a values varying from 12.25 and 17.25 and indicate that the acidity of these molecules in aqueous phase increases while the acidity in gas phase decreases with increasing chain length of these acids.

SPECTROSCOPIC ANALYSIS OF 3-NITROFLUORANTHENE AND FLUORANTHENE BASED ON AB INITIO CALCULATIONS

Obie Allen IV, Glake Hill, Wojciech Kolodziejczyk

Interdisciplinary Center of Nanotoxicity, Department of Chemistry and Biochemistry, Jackson State University

Polycyclic Aromatic Hydrocarbons (PAH's) have been well documented to be linked to various cancers, diseases, and abnormal fetal development from their exposure. PAH are distributed through our environment by soil sediments, flowing bodies of water, and through the air from burning fossil fuels. Spectroscopic analysis was performed on 3-Nitrofluoranthene and Fluoranthtene with ab initio calculations using MP2 method with 6-31G(d,p) basis-set. In addition, analysis of thermodynamic properties (heat capacity, entropy, enthalpy, and Gibbs free energy) were investigated with the same basis-set.

TWISTING MOTIONS IN $[FE(BPY)_3]^{2+}$ ARE INTIMATELY CONNECTED TO SPIN STATE, STERICS, AND FE−N BOND STRENGTH

Daniel C. Ashley and Elena Jakubikova*

Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695, United States

Ligand twisting motions in six-coordinate tris-chelate transition metal complexes have long been recognized as a potential reaction coordinate for racemization by converting the complex from octahedral (O_h) to trigonal prismatic symmetry. These pathways have been previously established as the Bailar twist (conversion to D_{3h} symmetry) and the Ray-Dutt twist (conversion to C_{2v} symmetry). Twisting motions have been thoroughly demonstrated as being associated with changes in spin state, and are therefore of relevance not just to thermal isomerization pathways, but spin-crossover (SCO) and intersystem crossing (ISC) mechanisms as well. In this work we use density functional theory (DFT) calculations to probe the structural and energetic features of idealized Bailar and Ray-Dutt twisting mechanisms for singlet, triplet, and quintet $[Fe(bpy)_3]^{2+}$, which has been well-studied as a model for ISC of Fe(II) complexes relevant to photochemical applications. We found that the energies of the D_{3h} and C_{2v} trigonal prismatic structures were severely dependent on spin state, with thermally accessible species only being possible on the quintet surface, enforcing the necessary relationship between SCO and torsional motion. The Ray-Dutt twist on the quintet surface was calculated to proceed with a low barrier, and is likely the preferable isomerization mechanism for this complex. We additionally identified a new “distorted” Bailar twist of C_{3h} symmetry which is considerably lower in energy than the idealized D_{3h} structure. This results from a combination of both steric and electronic factors. Developing an understanding of the structural and energetic features of these twisting pathways is a necessary pre-requisite for evaluating how torsional motion may influence the potential energy surfaces relevant to ISC.

DYNAMIC FEATURES OF IONIC LIQUIDS SOLUTIONS WITH NON-POLAR SOLVENTS: MOLECULAR DYNAMICS STUDY

Nataliia Atamas

National Taras Shevchenko University of Kyiv, Physics Department,
2 Glushkov Ave., Kyiv 03124, Ukraine
atamasphys@mail.univ.kiev.ua

Ionic liquids (IL) are important to physics for two reasons: their vapor pressure is negligible at room temperature, hence their status as green solvents and de-pending on their irons, they can act as sophisticated solvation or reaction media (designer solvents). IL can dissolve a wide range of polar or non-polar organic or inorganic molecules, providing new paths to carry out chemical reactions or industrial separations. Spectroscopic and simulation evidence is suggesting the presence and importance of the formation of intermolecular cation-anion hydrogen bonds. Ion-cation interactions can to induce the formation of a percolation anion-cation network. The experimental data indicate that imidazolium-based ILs of type 1-alkyl-3-methyl-imidazolium exhibit an anomalous temperature dependence of the solubility of nonpolar compounds showing a decreasing solubility with increasing temperature. It was observed that the anomalous behavior is found to be even strengthened with increasing particle size.

The MD method was applied using a modified DL_POLY_4.05 with a time step of 2 fs. The long-range electrostatic interaction was taken into account by the Ewald method. In the calculations, the cations, anions, and atoms forming the molecules of the added substance were treated as solid charged model systems with a fixed geometry. The methyl in the dmim+ were treated as a pseudo-atom with the total charge. All the studies were conducted for systems composed of 192 dmim+ cations, 192 chlorine anions Cl–, and one solute molecule at T = 400 K. The unit cell volume was calculated from the experimental values of the ionic liquid density at T = 400 K. The calculations used periodic boundary conditions. The electrostatic interaction at short distances was described using point charges on each atom. The interaction between dmim+ and Cl– molecules in the ionic liquid was described using the Buckingham potential for interactions at short distances. The Berendzen thermostat was used to stabilize the system in the $N V T$ -ensemble.

Analysis of the data allowed to establish: (1) The salvation effect in systems ionic-liquid ($dmim^+/Cl^-$) - non-polar solute molecules has qualitatively similar to the behavior of the hydrophobic hydration of small nonpolar particles in liquids like water. (2) The results of the computer experiment for <Etot> for the dmim+/Cl– non-polar solutions at T = 400 K show that the intermolecular interaction <Etot> does not depend on the physical characteristics of the structural and non-polar substances dissolved. Therefore, as a possible selection criteria for the data analysis is not appropriate to consider the thermodynamic and structural characteristics of the system. In this case, need to do analysis of its dynamic properties. (3) Based on the data obtained from MSD and VAF the different diffusion mechanisms of nonpolar solute molecules in IL ware determined.

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EXPOSURE OF TILAPIA TO IRON OXIDE NANOPARTICLES: EFFECTS OF PARTICLE MORPHOLOGY ON ACCUMULATION, ELIMINATION AND HEMATOLOGICAL RESPONSES

Mehmet Ates[1], Veysel Demir[1], **Zikri Arslan**[2], Hasan Kaya[3], Sevdan Yılmaz[3]

1.Tunceli University, Faculty of Engineering, Tunceli, 62000, Turkey
2. Jackson State University, Jackson, MS 39217 USA
3. Canakkale Onsekiz Mart University, Canakkale, 17100, Turkey

Effects of chronic exposure to alpha and gamma iron oxide nanoparticles (α-Fe_2O_3 and γ-Fe_2O_3 NPs) were investigated through exposure of tilapia (*Oreochromis niloticus*) to 0.1, 0.5 and 1.0 mg/L suspensions for 60 days. Accumulation was largest in spleen followed by intestine, kidney, liver, gills, brain and muscle. γ-Fe_2O_3 NPs showed higher Fe in all organs. Accumulation in spleen was fast and independent of NP concentration reaching to maximum levels by the end of the first sampling. Despite negligible ranging dissolved Fe levels in water, gills showed accumulation of through dissolved Fe from metastable γ-Fe_2O_3 polymorph. Ingested NPs cleared from the organs completely within 30-day elimination period, except the liver and spleen. Liver contained about 31% of α- and 46% of γ-Fe_2O_3, while spleen retained about 62% of α- and 35% of the γ-polymorph. No significant disturbances were observed in hematological parameters, including hemoglobin, hematocrit, red blood cell and white blood cell counts ($p > 0.05$). Serum glucose (GLU) levels decreased in treatments exposed to 1.0 mg/L of γ-Fe_2O_3 NPs at day 30 ($p < 0.05$). In contrast, GLU levels increased during the elimination period for 1.0 mg/L α-Fe_2O_3 NPs treatments ($p < 0.05$). Transient increases occurred in glutamic oxaloacetic transaminase (GOT), glutamic pyruvic transaminase (GPT), and lactate dehydrogenase (LDH). Serum Fe levels did not change during exposure ($p > 0.05$), but increased significantly within elimination period due to mobilization of ingested NPs from liver and spleen to blood. Though respiratory burst activity was not affected ($p > 0.05$), lysozyme activity (LA) was suppressed suggesting an immunosuppressive effects from both Fe_2O_3 NPs ($p < 0.05$). In contrast, myeloperoxidase (MPO) levels increased significantly in treatments exposed to α-Fe_2O_3 NPs ($p < 0.05$), and the effect from γ-polymorph was marginal ($p \geq 0.05$). The results indicate that morphological differences of Fe_2O_3 NPs could induce differential uptake, assimilation and immunotoxic effects on *O. niloticus* under chronic exposure.

COMPUTATIONAL CHEMISTRY APPLICATIONS IN THE ENVIRONMENT

Dajah Barnes, **Tiffany Bryant** , **Tyeashia Carson**, Ashley Egerson, **Devario Marzittie**,
Mikala Sims, Anastasiia Golius, and Jerzy Leszczynski

Interdisciplinary Center for Nanotoxicity, Department of Chemistry & Biochemistry,
Jackson State University, 1400 John R. Lynch St, Jackson, MS 39217

The research projects focused on quantum chemistry application for solving environmental problems. Two topics were related to development of new approaches for drinking water purification. Two cases of environmental contaminants adsorption on metal oxides clusters were studied. Two other projects focused on problems related to the ozone layer. The role of water molecules in the ozone depletion was studied using computational approach. In the remaining two projects, different properties of selected pollutants were estimated in order to understand their behavior in the environment.

THE TRANSITION TO THE DARK SIDE: MAKING KOHN-SHAM DFT GIVE THE RIGHT ANSWER FOR THE RIGHT REASON*

Rodney J. Bartlett, Prakash Verma, Jin Yifan, Duminda Ranasinghe

Quantum Theory Project
University of Florida
Gainesville, FL, 32611

We define a ‘consistent’ DFT method as one whose *potential* is sufficiently accurate that the KS eigenvalues offer reasonable approximations to the exact principal ionization energies for each electron in a molecule, analogous to, but better than Koopmans’ theorem for Hartree-Fock; while the total energy properties obtained from the corresponding functional remain accurate. The demands on the potential are not met by any of the currently used DFT methods. However, *ab initio dft*, which, unlike any other KS-DFT method, has to converge to the right answer in the basis and correlation limit, shows that such a consistent method exists and shows improved numerical performance. The critical element in *ab initio dft* is the use of the optimized effective potential strategy to provide local, multiplicative exchange-correlation potentials from orbital dependent functionals, but this is not practical for large scale applications. Instead, we introduce the QTP(00) and (01) functionals by simply fitting the 5 (4) Ip’s of water to a range-separated functional composed of conventional density dependent exchange and correlation pieces. With no other empiricism, we report activation barriers for reactions, molecular structure, ionization potentials, and TDDFT excited states, emphasizing core-excitation spectra and Rydberg states.

*This work is supported by the U. S. Air Force Office of Scientific Research.

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SYNTHESIS, CHARECTERIZATION AND PHOTOPHYSICAL PROPERTIES STUDIES OF HYDROCHAR AND BIOCHAR MATERIALS BY HYDROTHERMAL CARBONIZATION METHOD

Salma Begum, Azmain Alamgir, Avijit Pramanik, Paresh C. Ray*

Department of Chemistry and Biochemistry, Jackson State University, Jackson, MS 39217, USA

The process that termed hydrothermal carbonization is a thermal treatment of water mixed with organic substances such as saccharides (glucose, sucrose or starch) at ~220^{o}C-250^{o}C temperature gives rise to water-soluble organic substances and a carbon rich solid product (hydrochar). Biochar is produced through pyrolysis or gasification processes that heat biomass in the absence or under reduction of oxygen. Cellulose is the most promising material as it is by far the most abundant and inexpensive saccharide available is used in this experiment. Wang et al. were the first to report on the hydrothermal treatment of sucrose as a way to produce carbonaceous microspheres loaded with noble metal nanoparticles. In this experiment we investigate the potential of cellulose precursor for the production and to study the photophysical properties of highly functionalized carbonaceous materials such as hydrochar and biochar via UV-visible, Fluorescence and Raman Spectra. The product yield suggests that the hydrothermal carbonization of cellulose is an effective way to increase the turnover time of carbon contained in the biomass. From a chemical point of view the hydrochar and biochar contain a high amount of oxygen which is present both in the core and the shell of the carbonaceous microspheres.

Key words: Hydrothermal carbonization, Cellulose, Biochar, Hydrochar, UV-visible, Fluorescence, Raman spectra

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COMPUTATIONAL APPROACHES TO DESIGN DIFFERENT ENERGY STORAGE AND PHOTOVOLTAIC DEVICES

Shameka Bell, **Timaria Ford**, Charlena Jackson, **N'waynah Littleton**, Jakayla Marzittie,
Tiasia Williams, Juganta Roy, and Jerzy Leszczynski

Interdisciplinary Center for Nanotoxicity, Department of Chemistry & Biochemistry,
Jackson State University, 1400 John R. Lynch St, Jackson, MS 39217

These projects focused on hydrogen storage devices, carbon sequestration process, and two different types of photovoltaic cells (polymer-fullerene and dye-sensitized) using computational approach. This research comprises six different projects highlighting the up-to-date information in the respective fields of the projects. The projects focused on the working principle of the devices, properties of the materials, and different computational tools. Gaussian 09 package was used to extract research results (e.g. energetic and structural features) from the calculation to design the devices for better performance.

COMPUTATIONAL DESIGN OF NEW ENZYME ACTIVITIES

Tore Brinck

Department of Chemistry, KTH Royal Institute of Tecnology, SE-10044 Stockholm, Sweden.
tore@physchem.kth.se

There is an increasing interest in the redesign of enzymes to alter their reaction specificity. We have largely focused on the design of enzymes that catalyze the Diels-Alder, a reaction of great importance in organic chemistry that is rare in nature.[1-3] On the basis of quantum chemical calculations, we create theozyme models of the transition state, and mine the Protein Data Bank (PDB) for enzymes that have active sites with the proper functions for transition state stabilization. Using a combination of methods, including extensive molecular dynamics (MD) and large-scale quantum chemistry (QC) calculations, we devise active-site mutations that optimize the enzymes with respect to substrate binding and transition state stabilization. The relatively poor performance of designed Diels-Alderases[1-4] that utilize hydrogen bond catalysis have led us to suggest an alternative acid-base mechanism for catalysis. In this presentation, I will review our attempts of using enzymes based on ketesteroid isomerase (KSI) for catalyzing this mechanism.[5] I will also present applications to KSI and other enzymes of a novel method[6,7] for predicting contributions of individual residues to the catalytic efficiency of an enzymatic reaction using fragment molecular orbital theory (FMO).[8]

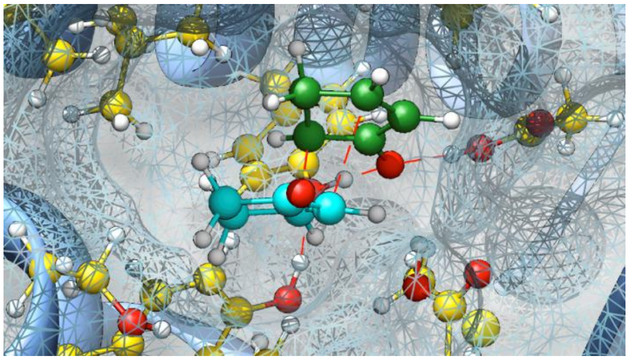

Figure 1: Acid-base catalysis of the Diels-Alder reaction in KSI.

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COMPUTATIONAL CHEMISTRY APPLICATIONS IN TECHNOLOGY

Lichelle Brown, Syporia Harris, BreAuna Law, **Jamie Lewis**, **Mike Ragsdale**, RaQuan Young,
Karina Kapusta, and Jerzy Leszczynski

Interdisciplinary Center for Nanotoxicity, Department of Chemistry & Biochemistry,
Jackson State University, 1400 John R. Lynch St, Jackson, MS 39217

These research projects covered such topics as light-emitting diodes (LED), sensors, and lithium-ion batteries. The task was to visualize the molecule, optimize the structure, and perform calculations using Gaussian Program Package. Two projects focused on calculating the absorption spectra for the compounds that can be used as LED materials. The goal of two other projects was to calculate the energy gap that can show the efficiency of a sensor. The reduction potential and geometry parameters of the solvent for a lithium-ion battery were calculated in two remaining projects.

APPROACHING REALITY

Timothy Clark

Computer-Chemistry-Center, Friedrich-Alexander-Universitaet Erlangen-Nuernberg, Naegelsbachstrasse 25, 91052 Erlangen, Germany.

Semiempirical (neglect of diatomic differential overlap, NDDO) molecular orbital (MO) calculations without local approximations are now possible for 100,000 atoms or more with the massively parallel EMPIRE program.[i] Calculations on systems of this size or with periodic boundary conditions for repeat units up to 50,000 atoms[ii] make realistic nanoscale systems accessible to MO theory, even for flexible systems, for which thousands of snapshots need to be calculated.

The importance of such calculations lies in the fact that we are no longer limited to small or homogeneous, perfect systems, but can now include defects, dopants, impurities or domain boundaries in the calculations, or even calculate amorphous systems.

Examples of the use of such large-scale calculations, both for electronic devices and biological systems, will be described.

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NATURE OF π-STACKING INTERACTIONS OF AROMATIC NITRO COMPOUND DERIVATIVES

Christopher Copeland, Devashis Majumdar, Jerzy Leszczynski

Interdisciplinary Center for Nanotoxicity, Department of Chemistry & Biochemistry,
Jackson State University, 1400 John R. Lynch St, Jackson, MS 39217

The nanotechnological revolution of the past two decades has placed an unprecedented focus on discovery and development of novel materials for energy production and storage, medicinal applications, and environmental health to name a few. At the dawn of this revolution, boron nitride (BN) nanostructures began to receive a notable amount of research interest, though not as much as their carbon counterparts. They have the capability of taking on various structures such as nanosheets, nanotubes, nanocones, hexagonal bulk crystals, fullerenes, and many more. A direct comparison of the structural analogues shows that boron nitride nanomaterials have physical and chemical attributes superior to that of carbon including higher thermal stability, chemical inertness, and constant band gaps.

Aromatic compounds containing nitro groups ($-NO_2$) generally referred to as nitroaromitic compounds (NAC), are considered as environmental contaminants and also pose a toxic threat to many organisms including humans. These compounds find elevated use in industry as precursor compounds in the production of explosive materials given the ease of chemical modification due to their aromaticity. Also, a very high level of toxicity to humans is associated with these compounds. The goal of this research project is to investigate the nature of interactions between nitro compound derivatives and (BN) scaffolds given the potential to act as molecular sieves. In recent years, it has been shown accurate predictions of the electronic structure of graphene-nitroaromatic complexes. Within the DFT/M06-2X framework, several thermodynamic parameters and binding energies have been computed using the cc-pVDZ basis set. The computed energies were refined using the cc-pVTZ basis set and corrections for basis set superposition and dispersion energies were included. Unlike their carbon analogues, the frontier molecular orbitals, primarily π in character, exhibit localization and separation on either side of the BN nanosheets. Because only the *meta*- and *para*- substituted nitro compounds have been studied, it is hypothesized that a linear free energy relation can be determined for all compounds of this class interacting with BN nanosheets.

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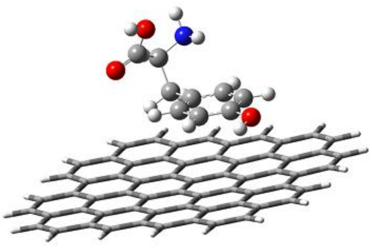
Faculty Advisor: Jerzy Leszczynski, jerzy@icnanotox.org

DENSITY FUNCTIONAL THEORY STUDY ON THE INTERACTIONS OF TYROSINE WITH GRAPHENE

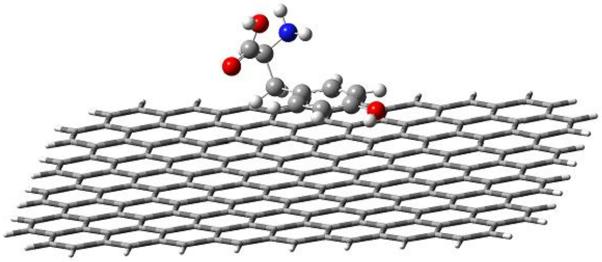
Dalia Daggag, Jovian Lazare, and Tandabany Dinadayalane*

Department of Chemistry, Clark Atlanta University, 223 James P. Brawley Drive, S.W., Atlanta, GA 30314, E-mail: dtandabany@cau.edu

Density functional theory (DFT) calculations were performed to investigate the interactions between the aromatic amino acid tyrosine (Tyr) with two finite size graphene sheets. Small graphene (G_S) consists of 62 carbon atoms and large graphene sheet (G_L) consists of 186 carbon atoms. The edges of these two graphene sheets were terminated with hydrogen atoms. Conformational analysis was done for tyrosine using MMFF force field implemented in Spartan '14. Three lowest energy conformers of tyrosine were chosen to examine the binding with graphene sheets. In our study, we considered four orientations for each of the three different conformers of Tyr to study interactions with G_S and G_L. A detailed computational investigation of the interactions between graphene and Tyr will provide knowledge required for graphene-based biological/biocompatible applications such as biochemical sensors and detection of Tyr in urine. M06-2X functional with 6-31G* basis set was used for complete optimizations of the fragments and complexes. Binding energies with and without basis set superposition error (BSSE) were calculated. Our aim in this study is to answer the following questions: (i) Which conformer of Tyr provides the most stable complex? (ii) What is the preferred orientation of Tyr with graphene (□-□ vs. C□H/N□H···□)? (iii) How does the size of graphene sheet affect the binding strength? Our results indicate that Tyr prefers to orient parallel (□-□ interactions). The size effect of graphene is almost negligible in case of tyrosine.



G_S-Tyr-1



G_L-Tyr-1

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PREDICTING THE INTERACTIONS OF RECEPTORS FOR CO_2 AND NITRATES AND THEIR ANALYTES

Mawuli Deegbey and Steven R. Gwaltney

Department of Chemistry, Center for Computational Sciences, and Center for Environmental Health Sciences, Mississippi State University, Mississippi State, MS 39762

Human and natural activities can cause a major decline in the levels of oxygen in water, resulting in environmental conditions such as hypoxia (low oxygen content) or anoxia (no oxygen). These conditions greatly affect the lifecycle of microscopic organisms, fish, and mammals, thereby posing a threat to the sustainability of seafood and fishing industries. The northern Gulf of Mexico is the second largest zone of coastal hypoxia due to excess nutrient from the Mississippi River and Atchafalaya River discharge. The major causes are acidification of water from dissolved CO_2, and eutrophication of waterbodies from nutrients (primarily nitrogen and phosphorus). The use of chemical sensors has proven to be valuable in environmental monitoring. These chemical sensors consist of a receptor that selectively interacts with the target analyte. The overall goal of this project is to develop robust and rapid sensors for detection of CO_2 and nitrates present in water. Several organic receptors with high sensitivity will be explored, synthesized, and incorporated into conjugated polymers for contaminant detection using experimental and computational design. We have employed computational studies to model receptor-analyte interactions, determine binding affinities for the proposed receptors, and identify and screen new receptor chemistries. This poster presents the results for some of the proposed receptors.

REORGANIZATION ENERGIES, IONIZATION POTENTIALS, AND ELECTRON AFFINITIES OF 4- ([2,2'-BITHIOPHENE]-5-YL) PYRIDINE AND 4-[5-(FURAN-2-YL)THIOPHEN-2-YL] PYRIDINE

Alva Dillon, Christopher Copeland, and Dr. Glake Hill

Jackson State University, 1400 John R. Lynch St Jackson, MS 39217

Organic chemists are now, possibly more than ever, getting their hands wet with organic-based electronics gaining the chance to produce more cost effective and efficient materials than their inorganic competitors. Though, not as efficient, they give way to physical possibilities such as flexible electronic devices. The current state of organic optoelectronics is to engineer efficient semiconducting light sources that are more powerful than the conventional incandescent and fluorescent lighting. For example, using OLEDs as a light source is more environmentally friendly, energy efficient, safer, and has broad applicability in a multitude of electronics.

The purpose of the project is to evaluate the efficiency of various organic semiconductors for use in organic field-effect transistors. This study characterized several ordered and disordered halogen-bonded crystals for various chemical properties including reorganization energies, ionization potentials, electron affinities, and electron mobilities via theoretical, density functional theory (DFT) methods. From the aforementioned characteristics, one is able to obtain metrics on electron and hole transporting capabilities. This work, in conjunction with analytical techniques, aim to standardize an efficient means for developing new nanomaterials for use in electronics. In this work, the DFT/B3LYP level of theory indication that the engineered semiconductor materials exhibit ambipolar characteristics.

COMPUTATIONAL CHEMISTRY APPLICATIONS IN HEALTH

Lydia Fields, Cameron Ford, Salonna Marzette, Asia Morgan, **Chyna Stewart**, **Hollye Weekes**,
Wojciech Kolodziejczyk, and Jerzy Leszczynski

Interdisciplinary Center for Nanotoxicity, Department of Chemistry & Biochemistry,
Jackson State University, 1400 John R. Lynch St, Jackson, MS 39217

In these projects, molecules that have significant impact on human health, such as anticancer drugs and polyaromatic hydrocarbons (PAH), were studied. The obtained results indicated how to optimize the structure of molecules and get data such as infrared, UV-Vis spectra.

A FULL ELECTRONIC STUDY OF METAL COMPLEXES AS ANTITUMOR DRUGS

Latasha S. Franklin[1], Wojciech Kolodziejczyk[1,2], Glake Hill[1]

[1]*Interdisciplinary Center for Nanotoxicity, Jackson State University, Department of Chemistry and Biochemistry*
[2]*Wroclaw Medical University, Department of Physical Chemistry, Wroclaw, Poland*

In recent years, there has been an increase in the prevalence of metal complexes used medicinal purposes. Particularly, vanadium, as a trace bioelement, displays a variety of biological properties. This metal exhibits potent anti-HIV effects towards infected immortalized T cells, as well as, antimicrobial, antitumor, and insulin-enhancing effects. In particular, the involvement of oxovanadium (IV) complexes in the treatment of malignant tumors will be studied, theoretically. Prior experimental studies have revealed that VO(PAHN)(phen) exemplifies behavior similar to the infamous antitumor drug, cisplatin. Both having an inhibitory concentration of 50%. It is imperative to study the interaction of this compound with relevant biomolecules and their model systems. Steric differences, electrostatic potential surfaces, DNA binding, and other chemical properties of oxovanadium(IV) complexes and cisplatin will be investigated by utilization of computational means. Potentially, an inexpensive, more effective and less toxic antitumor drug will be developed to assist in the treatment, prevention, and eradication of cancerous cells.

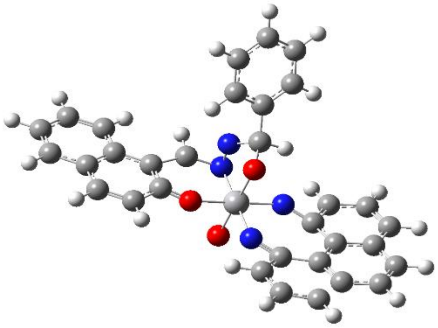

Figure 1-[VO(PAHN)(phen)]- PAHN is 4-pyridinecarboxylic acid, 2-[(2-hydroxy)-1-naphthalenylene] hydrazide, phen is 1,10-phenanthroline

CHALLENGES IN THE PREDICTION OF ENERGETIC MATERIAL PERFORMANCE AND SAFETY

Laurence E. Fried

Materials Science Division, Lawrence Livermore National Laboratory
L-282, 7000 East Ave., Livermore, CA 94550

Energetic materials (propellants, explosives, and pyrotechnics) store large quantities of energy, and can release this energy on a timescale as short as 1 ns. Energetic materials are used in a wide variety of industrial and military applications. Despite years of study, many of the safety and performance features of energetic materials are challenging to predict.

In my presentation, I will give an overview of issues in the prediction of energetic materials performance and safety. Many properties of interest are chemical in nature, but it is also important to understand the coupling between chemistry at the molecular scale and properties at the crystal scale (usually 1-100 μm) and the continuum scale (generally defined to be greater than 100 μm).

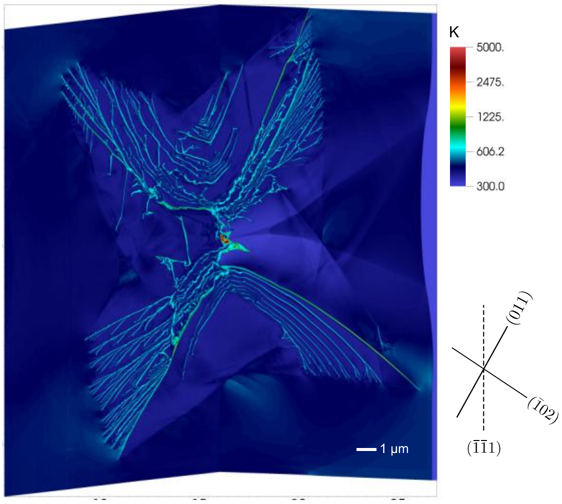

Figure 1: A continuum simulation of crack formation in the energetic molecule HMX.[1]

I will discuss recent progress in predicting properties of single energetic molecules, and in predicting the condensed phase reactivity of energetics with a variety of quantum methods. Next, I will discuss how grain-scale simulations can be constructed in the framework of finite element methods (see Figure 1), and current limitations in the approach when it is applied to grain scale phenomena.

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A PROTONATION ROLE IN THE FORMATION OF DOUBLE-STRANDED POLY(A)

Anastasia Golius[1], Leonid Gorb[2], Margarita Zarudnaya[3], Andriy Potyahaylo[3], and Jerzy Leszczynski[1]

1. Interdisciplinary Center for Nanotoxicity, Department of Chemistry and Biochemistry, Jackson State University, Jackson, Mississippi, USA
2. HX5, LLC, Vicksburg, Mississippi, USA
3. Institute of Molecular Biology and Genetics, Kyiv, Ukraine

The formation of intra- and intermolecular double oligo(A)-helices of different stability is considered as a possible physical mechanism of mRNA poly(A) tail functioning in a number of biological processes. The formation of double helices is induced by intermolecular proton transfer from proteins specifically interacting with Poly(A) to the N1 nitrogen atom of adenine residues.

Our main purpose is to study structure of double-stranded and single-stranded Poly(A) at different ions concentration and at different protonation level. All atoms Molecular Dynamic simulation is an effective tool to study some biological processes on atomistic level. Calculations have been done with NAMD program package and charmm36 force field parameters.

Three different Poly(A) structures with different level of protonation were considered: not-protonated, 60% protonated and 100% protonated. Calculations for single-stranded RNA have been done as well.

As the result, 100 ns trajectories were calculated for each case. Fully protonated complex shows good stability during whole time of the simulation, when unprotonated complex start to lose its initial structure just after 5 ns of the trajectory. Analysis of geometrical parameters has been done for each system.

PERMEABILITY OF BIOLOGICAL MEMBRANE TO ENERGETIC COMPOUNDS: COMPUTATIONAL STUDY

Anastasia Golius[1], Olexander Isayev[2], Leonid Gorb[3] and Jerzy Leszczynski[1]

1. Interdisciplinary Center for Nanotoxicity, Department of Chemistry and Biochemistry,
Jackson State University, Jackson, Mississippi, USA
2. Division of Chemical Biology and Medicinal Chemistry, Eshelman School of Pharmacy,
University of North Carolina at Chapel Hill, North Carolina, USA
3. HX5, LLC, Vicksburg, Mississippi, USA

In the present work, we focused on interaction of energetic compounds with cell membrane with different computational approaches. Five energetic compounds were chosen for the study: TNT, DNT, DNAN, NTO and anion of NTO. Those compounds were chosen based on the fact that there is not enough data available about their interaction with biological systems and at the same time they are widely used nowadays for different purpose.

One of the computational tools that were used is all atom Molecular Dynamic simulation with NAMD 2.9 program package. In order to obtain free energy profile for penetration of small molecules through the lipid bilayer Umbrella Sampling technique were implemented. Estimated free energy profiles have shown the location in the membrane where is the highest probability for the compound to be found. Additionally, partition coefficients were calculated from the profiles and results are in good agreement with experimental data. COSMOmic is another computational approach that allows predicting permeation for small molecules for relatively short period of time; however, it was shown that it has difficulties in estimation of free energy profiles.

TOXICITY OF NITROAROMATIC COMPOUNDS: A QUANTUM CHEMICAL AND QSAR BASED STUDY

Aminah Gooch[1], Natalia Sizochenko[1], Bakhtiyor Rasulev[1,2], Leonid Gorb[1,3], Jerzy Leszczynski[1]

1. Interdisciplinary Center for Nanotoxicity, Department of Chemistry and Biochemistry Jackson State University, Jackson, MS 39217
2. Center for Computationally Assisted Science and Technology, North Dakota State University, Fargo, ND 58108
3. HX5, LLC, Vicksburg, MS, 39180

The toxicity data of 90 nitroaromatic compounds related to their 50% lethal dose concentration for rats (LD_{50}) were compiled and used to develop quantitative structure-activity relationship (QSAR) models. Quantum-chemical calculations along with descriptor data generated using software products such as DRAGON, PaDEL and HiT-QSAR were utilized to generate a number of molecular descriptors. Multiple regression analysis was applied to generate correlation models. Predictive ability of the models was also assessed. The toxicity of nitroaromatic compounds depends on a number of factors, such as the number of nitro-groups and the presence of certain structural fragments. The developed models which are based on the largest to date dataset of nitroaromatics *in vivo* toxicity showed a good predictive ability. This can be important knowledge to use in a preliminary assessment of nitroaromatic compounds' toxicity to mammals.

FROM CHEMICAL STRUCTURE TO ENVIRONMENTAL HAZARD: EXPLOITING QSAR FOR SCREENING, PRIORITIZATION AND SAFER ALTERNATIVES' DESIGN

Paola Gramatica

QSAR Research Unit in Environmental Chemistry and Ecotoxicology, Dep. of Theoretical and Applied Sciences (DiSTA), University of Insubria, Varese, Italy.
paola.gramatica@uninsubria.it; http://www.qsar.it

345.000 of the several millions of commercially produced substances, listed by the Chemical Abstracts Services Registry, are regulated as priority chemicals. However, a higher number of compounds could be potentially dangerous for the environment and also humans and, in fact, new chemicals are continuously identified as emerging pollutants. The European regulation REACH (Registration Evaluation Authorization and restriction of Chemicals) will help in identifying hazardous chemicals, because a risk-based evaluation is required to evaluate the impacts of chemical uses or releases, for regulatory action, and to set priorities for pollution prevention. The time and resources, however, are not reasonably available to test all of these chemicals for their effects of potential concern on human and environmental health. Therefore, modeling tools for screening big sets of compounds, in order to prioritize most hazardous chemicals and then to focus the limited resources on selected chemicals for a more rigorous evaluation, will yield the greatest environmental and socio-economic benefits. Computational models, based on the chemical structure and the already available experimental evidences, such as Quantitative Structure-Activity Relationships (QSARs), are highly useful in chemical screening in order to identify compounds of the highest concern, among those without experimental data or even not yet synthesized. The important preliminary point is that they must be carefully externally validated for their predictivity [1a-d]. Some examples of screening and priority setting for the assessment of some hazardous properties/activities will be presented, in particular for Substances of Very High Concern (SVHCs), such as Endocrine Disruptors (EDs) or PBTs (Persistent Bioaccumulative Toxics), for which in REACH an authorization is requested for using. The inherent tendency of a compound to be PBT can be identified by the PBT Index model [2, 3], included in our software QSARINS [4a, b]: examples will be presented for Flame Retardants [5], Personal Care Products (PCPs) [6] and Active Pharmaceutical Ingredients (APIs) [7]. Externally validated QSAR models, specifically developed for the ecotoxicity of PCPs and APIs on various aquatic organisms and carefully verified for their Applicability Domain, will be presented to define a cumulative Aquatic Toxicity Index (ATI) for about 500 PCPs [8] and more than 1000 APIs [9]. Moreover, new QSAR models for the prediction of both ATI can be applicable in QSARINS for planning non-environmentally hazardous PPCPs (Pharmaceutical and Personal Care Products).

All the presented screening and priority setting tools could be usefully applied *a priori*, in the benign by design approach of Green Chemistry, before the chemical synthesis of safer alternatives to dangerous compounds. In this way, the possibility to continuously contaminate the environment with "regrettable substitutions", which could be recognized only after they have been introduced to the market, and evidence of environmental and human health concerns have been manifested, could be highly reduced.

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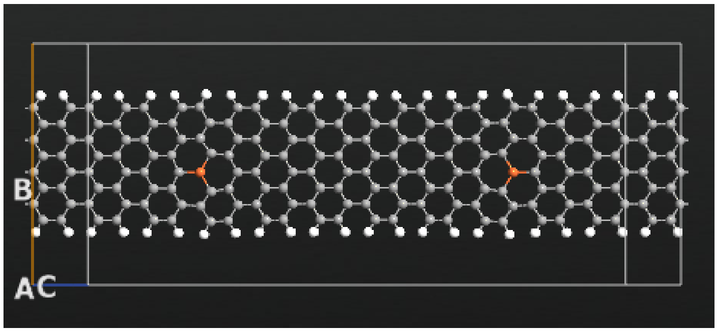
GRAPHENE NANORIBBONS WITH SUBSTITUTIONAL TRANSITION METAL ATOMS AS NANOSCALE SPIN FILTERS.

Frank Hagelberg

Department of Physics and Astronomy, East Tennessee State University,
Johnson City, TN 37614

Graphene nanoribbons (GNRs) well-known candidates for conductors in nanoelectronic circuits,[1] since they are chemically inert and mechanically stable, and thus can be easily handled and exposed to relatively high operating temperatures. Recently, it has been predicted that H-terminated single-walled carbon nanotubes of the zigzag type (zSWCNTs) can be used as gates in a spin valve or spin filter circuit due to the antiferromagnetic nature of their electronic ground state, characterized by unpaired electrons with opposite spin orientation at either end of the tube.[2,3]

In this contribution, the spin filter properties of analogous systems, namely zigzag graphene nanoribbons (zGNRs), are investigated by a non-equilibrium Green's function (NEGF) procedure.[4] The model shown in the figure, consisting of a zGNR transmission element between zGNR electrodes with two substitutional atoms, does not include metal leads and so avoids spin polarization quenching due to interface effects. It is shown that spin current with sizable degrees of spin polarization is generated as allowance is made for substitutional transition metal atoms in the zGNR network. This effect is discussed as a function of several parameters, among them the number, the type, and the substitutional sites of the transition metal atoms, and further the zGNR dimensions.



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BIOGEOCHEMISTRY OF THE GRAND BAY NATIONAL ESTUARINE RESERVE IN THE NORTHERN GULF OF MEXICO

Jacqueline Q. McComb[a], Eric Gulledge, Turquoise Alexander, Taimei Harris**, Fengxiang X. Han[a, b] ***, Christian Rogers[a], and Paul B. Tchounwou[a]

[a]*Environmental Ph.D. Science, Jackson State University, 1400 J.R. Lynch Street, Jackson, MS 39217, U.S.A.*

[b]*Department of Chemistry and Biochemistry, Jackson State University, 1400 J.R. Lynch Street, Jackson, MS 39217, U.S.A.*

**Fengxiang X. Han, Phone: (601) 979-3487; Email: Fengxiang.han@jsums.edu*

Understanding biogeochemistry of the Grand Bay is essential for better utilization and protection of national coastal ecosystems. About 17.5 millions of waste water containing P was accidently released into Bangs lake of the Grand Bay Reserve. The current biogeochemistry after 10 years of the accident is not clearly studied. The hypothesis of this study is that 1) the leaking accident caused a long-term biogeochemical changes in the reserve; 2) trace elements and heavy metals have been significantly accumulated in the reserve due to all anthropogenic sources, resulting potential concerns on the sea food safety. The aim of this study is to investigate biogeochemistry of P, trace elements, heavy metals and carbon in the Grand Bay National Estuarine Research Reserve of the northern Gulf of Mexico. The trace elements and heavy metals include As, Pb, Zn, Cu, Ni, Cr, Cd, Co, Se etc. The phosphorus as affected by earlier P containing waste water leaking and residual P chemistry will be discussed. The results show that P, Hg, Cd and to some extent, As and Pb have been significantly accumulated in soils. The strongest correlations were found between concentrations of Ni and total organic matter contents. The correlations decreased in the order: Ni > Cr > Sr > Co > Zn, Cd > Cu> Cs. Strong correlations were also observed between total P and concentrations of Ni, Co, Cr, Sr, Zn, Cu, and Cd. This may be related to the P spilling accident in 2005 in the Bangs Lake site.

Key words: Grand Bay, biogeochemistry, trace elements, heavy metals, carbon sequestration, global warming, phosphorus.

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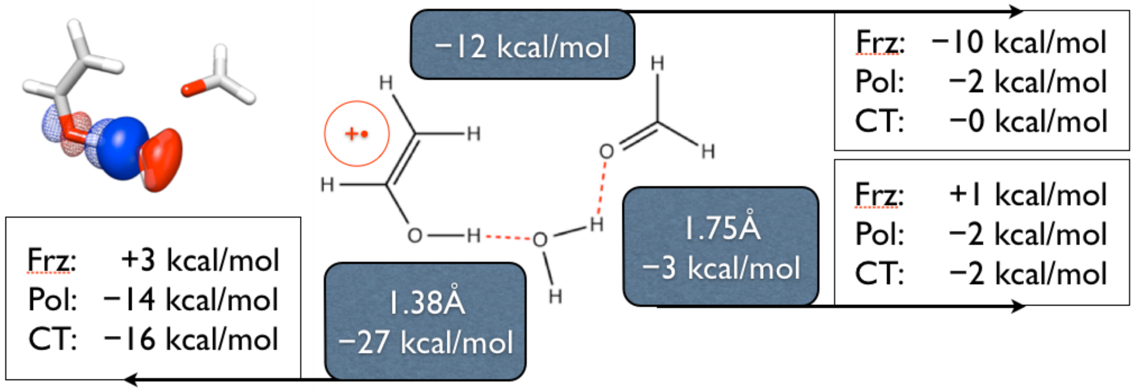
SOME NEW DEVELOPMENTS IN DENSITY FUNCTIONAL THEORY FOR CALCULATING AND ANALYZING INTERMOLECULAR INTERACTIONS

Martin Head-Gordon

Kenneth S. Pitzer Center for Theoretical Chemistry,
Department of Chemistry, University of California; and
Chemical Sciences Division, Lawrence Berkeley National Laboratory,
Berkeley CA 94720, USA.

Density functional theory (DFT) is the most widely used electronic structure theory. Crucial to its future is the problem of designing functionals with improved predictive power. I shall describe a new approach to functional design, “survival of the most transferable”, and show how the resulting functionals offer unprecedented accuracy for DFT calculations of intermolecular interactions. As a counterpoint to this vital numerical development, I will describe a new approach to obtaining physical insight into DFT calculations of intermolecular interactions. This energy decomposition analysis (EDA) separates interactions associated with frozen fragment electronic structure, from induced electrostatics, and forward and backwards charge transfer. I will present a variety of examples, such as the triplex between vinyl alcohol radical cation, formaldehyde and water, which is a rearranged form of the glycerol radical cation.

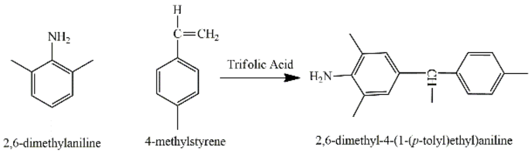


MICROWAVE ASSISTED SYNTHESIS OF CHIRAL ALKYLATED-ANILINE AND ITS CHARACTERIZATION IN PROTEIN AND DNA MOTIFS USING SPECTROSCOPY AND MOLECULAR MODELING

[1]Jabari Jackson, [1]Maria Muhammad, [1,2]Chirantan Sen Mukherjee, [1]Bidisha Sengupta*, [1]George Armstrong

[1]Department of Chemistry, Tougaloo College, Tougaloo, MS

Microwave irradiation offers a convenient way to synthesize optically active alkylated aniline following the protocol given below. It is rapid and inexpensive with almost 70% yield. Aniline, arylamines and heterocyclic aromatic amines are known carcinogens. Recently aniline mustard has come into prominence as novel anticancer agent. In this study, we like to explore the binding behavior of DMPA in naturally occurring drug carrier protein human serum albumin (HSA) and duplex and tetraplex DNAs, in order to understand its therapeutic importance. We have used spectroscopic and molecular modeling tools to find out the binding constant, sites and energy for the association. Several binding sites have been noted by docking studies and some amino acids namely lysine, alanine, leucine, and glutamic acid have been found to play crucial role in the binding process with protein. Further studies are underway.



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CLASSIFICATION OF BACTERIA BY SURFACE ENHANCED RAMAN SPECTROSCOPY AND PRINCIPAL COMPONENT ANALYSIS

Stacy J. Jones[1], Sudarson Sekhar Sinha[1], and Paresh Ray[1]

Department of Chemistry and Biochemistry, Jackson State University, Jackson, MS 39217[1]

Food contamination by pathogens provides a significant health concern in the United States. 48 million Americans become ill by eating contaminated food each year, resulting in more than 3,000 deaths and more than 100,000 hospitalizations. Currently, the USDA recommends conventional bacteria culturing for detection and identification of foodborne pathogens. This involves enrichment, colony isolation, and confirmation. Other potential methods including DNA amplification using polymerase chain reaction (PCR), antibody-based assays, and mass spectroscopic techniques. Unfortunately, due to instrumentation and aseptic requirements, these techniques are significantly limited. In addition, false identifications, numerous reagents, and multiple-steps make these alternative inconvenient. Consequently, the development of a portable, rapid and sensitive biosensors with on-the-spot interpretation of results is beneficial for testing. Surface enhanced Raman spectroscopy is an alternative approach that satisfies most of the requirements for on-site testing; it is specific, noninvasive, nondestructive, and can be rapidly performed. In this research, foodborne bacteria are quickly detected and identified using ferritin-silver nanoparticle assemblies. Surface-enhanced Raman scattering (SERS) provides rapid fingerprinting of biomaterial in a non-destructive manner and principal component analysis (PCA) is used to discriminate between several types of bacteria, including *E. coli* and *Salmonella*.

NEW APPROACH FOR THE CONSTRUCTION OF STO-3G FAMILY BASIS SETS

K. Kapusta[1,2], E. Voronkov,[3] S. Okovytyy,[1,2] V. Korobov,[2] and J. Leszczynski[1]

[1]*Interdisciplinary Nanotoxicity Center, Jackson State University, Jackson, MS, 39217, USA*
[2]*Oles Honchar Dnipropetrovsk National University, 72, Gagarin Ave., Dnipropetrovsk, 49010, Ukraine*
[3]*V. Lazaryana Dnepropetrovsk National University of Railway Transport, 2, Lazaryana Str., Dnipropetrovsk, 49010, Ukraine*

New approach for construction of STO-nG(r) family of basis sets has been proposed. The coefficients used for approximation of the Slater-type orbital (STO) by three Gaussian-type orbitals (GTO) calculated initially by Steward have been recalculated. Newly obtained coefficients have been used for the construction of the initial STO-3G(r) and physically adapted STO(I)-3G(r)$_{mag}$ basis sets.

The Mathcad program package with minerr solving block has been used to perform the approximation of STO by GTOs. Initially the values of α and d have been obtained for the n = 1, 2, 3, 4, 5, 6, 7 orbitals (1s, 2s, 2p, 3s, 3p, 3d, etc.). The next step has involved calculation of contradicted exponents (α_{2s}=α_{2p}, α_{3s}=α_{3p}, etc.) and corresponding contraction coefficients. The obtained results for uncontradicted and contradicted exponents α and contraction coefficients have been used to construct the zero-order STO-3G(r) basis set. The efficiency of the method has been tested by the calculation of the atomic energies at Hartree-Fock level. The atomic energies calculated with the newly constructed basis set have lower values then one obtained using standard basis set.

The initial STO-3G(r) set of atomic orbitals has been extended by adding of first-order correction functions for the calculation of magnetic properties of compounds. The efficiency of constructed such way STO(I)-3G(r)$_{mag}$ basis set has been illustrated by calculation of the magnetic susceptibility for set of molecules using HF and DFT levels of theory. All calculations have been performed for the molecules with the experimental geometry. The results presented in Table 1 show good agreement with the experimental values for the most of the molecules.

Table 1
Diamagnetic susceptibility of molecules, χ (cgs-ppm/mol) (sign is reversed)

	Original STO(I)-3G$_{mag}$				STO(I)-3G(r)$_{mag}$				
Molecule	HF	BP86	B3LYP	PBE1PBE	HF	BP86	B3LYP	PBE1PBE	Experiment [a]
C_2H_6	29,05	28,65	28,50	28,85	29,03	28,62	28,48	28,83	27,4
C_2H_4	20,32	19,31	19,50	19,43	20,31	19,29	19,48	19,41	19,7
C_2H_2	22,20	21,40	21,62	21,44	22,23	21,41	21,63	21,46	20,8
CH_4	18,06	18,06	17,91	18,12	18,06	18,06	17,91	18,12	17,4
CO_2	23,83	23,01	23,18	23,16	23,80	22,98	23,15	23,13	21
CH_2O	9,01	7,03	7,39	7,36	9,01	7,02	7,38	7,35	6,86

H_2O	14,29	14,50	14,47	14,42	14,28	14,50	14,47	14,41	13,12
NH_3	16,77	16,77	16,71	16,77	16,77	16,80	16,73	16,78	16,3
HF	10,61	10,91	10,85	10,79	10,61	10,91	10,85	10,79	10,4
SiH_4	21,52	22,58	22,08	22,53	21,51	22,56	22,06	22,51	20,4
H_2S	27,51	27,78	27,70	27,74	27,50	27,77	27,69	27,73	25,5
CO	13,15	13,21	13,25	13,07	13,15	13,21	13,24	13,07	11,8
F_2	11,93	10,31	10,61	10,71	11,92	10,30	10,60	10,70	9,63

[a] CRC handbook of Chemistry and Physics (91st ed.) / Haynes, W. M. ed. – CRC Press Taylor & Francis Group, 2011.

Table 2 illustrates the parameters of the linear regression for results from table 1.

Table 2
The parameters of the linear regression equation $\chi_{expt}=A^* \chi_{calc} + B$ for Table 1

	Original STO(I)-3G$_{mag}$				STO(I)-3G(r)$_{mag}$			
	HF	BP86	B3LYP	PBE1PBE	HF	BP86	B3LYP	PBE1PBE
R	0,9925	0,9940	0,9948	0,9945	0,9926	0,9940	0,9948	0,9946
A	0,97	0,93	0,95	0,94	0,97	0,94	0,95	0,94
B	-0,89	0,15	-0,14	0,02	-0,90	0,15	-0,15	0,01

In the case of BP86 and B3LYP functionals the values of correlation coefficients (R) are virtually the same for both basis sets used. However, the slope for one constructed using the new approach is closer to 1 and the intercept closer to zero.

Table 3 illustrates the results of calculation of ^1H nuclear magnetic shielding tensors for the set of test molecules. The values obtained using of the newly constructed basis set show better agreement with experimental data.

Table 3
^1H nuclear magnetic shielding tensors σ (ppm) and the parameters of the linear regression equation σ expt=A* σ calc + B

	Original STO-3G$_{mag}$				STO(I)-3G(r)$_{mag}$				
Molecule	HF	BP86	B3LYP	PBE1PBE	HF	BP86	B3LYP	PBE1PBE	Experiment
C_2H_6	31,58	31,10	31,21	31,15	31,58	31,09	31,21	31,14	29,86 [b]
C_2H_4	26,87	26,51	26,66	26,47	26,86	26,50	26,65	26,46	25,43 [c]
C_2H_2	30,99	31,22	31,27	31,09	30,94	31,16	31,21	31,03	29,28 [d]
CH_4	31,59	31,33	31,37	31,31	31,59	31,33	31,37	31,31	30,61[e]
H_2O	31,6	32,2	32,0	32,0	31,6	32,1	32,0	31,9	30,2 [f]
NH_3	31,7	31,7	31,7	31,7	31,6	31,7	31,6	31,6	30,7 [e]
HF	29,5	30,8	30,4	30,4	29,5	30,8	30,4	30,3	29,2 [f]

R	0,9590	0,9467	0,9482	0,9504	0,9594	0,9499	0,9521	0,9542
A	0,9666	0,8553	0,8869	0,8681	0,9700	0,8610	0,8937	0,8749
B	-0,1932	2,8659	1,9201	2,5767	-0,2819	2,7098	1,7313	2,3898

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The new approach proposed here for the recalculation of coefficients can be used for improvement of recently developed by our group STO(I)-nG and STO(II)-nG basis sets for calculation of magnetic and electric properties of organic compounds.

MOLECULAR DOCKING COMBINED WITH CLASSIFICATION-AND REGRESSION-BASED QSTR MODELS OF THE ENDOCRINE-DISRUPTING ACTIVITY OF POLY- AND PERFLUOROALKYL SUBSTANCES

Supratik Kar[1], Marisol Sepulveda[2], Jerzy Leszczynski[1*]

[1]Interdisciplinary Center for Nanotoxicity,
Department of Chemistry and Biochemistry,
Jackson State University, Jackson, MS-39217, USA

[2]Department of Forestry and Natural Resources,
Purdue University , West Lafayette, Indiana 47907, USA

Exposure to poly- and perfluoroalkyl substances (PFASs), an emerging class of endocrine disrupting halogenated pollutants, has been linked to thyroid toxicity in human populations across the globe. The PFASs can compete with thyroxine (T4) for binding to the human thyroid hormone transport protein transthyretin (TTR) which may lead to reduce thyroid hormone levels leading to endocrine disrupting activity. Distress about their environmental fate and endocrine-disrupting activity has initiated several research projects, but the amount of experimental data available for these pollutants is limited. In this background, twenty-four PFASs, together with 6 structurally similar natural fatty acids binding capacity in a radioligand-binding assay values were modeled with classification- and regression-based quantitative structure-toxicity relationship (QSTR) tools using simple molecular descriptors obtained from chemical structures of the compounds to identify the responsible structural features and fragments of these diverse class of PFASs. Additionally, docking study performed employing the crystal structure complex of TTR with bound 2,´6´-difluorobiphenyl-4-carboxylic acid (PDB: 2F7I) to constitute the receptor model for human TTR provided corroborating evidence for these binding interactions and indicated multiple high-affinity modes of binding. The developed *in silico* models therefore provide an understanding of important structural attributes of these chemicals and may provide important information for the design of chemicals for future synthesis of molecules as well as may serve as an efficient query tool for screening of large databases with diminished systemic toxicity profile.

THEORETICAL STUDY OF FORMATE, TARTRATE, TARTRONATE AND GLYCOLATE PRODUCTION FROM 6-CARBON TRIOXYLATE INTERMEDIATE IN THE CITRIC ACID CYCLE

Mehedi Khan, Jing Wang, Jerzy Leszczynski

Interdisciplinary Center for Nanotoxicity, Department of Chemistry & Biochemistry, Jackson State University, Jackson, MS 39217

Creation of first living cell from unanimated object is always a big query for scientists. Man has been searching the answer for long time. But still a long path is ahead to unveil this super mystery. In autotrophic theory, citric acid cycle is the engine to all biogenesis. Recently, glyoxylate was proposed to be the central starting materials for formation of components of the citric acid cycle[1] such as sugars, amino acids etc. It was proposed that glyoxylate, under highly basic condition, forms α keto acids and sugars via dihydroxyfumarate (DHF) intermediate. But experimentally tartrates along wi;th some oxalate, glycolate and tartronate were found[2] as end products.

There is no good explanation for this difference between expected and observed products.To shed a light on these differences we investigated selected reactions leading to the formation of formate, tartrate, glycolate and tartronate from 6 carbon trioxylate, a very important intermediate in Butch et al [2] experiment. We proposed pathways for each reaction by identifying reactants, products and the transition states. The pathways were explored at M06-2X/6-311+G(d,p) level. The polarizable continuum model (PCM) self-consistent reaction field was employed to evaluate the solvent effects (water as solvent). The studied models were fully optimized by analytical gradient techniques. The force constants were determined analytically by the analysis of harmonic vibrational frequencies for all of the compounds. An intrinsic reaction coordinate (IRC) analysis was carried out to ensure that each transition state corresponds with the correct minima. We calculated activation energy, enthalpy change, Gibb's free energy change, rate of reaction etc. to obtain information on the whole system.

In tartrate production from 6 carbon trioxylate intermediate, it involves decarboxylation, proton transfer, protonation, carboxylation, hyroxylation and fragmentation (formate production) reaction. The results reveal that two decarboxylation and one fragmentation reaction are rate determining steps with the highest energy barrier with 20 and 23 kcal/mol respectively. Other steps have very low activation energy. In the process of glycolate production, first decarboxylation has an energy barrier of 23 kcal/mol. Then proton transfer, carboxylation and hydroxylation are almost barrier less and thus form formate and tartronate. The last of this process is a one step SN2 reaction to form glycolate from tartronate which is a simultaneous decarboxylation and protonation reaction. It shows exceptionally large amount of energy barrier of 45 kcal/mol. This is due to highly stable tartronate molecule therefore breaking that bond requires such high energy. We identified this step as the rate determining step of glycolate production. The last reaction series produce equal amount of tartronate and tartrate molecule. Here the 6 carbon trioxylate decarboxylates and then combines with glyoxylate which is almost barrier less process (1.4kcal/mol). Following steps include hydroxylation, protonation and fragmentation process to finally give tartronte and tartrate molecule. Most of these reactions have very low energy barrier. Our results justify the high probability of these reactions.

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A COMPREHENSIVE COMPUTATIONAL ANALYSIS OF CATHINONE AND ITS METABOLITES USING QUANTUM MECHANICAL APPROACHES AND DOCKING STUDIES

Wojciech Kolodziejczyk[a,b,*], Supratik Kar[b], Glake A. Hill[b], Jerzy Leszczynski[b]

a) *Department of Physical Chemistry, Wroclaw Medical University, ul. Borowska 211A, 50-556 Wroclaw, Poland*
b) *Interdisciplinary Center for Nanotoxicity, Jackson State University, Jackson, MS 39217*
* *Corresponding author: dziecial@icnanotox.org, Tel: +16019790291*

Conformers of the psychoactive compound of the *Khat* plant cathinone along with its amino alcohol metabolites norephedrine and norpseudoephedrine have been calculated using DFT (M062X/B3LYP) and MP2 levels of theory for gas and solution phases. Gas phase studies revealed that cathinone has two, norephedrine has four and norpseudoephedrine has three low energy conformations with all conformers connected by rotational transition states. To understand the solvent effect to the energetic profiles of the studied species, the conductor-like screening model is employed within aqueous medium. It explains lowering of energy of all studied conformers in solution. The molecular electrostatic potential surface data for each molecule revealed likely reaction sites for the studied molecules. The computed IR spectra for cathinone and its metabolites have been compared with experimental data and rotational transition states connecting all conformers have been reported. The natural bond orbital (NBO) analyses for only ligands and separately for their complexes with amino acid residues in protein pockets from the docking results are also performed to corroborate the results obtained from the MP2 and DFT calculations. The comprehensive computational study explore important amino acid residues and stabilizing energy of the studied molecules with the interacting proteins along with the reason behind the difference in potency for cathinone's metabolites.

QUANTUM-CHEMICAL APPROACH TO THE INHIBITION MECHANISM RESEARCH.

Vitalina Kukueva

State Institution "The Institute of Environmental Geochemistry”
03680, Kiev, Palladin av. 34a

Inhibiting behavior of halon alternatives under different fire suppressing conditions can be understood and assessed effectively using computer simulations. Computer modeling is becoming better defined and much easier to carry out, in comparison with full-scale fire tests. A combination of laboratory and numerical studies with validation by fire tests, will make the selection of halon alternatives much more efficient and effective. The implications for flame suppression by haloalkanes are discussed [1].

The various possible elementary reaction in different ranges of temperature profile of the flame have been researched in this paper by ab initio Hartry-Fock method. If we analyze the results of Quantum Chemical analysis (Table 1), the right to say that the thermal decomposition of the molecule inhibitor likely to happen than chemical transformation in the interaction of radicals fuel. It is characteristic that is more likely to be degradation products and $CF_2^{\bullet\bullet}$ and HF (table 1, 5 and 6 stages). This path will lead to a partial termination inhibitory loop formed by so much as a neutral molecule HF with a strong chemical bond and stable biradicals $CF_2^{\bullet\bullet}$ [2]. In the scientific literature there are no reports of splitting hydrogen atoms from saturated compounds using particle $CF_2^{\bullet\bullet}$ [3]. The results of our calculations are correlated with other ab initio calculations [4] for the enthalpies and geometrical parameters of the studied molecules. Too low reactivity of $CF_2^{\bullet\bullet}$ with neutral molecules also confirmed.

Table 1. Energy elementary steps that occur in the interaction fluoromethane fuel calculated by ab initio with the base set 6 -31G *.

№	Elementary reactions	Reaction energy, E, kcal/mol
1	$CHF_2^{\bullet} + CH_3^{\bullet} \rightarrow CF_2^{\bullet\bullet} + CH_4$	77.7
2	$CF_3^{\bullet} + CHF_2^{\bullet} \rightarrow CF_2^{\bullet\bullet} + CHF_3$	21.7
3	$CHF_3 \rightarrow CF_3^{\bullet} + H^{\bullet}$	91.0
4	$CHF_3 \rightarrow CF_2^{\bullet\bullet} + HF$	66.8

Our calculations (table 1) explained the diminished inhibition efficiency of fluorine containing compounds by formation of stable biradical $CF_2^{\bullet\bullet}$ and HF molecules with high bond energy, that prevent the important stage of inhibition cycle – regeneration of inhibiting agents.

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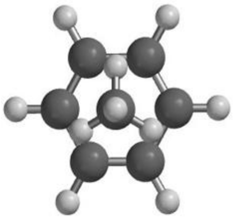
COMPUTATIONAL STUDY OF THE BINDING OF $(CH_4)_N$ (N=1, 2) WITH SMALL POLYCYCLIC AROMATIC HYDROCARBONS

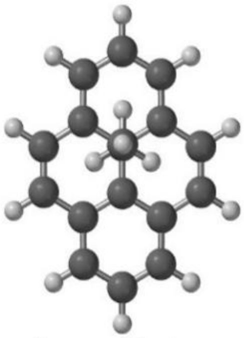
Jovian Lazare, Dalia Daggag, and Tandabany Dinadayalane*

Department of Chemistry, Clark Atlanta University, 223 James P. Brawley Drive, S.W.,
Atlanta, GA 30314; E-mail: dtandabany@cau.edu

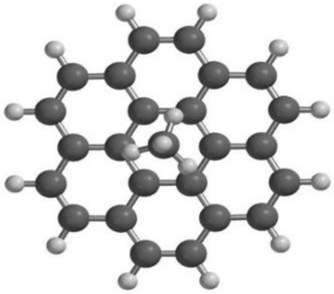
We explored the binding of single and double methane with smaller cyclic/polycyclic aromatic hydrocarbons (benzene, pyrene, and coronene). Density functional theory (DFT) calculations were used to investigate the binding energies. All the calculations were performed using meta-hybrid M06-2X functional in conjunction with 6-31G(d) basis set. Optimized geometries were used to obtain the correction for Basis Set Superposition Error (BSSE). In our computational study, a systematic investigation of binding of one and two methane with the above-mentioned mono- and poly-cyclic aromatic systems was carried out by considering several possibilities. The possibilities of different binding modes of methane with aromatic systems include three C□H···□, two C□H···□, one C□H···□. We considered two methane molecules binding from the same side or opposite side of the plane of pyrene and coronene molecules. This detailed computational investigation of binding of methane with model aromatic compounds will provide knowledge required for experimentalists developing materials for methane storage or sensors. The primary goals in this study are to answer the following questions: (i) How many C□H···□ interactions of methane exist in the most stable complex for each system? (ii) How does the binding strength change going from small to large aromatic systems as well as one to two methane? Our results show that one C□H···□□interaction produces the most stable complex in benzene system but three C□H···□ interactions exist in the most stable complexes involving pyrene and coronene. The binding energies for two methane molecules with the aromatic hydrocarbons are considerably larger than that of single methane binding with respective aromatic system.



Benzene-Methane



Pyrene-Methane



Coronene-Methane

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IMPACT OF THE DYE CONFORMATION ON INTERFACIAL ELECTRON TRANSFER IN Dye-TiO_2 ASSEMBLIES

Chang Liu and Elena Jakubikova

Department of Chemistry, North Carolina State University, Raleigh, NC 27695

Interfacial electron transfer (IET) is one of the crucial steps in light-harvesting process that occurs in dye-sensitized solar cells. Computational studies of IET in dye-semiconductor assemblies are often based on a static structural model obtained by optimization of the system at 0 K. Dye sensitizers anchored to a semiconductor will, however, display a range of conformations at room temperature, which can impact the efficiency of the IET in these systems. This work investigates the influence of the dye sensitizer conformation on the IET in a model dye-semiconductor assembly, represented by isonicotinic acid anchored to (101) surface of TiO_2 anatase. Molecular dynamics (MD) at the DFTB level of theory was utilized to obtain 200 sample conformations of the dye-semiconductor assembly at room temperature. Wavepacket dynamics was then employed to investigate the IET upon population of LUMO and LUMO+1 orbitals of the isonicotinic acid in all samples. The conformation of the dye does impact both long-term and short-term IET behavior. Moreover, the characteristic IET time, especially the short-term behavior, was found to be correlated with the orbital energies of the dye sensitizer, the amount of the electron density on the carboxylic acid linker, as well as the number of available acceptor states in the TiO_2 semiconductor. While our results suggest that the main features of the system can be described adequately by a static DFT structure model at 0 K, the presence of various conformations at room temperature leads to a distribution of the IET rates with a median rate faster than that of the IET rate obtained for the static DFT structure, especially for the more complicated long-term IET behavior.

COMPUTATIONAL STUDY OF SODIUM CHLORIDE (NaCl) MOLECULES WITH EXPLICIT WATER MOLECULES IN GAS AND AQUEOUS SOLUTIONS

Kimberly Madison,[1] **Takia Smith**,[1] Wojciech Kolodziejczyk,[1,2] Glake Hill[1]

1. Interdisciplinary Center for Nanotoxicity, Jackson State University, Department of Chemistry and Biochemistry

2. Wroclaw Medical University, Department of Physical Chemistry, Wroclaw, Poland

Radiation can damage DNA directly or indirectly. Radiation energy can either be deposited directly into the DNA molecule causing excitation and ionization of the molecule, or radiation may interact with the molecular environment surrounding DNA, i.e., water, salts, proteins, and oxygen molecules. The indirect process of DNA damage can result in the formation of low energy electrons (LEEs) and hydroxyl radicals by the radiolysis of water and solvated electrons. Water and sodium chloride molecules have been simulated using a M06-2X functional to analyze the local molecular environment surrounding DNA.

ABIOTIC CONVERSION OF CYSTEINE TO URACIL WITH A MECHANISTIC STUDY

Ali Mirchi, Jing Wang, and Jerzy Leszczynski

Interdisciplinary Center for Nanotoxicity, Jackson State University, Jackson, MS 39217

Origins of life studies represent an exciting and highly multidisciplinary research field. In this research we focus on the contributions made by theory, modeling and simulation to addressing fundamental issues in the domain and the advances these approaches have helped to make in the field. Theoretical approaches will continue to make a major impact at the "systems chemistry" level based on the analysis of the remarkable properties of nonlinear catalytic chemical reaction networks, which arise due to the auto-catalytic and cross-catalytic nature of so many of the putative processes associated with self-replication and self-reproduction. In this way, we describe a novel synthesis of uracil from cysteine under prebiotically feasible conditions is presented here. This generation of uracil from cysteine mimics modern biology in the use of amino acids to synthesize nucleobases. We then discuss computationally-based molecular modeling techniques that are currently being deployed to investigate various scenarios relevant to the origins of life.

ADSORPTION ANALYSIS OF SELECT CHLOROPHENOL DERIVATIVE'S BINDING INTERACTIONS WITH THE SIDEWALL OF SINGLE-WALLED CARBON NANOTUBES: THROUGH THE MICROSCOPE OF DENSITY FUNCTIONAL THEORY

Quentarius Moore and Jerzy Leszczynski

[1]*Interdisciplinary Center for Nanotoxicity, Department of Chemistry & Biochemistry, Jackson State University. Jackson, MS*

Chlorophenols are one of many priority water pollutants whose ecological risk and toxicity are biomagnified through the food chain. Chlorophenols have been studied by the Environmental Protection Agency (EPA) and published within their series of public health statements about hazardous substances and their health effects. These compounds are known to be a group of chemicals that have between one and five chlorines added to a phenol molecule. All of the 19 possible chlorophenols are solid at room temperature, with the exception of 2-chlorophenols. Some of the uses and production of these compounds have stemmed from the likes of actions such as, chlorophenols possessing two or more chlorines being used as or converted into pesticides, 2-chlorophenols being used as antiseptics, mono- and di- chlorophenols being produced when phenols are chlorinated after disinfecting waste water, and during the bleaching of wood pulp with chlorine for the production of paper and wood at sawmills. Chlorophenol exposure to sawmill workers in 1982 showed adverse health effects to the workers. 2,4,6-trichlorophenol has previously been reported to lymphomas and leukemia in male rats and hepatic tumors in mice. The most concerning aspect of chlorophenols is that many residues can still be found in the environment long after the use of chlorophenols was discontinued. These compounds are soluble in water and can leach from the soil to groundwater. Since these pollutants are so persistent, they should be removed from industrial plant waste water before discharge into the environment or into municipal sewer systems.

Contributions made by the study and use of single walled carbon nanotubes (CNTs) as a multifunctional material in gas storage elements, sensors, nano drug carrier, field-effect transistor in electronic devices, optical devices, quantum computers, organic photovoltaic devices, sorbent and nanocomposites have been numerous since their discovery by Iijima in 1991. CNT are hollow tubular structures that are a carbon allotrope which can be made to be single-walled or multi-walled. CNTs are promising materials for these applications in view of their unique structural, mechanical, and electronic properties. Over the past 25 years, some of the most intriguing properties of CNTs are their large surface area to volume ratio, high chemical stability, transport properties, high electrical conductivity, field effect transistor properties, and quasi ballistic conductance. Most of the research for these applications focuses on the functionalization of the side walls with aromatics to form materials that exploit the electronic and mechanical properties of CNTs. Many research groups have succeeded in understanding and making CNTs functionalized by attaching various functional groups such as aromatic molecules, polymers, porphyrins, quantum dots, and dyes through either covalent or noncovalent bonding. One exceptional reason to why SWCNTs are so extensively researched for electronic applications such as sensors lends its significance to that the electronic conductance of SWCNTs can change significantly when gases or biomolecules are absorbed to their surfaces. Thus allowing the sensor to respond to surface coverage instead of concentration of the molecule of interest. In turn, making the device well suited for the detection of molecules such as chemical weapons agents & explosives which are known to exist in very low concentrations. Evidence to why the studies of their adsorption/binding characteristics are imperative to deducing suitable parameters for SWCNTs to optimize previously mentioned applications.

This work is focused on investigating the potential of semiconducting open ended (6,0) zig-zag single-walled CNTs to act as an sorbent for chlorophenols in aqueous solution through non-covalent attachment due to the aromatic ring. Through literature, we see that the interaction is strong enough that the guest molecule may be irreversibly absorbed to the hydrophobic surface of the CNT, leading to a self-assembled, highly stable structure in aqueous solutions.

We investigated the binding interactions of the system through implementing density functional theory to predict a stable structure as well as to calculate the energy of binding, enthalpy of binding, and Gibbs free energy of binding. Full optimization and frequency calculations were carried out at M06-2X/6-311G using an implicit solvation model. The two solvents used were: methanol and ethanol. All calculations were carried out using the Gaussian 09 code. We also observed the distance between the chlorophenols and CNT to confirm that binding occurred through π-π stacking. We observed through our studies that the hydrogen of the –OH tends to rotate towards the surface of the carbon nanotube. Adsorption of chlorpophenol derivatives does not drastically change the structure of the CNT.

Through studying the adsorption energies of chlorophenols on CNTs, we are able to predict the interactions between the two systems and speculate on the potential use of these CNTs as a means of retracting certain chlorophenols from aqueous solutions. This application would be beneficial for water treatment, curving the amount of chlorphenols from by-products, environmental cleanup and limiting human consumption and long-term exposure to high levels of these contaminants. So computational studies of their adsorption characteristics are imperative for understanding the mechanisms of binding and optimizing experimental conditions leading to efficient adsorption of chlorophenols from water matrix by CNTs.

Keywords- Density Functional Theory, Carbon nanotube, Chlorophenol, Adsorption, Water pollution

NEW METRICS FOR THE REACTIVITY AND STABILITY OF ANTIOXIDANT FULLERENOLS

Devin Mulvey and Dr. Kristen Lewis

[1]*Department of Chemistry and Biochemistry, Bloomsburg University of Pennsylvania, 400 East Second Street, Bloomsburg, Pennsylvania, United States*

The antioxidative qualities of fullerenols allow for their potential use in the prevention and treatment of diseases in which oxidative damage is involved, (e.g., neurological diseases, such as Parkinson's disease or Alzheimer's disease, and cancer). Although many studies have been conducted in discovering the various applications and overall behavior of fullerenols, additional research is warranted to better interpret fullerenols on the atomistic level. The exact structure of many synthesized fullerenes remains unknown and are difficult to obtain experimentally because most syntheses unintentionally form multiple isomers with varying degrees of hydroxylation. Thus, in silico methods have been employed to further study the structure and stabilities of the fullerenols. The objective of this project is to investigated the effect of hydroxylation and hydroxyl distribution on the stability and structure of fullerenols as well as determine the potential use of reduction potential and hydroxyl distribution as new metrics for fullerenol stability and reactivity. The adiabatic ionization potential, electron affinity, and relative reduction potential of fullerene C_{60} and fullerenols $C_{60}(OH)_n$ (n=12, 22, 24, and 36) were calculated to determine the effect of increasing hydroxylation on antioxidant activity. Electrostatic potential maps were also generated for each fullerenol to determine how positive centers relate to hydroxylation. Additionally, six conformations of $C_{60}(OH)_{22}$ were studied to determine the effect of hydroxyl distribution on fullerenol stability. All calculations were computed at the B3LYP/6-31G** level of theory using the Gaussian '09 software package. Fullerenols $C_{60}(OH)_{22}$ and $C_{60}(OH)_{36}$ proved to be the most effective at scavenging negative charge and the most promising antioxidants due to their high electron affinities, high reduction potentials and low ionization potentials. The electrostatic potential maps supported this finding and revealed that n=22 and n=36 had the most positive centers. The relative energies of n=22 conformations revealed that fullerenol stability is heavily dependent upon hydroxyl distribution. The combination of these results revealed that the relative positioning of hydroxyl groups determines the reactivity and stability of fullerenols. As such, it was concluded that hydroxyl interactions on the fullerene cage largely determine a fullerenol's structural stability, the formation of positive centers on its cage, and its propensity to scavenge negative charge.

NEW DEVELOPMENTS IN THEORETICAL ASSESSMENTS OF ISOTOPE EFFECTS

Piotr Paneth

Institute of Applied Radiation Chemistry, Lodz University of Technology, Zeromskiego 116 90-924 Lodz, Poland

Isotope effects deliver powerful tool for studying mechanisms of chemical and biochemical processes. Classical, and thus far the most effective, way of their use relies on comparison of experimentally determined values with theoretical predictions made for alternative pathways. In recent years our understanding of origins of isotope effects, and the methodology of their theoretical calculations have grown. These developments will be discussed and illustrated by examples from our laboratory.

CHALLENGES IN MODELING ATOMIC SCALE SURFACES AND INTERFACES

Henry P. Pinto

School of Physical Sciences and Nanotechnology, Yachay Tech University, 100119-Urcuqui, Ecuador, E-mail: pinto@yachaytech.edu.ec

The impressive development of nanotechnology has already reached high controllability levels on the matter and it is clear that future technologies will depend upon our ability to manipulate atoms accurately. Within this context, many technological applications rely upon the surface and/or interface rather than bulk material properties. For this reason, the study of the composition and electronic properties of materials is the key to understand material properties.

This talk will provide an overview of the challenges when modeling surfaces and interfaces focusing in (**i**) Prediction and interpretation of photoelectron spectroscopy on pyrite $FeS_2(001)$ surfaces and Au(111)/MUD (MUD=11-mercaptoundecanol) interface: Photoelectron spectroscopy is a powerful technique that allows determining the composition and electronic structure of any material. The observed spectrum depends on the material composition as well as on the frequency of the incident radiation (X-rays or UV) that allows extracting either the information of the topmost atomic layers or bulking part of a specific surface or interface. The interpretation of such experiments is challenging but density-functional theory can provides fundamental insights that allow reproducing the observed spectra considering the actual atomic structure of the material. Basically, electronic structure calculations are applied and properly combined with corrections due to atomic subshell photoionization cross-sections and inelastic mean free path for the electrons. (**ii**) Molecular electronics: the development of practical molecular electronics relies on the identification of molecule-surface combinations where the molecule is bound to the surface; in this section is presented the electronic manipulation of Nickel-tetraphenylporphyrin (NiTPP) adsorbed on a pristine Si(100) surface. Experimentally this molecule is manipulated using low-temperature scanning tunneling microscopy (STM) creating a molecular switching device. Theoretical calculations combined with atomic resolution STM are a powerful toll that allows the understanding of precise molecule manipulation. (**iii**) Graphene is perhaps the most influential material in science; it has an infinite two-dimensional layer with sp^2 hybridized carbon atoms arranged in a honeycomb crystal lattice. This system is a unique 2D crystal (one atom thick) of carbon that has an electronic structure with linear dispersion close to the Fermi level described as massless Dirac fermions. Experimental studies of grain boundary loops in graphene (flower-like defects) have attracted the scientific interest given the new electronic properties observed as well as the induced mechanical properties that it might have. This topological defect has the lowest energy per dislocation core among all the known topological defects in graphene that appears as result of the joint of mobile dislocations. Simulations using density-functional theory allow us to understand the electronic and magnetic properties of these flower-like defects.

“IMPENETRABLE” MOLECULAR VOLUMES IN NONCOVALENT INTERACTIONS

Peter Politzer and **Jane S. Murray**

Department of Chemistry, University of New Orleans, New Orleans, LA 70148 USA

*Author for correspondence: Jane S. Murray. E-mail: jsmurray@uno.edu

The van der Waals radii of atoms are typically based upon an arbitrarily-defined intermediate value of the distances between non-bonded but interacting atoms in crystals [1-4]. Accordingly, as has been pointed out [3,4], the sum of van der Waals radii is often not a reliable criterion for the existence of a noncovalent bond; a noncovalent interaction can have a separation several tenths of an Angstrom greater or less than the sum of the respective atoms' van der Waals radii. Similarly ambiguous is therefore the term “impenetrable volume” that is sometimes applied to the volume of a molecule that is encompassed by overlapping “atomic spheres” with van der Waals radii.

For each of a series of molecular complexes A---B at their equilibrium separations, we have determined the electronic density contour that corresponds to separate but nearly touching molecular surfaces for A and B. These surfaces, which exclude some small portions of the electronic densities of A and B, can be viewed as enclosing the “impenetrable” volumes of A and B. The results for a series of eight complexes will be presented and discussed.

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SELECTIVE ZN(II) SENSING RAMAN PROBE FOR SCREENING OF PROSTATE CANCER CELLS

Avijit Pramanik, Suhash R. Chavva, Bhanu P. V. Nellore, Stacy Jones and Paresh Chandra Ray

Department of Chemistry and Biochemistry, Jackson State University, Jackson, MS 39217

Early stage identification of cancer is very important to cure from the chronic disease. Mobile zinc signatures can be used as a biomarker for prostate cancer prediction, opening the route for the early diagnosis of cancer. Clinicians need a reliable tools which can offer fast, highly sensitive and selective mobile Zn(II) concentration in live cells. Raman sensor hold high promise for in-vivo sensing of cancer, where near IR light can be easily used to avoid tissue auto-fluorescence and to enhance tissue penetration depth. The current work report to design of novel and highly efficient surface enhanced Raman spectroscopy (SERS) probe using *p*-(imidazole)azo) benzenethiol attached gold nanoparticle as a Raman reporter, which has the capability to identify prostate cancer cells based on Zn(II) sensing. Reported data show that after binding with Zn(II), Raman reporter attached gold nanoparticle forms assembly structure, which allows selective detection of Zn(II) even at 0.1 parts per billion (ppb) concentration. Experimental data shows that SERS probe can distinguish metastatic cancer cells from normal prostate cells very easily. Reported results demonstrated that this sensor's sensitivity is as low as 5 cancer cells/mL. Designed Raman probe has the capability to be used as chemical toolkit for determining Zn(II) concentrations in the biological sample.

Key words: *p*-(imidazole)azo) benzenethiol, Zn(II) sensor, Prostate Cancer Cells, Raman Spectroscopy and SERS probe.

Acknowledgments: The research supported by National Science Foundation (PREM NSF DMR-1205194) and NIH/NCRR (Award Number: G12RR013459) & NIH/NIMHD (Award Number: G12MD007581) for supporting the Analytical Core Laboratory Facilities

MATERIALS INFORMATICS: COMPUTATIONAL AND DATA MINING APPROACHES TOWARDS RATIONAL DESIGN AND TOXICITY ASSESSMENT OF NANOMATERIALS

Bakhtiyor Rasulev

Center for Computationally Assisted Science and Technology, North Dakota State University, Fargo, ND

For the last two decades, breakthrough research has been going on in all aspects of materials science, including nanotechnology at an accelerated pace. New materials of unprecedented functionality and performance are being developed and characterized. Moreover, the need in new materials of desired functionality and performance is increases in an exponential way.

Here we show the adaptation and application of various computational and cheminformatics methods in functional materials / nanomaterials properties prediction, including physico-chemical, and toxicological. Since functional materials are complex entities from chemical point of view the study of nanomaterials requires an interdisciplinary approach, involving multiple aspects ranging from physics and chemistry to biology and medicine. We show how the combination of computational chemistry, databases of experimental data, data mining and cheminformatics approaches can help in rational design of various materials with improved properties, and assist with risk assessment. The predicted properties can range from physico-chemical to toxicological and pharmacological, including drug delivery capabilities and interaction with target proteins. The discussed materials include metal oxides, metals, functionalized fullerenes and carbon nanotubes.

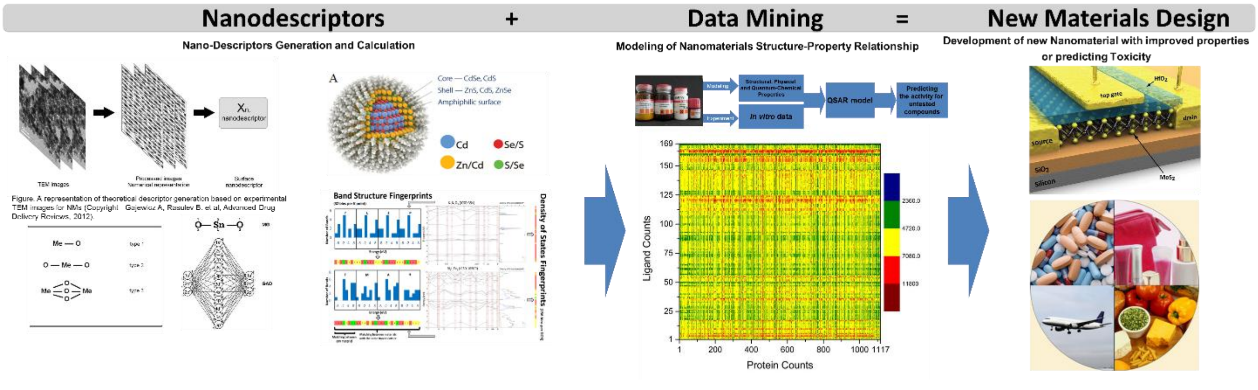

Figure. An overall scheme of cheminformatics and materials informatics methods applications for materials (nanomaterials) characterization and design

DESIGN OF NEW ARYLAMINE DERIVATIVES FOR DYE-SENSITIZED SOLAR CELLS EXPLORING DIRECT QSPR AND FIRST PRINCIPLES APPROACH

Juganta Roy[1], Supratik Kar[1], Henry Pinto[2] and Jerzy Leszczynski[1]

[1] *Interdisciplinary Center for Nanotoxicity, Department of Chemistry and Biochemistry, Jackson State University, Jackson, MS-39217, USA*
[2] *Yachay Tech University, School of Physical Sciences and Nanotechnology, 100119 Urcuquí, Ecuador*

Due to the flexibility in the aspect of cheap fabrication and environmental-friendly properties, dye-sensitized solar cells (DSSCs) have received increasing attention in recent years. In DSSCs, a photosensitizer (dye), adsorbed on the mesoporous semiconductor surface (here TiO_2), which is responsible for capturing the sunlight. In the presented work, we have employed a sequence of computational study to design new and higher power conversion efficient photosensitizer than the existing DSSCs. The quantitative structure-property relation (QSPR) approach and first principles density functional theories (DFT) were combined to understand the basic electron transfer mechanism as well as material properties of a huge number of arylamine organic dyes acting as dye-sensitizers from diverse chemical classes for the DSSCs.

We developed QSPR models for each chemical classes to link the quantitative relationship between the overall power conversion efficiency (PCE) and computed quantum as well as structural descriptors for the studied arylamine derivatives. Identified properties and structural fragments derived from QSPR employed to design the new dye-sensitizer with higher PCE. To study the interface of newly designed photosensitizers/TiO_2, we have employed Perdew-Burke-Ernzerhof (PBE) functional with on-site Coulomb interactions corrections. We have considered 9 atomic layers of the most widely used TiO_2 (101) surface to mimic the bulk TiO_2. Computed partial density of state and band gaps are used to evaluate the newly designed photosensitizers. Therefore, the combined techniques can accelerate the design of new dye sensitizers with higher PCE for DSSCs.

Key Words: Dye-sensitized solar cell, Arylamines, QSPR, Interface, Photosensitizers, PCE.

AB INITIO STUDY OF THE BINDING OF CO2 WITH NITROGEN CONTAINING COMPOUNDS

Lakeeta Sanders, Sadia Nowshin, and Glake Hill

Interdisciplinary Center for Nanotoxicity, Jackson State University, Jackson, MS 39217

The recent critical issue of degrading water quality in the MS Gulf Coast requires the development of technology that can analyze and detect pollutants in the water. Water quality is important for sustaining life and proper functioning of the ecosystem. This ecosystem yields food and economic development for many along the coastal US. It is critical to detect and remove pollutions before this ecosystem is destroyed. However, there remains very few options to detect these changes within the water system. One such change that would be important to detect is in the concentration of CO_2, a byproduct of many polluting processes. There are a number of potential compounds that can be used to detect CO_2 due to the binding properties of the molecule. In this work, he project explores the absorption of carbon dioxide in water with two well known CO_2 binding compounds. The binding constants and other energetic information will be discussed. Proper understanding of these constant will lead to a predictive understanding of which compound is better suited for CO_2 absorption and detection.

UNIVERSAL LOCAL DENSITY OF STATES FOR NANOPLASMONICS: FROM ENERGY TRANSFER TO STRONG COUPLING TO LOSS COMPENSATION AND SPASING.

Tigran Shahbazyan

Jackson State University, Department of Physics, Atmospheric Sciences and Geoscience,
1400 J.R. Lynch Street Jackson, MS 39217 U.S.A.

We derive a general expression for local density of states (LDOS) in any metal-dielectric nanoplasmonic system in the frequency range dominated by a localized plasmon mode. By including, in a systematic way, the Ohmic losses, we show that the plasmon LDOS is simply the local field intensity normalized by the system absorbed power. We obtain the explicit formulae for energy transfer (ET) between quantum emitters and plasmon modes as well as between donors and acceptors situated near a plasmonic nanonostructure. In the latter case, we show that the plasmon-assisted ET rate is proportional to the LDOS product at the donor's and acceptor's positions, and establish a universal condition for the transition between the Forster-dominated and plasmon-dominated ET regimes. For multiple QEs interacting with plasmon modes, we obtain explicit conditions for the onset to strong coupling regime and, for pumped systems, for loss compensation.

COMPUTATIONAL CHEMISTRY INVESTIGATION OF FATE AND EFFECTS OF SOME MUNITION COMPOUNDS

Manoj K. Shukla

US Army Engineer Research and Development Center, Environmental Laboratory, Vicksburg, MS 39180

Research in modern explosives is driven by the need for the development of low vulnerable munitions, which are safe in handling and have reduced response to unplanned aggressive stimuli and at the same time without compromising their potency compared to conventional explosive compounds. These modern munitions are collectively called as insensitive munitions. Manufacturing, storage and application of these munitions can lead to environmental contamination. This talk is devoted to application of advanced computational chemistry methods in determining fate and effects of munitions compounds in the environments. For example, some of the munitions compounds undergo photo-transformation and computational chemistry methods can be reliably used to predict photodegradation products and their kinetics. Adsorption of high energy military contaminants on different surfaces is an important area of research. Such investigations can provide significant information on components of soils responsible for munition retention. Similarly, computational chemistry methods can be utilized for the development of multifunctional polymeric materials for application in environmental remediation.

PREDICTING PROPERTIES OF POLYMERIC NANOPARTICLES: ZETA-POTENTIAL AND HEMOLYTIC ACTIVITY

Natalia Sizochenko, Jerzy Leszczynski

Interdisciplinary Nanotoxicity Center, Department of Chemistry and Biochemistry, Jackson State University, Jackson MS, USA

Various properties of polymeric nanoparticles can be predicted using simulation methods. However, all atoms simulations or even molecular dynamics modeling require a lot of computer time. Reliable modeling of infinite molecular compounds like polymers or semi-infinite molecular compounds as polymeric nanoparticles is a challenge for quantum chemists. It is critical to determine a reasonable size, which represent an infinite structure accurately.

Density functional theory (DFT) calculations were applied to model polymer conjugates of interest. Standard Gaussian 09 code was applied to optimize structures with the nonlocal hybrid Becke three-parameter Lee−Yang−Parr (B3LYP) level of theory with the 6-311G(d) basis set. The geometry was optimized at the neutral singlet ground state. When several conformations for studied polymers were possible, the structure with the lowest energy geometry was used.

Using DRAGON software, simple parameters were calculated for part of polystyrene chain with one functional group (candidate polymeric repeat unit).

Both DFT- and DRAGON-based parameters were used for quantitative structure-property analysis. Molecular parameters were used to predict zeta potentials and hemolytic activity of 17 polystyrene conjugates.

In order to compare developed model, the molecular dynamics simulations would be performed using DL_POLY package.

NEW PARADIGMS IN THE PHOTOPHYSICS OF HYDROGEN-BONDED MOLECULAR SYSTEMS

A. L. Sobolewski

Institute of Physics, Polish Academy of Sciences, Warsaw, Poland
E-mail: sobola@ifpan.edu.pl

Near the turn of the century, the discovery and theoretical characterisation of hitherto unknown photoreactive electronically excited states in heteroaromatic molecules [1] established the so-called πσ* states as a new paradigm in molecular photophysics [2]. In these states, one electron is excited from a π orbital of an aromatic ring to the σ* orbital localized on an acidic molecular moiety XH (where X is an oxygen or nitrogen atom and H is a hydrogen atom). The πσ* states are dissociative with respect to the detachment of the hydrogen atom. Excitation of a molecule into a πσ* state results in a instantaneous (fs) dissociation of the hydrogen atom [3].

When the departing hydrogen atom forms an intra- or an inter-molecular hydrogen bond (HB), new photophysical phenomena may appear. Thus:

1. In proton accepting saturated solvents (water, ammonia, etc.) hydrogen atom is spontaneously ionized and provides the source of solvated electrons [4].
2. In DNA base pairs and in peptides the conical intersection between the electronically excited state and the ground state for proton-transfer reaction along HB bridges provides a very effective mechanism for explanation of the photostability of living matter [5].
3. The mechanisms that govern the motion of protons along intra-molecular HB has allowed the design of bistable molecular photoswitches [6].
4. The mechanisms that govern the motion of protons along inter-molecular HB may provide a template for designing of macromolecular systems, which are able to oxidize water using solar radiation [7,8].

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ADVANCED COMPUTATIONAL STUDIES OF NUCLEIC ACIDS. ADVANTAGES AND LIMITATIONS.

Jiří Šponer

Institute of Biophysics, Academy of Sciences of the Czech Republic, Královopolská 135, 612 65 Brno, Czech Republic

Ph: (420) 541517-133 Email: sponer@ncbr.muni.cz

Due to steady developments of computer hardware and software in the last decades, computational methods have become key tools to understand structural dynamics, function and evolution of nucleic acids. In my talk, I will introduce two important classes of computational methods that are used in studies of nucleic acids, namely, advanced quantum-chemical calculations and classical atomistic explicit solvent molecular dynamics simulations. I will explain how to correctly combine these methods with diverse types of experimental information and to avoid misinterpretations that are widespread. The main limitation of the MD technique is the force field approximation, which is becoming more and more visible with advance of microsecond-to-millisecond time scales and enhanced-sampling methods. The main limitation of QM is the lack of Boltzmann sampling, which precludes any assessment of stabilities of biomolecules in a thermodynamics sense. Nevertheless, wisely used computational and modelling techniques can bring unique insights into the complex world of RNA and DNA molecules that are not obtainable by any available experimental techniques. I will illustrate application of computational methods using selected examples from our research, including recent developments of nucleic acids force fields, attempts to use large-scale QM calculations to compute complete nucleic acids building blocks, studies of DNA quadruplex folding and proposal of an origin-of-life scenario leading from formamide to first RNAs.

SYNTHESIS OF MoS2 QUANTUM DOTS AND THEIR APPLICATION TO BIOIMAGING AND TREATMENT OF MULTIDRUG-RESISTANT BACTERIA

Carrie Sweet, Stacy Jones, Avijit Pramanik, and Dr. Paresh Ray

Department of Chemistry and Biochemistry, Jackson State University, Jackson, Mississippi 39217, United States

Water-soluble photoluminescent MoS_2 quantum dots were synthesized by a facile bottom-up hydrothermal approach from sodium molybdate and L-cysteine precursors. These quantum dots exhibit a strong blue emission at 430 nm under ultraviolet irradiation. The suitability of MoS_2 quantum dots as photoluminescent probes for bioimaging was assessed using SkBr3 cancer cells. Furthermore, MoS_2 quantum dots exhibit quenching and upconversion of photoluminescence in the presence of the antibiotic tetracycline due to an energy transfer event. Because of the interaction between MoS_2 quantum dots and tetracycline, a potential synergistic effect may exist for the treatment of multi-drug resistant bacterial infections that are immune to tetracycline alone.

MULTIFUNCTIONAL FLUORESCENCE NANOPROBES FOR DETECTION AND IDENTIFICATION OF COMPLEX CIRCULATING TUMOR CELLS.

Avijit Pramanik, **Aruna Vangara**, Bhanu Priya Viraka Nellore, Sudarson Sekhar Sinha, Suhash Reddy Chavva, Stacy Jones, and Paresh Chandra Ray*

Department of Chemistry and Biochemistry, Jackson State University, Jackson, Mississippi 39217, United States

Recently Circulating tumor cells (CTC) are gaining huge attention for their complexity and metastasis relapse in cancer development. The CTCs are found low range in blood sample about 1-10 cells/ml and also possess heterogeneity due to epithelial mesenchymal (EMT) transitions. Our current findings are a new approach to detect accurately and capture these complex CTCs from the blood samples. This article reports the development of a new class of multifunctional fluorescent–magnetic nanoprobes for targeted capturing and accurate identification of heterogeneous CTC. A facile design approach for the synthesis and characterization of these multifunctional nanoprobes that exhibit excellent magnetic properties and emit very bright and photostable multicolor fluorescence at red, green, and blue under single excitation wavelength 380 nm is reported. We demonstrated with experimental results that multicolor fluorescence imaging can be used for mapping epithelial, mesenchymal and stem cell CTCs simultaneously, which indicates that nanoprobes are capable of characterizing circulating tumor cells heterogeneity by accurately identifying the multiple subpopulations of CTC from blood samples. The current clinical methods in the market are for CTCs detection but our method can separate and detect simultaneously via fluorescence imaging technique. We performed CTC detection on spiked 15ml whole blood samples so we are in progress towards a better design of this nanoprobe to enhance sensitivity of CTCs detection in about 7.5 ml of blood sample.

Keywords:
Single wavelength excitation, heterogeneous circulating tumor cell capturing, mapping of epithelial, mesenchymal and stem cells simultaneously, multifunctional fluorescent−magnetic nanoprobes, fluorescence imaging.

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UNDERSTANDING A MECHANISM OF GUANINE INTERACTING WITH HYDROXYL RADICAL IONS TO 8-OxoG AND FapyG: A THEORETICAL STUDY

Sharnek Walker,[1] Glake Hill**,**[1] and Wojciech Kolodziejczyk[1,2]

1. Interdisciplinary Center for Nanotoxicity, Jackson State University, Jackson, MS 39217
2. Wroclaw Medical University, Department of Physical Chemistry, Wroclaw, Poland.

As humans, we are exposed to these toxic ions from inhalation, direct contact, and ingestion. Once inside the body it is possible the ion can attach to macromolecules that are important to many processes the body needs to function properly. The metals and reactive oxygen species (ROS) are known to cause oxidative stress to DNA. Oxidative stress from ROS have been linked to diseases like cancer and Alzheimer's. Thus, the function of the Watson and Crick bases are functioning differently than mutated bases. The production of ROS can modify lipids, proteins, and nucleic acids, which are all important to the human body. In this work, we attempt to gain knowledge of the mechanism that radical hydroxyl ions have when interacting with nucleobase, guanine. As we know, the DNA may be modified. This can happen as a result of UV-VIS radiation, inter- and intra-strand cross linking or reaction with radicals. Especially exposure to metal and radical ions impact the living organism by disturbing fundamental biological processes. Every single modification may lead to cancer or any other genetic disease. Exposure to metal and radical ions impact the living organisms by disturbing fundamental biological processes. We performed all calculations using the density functional theory B3LYP functional accompanied with 6-31G (d,p) and 6-311+G (d,p) basis sets. Solvent properties were treated using the SMD model. In this work, we attempt to gain a better understanding of molecular changes in nucleobase, guanine.

In this paper we have studied a reaction path from Guanine to 8-oxo-Guanine proposed by N. R. Jena et all using density functional theory (B3LYP) employing 6-31G(d,p) and 6-311+G(d,p) basis sets. Our calculations shows that reaction can be activated very easily with ·OH radical with barrier energy 4.01 kcal/mol but next stage of reaction path needs higher energy to activate. It suggests that full reaction path needs catalyst like enzyme to occur. NBO analysis of each stage of the reaction path has been preformed.

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CHEMISTRY OF AMYLOID-BETA PEPTIDE AGGREGATION: EXPERIMENTAL AND COMPUTATIONAL STUDIES USING TRYPTAMINES AND HYDROXYFLAVONES AS INHIBITORS

Brianna Walley, Ja'Nautica Bee and Bidisha Sengupta*

Department of Chemistry, Tougaloo College, Tougaloo, MS 39174, U.S.A

bsengupta@tougaloo.edu

The unfolding process of amyloid-beta (Aβ) peptide is followed by oligomerization, protofibril formation producing aggregated plaques at the end. These fibrils develop Alzheimer's disease. Salt concentrations, types and pH play varied and important roles in the overall unfolding process of the peptide. Neurotransmitter tryptamines serotonin and melatonin play mixed functions in inhibiting the aggregations. Plant flavonoids also show interesting effects when present in the peptide solutions. The hypothesis of this research is that hydroxy and methoxy substituents present in tryptamines and hydroxyflavones decreases the rate of the formation of aggregates to a significant extent, while when they are present together, can prevent aggregation. We have performed experimental and computational studies on these systems. Further studies are underway.

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COMPARATIVE THEORETICAL STUDY OF OXYGEN ADSORPTION ON NEUTRAL AND ANIONIC AG_N AND AU_N CLUSTERS (N = 2 – 25)

Meng-Sheng Liao, **John D. Watts**, and Ming-Ju Huang

Department of Chemistry and Biochemistry, P. O. Box 17910, Jackson State University, Jackson, Mississippi 39217, USA

Using density functional theory (DFT), we have performed a theoretical comparative study of oxygen adsorption on neutral and anionic Ag_n and Au_n clusters in a large size range of $n = 2 – 25$. Ionization potentials (IPs) and electron affinities (EAs) of the pure clusters and the $M_n^q–O_2$ binding energies $E_{bind}(M_n^q–O_2)$ in the $(M_nO_2)^q$ complexes (M = Ag, Au; q = 0, −1) were determined. Three density functionals, BP86, revPBE, and B3LYP were used in the calculations, among which the BP86 functional gives the best results for IPs and EAs, while B3LYP gives the best results for $E_{bind}(M_n^q–O_2)$. A number of differences between the silver and gold clusters and their reactivities toward O_2 adsorption are accounted for by the calculations. One interesting result is that the calculated $Au_n^-–O_2$ binding energies are in good, quantitative agreement with the measured relative reactivities of the Au_n^- cluster anions toward O_2 adsorption.

Key words: density functional calculations; catalysis; quantum chemistry; intermolecular interactions; dioxygen ligands; coordination modes

SINGLE PARTICLE ICP-MS (SP-ICP-MS) FOR MEASUREMENT OF SIZE OF SILVER NANOPARTICLES (AGNPS)

Jeremy White and Zikri Arslan

Department of Chemistry and Biochemistry, Jackson State University, Jackson, USA

Silver nanoparticles (AgNPs) possess antibacterial properties and thus are being used in numerous consumer and food products. Ion release and other toxicological properties are affected by the size of the AgNPs. As a result, understanding the stability and particle distribution is important to accurately predict toxicological impact of the AgNPs on human and environmental health. Transmission electron microscopy provides information with regard to size distribution in powders. Dynamic light scattering technique is suitable for measuring hydrodynamic size distributions, but lacks the sensitivity to detect NPs at low concentrations. Inductively coupled plasma mass spectrometry (ICP-MS) is a sensitive technique and can provide information about the AgNPs in solution at very low levels, even in the presence of single particles. In this study, we utilized uncoated, PVP- and oleic acid (OLA)-coated AgNPs within a size range of 20-30 nm. We employed single particle (sp) ICP-MS in very dilute solutions of the AgNPs to determine the particle size distribution. Water, methanol (MeOH), dimethylsulfoxide (DMSO) and tetramethylammonium hydroxide (TMAH) were examined as solvents. Water and TMAH was found to be most suitable solvents in terms of NP stability and gathering precise size information. MeOH yielded size distribution much smaller than listed particle sizes, while DMSO was not suitable for ICP-MS measurements. Various concentration of TMAH was examined for all AgNPs. A concentration of 5 and 10% provided accurate estimate of AgNPs.

THE RESPONSE ELECTRON–ELECTRON REPULSION ENERGY AND ENERGY COMPONENT ANALYSIS IN AN ASSESSMENT OF STERIC REPULSION IN ETHANE'S ROTATIONAL BARRIER

E. A. Salter and **A. Wierzbicki**

Department of Chemistry, University of South Alabama, Mobile, AL 36688

Previously, we showed how to compute 2-electron properties as responses (energy derivatives) in the coupled-cluster (CC)/many-body perturbation theory (MBPT) models and demonstrated that the correlation energy (ΔE) is the sum of response kinetic (ΔT) and electron-nuclear attraction (ΔV) energies and the response electron repulsion (ΔV_{ee}) energy. Thus, evaluation of total V_{ee} in the CC/MBPT models is quite simple: For total energy (E), total 1-electron responses (T and V), and nuclear-nuclear repulsion energy (V_{NN}), $V_{ee} = E - V_{NN} - T - V$ is the true 2-electron response value.

As the CC/MBPT energy is a simple sum of components, we have applied component energy analysis to assess the role of "steric repulsion" in the case of ethane's rotational barrier. We find that the higher-energy eclipsed geometry is actually favored versus staggered in the two repulsion energies (V_{NN} and V_{ee}), while decisively disfavored in electron-nuclear attraction energy (V). This is in agreement with earlier SCF-based results. Our best quality calculations (CCSD/cc-pVQZ) attain practical Virial Theorem compliance (i.e., agreement among the kinetic energy, potential energy, and total energy representations of the barrier) in assigning 2.70 ± 0.06 kcal/mol to the barrier height; -195.80 kcal/mol is assigned to the drop in "steric repulsion" upon going to the eclipsed geometry. This demonstrates, contrary to the commonly held belief, that steric repulsion is not responsible for any fraction of the~3 kcal/mol barrier.

IN SITU RAMAN SPECTROELECTROCHEMICAL STUDY OF TRANSFORMING GRAPHENE OXIDE INTO HOLEY GRAPHENE OXIDE

A.B.M. Zakaria[1] and Danuta Leszczynska*[2]

[1]*Department of Chemistry and Biochemistry, Jackson State University, Jackson, MS 39217*
[2]*Department of Civil and Environmental Engineering, Jackson State University, Jackson, MS 39217*

Holey Graphene Oxide (HGO), a new form of graphene material with oxidative nanoholes in its basal plane, has captured the attention of the scientific community due to its increased catalytic sites associated with the holes. This newly explored graphene surface exhibits potential for use in future generations of electronics and renewable energy applications. Most recently, we reported for the first time, a successful synthesis of HGO by using a two-step electrochemical method.[1] We also extensively characterized this new material by using AFM, SEM, TEM, FTIR, Raman spectroscopy, XPS and cyclic voltammetry. However, none of the instrumental techniques alone can be a probe to give the mechanism and the sequence of events of the formation HGO.

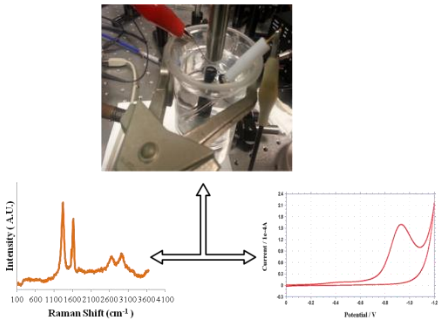

Figure: Schematic presentation of in-situ instrumentation.

Driven by this need, in this abstract, we report a real-time monitoring of the transformation of GO into HGO by combining Raman spectroscopy with electrochemistry. In this work, an in situ measurement have been carried out during potential dependent reduction and re-oxidation of GO immobilized on a conducting substrate of 3-aminopropyltrimethoxysilane (APTMS) modified glassy carbon electrode. It has been observed that during electrochemical reduction of GO, D/G intensity ratio was increased from 0.91 to 1.23 and decreased from 1.23 to 1.01 during followed by the oxidation of reduced graphene oxide (RGO). It has also be shown that the crystallite size, L_a of GO, RGO and HGO were 52 nm, 39 nm and 38nm respectively.

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