台灣理論計算分子科學學會會員大會
General Meeting of Taiwan Theoretical and Computational Molecular Sciences Association
(T^2CoMSA)

暨

2015 年理論計算化學小組九月研討會
TCCAT September Conference 2015

Program

September 8, 2015

松柏講堂, Chemistry Department, National Taiwan University

09:00-09:30 registration opens

09:30-10:00 General Meeting of Taiwan Theoretical and Computational Molecular Sciences Association (T2CoMSA)

（Chair：Jyh-Chiang Jiang）

NO.01 10:00-10:20 **Yu-Jie Zhong** 鍾雨潔 (Academia Sinica)
"The Anisotropy in Charge Mobility of Rubrene"

NO.02 10:20-10:40 **Chen-Hao Yeh** 葉丞豪 (National Taiwan Normal University)
"Density Functional Theory Calculation on the NO Dissociation and Conversion to N_2O Mechanism Catalyzed by Cu_4 cluster in ZSM-5 (Cu_4-ZSM-5) and Bimetal Cu_3Fe in ZSM-5 (Cu_3Fe-ZSM-5)"

NO.03 10:40-11:00 **Yu-Chih Chen** 陳鈺智 (National Taiwan University of Science and Technology)
"Methane activation on Ir-doped TiO_2 (110) and IrO_2/TiO_2 (110) surfaces- a density functional theory study"

NO.04 11:00-11:20 **Ya-Chiao Wang**王亞喬 (National Taichung University of Education)
"A theoretical study of the structures and photoelectron spectra of $C_2(C_{60})_2$ and $C_2H_2(C_{60})_2$"

（Chair：Jer-Lai Kuo）

NO.05 11:20-11:40 **Chien-Pin Chou** 周建斌 (National Chiao Tung University)
"Zhang-Zhang Polynomials as a Novel Local Aromaticity Index for Benzenoid Hydrocarbons"

NO.06 11:40-12:00 **Bing-Hau He** 何秉澔 (National Chiao Tung University)
"Constructing Homogeneous Solutions of Kinetic Energy Operator in Schrödinger Equation of Helium Atom"

12:00-13:30 lunch (學會第一屆第三次理監事會議)

（Chair：Hayashi Mishitoshi）

NO.07 13:30-13:50 **Timothy Click** 柯明 (National Chiao Tung University)
"The Allosteric Effects of CRIPT Peptide upon Binding to PSD-95 PDZ3"

NO.08 13:50-14:10 **Jake Tan** 洪于玉 (Academia Sinica)

“Coupling of Intermolecular Proton Bond (IPB) Stretch with C-O stretch in Zundel Dimers of $(MeOH)_2H^+$ *and* $(Me_2O)_2H^+$*”*

NO.09 14:10-14:30 **Chun Yin Chen** 陳俊吟 (National Taiwan Normal University)

“A Theoretical Investigation on the Mechanism and Application of Quantum Interference Effect in Single Molecule Electron Transport”

NO.10 14:30-14:50 **Liang Chun Lin** 林亮君 (Academia Sinica)

“Substituent effect toward the temperature dependence of R1R2COO + Water reaction”

14:50-15:10 Coffee Break

（Chair：Kaito Takahashi）

NO.11 15:10-15:30 **Cheng-Han Yang** 楊承翰 (Fu Jen Catholic University)

“Probing Water Microsolvation Dynamics of Proteins toward Photochemical Application”

NO.12 15:30-15:50 **Mawan Nugraha** (National Taiwan University of Science and Technology)

“Selectivity Study of Pd(111), PdAu(111) and PdHg(111) Catalysts for H_2O_2 *Direct Forming: A Theoretical View”*

NO.13 15:50-16:10 **Chin-Chai Fan** 范錦財 (National Chiao Tung University)

“Parameterization of DFTB3 for Water Clusters by using an Automatic DFTB Parameterization Toolkit (ADPT)”

16:10-17:10 Poster

P01	Hung-Lung Chou	Combined Experimental and Computational Studies of $Na_2AxByFe(CN)_6$ for Aqueous Sodium-Ion Batteries
P02	Chia-Ning Yang	Molecular Modeling Studies of the SAGA Deubiquitinating Module Structural and Functional Variance Caused by Sgf73/Y57A
P03	Ching-Chen Wu	Study of Poly (3, 4-ethylenedioxythiophene)/MnO_2 as Composite Cathode Materials for Aluminum-Air Battery: DFT Simulation Studies

P04	Yu-Ming Su	Catalytic Oxidation of CO over CeO2 and $CeGd_{0.1}O_2$ Nanoparticles: DFT Simulation Studies
P05	Yi-Tsao Chen	On the Structure Variation of DNA-RNA Hybrid in the Ago Protein
P06	Shiuan-Yau Wu	Density-functional Calculations of Alkane Conversion on Platinum Decorated Graphene Oxide Sheets
P07	Gou-Tao Huang	A Computational Study of Sulfur Transfer in Mercaptopyruvate Sulfurtransferase
P08	Arpita Varadwaj	Can entirely negatively charged covalently bound atoms in two different molecules interact attractively? A theoretical (and experimental) prospective
P09	Ge Yung Chi	QM/MD Simulations on the Proton Coupled Electron Transfer of Prostaglandin H_2 Isomerization by Prostacyclin Synthase
P10	Nixon Raj N	Allosteric Effects Of Mn^{2+} Ion In Cell Death Related Nuclease (Crn4)
P11	Huang Chi-Chang	Anomalous Exo Selectivity in Diels–Alder Reactions: A Computational Study
P12	Ming-Yi, Huang	Investigation of Water Coupled Conformational Dynamics of Thromboxane and Prostacyclin syntheses by Molecular Dynamics Simulation and Small-Angle X-ray Scattering
P13	Chun-Chih Chang	Quantum-Chemical Calculations of Dehydrogenation of Butane to Butene on Rhodium Nanoclusters (Rh13) Supported on Unzipped Graphene Oxide
P14	Yu-Huan Lu	Adsorption and Dissociation of H_2O molecule on α-Al_2O_3 (0001) Surface:A Computational Study
P15	I-Hsiang, Lin	Nitrogen-doped carbon nanotubes as a metal-free catalyst for CO oxidation
P16	Tong, Yu -Jhe	Density functional study of oxidation reaction on W(111) and Pd-modified W(111) surface
P17	Chia-Ming Chang	Interactions between Ligands and Kinases: Molecular Simulations, and Kinase Assays
P18	PeiKang Tsou	A Study of the Reaction Mechanism of Wittig Rearrangements by *Ab Initio* Computations

P19	Amol Deshmukh	Tetrahedral Silsesquioxane Framework: A Feasible Candidate for Hydrogen Storage
P20	Wen-Cheng Liu	Temporary Anion States of Aza-Derivatives of Furan, Pyrrole, and Thiophene

17:10-17:30 Closing (Awards) Ceremony （Chair：Hsiao-Ching Yang）

The Anisotropy in Charge Mobility of Rubrene

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An analytic form of mobility was developed to account for the anisotropic mobility observed in molecular crystals. We formulate the mobility in terms of the diffusion coefficient through the Einstein's relationship. Based on the fluctuation-dissipation theorem[1], the diffusion is related to the friction coefficient, and the latter is expressed in terms of force-force correlation function. We propose to evaluate the correlation function with polarons that are coupled with local and non-local phonons, which was obtained with a Merrifield transformation[2], and the result was expressed for an orthorhombic crystal such as rubrene. In the theoretical development, it is assumed that the scattering of thermal fluctuation is mainly through optical phonons, and scattering is originated from the inelastic interaction between the polaron and phonons.

With numerical calculation, we found that the anisotropy of mobility calculated is close to experimental observations. In our theoretical model, the anisotropy in mobility is mainly from the anisotropic effective mass of the polarons, which is determined by the energy band structure, or the electron-electron coupling and the crystal structure. Moreover, we show that the temperature dependence of mobility follows the power law observed, $\propto T^{-1.91}$ (140 - 230 K),[3] which mainly is determined by the inelastic scattering of acoustic phonons.

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Density Functional Theory Calculation on the NO Dissociation and Conversion to N_2O Mechanism Catalyzed by Cu_4 cluster in ZSM-5 (Cu_4-ZSM-5) and Bimetal Cu_3Fe in ZSM-5 (Cu_3Fe-ZSM-5)

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Zeolite-based catalysts have been investigated as a well-known catalyst in a selectively catalytic reduction (SCR) in the conversion of NO molecule. First we simulated the formation and adsorption of pure metal Cu_4 and bimetal Cu_3Fe clusters in ZSM-5 (Si/Al ratio = 95). By using ab-initio molecular dynamic simulation, both Cu_4 and Cu_3Fe clusters would form from metal atoms in the framework of ZSM-5 at 550K, in good agreements with experimental observation [1]. In addition, the calculated results by periodic DFT calculations demonstrate that the most stable structures of both Cu_4 and Cu_3Fe clusters in ZSM-5 are both T_d configuration. Second, the calculated N—O bond length would be elongated from 1.15Å to 1.25 ~ 1.30 Å in the adsorption of NO on metal-cluster stabilized zeolites (both Cu_4-ZSM-5 and Cu_3Fe-ZSM-5), being longer than the counterparts on single-atom-metal anchored zeolites. Furthermore, the calculated N—O bond cleavage barrier on Cu_3Fe-ZSM-5 was lower than its counterparts on Cu_4-ZSM-5, indicating that the Cu_3Fe-ZSM-5 might enhance the conversion of NO molecule. In the mechanism of NO conversion reaction, the co-adsorption of two NO molecules on Cu_3Fe-ZSM-5 was carried out and subsequently produce N_2O molecule. Incidentally, to understand the electronic properties, we performed the calculation of Bader charge analysis and local densities of states, and the result was explicable.

References

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Methane activation on Ir-doped TiO_2 (110) and IrO_2/TiO_2 (110) surfaces- a density functional theory study

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The long-term anticipated decline of oil combined with the emergence of advanced technology for shale gas extraction make methane is considered as great potential alternative hydrocarbon feedstock for chemical industry. Accordingly, the chemical conversion of methane to value-added chemical products would be enormous beneficial. For this purpose, it is necessary to search for a catalyst that can activate methane at mild temperature. In this work, theoretical calculations were performed to explore such characteristics of Ir-doped TiO_2 (110) and IrO_2/TiO_2 (110) surfaces. The result shows that the binding energy of a CH_4 molecule with the Ir-doped TiO_2 (110) surface is 0.81 eV which is higher than that with IrO_2 (110) surface. On the Ir-doped TiO_2 (110), the first C-H bond breaking is relatively easy with a kinetic barrier of 0.54 eV and exothermicity of 0.78 eV. Binding energy of CH_4 with the IrO_2/TiO_2 (110) is 0.85 eV. The first C-H bond breaking reaction the IrO_2/TiO_2 (110) needs to overcome a kinetic barrier of 0.58 eV, and the reaction is exothermic by 0.92 eV. On the both surfaces, the first C-H bond breaking preferred by molecular-mediated mechanism since the kinetic barriers are significantly smaller than methane desorption energy. The calculated results indicate that Ir-doped TiO_2 (110) and IrO_2/TiO_2 (110) surfaces possess the same capability with IrO_2 (110) surface in methane activation.

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A theoretical study of the structures and photoelectron spectra of $C_2(C_{60})_2$ and $C_2H_2(C_{60})_2$

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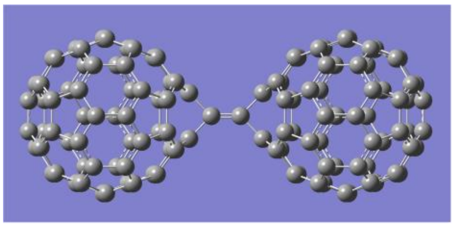
The equilibrium structures and harmonic vibrational frequencies of the molecule, cation and anion of end-bonded (**1**) and side-bonded (**2**) $C_2(C_{60})_2$, together with *cis*- (**3**) and *trans*-$C_2H_2(C_{60})_2$ (**4**), were computed by the density functional theory (B3LYP) associated with the 3-21G and 6-31G(d) basis sets. The photoelectron spectra were simulated by computing Franck-Condon factors with the approach developed by our group [1], in which the model of harmonic oscillator including the Duschinsky effect was adopted. It was found that *trans*-$C_2H_2(C_{60})_2$ belongs to the C_{2h} point group, whereas the other molecules studied belong to the C_{2v} point group. Each molecule has a distinct pattern in its photoelectron spectrum. The adiabatic ionization energies and adiabatic electron affinities are also obtained. The theoretical prediction of the photoelectron spectra and ionization energies of these molecules serves as a reference for future experimental identification of the species.



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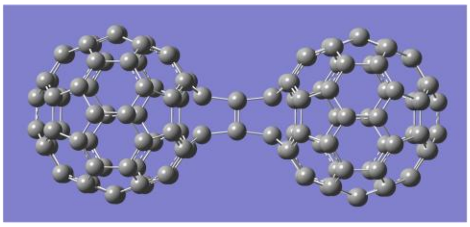

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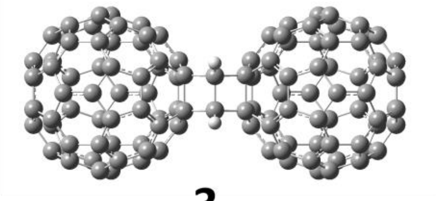

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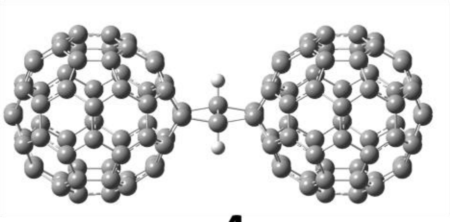

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Reference

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Zhang–Zhang Polynomials as a Novel Local Aromaticity Index for Benzenoid Hydrocarbons

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We present a new local aromaticity index, Zhang–Zhang Index (ZZI), for benzenoid hydrocarbons (polycyclic aromatic hydrocarbons, PAH) based on their Zhang–Zhang polynomials. The Zhang–Zhang (ZZ) polynomial, *aka* Clar covering polynomial, is a combinatorial tool that brings the concept of Clar sextets and Kekulé structures into a mathematical polynomial[1]. The Zhang–Zhang polynomial $ZZ(S,x)$ of a benzenoid system S is defined as

$$ZZ(S,x) = \sum_{i=0}^{Cl} C_i x^i,$$

where Cl is the Clar number of a given benzenoid S and C_i is the number of conceivable Clar covers of order i. A Clar cover of order i contains exactly i aromatic sextets. We have developed an efficient algorithm and a computer code, named **ZZCaluclator**[2], which is capable of computing the ZZ polynomials of peri-condensed benzenoid systems with 500 atoms easily and more than 100,000 atoms for cata-condensed benzenoid systems. The Zhang–Zhang Index of any hexagonal ring h in the benzenoid system S is defined as

$$ZZI(S,h) = \frac{ZZ(S-h,1)}{ZZ(S,1)},$$

where $S-h$ is the substructure removing all six atoms of the ring h from S. Numerical benchmark of ZZI for many benzenoid systems shows similar results to other *ab initio* local aromaticity indexes, such as NICS, HOMA, and PDI. However, those *ab initio* indexes require large amount of computational time, whereas ZZI can be computed in seconds. With a new feature on the previously developed Zhang–Zhang polynomial graphical toolkit (**ZZDecomposer**)[3], computing local aromaticity index of benzenoid systems has been made intuitive and fast.

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Constructing Homogeneous Solutions of Kinetic Energy Operator in Schrödinger Equation of Helium Atom

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Finding the exact, analytic wave function for a helium atom is one of the unsolved fundamental problems in quantum mechanics. This system serves as a model for understanding electron correlations. Equipped with the knowledge of the exact form of correlation between two electrons, one can go further and develop the compact expressions for multi-electron systems, and ultimately construct a new theory of quantum chemistry based on such explicitly correlated wave function ansätze.

The Schrödinger equation of a helium atom can be transformed as a set of inhomogeneous linear PDEs of the kinetic energy operator. Finding the full set of homogeneous solution of an operator is very important in solving the corresponding inhomogeneous PDE. In this work, we write the homogeneous solution as a power series of a selected coordinate system with unknown coefficients. The recurrence relations can be obtained from the substitution of the power series into the homogeneous equation. By solving the recurrence relations, we would obtain the homogeneous solutions.

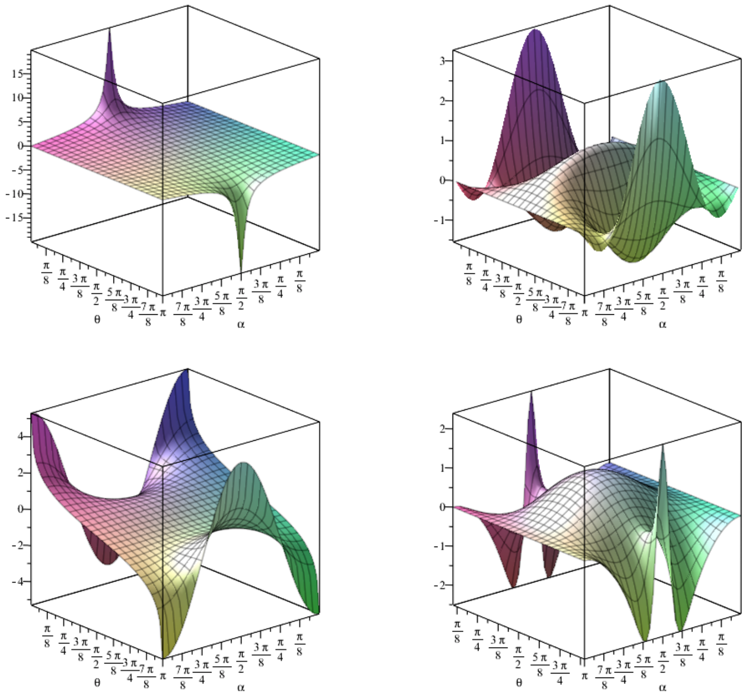

Figure 1: Selected homogeneous solutions of the kinetic energy operator.

The Allosteric Effects of CRIPT Peptide upon Binding to PSD-95 PDZ3

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The study of allostery has become a major focal point over the past decade; protein allostery offers the potential of designing new drugs that affect catalysis indirectly. The third domain of PSD-95/Discs Large/ZO-1 domain (PDZ3, Figure 1) has been extensively studied both experimentally and computationally. Some of the more recent studies have shown that PDZ3 exhibits allostery when binding to other proteins like the CRIPT peptide. From a computational standpoint, Monte Carlo simulations[1], elastic network models (ENMs)[2], and statistical coupling analysis (SCA)[3] have been used to determine potential allosteric pathways. Silvestre-Ryan et al.[4] developed fluctuation matching as an alternative to map potential allosteric pathways using a two-site ENM on subtilisin Carlsberg. In this work, we extend their work by using a three-site ENM (Figure 2) for fluctuation matching to enhance the resolution for finding potential allosteric pathways within PDZ3 and compare our results with previous work.

Figure 1 PDZ3 complexed with CRIPT peptide

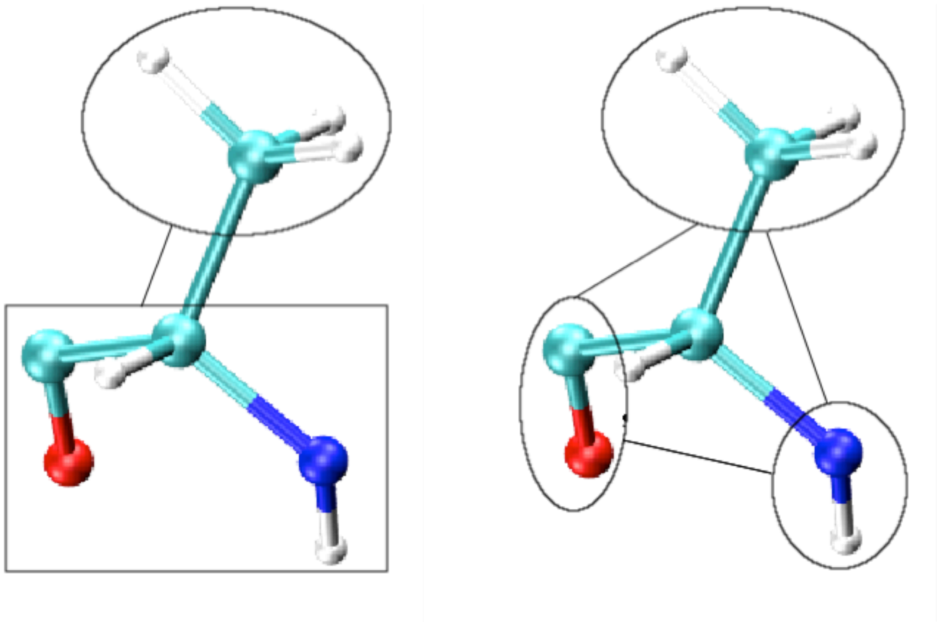

Figure 2 2-site (left) and 3-site (right) representations of the coarse-grain models

References

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Coupling of Intermolecular Proton Bond (IPB) Stretch with C-O stretch in Zundel Dimers of $(MeOH)_2H^+$ and $(Me_2O)_2H^+$

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The strong doublet at 1000 cm^{-1} in the predissociation spectrum of Ne•••$H_5O_2^+$ had captured the attention of several spectroscopist [1]. At the vicinity of the said frequency, the intermolecular proton bond stretch is expected to be found. Such vibrational signature became an enigma since intuitively one expects to observe a strong single peak instead of two. Simulations to unravel the identity of the doublet were found to be difficult that it took a full 15-dimensional calculation by Meyer and coworkers to understand its origin [1-2]. To date with, it is established that the coupling between the IPB stretch and the combination band due to water wagging and O-O stretch is responsible for the said signature. Alcohols and ethers are expected to exhibit C-O stretches at 970-1250 cm^{-1} window, opening the possibility of coupling with IPB stretch. Such speculation is further intensified by three intense peaks observed [2] at the spectra of Ar•••$(MeOH)_2H^+$ and Ar•••$(Me_2O)_2H^+$. In this study, we investigate the coupling of C-O stretches with IPB stretch and how such intermode interaction manifests in the overall spectrum. Ab initio methods at the level of MP2 and CCSD(T) (if possible) were used to minimized and calculate the vibrational normal modes. The potential and dipole surfaces are constructed by scanning along a few key normal modes. The reduced dimensional vibrational Schrödinger equation was numerically solved by a pseudospectral method: Discrete Variable Representation (DVR) [3]. It was found out that compare with the peak positions, the intensities are more sensitive with the basis set used. For the case of $(MeOH)_2H^+$ it was found out that O-O stretch (ν_1), out of phase C-O stretch (ν_3) and CH_3 twist (ν_4) couples with IPB stretch (ν_2). While for $(Me_2O)_2H^+$, the in phase C-O-C bend and out of phase symmetric C-O stretch interacts with IPB stretch.

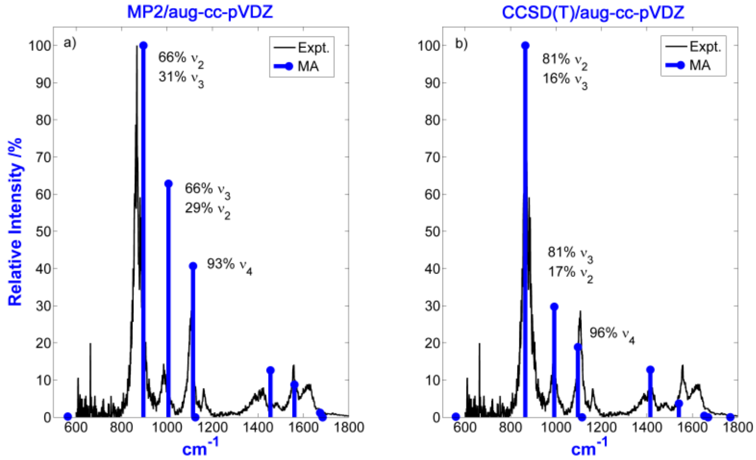

Figure 1: Four dimensional DVR calculation for $(MeOH)_2H^+$. a) MP2/aug-cc-pVDZ and b) CCSD(T)/aug-cc-pVDZ. In both figures, the blue dots refer to the transition of the first few vibrational states relative to the ground vibrational state.

References

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A Theoretical Investigation on the Mechanism and Application of Quantum Interference Effect in Single Molecule Electron Transport

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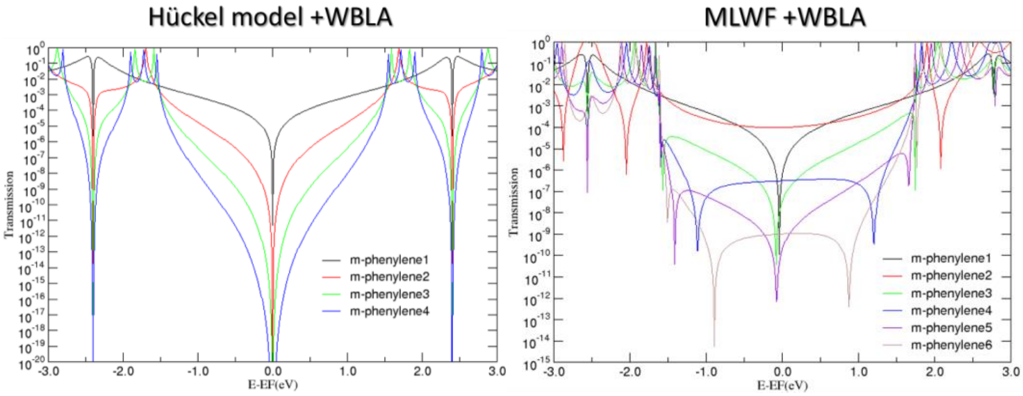
As the size of the integrated circuits (IC) gets smaller, single-molecule electron transport becomes an important issue. Electron transport in single molecules is often accompanied and strongly influenced by quantum interference effect (QIE) [1]. Here we investigate QIE in single -molecule electron transport in the hope that this effect can be utilized to design different electric device component. Previous literatures have reported successful synthesis of a molecular turnstile based on the phenyl-acetylene macrocycle (PAM) architecture [2], which consists of a central rotor and an outer stator. The rotor, with electron donating and electron withdrawing substituents, can be rotated by an external electric field. The conductance through this molecule varies with different rotating angles. We observe a sudden transmission drop at some particular rotating angles, seemingly from the destructive QIE. The variations of the molecular orbital distribution and energy with rotation for this system are investigated in detail. Inspired by a recently reported single-molecule electric revolving door device (SMERD) [3], we propose an improved version for this device (2G-SMERD) which has a large on-off conductance ratio ($>10^4$) and that their open and closed states can be operated by a smaller external electric field (1.0-1.5V/nm) [4]. We notice in the above case studies that the destructive QIE may take a completely different characteristic transmission lineshape in different molecular systems [5]. We examine the odd-even symmetry effect in the destructive QIE phenomenon.



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Substituent effect toward the temperature dependence of R1R2COO + Water reaction

Liang-Chun Lin(林亮君)[1,2] ,Kaito Takahashi[2](高橋開人),Jim Jr-Min Lin[1,2](林志民)
[1] Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan
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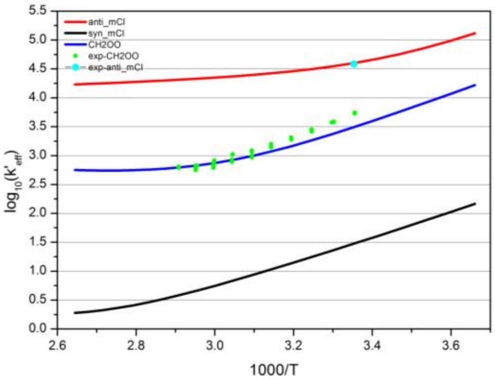
Atmospherically relevant R_1R_2COO, so-called Criegee intermediates(CIs) are the key intermediates in the ozonolysis of different kinds of alkenes. Alkenes are released to the troposphere in very large amount from biogenic and anthropogenic sources. CIs reactions with atmospheric abundant water vapours is considered to be a very important issue in atmospheric chemistry research. To model these processes, we consider CIs + H_2O and CIs + $(H_2O)_2$, ignoring CIs' reactions with bigger H_2O clusters. Considering temperature variance with altitude in atmosphere, temperature dependence of CI+water vapour reaction rate is important. However, temperature dependent rate was only measured recently for CH_2OO and there is no result for other substituted species. Therefore, in the present study we perform theoretical simulation on CH_2OO and CH_3CHOO (methyl CI) to quantify the temperature dependence of the rate constant.

We calculated temperature dependent rate constants on CH_2OO, anti-methyl CI, and syn-methyl CI reaction with $(H_2O)_{n,n=1,2}$. we utilized harmonic approximation, anharmonic correction, and anharmonic plus hindered rotor correction to simulate rate constants with the Multiwell program suite . The geometries, harmonic frequencies, and anharmonic correction coefficients for stationary points were calculated by B3LYP/6-311+G(2d,2p). In addition, the relative energies were modified by the complete basis set extrapolation using the QCISD(T) method.

In the following figure, we present our best estimate of the rate constants for CH_2OO, CH_3CHOO as well as the available experimental data. From the similarity between the experiment(green dot) and theory(blue line) we are confident that our protocol can accurately simulate CIs + water vapour reaction. Indeed the saturation of the negative temperature dependence of the CH_2OO +water reaction seen at higher temperatures($1000/T < 3$) is clearly reproduced in theory. From our theoretical simulation, we found that this is due to the difference in temperature dependence in the rate between the $CH_2OO + H_2O$ and $CH_2OO + (H_2O)_2$ reactions.



Now comparing the results for methyl-CI with CH_2OO. We notice that anti-mCI is more reactive than CH_2OO while syn-mCI is much slower. Furthermore, the temperature dependence of the rate is very different. For anti-methyl CI, rate constant difference between 273.15 K and 378.15 K is nearly 8 times. While for CH_2OO, the difference is approximately 30 times. The major reason is that anti-methyl Criegee is more reactive to water monomer than simplest Criegee and this compensates the negative temperature dependent behavior of wate dimer with CIs reaction.

Probing Water Microsolvation Dynamics of Proteins toward Photochemical Application

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Probing the water environment of a specifically interesting site in proteins thus may pave a way to understanding the underlying mechanism. Unfortunately, although enormous efforts have been made in the characterization of fundamental aqueous hydration phenomena on protein surfaces, little insight has been gained into water micro-solvation in protein. The newly-developed tryptophan analogue, (2,7-aza)Trp exhibits remarkable water catalyzed proton transfer properties. The resulting multiple emissions provide unique fingerprints that can be exploited for directly sensing a site-specific water environment in a protein. Here we selected thromboxane A_2 synthase (TXAS), an membrane protein containing five tryptophans, as a prototype to demonstrate the feasibility of (2,7-aza)Trp in probing water environments. The incorporation of (2,7-aza)Trp into TXAS proves (2,7-aza)Trp to be a novel optical probe that allows transmission of its surrounding water environment into unique fluorescence spectral features. With molecular dynamics (MD) simulation, we showing different hydration environments between the substrate access channel, water channel, and protein surface in TXAS. The superb water sensing capability in terms of N_1-H/N_2-H equilibrium thus provides an unprecedented tool for probing the water environment in bio-systems on a structural basis. In addition, we also probe the water environment near the connecting loop region of ribonuclease Tl (RNase T1). The resulting (2,7-aza)Trp59 triple emission bands and dynamics with MD simulation, lead us to propose two Trp59 containing conformers in RNase T1, namely, the loop-close and loop-open forms. Water is rich in the loop-open form around the proximity of (2,7-aza)Trp59, giving both N(1)-H and N(7)-H isomer emissions. Existence of N(2)-H isomer in the loop-open form, is mainly due to the specific hydrogen bonding between N(2)-H proton and water molecule that bridges N(2)-H and the amide oxygen of Pro60, forming a strong network. This points out that the Trp-water pairs appear to preferentially participate in a hydrogen bond network incorporating polar amino acid moieties on the protein surface and bulk waters.

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Selectivity Study of Pd(111), PdAu(111) and PdHg(111) Catalysts for H_2O_2 Direct Forming: A Theoretical View

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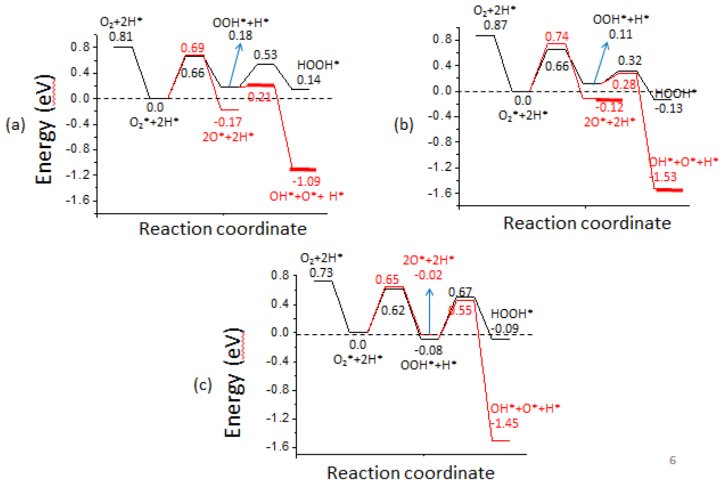
The exploration of green synthesis of H_2O_2 can be done by choosing direct catalyst which is abundant, high selectivity and non-toxic. The well-known catalyst in this area is the alloy of PdAu which has selectivity reach to 95%[1]. Since price of Au material is expensive, the alternative material need to be found. Some researcher[2] showed that the alloy of PdHg could perform more active catalytic reaction for H_2O_2 direct synthesis compare to that of PdAu alloy. However, the Hg has serious problem related to its poison characteristic for human and environment. The reported experimental performance of H_2O_2 direct synthesis catalysts lead to the question of how the mechanism of H_2O_2 forming using PdAu and PdHg. Although it has been known that there are reactions competition in H_2O_2 direct synthesis, i.e O_2 decomposition and OOH forming but the comparison between both reactions need to be explored more detail to support the experimental result.

To compare the surface species forming and their dissociation, we use a DFT approach. The study were conducted on three catalysts i.e. Pd(111), PdAu(111) and PdHg(111) with respect to the energy barrier of O_2 dissociation and OOH formation. The energy barrier can be used as a descriptor to select the best catalyst. The minimum energy path and the energy barrier were calculated using the climbing-image nudge elastic band (CI-NEB) approach.

The result showed that the energy barrier difference between O_2 dissociation and OOH forming is highest on PdAu(111), followed by that on PdHg(111) and Pd(111). The higher difference means the higher selectivity toward main product. At this case, although the PdHg has been reported to have highest catalytic activity but the best selectivity was showed by PdAu(111).



Potential energy surface on (a) Pd(111), (b) PdAu(111) and (c) PdHg(111)

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Parameterization of DFTB3 for Water Clusters by using an Automatic DFTB Parameterization Toolkit (ADPT)

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Automatic Density-Functional Tight-Binding parameterization toolkit (ADPT) is a recently proposed automatic program for optimizing parameter of Density-Functional Tight-Binding (DFTB) method[1]. ADPT is a bundle of tools, which creating the DFTB parameterization with the least manual effort. The main optimization tool implements the particle swarm optimization algorithm[2] to find the optimal values of DFTB parameters.

In this work, we develop a new set of H and O parameter to describe water clusters system. DFT B3LYP functional with cc-pVTZ basis set was selected as the reference *ab initio* level of theory and several database from literature for this parameterization. Preliminary, this parameter can produce the correct internal rotation energy curve of H_2O_2, and also the basic chemical properties of H_2, O_2, and H_2O molecules. We expect the parameter able to reproduce geometries, reaction energies, and hydrogen bonding interactions of water clusters with high accuracy in comparison with the reference data.

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Combined Experimental and Computational Studies of $Na_2A_xB_yFe(CN)_6$ for Aqueous Sodium-Ion Batteries

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With the increasing demand for renewable energy sources, large-scale energy storage system (EES) for grid application serves as an essential component because it is able to stabilize intermittent renewable energy, balance electricity generation and requirement between day-time and night-time, *etc*. Among those existing electrochemical energy storage technologies, aqueous rechargeable sodium-ion batteries (ARSB) have recently attracted considerable attention due to their safety, environmentally benign and low cost. Recently, sodium-rich metal hexacyanoferrate (II) ($Na_xM_yFe(CN)_6$, M=transitional metal) compounds with three-dimensional frameworks and large interstitial spaces were demonstrated as potential cathode materials toward ARSB applications. Herein, the combined experimental and computational studies were conducted to explore the influence of x/y ratio on their sodium storage capabilities of $Na_2A_xB_yFe(CN)_6$ synthesized by a facile wet-chemistry approach. It was found that the $Na_2A_1B_1Fe(CN)_6$ exhibited superior cycling stability (capacity retention: 75% after 200 cycles) than that of the $Na_2B_1Fe(CN)_6$ (capacity retention: 68% after 150 cycles) at 2C. From Density-Functional-Theory (DFT) calculation and Bader charge analysis, it revealed that their charge differences of A and B in the $Na_2A_1B_1Fe(CN)_6$ were higher than that of $Na_2A_1Fe(CN)_6$ and $Na_2B_1Fe(CN)_6$. It implied that the charges transferred from A and B to N atoms were easily occurred, resulting in the highly stability of C＝N bonding at fragment of －Fe－C＝N－. Consequently, the electronic effect acted as one of the critical factors to alter its cycling stability of $Na_2A_xB_yFe(CN)_6$ for ARSB.

KEYWORDS
Sodium-ion battery, Wet-chemistry approach, Density Function Theory (DFT)

ACKNOWLEDGMENT
We thank the NCHC and NTUST for their generous provision of computing time. We gratefully acknowledge financial support from the Bureau of Energy (BOE), Ministry of Economy Affair (MOEA), Taiwan.

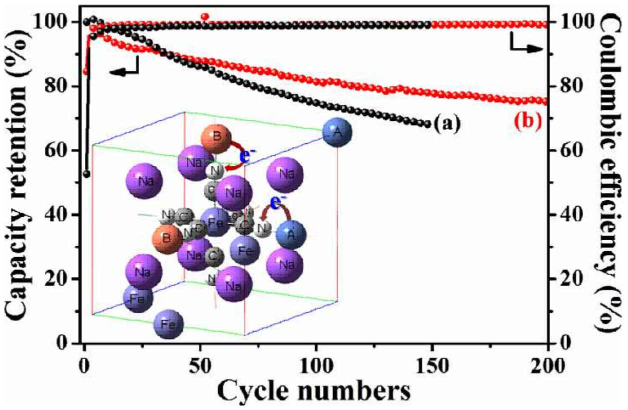

Figure 1 Discharge capacity retention and coulombic efficiency of (a) $Na_2B_1Fe(CN)_6$ and (b) $Na_2A_1B_1Fe(CN)_6$ measured at 2C. Inset illustrated its DFT model and charge transferring process of $Na_2A_1B_1Fe(CN)_6$.

Molecular Modeling Studies of the SAGA Deubiquitinating Module Structural and Functional Variance Caused by Sgf73/Y57A

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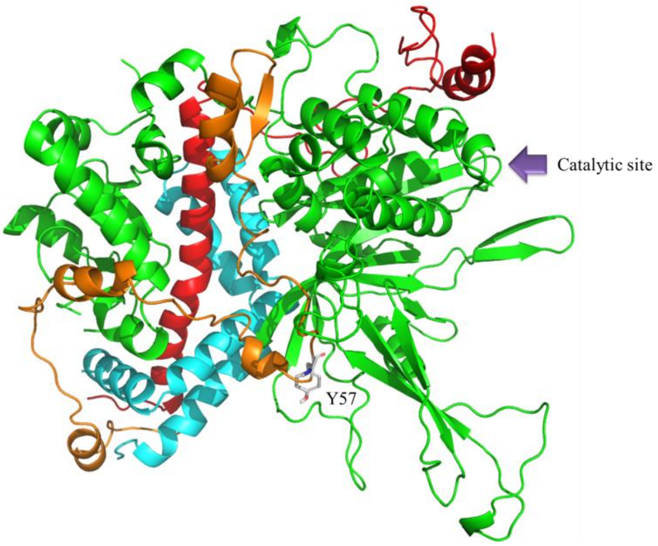
The SAGA (Spt-Ada-Gcn5-Acetyltransferase) complex, composed of 21 proteins, is a 1.8 MDa transcriptional coactivator with many functions. One function is to deubiquitinate histone H2B and this role is played by a module made of the ubiquitin-specific protease Ubp8, bound to Sgf11, Sus1, and Sgf73. Lately, it has been reported that a portion of the non-globular Sgf73 subunit which links the Ubp8 catalytic domain and the ZnF-UBP domain maintains the catalytic structural stability and activity. Moreover, biomolecular experiment suggested that mutations on Sgf73 introduce vulnerability of the whole module. In this study, we applied MD (molecular dynamics) simulations on WT and Y57A at two temperatures, 298 and 303 K, to investigate the structural instability caused by Y57A. Further test using PCA (principal component analysis) indicated the breathing motion on the catalytic site is varied, especially in the Y57A at 303 K. Our preliminary structural evaluation to correlate the Y57A, which is remote to the catalytic site, to the loss of deubiquitination function showed the lack of a hydrogen bond formed between Y57 and N403 on Ubp8 causes dynamic discrepancy onto the open/close motion of the entrance of the catalytic pocket.



SAGA deubiquitinating module made of Ubp8 (green), Sus1 (blue), Sgf11 (red), and Sgf73 (orange).

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Study of Poly (3, 4-ethylenedioxythiophene)/MnO_2 as Composite Cathode Materials for Aluminum-Air Battery: DFT Simulation Studies

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This study focused on the development of the composite electrode materials for an aluminum-air battery and improving the oxygen reduction reaction (ORR) of the air electrode by matching alpha- and beta- manganese dioxide (MnO_2) with poly-(3,4-ethylenedioxythiophene) (PEDOT) conducting polymer. The catalysts of α-MnO_2 and β-MnO_2 were prepared by hydrothermal method with different precursors, while PEDOT conducting polymer was subsequently deposited on the screen-printed electrodes (MnO_2/carbon paper) by oxidative chemical vapor deposition (oCVD). Material characteristics of prepared MnO_2 powder and PEDOT layer were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM) and Raman scattering spectroscopy. The half-cell polarization curve test is found to be strongly depended on the crystalline phases of MnO_2. From experimental observations and a density functional theory (DFT) study, the conductivity of PEDOT/α-MnO_2 was found to be higher than PEDOT/β-MnO_2 contributed to structural effect mediated improvements in charge transfer. As a result, integrating the deposition of PEDOT on MnO_2/carbon paper as composite cathode was suitable for the use in aluminum-air battery.

KEYWORDS
Manganese Dioxide (MnO_2); Poly(3,4-ethylenedioxythiophene) (PEDOT); Oxidative Chemical Vapor Deposition (oCVD); Aluminum-Air Battery; Density Functional Theory (DFT)

ACKNOWLEDGMENT
We thank both NCHC and NTUST for their generous provision of computing time. Financial support from the Ministry of Science and Technology No. MOST 103-2221-E-011-041 is also gratefully acknowledged.

Catalytic Oxidation of CO over CeO_2 and $CeGd_{0.1}O_2$ Nanoparticles: DFT Simulation Studies

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Gd-containing CeO_2 oxidation catalysts find wide application, due to their excellent redox properties; however, they are frequently partially deactivated by carbon monoxide (CO) poisoning. In this work $CeGd_{0.1}O_2$ nanoparticles (NPs) were synthesized using an atmospheric pressure plasma jet (APPJ) and their catalytic performance with respect to CO poisoning was studied. Additionally, the $CeGd_{0.1}O_2$ NPs were characterized by X-ray diffraction (XRD), scanning electron miscroscopy (SEM), transimission electron microscopy (TEM), temperature gravity analysis (TGA) and HAADF and Mapping. The XRD results showed that the high crystallinity of the $CeGdO_2$ NPs was similar to that of CeO_2. TEM showed that the $CeGdO_2$ NPs were well dispersed. The Gd doped into CeO_2 lattice was considered as main reason for the high catalytic activity of the $CeGd_{0.1}O_2$ NPs. A periodic density-functional theory (DFT) study was used to investigate the adsorption and oxidation reactions of CO on CeO_2(111) and $CeGd_{0.1}O_2$(111) surfaces.

KEYWORDS
Atmospheric pressure plasma jet (APPJ); DFT; CeO_2; $CeGd_{0.1}O_2$

ACKNOWLEDGMENT
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On the Structure Variation of DNA-RNA Hybrid in the Ago Protein

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RNA-induced silencing complex(RISC) plays a crucial role in RNA-interference(RNAi) which relates to transcriptional and post-transcriptional gene regulation in animals and plants. One of the proteins in RISC, Ago, is responsible for mediating distinct assembly and cleavage steps of RNAi catalytic cycle. The ligand of Ago protein is a DNA-RNA hybrid duplex. Previous studies[1] indicate that the dominant form of Ago's DNA-RNA hybrid resembles A-form. To investigate the relationship between the duplex structure and its specific sequence, we performed molecular dynamics simulation using the CHARMM36 force field. The initial model of the duplex was extracted from the X-ray structures of Thermus thermophilus Ago bound with the duplex ligand. We also employed the canonical structure of A and B forms of DNA to model the structures of the DNA-DNA and DNA-RNA strands recognized by ago in comparison with the results started from the structures extracted from X-ray. The backbone dihedral angles and properties relating to complementary base pairs calculated from all-atom MD simulations indicate that the RNA target strand has profound effects on the duplex structure. Moreover, the information about major groove and minor groove demonstrates that the DNA-RNA hybrid duplex deviates from original structure that is similar to A-form.

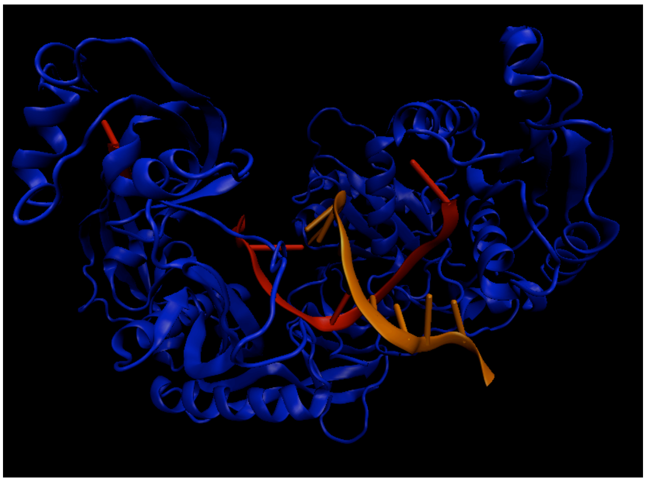

Figure 1: 3F73.pdb from Wang. et al. 2008. The Ago(blue) protein bound with the DNA strand(red) and the RNA strand(orange).

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Density-functional Calculations of Alkane Conversion on Platinum Decorated Graphene Oxide Sheets

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Graphene oxide (GO) is an attractive option for a suitable support regarding the dispersion of Pt particles and an improved control of size, because of the active oxygen atoms on the sheet. On the GO ($C_{48}O_{16}$) sheet (Pt/GO), we used two Pt atoms to match the mass of composition of Pt (about 32 %), within a range of experimental observations in a common Pt/GO hybrid synthesis. By means of calculations based on density-functional theory (DFT), we have investigated the conversion of methane on two platinum atoms supported with a graphene-oxide sheet (Pt_2/GO). In our calculations, alkane molecules including CH_4, C_2H_6, and C_3H_8 can be adsorbed around the Pt atoms of the Pt_2/GO sheet with adsorption energies of −0.51, −0.55 and −0.58 eV, respectively; all elongated C−H bonds in these molecules indicated that Pt atoms on that sheet can activate the C-H bond of alkane. The role of the GO sheet in the activation of C−H bond was clarified according to an analysis of the electronic density: the GO sheet induces the d-band of Pt atoms to generate several specific $d_z{}^2$ state features above the Fermi level, which enabled activation of the C-H bond on generating an evident area of overlap with the hydrogen s orbital of the C-H bond beneath the Fermi level. Upon a dioxygen molecule being added onto the Pt_2/GO sheet, this molecule can react with activated methane to form the methanol, but when ethane and butane as the reactants they were changed into ethene and butene, respectively, instead.

A Computational Study of Sulfur Transfer in Mercaptopyruvate Sulfurtransferase

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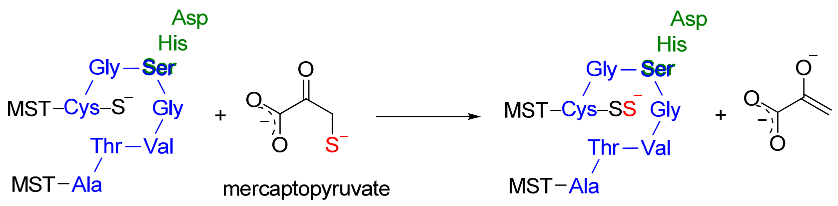
The mechanism of sulfur transfer in mercaptopyruvate sulfurtransferase (MST) is studied using a ONIOM(B3LYP/6-31G*:Amber) methodology. MST transfers a sulfur atom from a mercaptopyruvate substrate to its own cysteine (Cys248) residue, yielding the cysteine persulfide (Cys–SS$^-$).[1] Calculations show that the sulfane sulfur (S^0) transfer is more kinetically favorable than the SH transfer (Fig. 1). The Ser/His/Asp triad can help the deprotonation of the sulfhydryl group in mercaptopyruvate, initializing the sulfane sulfur transfer. In addition, the transferred sulfur atom interacts with the –NH/–OH groups of the loop by electrostatic interactions. The analysis of electrostatic potential and frontier orbitals shows that the specific conformation of the loop structure not only stabilizes the sulfhydryl and persulfide anions but also turns the persulfide anion more electrophilic.

a) Sulfane sulfur transfer



b) SH transfer

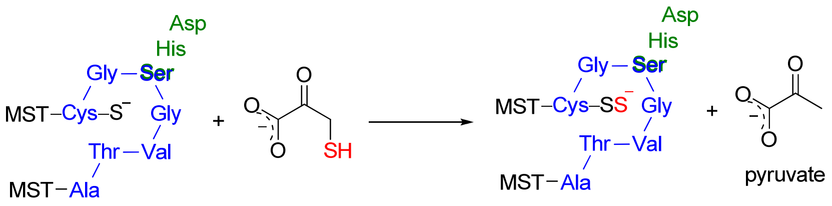


Figure 1. a) Sulfane sulfur transfer and b) SH transfer in MST. The triad is shown in green, and the loop in blue.

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Can entirely negatively charged covalently bound atoms in two different molecules interact attractively? A theoretical (and experimental) prospective

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Intermolecular noncovalent interactions (e.g., hydrogen bond, halogen bond, etc.) are crucial to many research fields, including, for example, chemistry, biology, crystallography, crystal engineering, nanomaterials science and technologies [1]. These are attractive by nature. Because of this, they can assist designing versatile supramolecular compounds for applications in biology, as well as in the development of materials for device applications. Water in its liquid and ice forms, and the specific structural patterns between the Watson-Crick base pairs (e.g., guanine-cytosine and adenine-thymine) that allow the DNA helix to maintain a regular helical structure, etc., are the consequences of the noncovalent interactions. Classically, these interactions are formed when two charged atoms of opposite polarities belonging to two molecules do sustain a long-range contact with each other. A number of features have recently been IUPAC recommended to identify and characterize such interactions in binary or multinary complexes [1]-[2].

It has been endorsed by the scientific community that similarly negatively charged atoms in different molecules (the fluorine atoms in the two perfluoromethane molecules, for example) when discover themselves in the close proximity to each other preclude to form noncovalent interactions [1]-[2]. This was specifically demonstrated for the highly electronegative and nonpolarizable fluorine atom in organofluorine compounds. For instance, it was suggested that the fluorine in these compounds is inefficient to halogen bond [3], even though there were other examples facilitated in the literature that have contradictorily demonstrated the fluorine atom in such compounds has the capability of forming halogen bonds, which is not unexpected when it carries a positive site on it, called σ_{hole} [4]. In this presentation, however, we will demonstrate that the former view on the potential inability of the covalently bound fluorine in molecules is not always true because there are numerous instances, which are yet to be thoroughly exploited, wherein an opposite scenario does exist. In particular, this study is focused to explore the natures of the fluorine atoms in perfluorobenzene (also called hexafluorobenzene), C_6F_6, and their capacities in forming noncovalent interactions. Our results have indicated that these atoms are entirely negative, evidenced by their totally negative electrostatic surface potentials both around and along the outer regions of the C–F bond axes. Even so, they can temper to attract the same fluorine atoms in the other C_6F_6 molecule(s) to form the $F^{-0.61e}\cdots F^{-0.61e}$ intermolecular interactions. The reliability of this unified interaction between the two similarly negatively charged fluorine atoms has only recently been propagandized experimentally using atomic force microscopy (AFM) and scanning tunneling microscopy (STM) techniques [5], as well as in the solid state 40 years ago [6].

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QM/MD Simulations on the Proton Coupled Electron Transfer of Prostaglandin H_2 Isomerization by Prostacyclin Synthase

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Prostacyclin synthases (PGISs) have been classified as cytochromes P450s with function in isomerization of endoperoxide substrate prostaglandin H_2 (PGH_2) to prostaglandin I_2 (PGI_2). However, these enzymes unlike typical P450s, they catalyze the peroxide isomerization without the need for either molecular oxygen or any external electron donors. Despite the postulated mechanism has been developed, how to abstract the proton of C6 and protonation C11 in PGIS catalytic mechanism remains a critical question. This work examines the issue of enzyme catalysis in terms of enzymatic confinement water dynamical concept and development of the substrate recognition mechanism. We describe the detailed structure dynamics and catalysis by means of Quantum Mechanics (QM) and Molecular Dynamics (MD) simulations. We observed that the nitrogen atom of Trp residue forms hydrogen network with two waters, which in turn form H-bonds to N287 with subsequent water molecule connection to the substrate head endoperoxide. Theoretical insights suggest this water bridge structure as a PCET shuttle delivering proton/electron to confer high product fidelity for PGIS catalysis. Furthermore, even if one of the water moved away, supplemental waters in the surrounding will substitute the position to stabilize the hydrogen-bonding network. This study emphasizes that the preorganized enzyme active site with confinement water dynamics can employ relatively fixed dipoles oriented towards transition state stabilization, as well as directing the PCET to the high fidelity PGI_2 isomerization from PGH_2 in the catalytic mechanism.

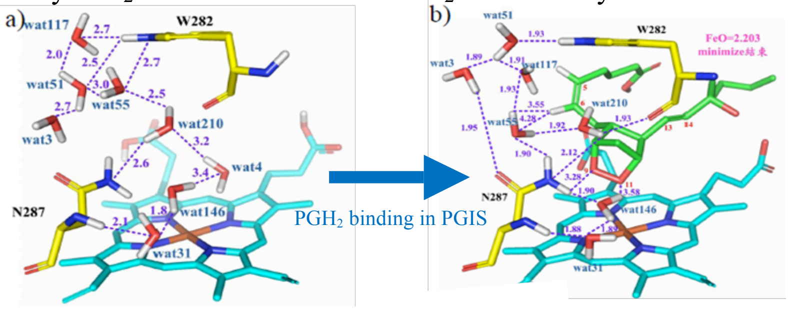

Figure 1 The preorganized enzyme active site with confinement water dynamics providing relatively fixed dipoles oriented towards TS stabilization and directing the PCET of PGI_2 isomerization.

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Allosteric Effects Of Mn^{2+} Ion In Cell Death Related Nuclease (Crn4)

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Cell Death Related Nuclease (CRN4) is a nuclease that plays a key role in apoptosis. In this work, we analyze the structure-property relationship of CRN4 by focusing on the allosteric coupling through the matrix of protein conformation. The basis of our analysis is trajectories of all-atom (Fig. 1) molecular dynamics (MD) simulation with explicit solvent. The coupling between amino acid residues in CRN4 is represented by a coarse grained elastic network model Fig. 2, in which the force constants of harmonic bonds are calculated from the statistics of inter-site distances via an algorithm called fluctuation matching [1]. By transforming consecutive segments of an all-atom trajectory into separate elastic network models, the anharmonicity in the finer grained scale is effectively represented. This analysis is referred to as the fluctuogram of protein dynamics [2]. The effects of Mn^{2+} unbound (apo) and bound (holo) are shown to enable a switch mechanism from inactive to active form of the protein. The inter-residue coupling responsible for the allostery is evidenced from the calculated fluctuogram. The residues playing pivotal role in the switching mechanism extend the vision of developing potential drug candidates targeting the protein.

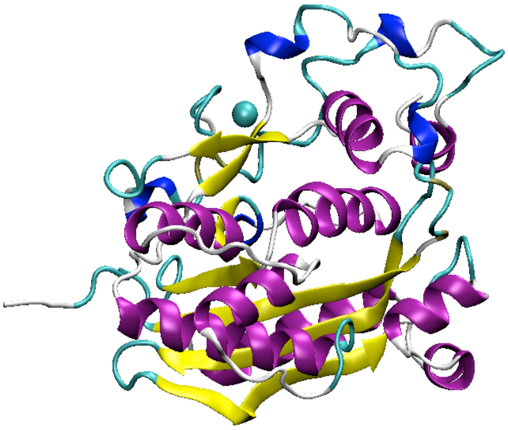

Figure 1: All-atom structure of CRN4

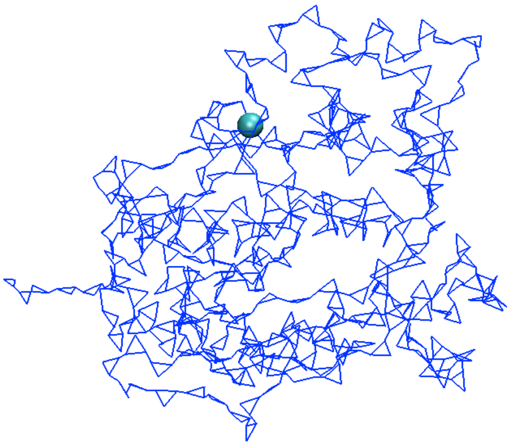

Figure 2: Coarse grained structure of CRN4

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Anomalous Exo Selectivity in Diels–Alder Reactions: A Computational Study

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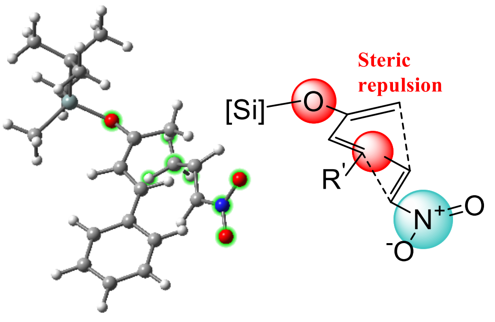
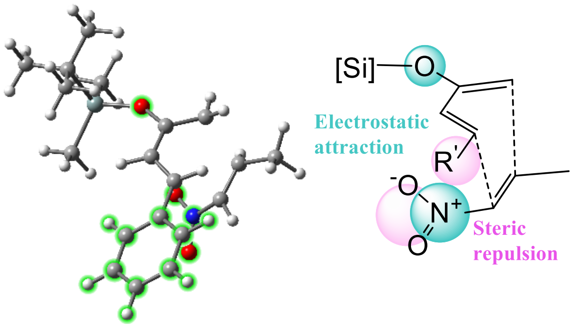
The Diels-Alder reaction is a powerful tool for the construction of six-membered rings with high regio- and stereo-selectivities. The *endo* selectivity (Alder's rule) has been widely recognized in the reactions of an electron-rich diene and an electrondeficient dienophile. However, *exo* selective Diels-Alder reactions in special cases have been investigated and reported. [1] The Diels-Alder reactions of a series of silyloxydienes and silylated dienes with acyclic α,β-unsaturated ketones and *N*-acyloxazolidinones was found the endo/exo stereochemical outcome is strongly influenced by the substitution pattern of the reactants. [2] We investigate theoretically the endo and exo reaction pathways for the Diels-Alder cycloadditions between various dienes and dienophiles with different electron withdrawing groups. While previous study predicted exo selectivity only in the case when both termini of the diene and the dienophile involved in the shorter of the forming bonds were substituted simultaneously, exceptions are found both computationally and experimentally. In this study, we investigate in detail the substitutional group effect on the stereoselectivity of Diels-Alder reactions, and propose a mechanism for the anomalous exo selectivity in these special cases.



Exo



Endo

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Investigation of Water Coupled Conformational Dynamics of Thromboxane and Prostacyclin Syntheses by Molecular Dynamics Simulation and Small-Angle X-ray Scattering

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Thromboxane synthase (TXAS) and prostacyclin synthase (PGIS) belongs to the cytochrome P450 (CYP450) family proteins, plays crucial roles in cardiovascular homeostasis. Despite the structural information about TXAS is still limited at present due to the lack of X-ray crystallographic structure, we building hTXAS simulation model with carefully re-examine to combines the SAXS (small-angle X-ray scattering) results, getting more structural information, such as the size and shape of the protein dynamic structure, the size of active site and the substrate access channel of hPGIS and hTXAS. According to the preliminary results, we have successfully investigated the water-coupled dynamic structures for the membrane proteins (i.e. prostacyclin synthase) and its counter protein (i.e. thromboxane synthase), by the approaches of molecular dynamics simulations and SAXS data analyses. It is of great importance to characterize the size and shape of the active sites as well as the water-assistant substrate access channels formed inside of the proteins in liquid.

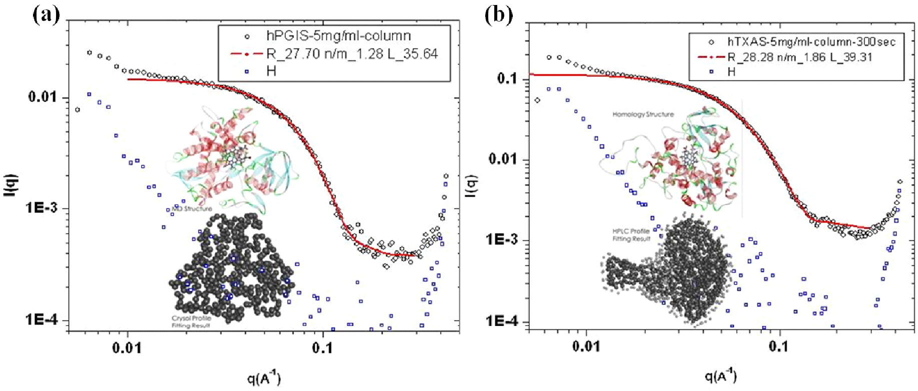

Figure. SAXS profiles and the fits of experimental data by the form factor of elliptical cylinder of the well dissolved (a) hPGIS and (b) hTXAS protein molecules. The 3D reconstructed structures obtained via the Monte Carlo simulation (represented by colored riboons) and the simulated structures based on the SAXS results (represented by black beads) of these two proteins are also given.

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Quantum-Chemical Calculations of Dehydrogenation of Butane to Butene on Rhodium Nanoclusters (Rh_{13}) Supported on Unzipped Graphene Oxide

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The catalytic activity of rhodium nanoclusters (Rh_{13}) on unzipped graphene oxide (Rh_{13}/UGO) has been investigated for comparison with Rh_{13} nanoclusters. We calculated the energies of adsorption of C_4H_{10} on Rh_{13}-L_s/UGO (where the L_s representing low symmetry shape of Rh_{13} nanocluster on unzipped graphene oxide) to have the largest energy, -0.52 eV, with C–H bonds of methyl (-CH_3) and methylene (-CH_2) being elongated from 1.098 to 1.140 Å and 1.104 to 1.145Å, respectively. Our proposed reaction path for the dehydrogenation of butane to butene on Rh_{13}-L_s/UGO, has the first barrier of 0.08 eV for dissociating the C-H bond of methyl group to form butyl (-C_4H_9), and the subsequent C-H bond scission on the 2nd degree carbon of methylene group to form 1-butene has an barrier of 0.14 eV. From our partial charge analysis, we found that UGO could tie up the bottom part of the Rh cluster to enable effective docking of the metal cluster on the UGO and to activate the metal atoms in the upper layer which exhibited greater activity towards the adsorption and dissociation of unreactive gaseous molecules such as buatne.

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Adsorption and Dissociation of H_2O Molecule on α-Al_2O_3(0001) Surface: A Computational Study

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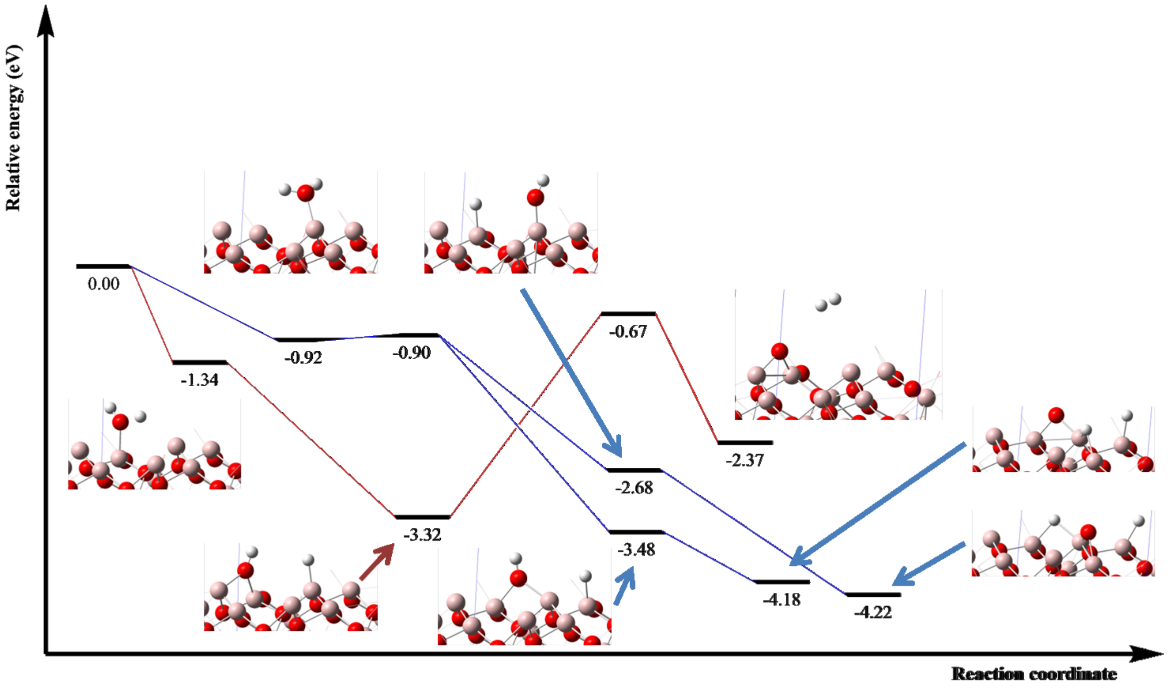
The microscopic reaction mechanism for the water adsorption/dissociation processes on the α-Al_2O_3(0001) surface was calculated using density functional theory with the all-electron triple numerical polarized basis sets. Both unit-cell and 2 × 2 supercell slab models were employed to investigate the coverage-dependent hydroxylation of the surface. Geometries of the molecular adsorbed intermediates, transition states, and the hydroxylated products were fully optimized, and the energetic reaction routes were clarified. The structure, and binding energy of theα-Al_2O_3(0001)−H_2O, α-Al_2O_3(0001)−OH, α-Al_2O_3(0001)−O, and α-Al_2O_3(0001)−H systems were also predicted. It was shown that the most favorable structure of α-Al_2O_3(0001)−H_2O corresponds to the coordination of water through its oxygen lone pairs with the α-Al_2O_3(0001) surface. Figure shows the mechanism of this study.



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Nitrogen-doped carbon nanotubes as a metal-free catalyst for CO oxidation

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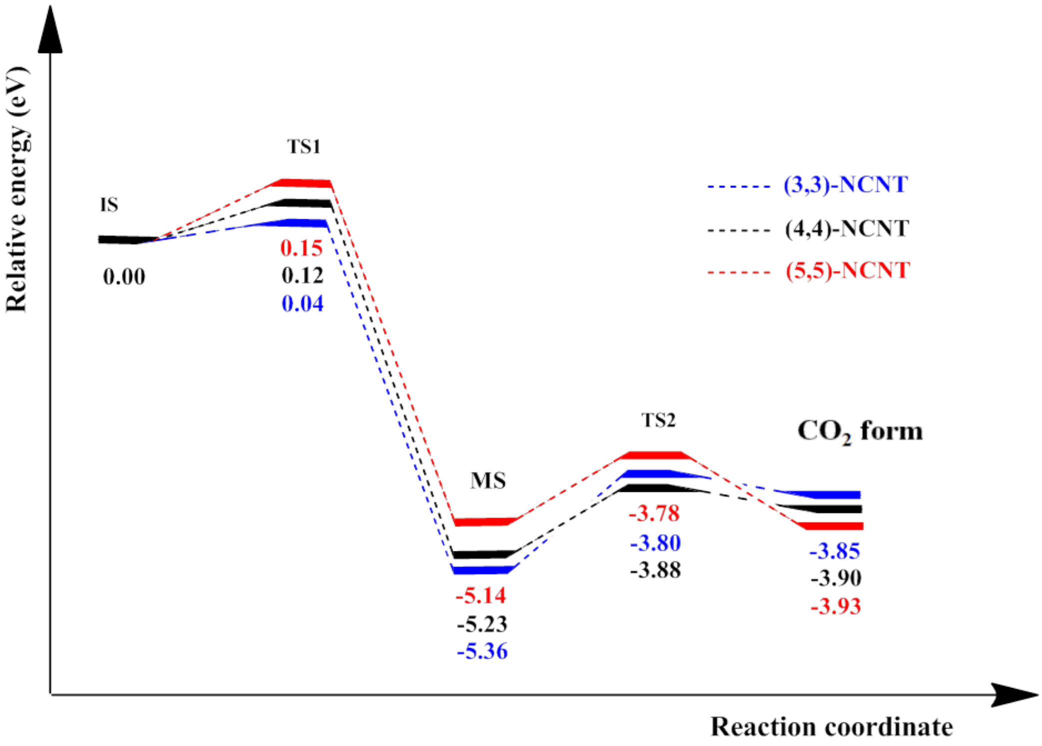
The oxidation of carbon monoxide (CO) on catalyst has attracted considerable research interest in recent years because it can remove CO from fuel cells or lowering CO pollution. An effective catalyst for CO oxidation need to comprise metal. We usually use noble metal catalyst for CO oxidation, but the noble metals (Pd, Au, and Pt) are rare and expensive. So we must to find the new catalysts replacing the noble metal. In our research, We have study CO oxidation by O_2 on nitrogen doped carbon nanotube (NCNT) with different diameter ((n,n)-NCNT (n= 3,4,5))by the density functional theory (DFT) calculations. We also find the reaction mechanism of CO oxidation and use NEB to map the potential energy surfaces. In our result, we show that the oxidation of CO energy barrier can reduce effectively. The result demonstrate that NCNT is a good, low-cost, and metal-free catalyst for CO oxidation.



Density functional study of oxidation reaction on W(111) and Pd-modified W(111) surface

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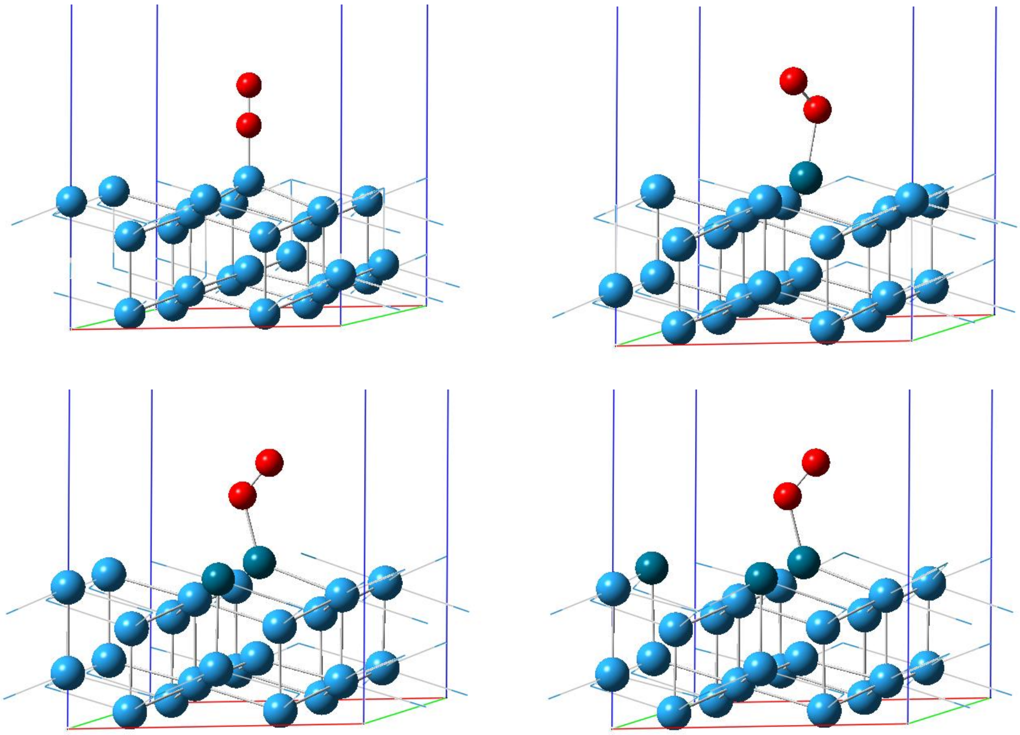

Tungsten is a material often be used in industry. Pd is more abundant and often shows similar catalytic properties to Pt. We choose the W(111) to discuss the oxidation reaction on this surface. In addition, we also use Pd to modify it.

We change the ratio of Pd-modified at Tungsten surface to discuss the oxidation reaction. With DFT calculation, we discuss different location of oxygen, and find the stable place to find out the mechanism of oxidation reaction on this surface.

And compare how many ratio of Pd cover has better for this reaction.

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Interactions between Ligands and Kinases: Molecular Simulations, and Kinase Assays

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Kinases are important target proteins for treatment of several diseases. In our study, we selected Glycogen synthase kinase-3β（GSK-3β）to study ligand-protein binding and developed small molecule inhibitors. When the activity of GSK3β is too high, it over-phosphorylates downstream proteins and causes some diseases such as cancer, inflammation, and Alzheimer's Diseases. This study utilized molecular docking, molecular dynamics simulation, and kinase assay to search new GSK-3β kinase inhibitors.

We used molecular docking method to do high throughput virtual screening in the ZINC Database and the Enamine Database to find out some potential small molecular compounds, and suggested these compounds for kinase assay. Among the 27 compound undergone kinase assay, 12 compounds were identified to be active. Moreover, thermodynamic integration MD simulation was also employed to aid in further inhibitor design.

The thermodynamic integration molecular dynamics simulation reproduced the relative protein-ligand binding free energy of a pair of analogous GSK3b kinase inhibitors of available experimental data well. The computation for the pair gave a $\Delta\Delta G$ of 1.0 kcal/mol, which was in reasonably good agreement with the experimental value of -0.1 kcal/mol, and the error bar was estimated to be 0.5 kcal/mol. The protocol was then applied to predict the affinity for other analogs as well as binding modes. The computed results will be reported and discussed.

In addition, a topic of ligand- p38 kinase complexes was investigated using MD simulation. The results will be discussed.

A Study of the Reaction Mechanism of Wittig Rearrangements by *Ab Initio* Computations

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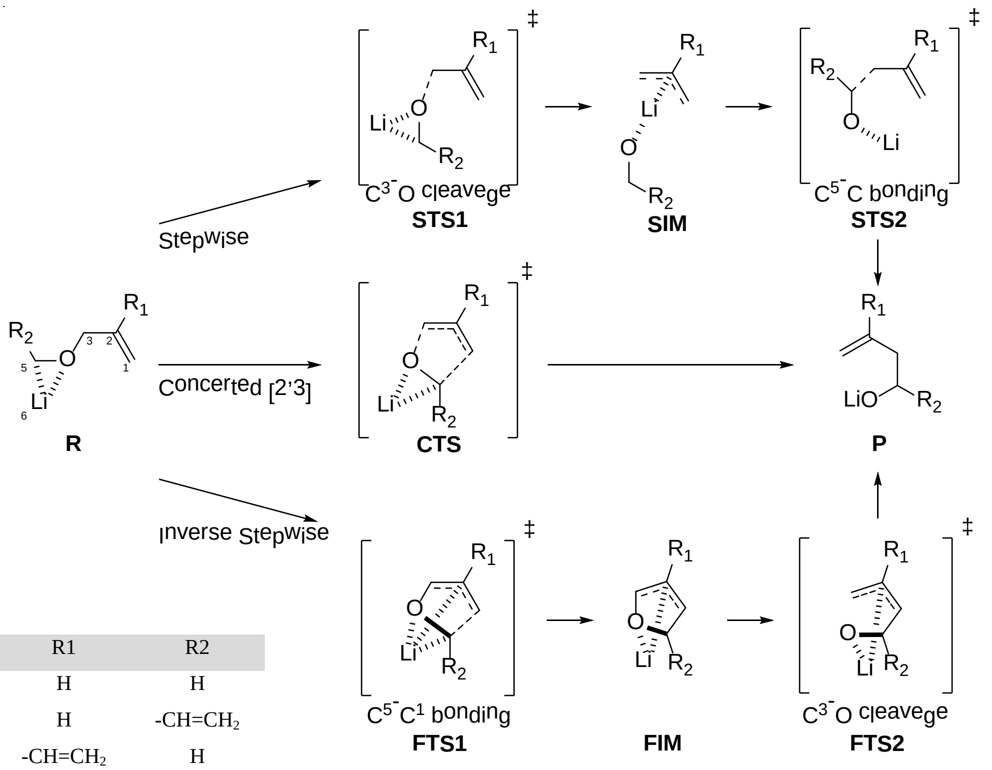
The high regio- and stereo-selectivity of Wittig rearrangement makes it a versatile tool in organic synthesis. The concerted [1,2] Wittig rearrangement is a orbital-symmetry forbidden process and is assumed to go through a stepwise pathway. An ionic and a radical pair are proposed as possible intermediates along this stepwise path. The [2,3] Wittig rearrangement is a concerted reaction with a high degree of stereocontrol. A inverse stepwise pathway has been found to form the [2,3] products.



	R1	R2
1	H	H
2	H	-CH=CH$_2$
3	-CH=CH$_2$	H

Three model compounds were used to analyze important reaction structures along the three reaction paths using the CASSCF and the unstricted M06-2X functionals, and the MRCI methods were used to calculate the reaction energies. Through the Boys localized molecular orbitals analysis, the transition state **2STS1** shows a biradical character. However, the ionized intermediate gives the lowest energy, indicating that there is an avoided crossing after the **2STS1**. The optimized geometries by both methods are similar for model **2**, and UM06-2X gives a better energy prediction for barrier heights. The two substituents provide different electron delocalization effects, which further guides the reaction pathway and the stereo-selectivity of the Wittig rearrangement.

Tetrahedral Silsesquioxane Framework: A Feasible Candidate for Hydrogen Storage

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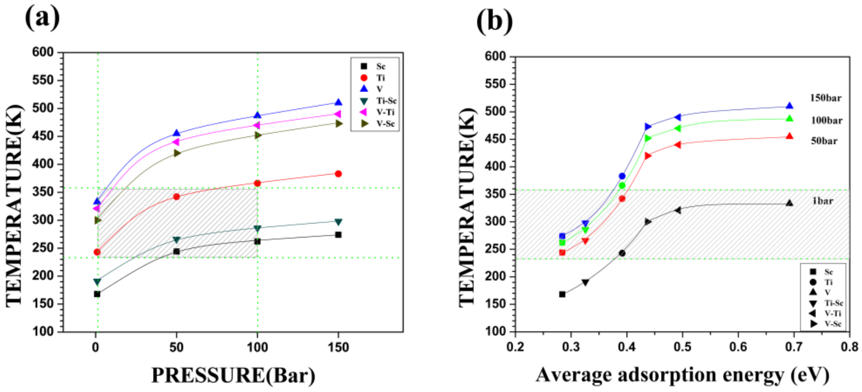
ABSTRACT

The search for new materials that can withstand tough demands of practical hydrogen storage for use in automotive transportation is currently receiving a great deal of attention from the scientific communitybecause of the urge of looking for the replacements of traditional energy resources like fossil fuels.In this work, the transition metals (TMs) decorated boron doped tetrahedral silsesquioxane frameworks (B-TSF) for application in hydrogen storage are investigated using first principles density functional theory calculations. We design this plausible hydrogen storage system based onthe knowledge of previous works by other groups including metal atom decoration for quasi-molecular H_2 adsorption,boron substitution into benzene rings to prevent metal clustering, and assembling the modified benzene rings and tetrahedral silsesquioxane cages into the framework for this study. Boron substitutiondid substantially enhance the TMs binding energy to the linker of B-TSF to suppress metal clustering as well as maintains stable hydrogen adsorptionenergy to TMs. It is found that average hydrogen adsorption energyenergies in Sc, Tiand VdecoratedB-TSF are 0.29 eV, 0.40 eV and 0.69 eV respectively with decent gravimetric density of 6.9, 5.6 and 4.15wt%. Gibbsfree energy calculations are also carried out to estimate theworking temperature and pressure ranges of using B-TSF as a hydrogen storage system.



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Temporary Anion States of Aza-Derivatives of Furan, Pyrrole, and Thiophene

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The Stabilized Koopmans' Theorem within long-range corrected density functional theory is used to calculate the energies of π* anion states of furan, thiophene, pyrrole, and their aza-derivatives. In this approach, stabilization is accomplished by varying the exponents of appropriate diffuse functions. The characteristics of these resonance orbitals are also analyzed. The obtained results have demonstrated that the SKT ωB97XD method can yield energies of π* anion states in agreement with the experimental data. These results will help us understand the electronic processes in five-membered heterocyclic, aromatic compounds.

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