台灣理論計算分子科學學會成立大會
Inaugural Meeting of Taiwan Theoretical and Computational Molecular Sciences Association
(T^{2}CoMSA)

暨

2014 年理論計算化學小組九月研討會
2014 TCCAT September Conference

Program

September 11, 2014

National Center for High-performance Computing, Hsinchu

09:00-09:50 registration opens

09:50-10:00 Opening Ceremony

（Chair：江志強）

NO.01 10:00-10:15 **Chih-Hao Chin** 金之豪 (Natl. Synchrotron Radiation Res. Center)
“Ab Initio Investigation of the Thermal Decomposition of 2*-butanol”*

NO.02 10:15-10:30 **Tung-Lin Wu** 吳東霖 (National Chiao Tung University)
“Theoretical Study on the Thiocyanide Formation of
3*-mercaptopyruvate Metal and Related Molecular Design”*

NO.03 10:30-10:45 **Tzung-Ying Jiang** 姜宗螢 (National Taiwan Normal University)
“Semi-Quantitative Assessment of Intersystem Crossing Rate: An
Extension of El-Sayed Rule to the Emissive Transition Metal
Complexes”

NO.04 10:45-11:00 **Wen-Chi Hsu** 許文綺 (National Taiwan Normal University)
“Computation of Relative Binding Free Energy for an Inhibitor and its
Analogs Binding with GSK3b *Kinase Using Thermodynamic*
Integration MD Simulation”

11:00-11:10 Photography

11:10-12:00 Inaugural Meeting of T^2CoMSA （學會成立大會議程請見附件檔案）

12:00-13:00 國家高速網路與計算中心計算資源需求座談 ＋ lunch

（Chair：蔡惠旭）

NO.05 13:00-13:15 **Hsing-Ta Chen** 陳信達 (Columbia University)
“Is decoherence always necessary in conjunction with the surface
hopping algorithm?”

NO.06 13:15-13:30 **Jake A. Tan** 洪于玉 (National Tsing Hua University)
“Sensitivity of the Intermolecular Proton Bond to Messenger’s
Existence and Flanking Group Motions: A Theoretical Study for the
Case of $(MeOH)_2H^+$*”*

NO.07 13:30-13:45 **Hsiao-Han Chuang** 莊曉涵 (National Taiwan University)
"Spectroscopic Study of the O-H Stretching Motions in $H^+(CH_3OH)_{1-3}X_{0-2}$*;* X=Ar and N_2*"*

NO.08 13:45-14:00 **Chun-Jui Tan** 譚俊瑞 (National Central University)
"Electron Transfer of Squaraine-Derived Dyes Adsorbed on a TiO_2 *Cluster in Dye Sensitized Solar Cells: A Density Functional Theory Investigation"*

14:00-14:20 Coffee Break

（Chair：孫英傑）

NO.09 14:20-14:35 **Wei-Chieh Chen** 陳葳潔 (National Taipei University of Technology)
"Effect of Anchoring groups on Optical properties and Aggregation of Organic dyes-A DFT study"

NO.10 14:35-14:50 **Ting-Yin Chen** 陳亭吟 (National Taipei University of Technology)
"Theoretical Insights into the Effect of Water on the Oxidative Decomposition of Propylene Carbonate in Lithium Ion Batteries"

NO.11 14:50-15:05 **Ting-Yi Wei** 魏廷伊 (National Taipei University of Technology)
"High-throughput Virtual Screening of Improved Cyclic Carbonates as Electrolyte in Lithium-ion Batteries"

NO.12 15:05-15:20 **Yu-Huan Lu** 盧禹寰 (Chung Yuan Christian University)
"Adsorption and Dissociation of the H_2O *Molecule on* γ-$Al_2O_3(110)$ *Surface: A Computational Study"*

15:20-16:20 Poster （P13~P34）

16:20-16:50 Closing (Awards) Ceremony

17:00-18:00 學會理監事會議

Ab Initio Investigation of the Thermal Decomposition of 2-butanol

Chih-Hao Chin (金之豪)
National Synchrotron Radiation Research Center, Hsinchu, Taiwan
chin.ch@nsrrc.org.tw

The pyrolysis mechanism of 2-butanol has been studied using accurate ab initio G3(MP2,CC)//B3LYP/6-311G(d,p) calculated followed by the kinetic analysis of various reaction pathways and computations of relative product yields. The computed PESs and molecular parameters have been used RRKM and RRKM-Master Equation methods calculated the rate constants of unimolecular reaction of 2-butanol and predicted the product branching ratios. The mechanism for decomposition involves direct elimination of water producing *E*- and *Z*-2-butene, and 1-butene, and C-C bond fission producing ethylene. Acetaldehyde, propionaldehyde, and propene were also observed in much smaller yields from C-C bond fission. Implementation of these pathways into an existing chemical kinetic mechanism improved the prediction of experimental product fragments speciation in shock tube oxidation [1]. Simulations of this combustion showed a change in the expected decomposition chemistry of 2-butanol, predicting increased production of *E*-2-butene or *Z*-2-butene instead of 1-butene. The most prominent reaction pathway for the decomposition of 2-butanol is *E*-2-butene. Good agreements between the predicted and measured results were obtained. These results of this study provide insight into the combustion of 2-butanol and will aid in the future development of alkene kinetic mechanisms.

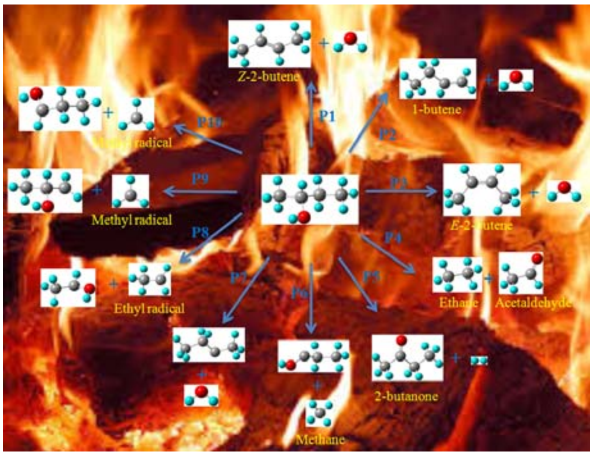

Figure 1: Thermal decomposition model starting from 2-butanol that shows the formations of the possibility products.

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Theoretical Study on the Thiocyanide Formation of 3-mercaptopyruvate Metal and Related Molecular Design

Tung-Lin Wu (吳東霖)[a], Jen-Shiang K. Yu(尤禎祥)[a,b,*]
[a] Department of Biological Science and Technology, National Chiao Tung University,
[b] Institute of Bioinformatics and Systems Biology, National Chiao Tung University,

In this study, computational design of efficient detoxification metal drugs to rescue for the cyanide poisoning by molecular simulation is attempted. Two molecules of 3-mercaptopyruvate (3-MP) are expected to chelate one metallic divalent cationic center (M^{2+}, M= Cu and Zn) to form stable four-coordinate complexes. Geometry optimization of the model complex **(1)**, bis[2-(2-thienyl)-glyoxylato-O,O'] copper(II) [1], is performed using various density functionals including BP86, B3LYP, TPSS, and PBE. The structure of **(1)** may be further reduced into **(2)** and optimized at identical levels. The geometries of the ligand coordinations remain almost identical compared to the structure of 3-MP calculated at high level CCSD theory. Transition state (TS) of **(2)** in the reaction of cyanide detoxification process is proposed (Figure 2): in this TS, the thiol group (–SH) tends to shift to cyanide and produce the thiocyanic acid. Subsequently, the thiocyanic acid approaches the oxygen atom of the carboxyl group and transfers the proton to oxygen, forming thiocyanide, which is less toxic and can be metabolized easily in urea. Energy profile of the dithiolation reaction is also constructed.

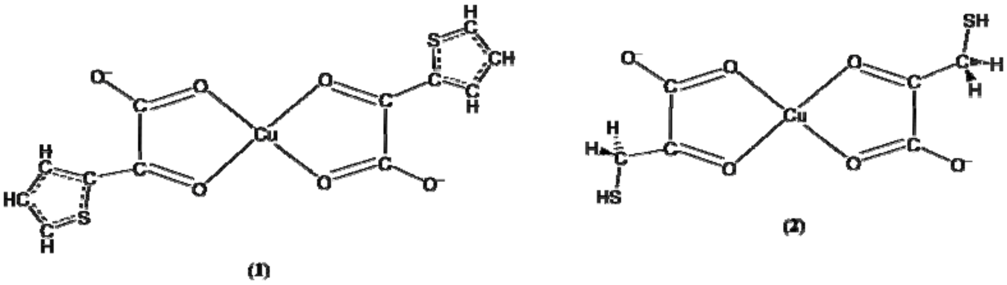

Figure 1. Molecular structures of **(1)** and **(2)**.

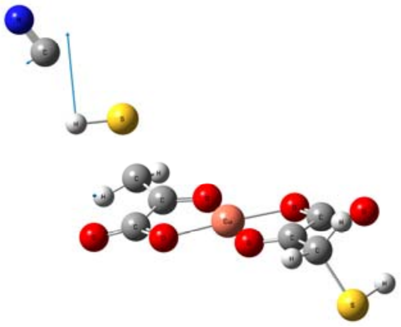

Figure 2. Vectors of the maginary frequency of the TS in the dithiolation reaction of **(2)**.

References

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Semi-Quantitative Assessment of Intersystem Crossing Rate: An Extension of El-Sayed Rule to the Emissive Transition Metal Complexes

Tzung-Ying Jiang(姜宗螢), Elise Yu-Tzu Li (李祐慈)
Department of Chemistry, National Taiwan Normal University, Taipei 116, Taiwan

The main goal of this study is to provide systematic elucidation of the parameters that influence S → T intersystem crossing (ISC). Particular attention is paid to: (i) the computation of $S_n \rightarrow T_m$ spin-orbit coupling strength based on a non-adiabatic approach, (ii) crucial factors that facilitate ISC, such as the atomic number, ligand structure, and particularly types of electronic transition, (iii) formulating a discussion on the standpoints of the fundamental photophysical theory. Combining the theoretical and empirical approaches, we propose the following empirical rules as general guidelines for assessing the ISC in a qualitative manner: (1) In general, the higher MLCT characteristic involved in the singlet and triplet excited states, the stronger the SOC integral. However, the strength of SOC also depends strongly on the detailed electronic structure of the states involved. (2) When the S_1 and T_1 originate from almost identical electronic transitions, the major ISC channel usually occurs via S_1 to higher T_m ($m > 1$) state, which has both a proper orbital transition and a smaller energy gap with S_1. (3) When the structure of the ligands involves extended conjugated systems and that the lowest excited states have a more dominating $\pi\pi^*$ character, the ISC originating from higher singlet excited states can be large enough to violate the Kasha's rule. (4) The overall SOC strength (and ISC rate) relies on a delicate balance between the one-electron SOC constant and the nature electronic structure of the involved states. In other words, the "heavy atom effect" might not be so heavily weighted after all; through a careful design, lighter elements may also exhibit similar emission efficiency with that of heavier elements. The theoretical approach in this study shall serve as a prototype to access the photophysics of TM complexes in both facile and precise manner beneficial to researchers in the field of optoelectronics.

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[3] El-Sayed, M. *J. Chem. Phys.* **1963**, *38,* 2834.

Computation of Relative Binding Free Energy for an Inhibitor and its Analogs Binding with GSK3β Kinase Using Thermodynamic Integration MD Simulation

Hsing-Chou Lee (李興洲), Wen-Chi Hsu (許文綺), An-Lun Liu (劉安倫), Chia-Jen Hsu (許嘉仁), Ying-Chieh Sun (孫英傑)
Department of Chemistry, National Taiwan Normal University
sun@ntnu.edu.tw; 60242014S@ntnu.edu.tw (W.C. Hsu)

Thermodynamic integration molecular dynamics simulation was used to investigate how TI-MD simulation preforms in reproducing relative protein-ligand binding free energy of a pair of analogous GSK3β kinase inhibitors of available experimental data, and to predict the affinity for other analogs. The computation for the pair gave a ΔΔG of 1.0 kcal/mol, which was in reasonably good agreement with the experimental value of -0.1 kcal/mol. The error bar was estimated at 0.5 kcal/mol. Subsequently, we employed the same protocol to proceed with simulations to find analogous inhibitors with a stronger affinity. Four analogs with a substitution at one site inside the binding pocket were the first to be tried, but no significant enhancement in affinity was found. Subsequent simulations for another 7 analogs was focused on substitutions at the benzene ring of another site, which gave two analogs with ΔΔG values of -0.6 and -0.8 kcal/mol, respectively. Both analogs had a -OH group at the meta position and another -OH group at the ortho position at the other side of the benzene ring. To explore further, another 4 analogs with this characteristic were investigated. Three analogs with ΔΔG values of -2.2, -1.7 and -1.2 kcal/mol, respectively, were found. Hydrogen bond analysis suggested that the additional hydrogen bonds of the added –OH groups with Gln185 and/or Asn64 were the main contributors to an enhanced affinity. Effect of displacement of crystal water molecules at binding site will be discussed. The prediction for better inhibitors should interest experimentalists of enzyme and/or cell assays.

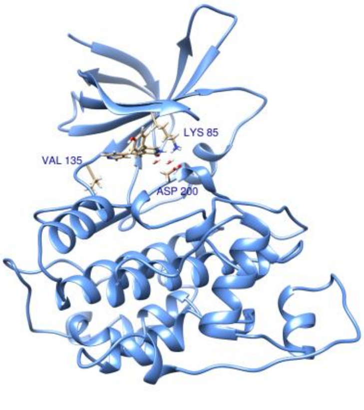

Figure 1: Binding of the reference compound with GSK3β kinase [1]

In addition, progress in using new module in Amber package, pmemd, and experimental measurement for finding new GSK3β kinase inhibitors will be reported and discussed. [2]

References

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Is decoherence always necessary in conjunction with the surface hopping algorithm?

Hsing-Ta Chen (陳信達) and David R. Reichman
Department of Chemistry, Columbia University, New York, USA
hc2602@columbia.edu

Fewest switches surface hopping (FSSH) [1] is a mixed quantum-classical method that has been widely used to simulate non-adiabatic processes. However, it is known that the over-coherence problem arises from the quantum-classical asymmetry and may cause a failure to properly predict Marcus scaling with the diabatic coupling for the spin-boson model [2]. To date, there are many decoherence schemes, such as augmented FSSH (A-FSSH) and 2nd order pure-dephasing, proposed for overcoming this problem.

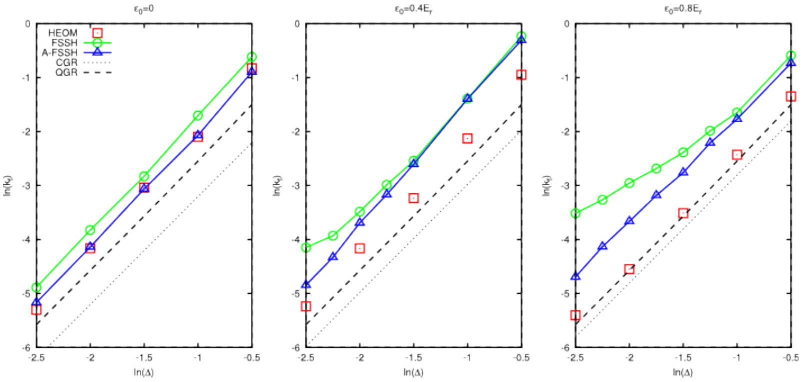

Figure 1: Transition rates (k_f) scaling with the diabatic coupling (Δ) compares the results of FSSH, A-FSSH, HEOM(exact) and the quantum/classical golden rule (QGR/CGR) for symmetric (left) and large-biased (right) spin-boson models.

Here, for the first time, we compare the results of various surface hopping algorithms against numerically exact methods for the spin-boson model. Within the Marcus regime, we find the failure is not general, but dependent on the parameters of the model. For broaden parameter regimes, decoherence reduces the over-estimated coherent oscillation, but does not recover the long-time behavior. In this talk, I will discuss the effects of decoherence to transition rates and population dynamics. Also, I will compare the efficiencies of different decoherence schemes and reveal their limitations.

References

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Sensitivity of the Intermolecular Proton Bond to Messenger's Existence and Flanking Group Motions: A Theoretical Study for the Case of $(MeOH)_2H^+$

Jake Acedera Tan[1,2,3] and Dr. Jer-Lai Kuo[1,3]
[1]Institute of Atomic and Molecular Science, Academia Sinica, Taipei, Taiwan
[2]Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan
[3]Taiwan International Graduate Program, Academia Sinica, Nangang, Taiwan
jaketan@gate.sinica.edu.tw and jlkuo@pub.iams.sinica.edu.tw

The behavior of the intermolecular proton bond (IPB) between the motion of the flanking groups and the presence of Ar messengers in $(MeOH)_2H^+$ were studied using Density Functional Theory (DFT) under B3LYP/6-311+G(d,p). The study was conducted by scanning the potential energy surface along a few key normal modes and solving the vibrational Schrödinger equation by means of eleven point finite difference. It was found out that the presence of Ar tunes the potential energy surface where the shared proton is trapped, resulting to a different distribution of intensities relative to the bare $(MeOH)_2H^+$. Moreover, it was confirmed that IPB is sensitive to the motion of the flanking groups [1]. In particular, IPB couples strongly with O-O stretch, out phase C-O stretch and out phase free O-H bend. Both bare and Ar-tagged cases had recovered three peaks in good agreement with the experiment [1]-[3], but the Ar-tagged captures the relative intensities. These results suggest the perturbative nature of the messenger on IPB. Lastly, isotope studies were performed to further understand the nature of IPB.

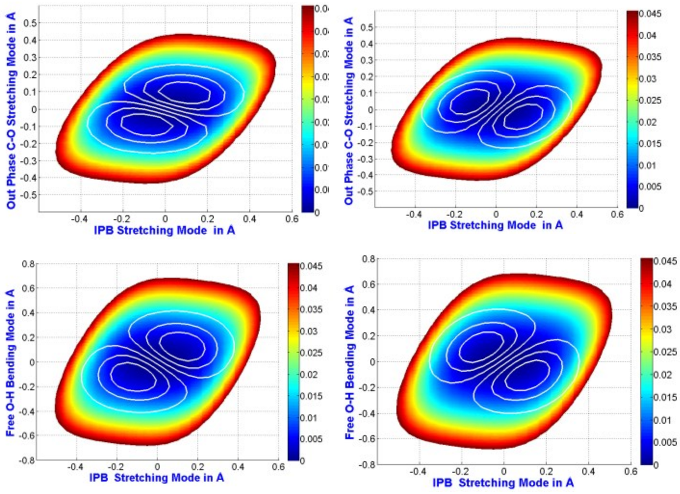

Figure 1: Mixing of the first excited states of IPB stretching mode with out of phase C-O stretching mode (upper row) and free O-H bending (lower row).

References

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Spectroscopic Study of the O–H Stretching Motions in $H^+(CH_3OH)_{1-3}X_{0-2}$; X=Ar and N_2

Hsiao-Han Chuang[a], Jer-Lai Kuo[b], Kaito Takahashi[b], Asuka Fujii[c]

[a] *Department of Chemistry, National Taiwan University, Taipei, Taiwan.*

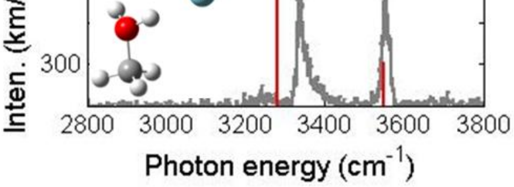
Nano Science and Technology Program, Taiwan International Graduate Program.

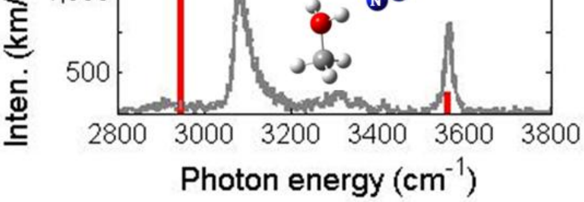
[b] *Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan.*

[c] *Department of Chemistry, Graduate School of Science, Tohoku University, Sendai, Japan*

hhchuang@phys.sinica.edu.tw

Tagging messengers (usually stable atoms or molecules) on ionic cluster can resolve the low-resolution infrared spectra of previous unobserved ions through vibrational pre-dissociation mechanism, and usually these messengers deliver the information of large size ionic cluster well [1]. Nevertheless, in the small cluster, they perturb the system by themselves and would not act as a "messenger" anymore. Infrared Pre-Dissociation (IR-PD) spectra of the mass-selected ionic cluster $H^+(CH_3OH)_{1-3}X_{0-2}$ (X=Ar and N_2) were observed, and both Ar and N_2 interfere the O–H stretching motion between 2800 to 3800 cm^{-1}. The observed sharp peaks are analyzed with theoretical simulations to find out how the messenger perturbs the system in the spectra via different vibrational calculation. In this work, expressions were derived in reduced dimension vibrational discrete variable representation (DVR) [2], which has high accuracy potential energy surface along several selected normal mode coordinates and has no coupling term between kinetic operators. After concerning the anharmonic effect and the coupling between different coordinates, simulation of covalent bond is in agreement with experimental results upon B3LYP/6-31+G(d,p) level, but overestimate the interaction between messenger and ionic protonated methanol cluster, see the figure below.





Reference

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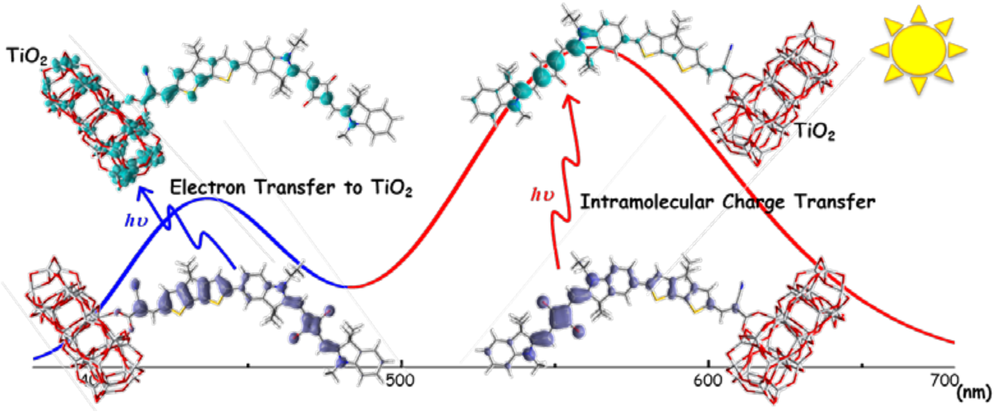
Electron Transfer of Squaraine-Derived Dyes Adsorbed on a TiO_2 Cluster in Dye Sensitized Solar Cells: A Density Functional Theory Investigation

Chun-Jui Tan, Wen-Hsin Tseng, and Hui-Hsu Gavin Tsai*
Department of Chemistry, National Central University, Jhong-Li City,
Tao-Yuan County 32001, Taiwan
hhtsai@cc.ncu.edu.tw

Squaraine (SQ) dyes are well-known for their intense absorption in the red/near-IR spectral regions, which closely match the spectral response of sun light. Thus, SQ dyes seem to show promise for utilization in dye-sensitized solar cells (DSCs). In this study, we employed density functional theory (DFT) as well as time dependent DFT to investigate the structural, optical and electron transfer properties of seven recently reported SQ-derived dyes adsorbed on a $(TiO_2)_{38}$ cluster with an anatase (101) surface, as a model for the corresponding DSCs. Particular efforts were given to calculate the proportion of the electron density of dye-$(TiO_2)_{38}$ systems transferred to the TiO_2 moiety, which allows us to investigate their electron injection mechanism. Our study shows the dye-$(TiO_2)_{38}$ systems follow different direct and/or indirect mechanisms of electron injection to TiO_2 depending on the orbital energy alignment between dye and TiO_2, the localization of the excited-state electron density, and the directionality of electron transfer upon excitation. JD10 and YR6 have two intense absorption bands due to their twisted structures and follow both direct and indirect electron injection mechanisms to TiO_2. JD10 and YR6 follow the indirect electron injection mechanism when their most intense and low-energy bands [$\pi(SQ) \rightarrow \pi^*(SQ)$ transition] are excited, where the excited-state electron density is distally away from the TiO_2 moiety; but follow the direct electron injection mechanism when less intense and high-energy bands are excited. Our study also shows that SQ dyes (e.g., SQ2 and SQ4) which have lowest unoccupied molecular orbital energies lower than the edge of the $(TiO_2)_{38}$ conduction band follow the indirect electron injection mechanism. Moreover, the electron injection of SQ dyes (e.g., SQ12) whose direction of electron transfer is away from the anchoring side upon excitation also follow an indirect electron injection mechanism. We found that the SQ-dyes which follow the indirect electron injection mechanism have lower experimentally observed short-circuit currents than those of the SQ-dyes which follow the direct electron injection mechanism. This study provides insights into the electron injection mechanisms of SQ-derived dyes adsorbed on TiO_2 upon photo-excitation. Furthermore, our calculations and findings give clues for designing new SQ-derived sensitizers in DSC applications.



Effect of Anchoring groups on Optical properties and Aggregation of Organic dyes-A DFT study

Wei-Chieh Chen (陳葳潔), Jyh-Chiang Jiang* (江志強)
Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei, 106, Taiwan, R.O.C
m10306112@mail.ntust.edu.tw

Dye-sensitized solar cell (DSSC) has been regarded as a next generation photovoltaic cell because of its low cost and high photon-to-current conversion efficiency.[1-2] Although DSSC has three components, which are equally important in terms of photovoltaic action, dye is inevitably essential since it generates electrons and holes. An efficient dye should have optical and physico-chemical characteristics of intense absorption in the visible-to-near IR region and strong chemical adsorption onto the TiO_2 surface.[3] Organic dye molecules have considerable importance in comparison with inorganic dye molecules by their applicability to green chemistry in DSSCs.[4] The limitations of organic dyes are reduced in molar absorption coefficient and increased dye aggregation. Especially, dye aggregation suppresses electron transport from the excited dye molecule to TiO_2 semiconductor surface resulting in lower DSSCs performance. Therefore, keeping in mind the requirement of efficient sensitizer and reduced tendency towards dye aggregation, we designed dyes based on D-π-A structure with three kinds of acceptors (CDM, CDT, and TP) and four different anchoring groups (COOH, CSSH, PO_3H_2, and SO_3H), and studied their optical properties using DFT and TDDFT methods. Our calculations indicate that PO_3H_2 and SO_3H are not suitable anchoring groups for efficient dyes due to its inefficient electron delocalization in LUMOs which will reduce the electron injection into the semiconductor surface. Also, we found that the dyes with CSSH and COOH anchoring groups have similar properties both in UV/vis spectra and molecular orbital (MO) diagrams. However, the calculation demonstrates that aggregation of the dyes with CSSH anchoring group are very less compared to that of COOH group, which will certainly increase the photo conversion efficiency of DSSCs. In this study, we report a new type of anchoring group for efficient dyes and it gives a good balance among several factors and we believe that it can be a good alternative to the inorganic dyes in DSSCs.

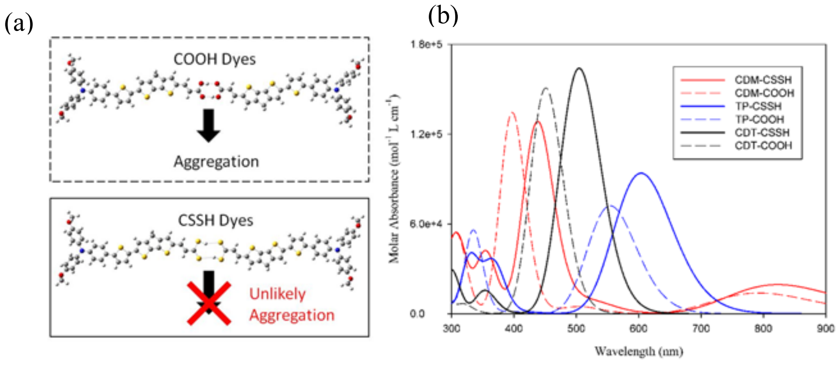


Figure. (a) The optimized structures of dyes with COOH and CSSH anchoring groups and (b) simulated absorption spectra for the different designed dyes.

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Theoretical Insights into the Effect of Water on the Oxidative Decomposition of Propylene Carbonate in Lithium Ion Batteries

Ting-Yin Chen(陳亭吟), Ermias Girma Leggesse and Jyh –Chaing Jiang*(江志強)

Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan (台灣科技大學化學工程學系)

*Corresponding author: jcjiang@mail.ntust.edu.tw

Lithium-ion rechargeable batteries are widely used in portable electronic devices as compared to the conventional batteries due to their high energy density and good environmental properties. However, there are still many challenges concerning the safety requirements. Propylene carbonate (PC) and lithium hexafluorophosphate ($LiPF_6$) have been extensively studied as electrolyte compositions for lithium ion battery. At open-circuit and during cell charge, the high potentials of several cathode materials may result in electrolyte oxidation. These highly exothermic electrolyte decomposition reactions are usually accompanied by the decomposition of the cathode material and gas evolution that will cause potential danger and reduced cyclic stability. The presence of trace amount of water is also believed to enhance the electrolyte decomposition reactions. In this study, density functional theory is applied to investigate the oxidative decomposition mechanisms of PC/$LiPF_6$ with water. The solvent effect is included using the implicit Solvation Model with Density method. Based on the calculation, there is a significant difference in the oxidative decomposition mechanism of $[H_2O\text{-}PC\text{-}PF_6]^-$ compared to $[PC\text{-}PF_6]^-$. For the $[PC\text{-}PF_6]^-$, HF is formed at the initial oxidation step; whereas, in $[H_2O\text{-}PC\text{-}PF_6]^-$ the elementary oxidation reactions, such as H_3O^+ formation and C-C bond-breaking, happen depending on the position of water. The energy barrier for the ring-opening step of $[PC\text{-}H_2O\text{-}PF_6^-]^+$ was found to be much lower than that of $[PC\text{-}PF_6^-]^+$. Our calculations suggest that, the initial oxidative decomposition products of PC in the presence of water are acetone radical, propionaldehyde radical and carbon dioxide, in agreement with experimental observation.

References

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High-throughput Virtual Screening of Improved Cyclic Carbonates as Electrolyte in Lithium-ion Batteries

Ting-Yi Wei(魏廷伊), Ermias Girma Leggesse, Jyh –Chaing Jiang(江志強)*

Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan

*Corresponding author: jcjiang@mail.ntust.edu.tw

Even though the demand for novel materials with specific properties increases significantly, the search for materials using experimental procedures is hindered by high costs and time-consuming procedures of synthesis. An alternative and new approach is to use theoretical methods systematically within a short period of time. In order to assist the discovery of lithium ion batteries which can offer high energy density, an electrolyte with a wide electrochemical window is essential. Among the commonly used cyclic carbonates, ethylene carbonate (EC) is the most studied organic solvent for lithium-ion cells. Some of the desired properties of EC include stability, high dielectric constant and its ability to form a stable solid electrolyte interface (SEI). However, it is viscous even at room temperature which results in low ionic conductivity in the electrolyte.

In this work, virtual structure library, consisting of 14,641 compounds, based on EC as a core structure were generated by employing R-group enumeration scheme using ChemAxon. High throughput computational screening was then carried out to identify potential solvents derived from EC. Molecular properties, such as, frontier molecular orbital energies, electron affinity, ionization potential, chemical hardness and dipole moment, were selected as descriptors and calculated relative to EC. Finally to illustrate the potential of the selected molecules and the screening technique, the reductive and oxidative decomposition mechanism of the representative molecule was compared with EC.

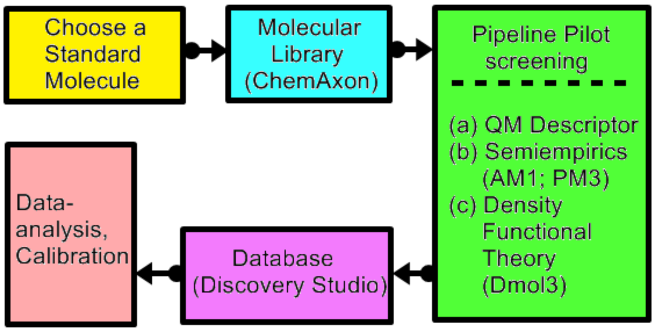

Figure 1: The workflow of screening LIB solvent

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Adsorption and Dissociation of the H_2O Molecule on γ-Al_2O_3(110) Surface: A Computational Study

Yu-Huan Lu (盧禹寰), Hsin-Tsung Chen* (陳欣聰)
Department of Chemistry, Chung Yuan Christian University, Chungli 32023,
Taiwan
dennis2353653@gmail.com, htchen@cycu.edu.tw

The adsorption and dissociation of water have been studied by the density functional theory (DFT) calculations in conjunction with the projected augmented wave approach. In this study, the potential energy surface of the water decomposition on the γ-Al_2O_3(110) surface was constructed. It was shown that the barriers for the stepwise H_2O dehydrogenation reaction, $H_2O \rightarrow OH_{(ads)} + HO_{(ads)}$is 0.18 (for HO−H bond activation) eV. Calculations show that the formation of γ-Al_2O_3(110)−O + $H_{2(gas)}$ from γ-Al_2O_3(110) + H_2O is exothermic by 3.96 eV. The structure, vibrational frequency, and binding energy of the γ-Al_2O_3(110)−H_2O, γ-Al_2O_3(110)−OH, and γ-Al_2O_3(110)−H systems were also predicted. It was shown that the most favorable structure of γ-Al_2O_3(110)−H_2O corresponds to the coordination of water through its oxygen lone pairs with the γ-Al_2O_3(110) surface (at its top position). For the OH and H systems are both on bridge sites.

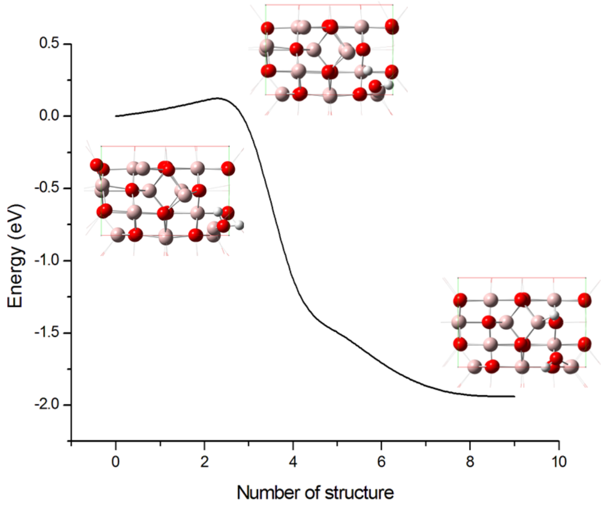

Figure 1: Potential energy diagram of transition state search for H_2O-γ-Al_2O_3(110) system, calculated at the PBE level.

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A Quantum Four-Element Approach to Characterization of Mixture Toxicity of Organic Compounds

Chia M. Chang (張家銘)
Environmental Molecular and Electromagnetic Physics (EMEP) Laboratory,
Department of Soil and Environmental Sciences, National Chung Hsing
University, Taichung 40227, Taiwan
abinitio@dragon.nchu.edu.tw

In our previous work, the concept of the four-element theory has been used to make assumptions on how to combine four types of quantum chemical descriptors, which governed electron flow, electrostatic, polarization and hydrophilic interactions, to predict diverse experimental results with a quantitative structure-property or structure-activity (QSPR/QSAR) analysis [1-3]. This approach was successfully applied to predict many kinds of reactions of metal ions and organic compounds in aqueous solutions – such as, hydration, diffusion, deprotonation, precipitation, redox reaction, and complexation; onto solid surfaces – such as, adsorption, ion exchange reaction, and sorption by organoclay; and for biological activity – such as, median effective concentrations measured from *Photobacterium phosphoreum* and *Chlorella vulgaris*.

In the present study, this quantum four-element approach was employed to evaluate the joint effects of mixture organic compounds - such as, benzene and its derivatives, non-polar narcotic chemicals, and aromatic compounds. The median effective concentrations (log ($1/EC_{50M}$)) of mixtures of organic compounds to *Photobacterium phosphoreum* and *Scenedesmus obliquus* were investigated. The introduction of this approach improved the prediction accuracy and provided a basis for interpreting the chemical interactions that affect the toxicity of chemical mixtures.

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Investigation of Surface Modification of CdSe Quantum Dots and Ligands by Density Function Theory

Hung-Lung Chou[a*], Liang-Yih Chen[b], Ching-Hsiang Chen[b], Chia-Lu O[a]

[a] Graduate Institute of Applied Science and Technology, National Taiwan University of Science and Technology, Taipei, 106 Taiwan
[b] Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei, 106 Taiwan
E-mail: HLCHOU@mail.ntust.edu.tw

An interfacial mechanism for CdSe(111) slab with ligands has been proposed based on the microscopic analysis and DFT simulations. A compatible modeling consisting of a CdSe(111) slab and amine (BA and HA) and oleic acid is achieved. The results could help to understand the role of the electronic structure in bimetallic electrocatalysis for applications like solar cells. Further investigations into this interfacial mechanism of CdSe QDs NPs and the relation between the surface structure and relaxation are necessary. Though the results presented herein are based on the CdSe and ligands system, the findings give insight into the interfacial mechanism of the nanosized CdSe(111) QDs and pave the way for designing bimetallic catalysts with tailored properties at the atomic level.

Acknowledgement:
We thank the NCHC and NTUST for providing massive computing time. Financially support from the National Science Council is gratefully acknowledged. Financial support from the National Science Council under Contracts No. NSC 102-2221-E-011-025 and MOST 103-2221-E-011-041 are also gratefully acknowledged.

Polyvinyl alcohol nanofibres supporting Ag nanoparticles: Surface Enhanced Raman Spectroscopy and DFT Studies

Hung-Lung Chou[a*], C. M. Wu[b], F. D. Lin[c], and J. Rick[b], W. J. Lin[a], W. C. Chen[a], Y. Lee[a]

[a] Graduate Institute of Applied Science and Technology, National Taiwan University of Science and Technology, Taipei, 106 Taiwan
[b] Department of Materials Science and Engineering, National Taiwan University of Science and Technology, National Taiwan University of Science and Technology, Taipei, 106 Taiwan
[c] Department of Fiber and Composite Materials, Feng-Chia University, 40724, Taiwan
[d] Department of Chemical Engineering, National Taiwan University of Science and Technology, National Taiwan University of Science and Technology, Taipei, 106 Taiwan

E-mail: HLCHOU@mail.ntust.edu.tw

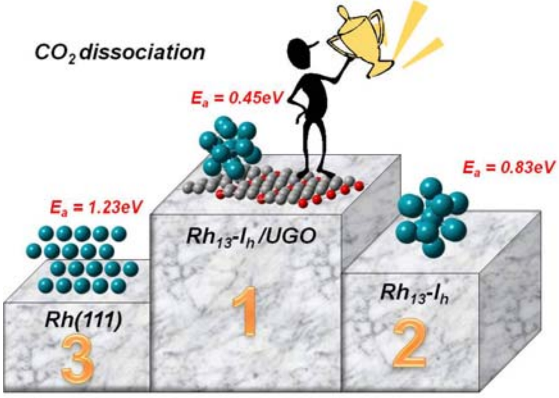
The interaction of polyvinyl alcohol (PVA) nanofibers with silver nanoparticles (mean diameter 8nm) has been modeled using density functional theory (DFT) calculations. The physical adsorption of PVA through the hydroxyl group, to the Ag, and its corresponding molecular orientation was compared with experimental results obtained from surface-enhanced Raman scattering (SERS) studies of the same material. A good agreement was found between the computational model of the vibrational spectrum of the adsorbate and the experimentally observed SERS. In general, aliphatic capping molecules are used to passivate the surface of Ag55 nanocrystals (55 = atomi number of Ag). In this study, a density function theory (DFT) simulation was employed to show binding energies and electron contour map analyses of Ag55 with polyvinylalcohol (PVA). Here we show that the PVA interacts with the Ag nanoparticle’s surface, through the OH fragment, thereby contributing significantly to the increase in SERS activity.

Acknowledgement:
We thank the NCHC and NTUST for providing massive computing time. Financially support from the National Science Council is gratefully acknowledged. Financial support from the National Science Council under Contracts No. NSC 102-2221-E-011-025 and MOST 103-2221-E-011-041 are also gratefully acknowledged.

Catalytic Enhancement of CO_2 Dissociation on Various Structures of Rhodium Nanoclusters (Rh_{13}) Supported on Unzipped Graphene Oxide – A DFT Study

Chun-Chih Chang (張鈞智), Jia-Jen Ho(何嘉仁)
Department of Chemistry, National Taiwan Normal University, No. 88, Section 4,
Tingchow Road, Taipei, Taiwan
E-mail: jancochang@gmail.com

The catalytic activity of rhodium nanoclusters (Rh_{13}) on unzipped graphene oxide (Rh_{13}/UGO) has been investigated to compare with that of Rh_{13} nanoclusters and that of Rh(111) surfaces. The binding energy of Rh atoms on UGO is less than the cohesive energy (- 5.75eV) of Rh bulk, indicating that the Rh atoms adsorbed on UGO tend to collect to clusters. In this work, we systematically calculated the CO_2 adsorption energies on various stable shapes of the Rh_{13} nanoclusters on unzipped graphene oxide and found that the Rh_{13}-I_h/UGO had the largest, -1.18eV with the C–O bond being elongated from 1.18 to 1.29 Å; accordingly, the dissociation barrier of CO_2 on Rh_{13}-I_h/UGO is the smallest (E_a = 0.45eV), indicating that the Rh_{13}-I_h/UGO might act as good catalyst to adsorbe and activate the scission of the C-O bond of the CO_2 . The data needed to support all the evidence of this result including electronic distribution, density of states,.. etc., have been calculated and provided.



Graphical abstract

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Efficient Oxidation Reduction Reaction Occurred on N-Doped Graphene Nano Ribbons

Chen Po-Tuan (陳柏端)[‡], Sun Chia-Liang (孫嘉良)[†], Hayashi Michitoshi (林倫年)[‡]
[‡] Center for Condensed Matter Sciences, National Taiwan University, Taipei 106, Taiwan.
[†] Department of Chemical and Materials Engineering, Chang Gung University, Kwei-San, Tao-Yuan 333, Taiwan.
r92222019@ntu.edu.tw

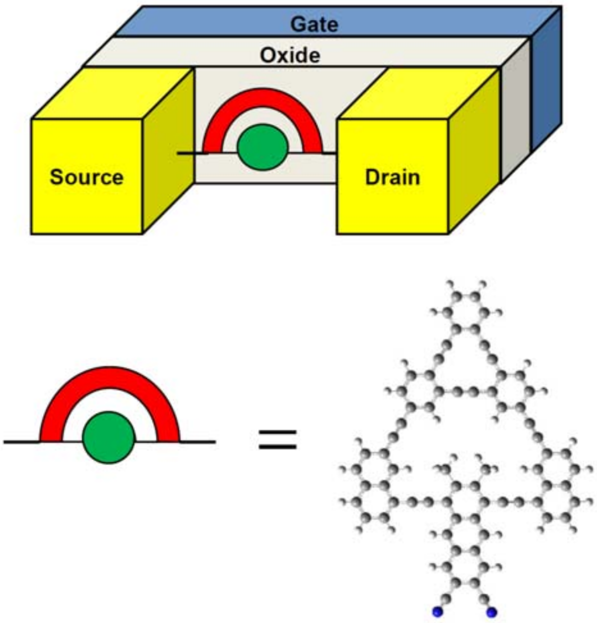
We have performed the calculations of O_2 and dissociated O_2 adsorbing on N-doped graphene nanoribbon (NGNRs) models using density functional theory to elucidate the origin of oxidation reduction reactions of NGNRs. Experimental X-ray photoelectron spectroscopy analysis suggests that the pyridinic-type N dopants play the major function of ORR in NGNR electrodes. In addition, the pyridinic-type N dopants can be contained in pyridine, pyridinium, or N in the graphene sheet with a nearby vacancy (NV) models. Thus, the significant N-doped ribbon models were constructed within 1D periodic boundary condition and we could theoretically examine the ORR properties naively at zigzag edge (Z) or armchair edge (A). Z-pyridine is exothermal for dissociated O_2 adsorbing, while Z-pyridinium is endothermal for dissociated O_2 adsorbing. A-pyridine is poor for dissociated O_2 adsorbing, and dissociated O_2 can be thermally preferable adsorbing on A-pyridinium. Interestingly, both of Z-NV and A-NV display the strongest adsorption abilities. The NV models can be the most potential candidate for ORR application.

Gate Control of Single-Molecule Machines

Liang-Yan Hsu,*,† Chun-Yin Chen,‡ Elise Y. Li,*,‡ and Herschel Rabitz*,†

†Department of Chemistry, Princeton University, Princeton, New Jersey 08544,
United States, and ‡Department of Chemistry, National Taiwan Normal
University, Taipei 11677, Taiwan
60242069s@ntnu.edu.tw

Artificial molecular machines are a growing field in nanoscience and nanotechnology.[1,2] This study proposes a new class of artificial molecular machines, the second-generation singlemolecule electric revolving doors (2G S-MERDs), a direct extension of our previous work [3]. We investigate destructive quantum interference with tunneling and conductance dependence upon molecular conformation in the 2G S-MERDs by using the Green's function method together with density functional theory. The simulations show that the 2G S-MERDs have a large on-off conductance ratio ($> 10^4$), and that their open and closed door states can be operated by an experimentally feasible external electric field (1 V/nm). Conductance - gate electric field characteristics are also introduced to illustrate the operation of the 2G S-MERDs.



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Ethylene Carbonate Adsorption and Decomposition on LiMn$_2$O$_4$ Cathode: A DFT study

Kai-Hao Tsau (曹凱皓), Yu-Tsung Liu (劉于琮) and Jyh－Chaing Jiang*(江志強)

Department of Chemical Engineering, National Taiwan University of Science and Technology,
Taipei, 106, Taiwan, R.O.C
m10206043@mail.ntust.edu.tw

The development of electrochemical energy storage technologies, such as lithium ion batteries (LIBs), will play a grand role in the advancement of alternative renewable energy sources. The adsorption and decomposition mechanism of electrolyte on the cathode surface of LIBs is one of the governing factors which control the stability, capacity and cyclic life. In this work, first principles calculations are used to study the adsorption and decomposition reaction mechanisms of ethylene carbonate (EC) on the (100) surface of fully discharged LiMn$_2$O$_4$, and the half-charged Li$_{0.6}$Mn$_2$O$_4$. The adsorption strength and electronic properties of various configurations are discussed by using density of states (DOS), projected density of states (PDOS) and electron density difference (EDD). Moreover, the initial decomposition mechanisms of EC on the surfaces is investigated by examining the minimum energy path between two minima using the climbing image nudged elastic band reaction-pathway sampling scheme. Even though adsorption and decomposition reaction can occur on the surfaces, for all configurations studied, the results show that the generation of gas is highly unlikely to occur at normal condition. In general, this work aims to give an insight about the initial stages in surface catalyzed electrolyte decomposition reactions on spinel cathode structure.

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Adsorption and Reaction of O_2 and C_2H_4 on Au_{38} and Cu_{38} Clusters: A Computational Study

Chen-Chi, Lee (李偵綺), Hsin-Tsung, Chen (陳欣聰)*
Department of Chemistry, Chung Yuan Christian University, Chung-Li, 32023, Taiwan
wacky20091@yahoo.com.tw, htchen@cycu.edu.tw*

The heterogeneously catalyzed epoxidation of alkenes is experimentally challenging, so we try to use theoretically method to find the better route. We have studied the adsorption of O_2 and C_2H_4 molecules on Au_{38} and Cu_{38} by using density functional theory (DFT) calculations. Some adsorption sites were discussed in this study and characterized as top, bridge, hollow, and hcp sites. Cooperative adsorption O_2 and C_2H_4 on Au_{38} and Cu_{38} clusters were investigated. To predict the competing reaction pathways for epoxide formation versus acetaldehyde formation on Au_{38} or Cu_{38} and search out a lower transition state, we use NEB method to map the potential energy surfaces. Results suggest that epoxidation proceeds via a surface oxametallacycle intermediate (OMME structure), such as a ring structure, Au-C-C-O-Au.

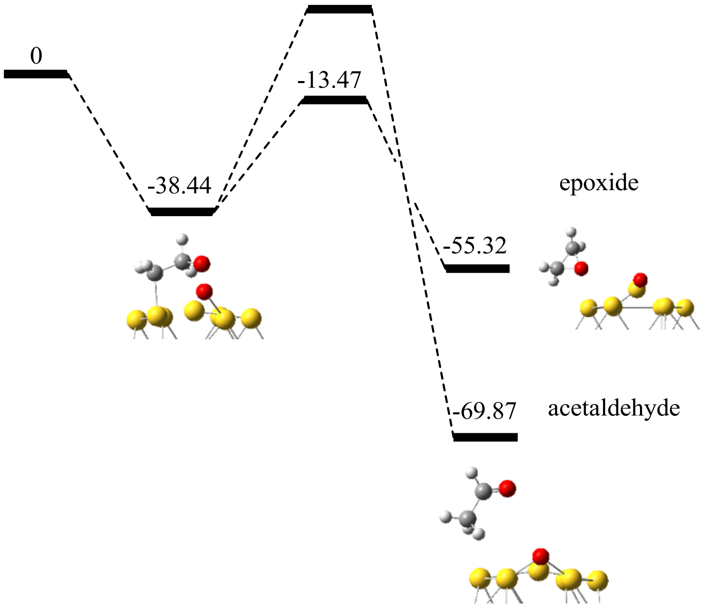

Figure 1: Potential energy diagram for the epoxide and acetaldehyde formation from ethylene and oxygen absorbed on Au_{38}.

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Methanol Synthesis from CO_2 Hydrogenation on Fe(111) Surface by DFT Study

Chia-Ni Li (李佳霓), Ming-Kai Hsiao (蕭銘凱), Su-Hong Tsai (蔡書弘), Hui-Lung Chen* (陳輝龍)*
Department of Chemistry and Institute of Applied Chemistry, Chinese Culture University, Taipei, 111, Taiwan
chl3@faculty.pccu.edu.tw

Methanol synthesis from CO_2 hydrogenation has been studied extensively in recent decades.[1-3] This reaction is very important for the industry since the methanol could be employed as the raw material for other synthetic hydrocarbons. In our work, we investigated the possible reaction mechanisms of methanol synthesis from CO_2 via density function theory calculations by VASP program. Our purpose of this study is to provide the more efficient method and suitable surface for CO_2 reduction/hydrogenation. We proposed three pathways for these reactions, as shown in Figure 1. The corresponding reaction energies and the structures of the reactants, transition states, and products have been determined and analyzed in detail. Our calculated results show that the CO_2 preferred to form the intermediate of formate (HCOO) in the first step and then proceed follow-up reaction mechanisms and different product formations. In all the reaction processes, it is found that the highest activation barrier energy is 27.84 kcal/mol. To explore this phenomenon in detail, we study the electron localization function (ELF), charge density difference, and electronic local density of states (LDOS).

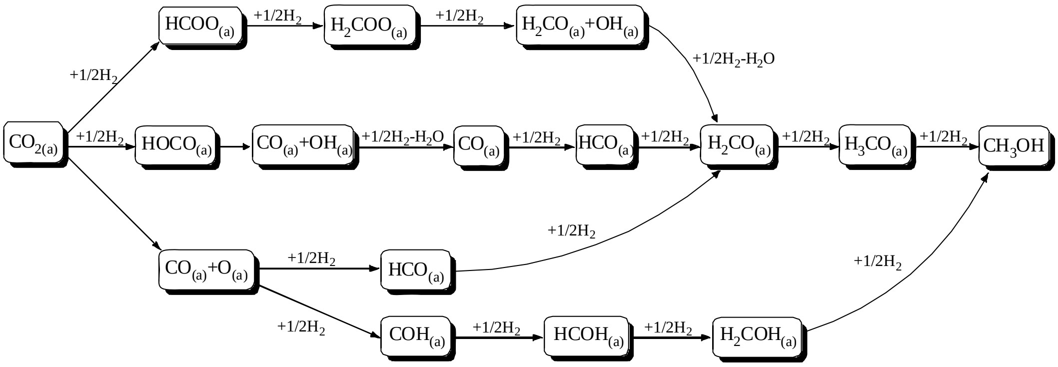

Figure 1. Schematic diagram of proposed paths for the reaction network of the (1) formate pathway, (2) RWGS pathway and (3) direct CO_2 dissociation pathway.

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Theoretical Calculations on the Oxidation of CO on the Carbon-Based Material Composed with Nickel Hydroxide and Reduced Graphene Oxide ($Ni_4(OH)_3$/rGO)

Chen-Hao Yeh(葉丞豪) and Jia-Jen Ho(何嘉仁)*

Department of Chemistry, National Taiwan Normal University,
No. 88, Section 4, Tingchow Road, Taipei, Taiwan
E-mail : mrprofya@gmail.com

Low-temperature CO oxidation is important and has been extensively studied via heterogeneous catalysis such as Rh, Pd, Pt, and Au. However, noble metals are costly and not abundant in nature. Nickel or nickel hydroxide clusters on reduced graphene oxide (rGO) are novel nanomaterial in the application to the electrochemical catalyst [1, 2]. In this work, we calculated the composition of Ni_4 and saturated hydroxyl GO and found that it formed $Ni_4(OH)_3$ locating on the exposed hollow site in the hydroxyl rGO and released 5.22 eV. Here we have calculated the CO oxidation reaction on the $Ni_4(OH)_3$/rGO with three possible mechanisms of CO oxidation reaction – LH, ER and carbonated mechanisms considered. Our results show that the activation energy of oxidizing the first CO molecule by ER mechanism is 0.12 eV, being smaller than that by LH (Ea = 0.61 eV) and by carbonated (Ea = 1.23 eV) mechanisms. Nevertheless, the reaction barrier of oxidizing the second CO molecule to CO_2 by ER mechanism increases to 0.47 eV, yet still lower than via LH (Ea = 1.07 eV), indicating the CO oxidation reaction could be carried out promptly by ER mechanism on the $Ni_4(OH)_3$/rGO catalyst.

Graphical Abstract

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A DFT Study of the Mechanisms of Cesium Fluoride-Mediated Claisen Rearrangement of Aryl Propargyl Ether.

Mengistu Gemech, Srinivasa Desikan and Shyi-Long Lee*

Department of Chemistry and Biochemistry, National Chung Cheng University, 168 University Road, Min-Hsiung Chiayi 621, Taiwan.

chesll@ccu.edu.tw

Ishii[1] and co-workers reported that the Claisen rearrangement of an aryl propargyl ether in the presence of CsF led to exclusive formation of 2-methylarylfuran in excellent yield. The accepted mechanism[2] for formation of arylfuran and arylpyran from aryl propargyl ether under the condition of Claisen rearrangement involves a concerted pericyclic [3,3]-sigmatropic rearrangement. A computational study of the mechanisms of the Claisen rearrangement of aryl propargyl ether in the presence of CsF has been performed by using DFT calculations. We found that the [3,3]- sigmatropic rearrangement is the rate limiting step for the formation of arylfuran with $\Delta G^{\neq}$ values of 39.2 and 37.1 kcal/mol in gas phase and in N,N-diethylaniline solvent, respectively. Furthermore, the calculation results reveal that the enolization of α-allenyl ketone suffered from a higher energetic barrier and indeed unlikely to allow the rearrangement reaction to proceed towards arylpyran cyclization. However, the abstraction of the α-hydrogen atom in the α-allenyl ketone has a very low activation barrier and is the favored pathway for the Claisen rearrangement of aryl propargyl ether in the presence of CsF.

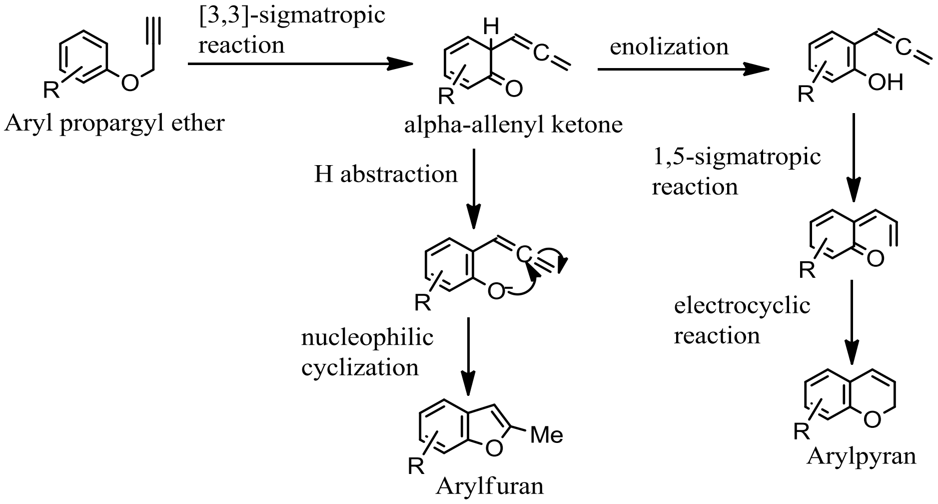

Fig. Accepted mechanism for formation of arylfuran and arylpyran from aryl propargyl ether under the condition of Claisen rearrangement.

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Theoretical study on the dethiolation mechanism of human mercaptopyruvate sulfurtransferase

Ying-Siao Chen[a] (陳盈孝), Jen-Shiang K. Yu[a,b] (尤禎祥)
[a] Department of Biological Science and Technology, National Chian Tung University,
Hsinchu City 300, Taiwan
[b] Institute of Bioinformatics and Systems Biology, National Chian Tung University,
Hsinchu City 300, Taiwan
e-mail: jsyu@mail.nctu.edu.tw

The human mercaptopyruvate sulfurtransferase (h-MST) is able to detoxify physiological cyanide poisoning, and the detoxification process involves the formation of persulfide followed by dethiolation [1]. At the stage of persulfide formation, the sulfur atom transfers from the 3-mercaptopyruvate (3-MP) to the Cys248 residue of the h-MST and produces the persulfidated Cys248 residue and pyruvate. In this study we aim at the mechanisms of the dethiolation process and propose a two-step reaction in the small model (Figure 1.a). The small model that consists of cysteine–glycine dipeptide and cyanide is preliminarily constructed to depict the potential energy surfaces (PES) by density functional theories (DFT) as well as the second order Møller-Plesset perturbation theory (MP2). In this model, cyanide reacts with the aforementioned persulfidated Cys248 residue and finally produces a less toxic thiocyanate via a two-step mechanism: the first step is the persulfide bond cleavage, while the second step involves the proton transfer. The energy barriers of the two steps are 55.5 kcal/mol and 40.1 kcal/mol at the level of B3LYP/6-311++G(d,p), while MP2 theory gives higher values at 55.0 kcal/mol and 45.7 kcal/mol using triple-zeta 6-311++G(d,p) basis set. The PES are further investigated in the protein system (PDB code: 4JGT), utilizing a two-layer ONIOM scheme. Simulations performed using the authentic protein structure at ONIOM(MP2:AMBER) level suggest a concerted route (Figure 1.b) with only one transition state, and the activation energy is computed at 58.4 kcal/mol. The high activation barrier in both of the small model and the protein system might explain the fatality of cyanide poisoning though the existence of MSTs *in vivo*.

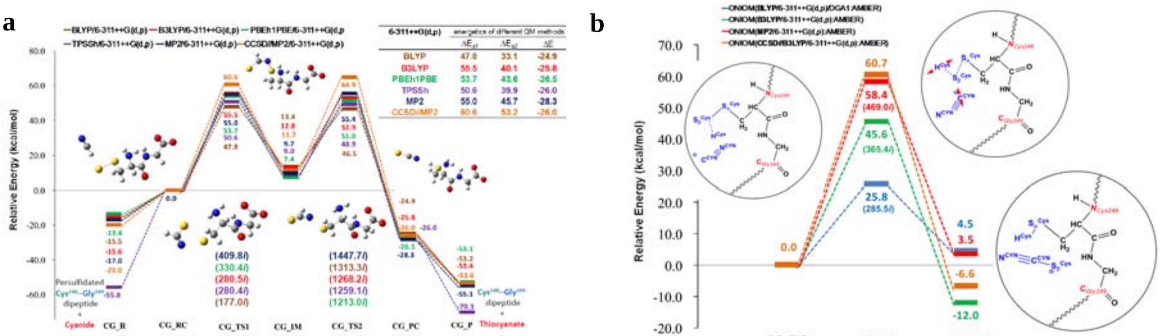

Figure 1: (**a**) PES in the small model. (**b**) PES in the protein system.

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Titanium decorated Boron doped Tetrahedral Silsesquioxane Framework: Efficient candidate for hydrogen storage

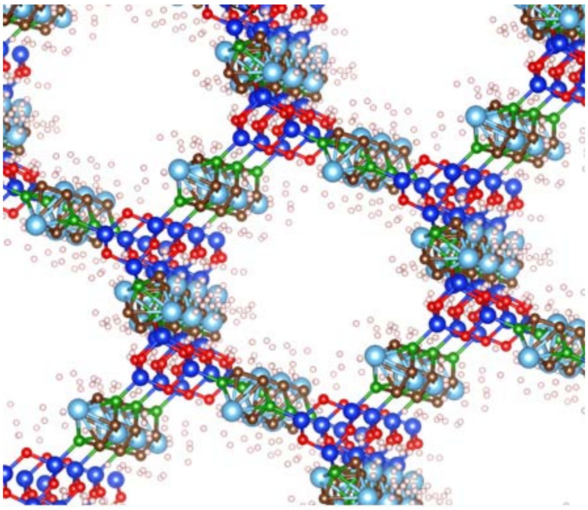
Amol Deshmukh[ab], Yun-Wen Chen[a],   Jer-Lai Kuo[a*]

[a] *Institute of Atomic and Molecular Science, Academia Sinica Taiwan.*

[b] *National Central University, Taiwan.*

E-mail address: damol92@yahoo.com

Hydrogen has been viewed as a clean energy carrier that could replace traditional energy sources such as fossil fuels, particularly for transportation applications including hydrogen fuel cell vehicles. The search for new hydrogen storage materials is currently receiving great attention from the scientific community. The porous material that can satisfy tough demand of practical hydrogen storage is needed for use in automotive application. Hydrogen storage capacity of Ti decorated boron doped TSF (Tetrahedral Silsesquioxane Framework) has been studied using first principle calculations. It is found that boron substitution on metal decorated TSF enhances interaction energy of Ti with TSF. A maximum of four hydrogen molecules can adsorb on single Ti atom with average adsorption energy 0.20 eV and gravimetric density of 5.56 wt %. Thermochemistry calculations were also carried out to study the effect of varying temperature on H2 adsorption on a substrate.



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Theoretical Study on Alkali-earth Metal Decorated Carbon Ring Based Molecular Materials with Boron and Nitrogen Substitution for Hydrogen Storage

謝涵如(Han-Ju Hsieh), 林逸庠(Yi-Shiang Lin), 童昱哲(Yu-Jhe Tong), 陳欣聰(Hsin-Tsung Chen)

Department of Chemistry, Chung Yuan Christian University, Chungli 32023, Taiwan

Abstract

Based on density-functional theory, the hydrogen molecule adsorbed on metal decorated carbon-based molecular complexes is revealed, and its effect on the hydrogen storage capacity is investigated. We find that carbon-based molecular complexes decoration with alkali-earth metal atoms is an efficient way to improve the hydrogen storage capacity. Moreover, in order to enhance their capacity to bind with more hydrogen molecules, we also discuss the strategy of modifying the carbon ring materials by subsisting carbon atom to boron or nitrogen up to three atoms. Our calculation results indicate that alkali-earth metal decorated carbon-based molecular materials with boron or nitrogen substitution has a significant effect on the hydrogen storage capacity. Furthermore, through a comparison study on the hydrogen adsorption behavior on Be-, Mg-, and Ca-decorated carbon-based molecular complexes, the factors relating to the hydrogen molecule are revealed. In the future, we hope this information will be useful for extending the study of graphene-based system for hydrogen storage.

Theoretical Calculations on Photochemistry of Commercial Photoinitiator Irgacure 907-(2-Methyl-4’-(methylthio)-2-morpholinopropiophenone)

Wan-Rou Tong(童琬柔), Jyh –Chaing Jiang(江志強)*

Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan

*Corresponding author: jcjiang@mail.ntust.edu.tw

A photoinitiator is a compound that undergoes a photoreaction on absorption of light, producing reactive species which are capable of initiating chemical reactions and then causing photopolymerization. It transforms a soluble liquid formulation into a hard and insoluble crosslinked polymer network. The cured coating is chemically and physically resistant and is used both to protect and decorate substrates such as plastics, wood and metal. Irgacure 907 (2-Methyl-4’-(methylthio)-2-morpholinopropiophenone) is a highly efficient type I α-aminoketone photoinitiator which is widely used to initiate the photopolymerization of chemically unsaturated prepolymers.

In this work, the photocleavage reaction mechanism as well as excited state properties and the underlying relaxation mechanisms upon photoexcitation of Irgacure 907 is investigated by using DFT calculations. To investigate mechanism, the excited state of singlet and triple were studied in detail. Based on our calculations, we have found that the radical formation for Irgacure 907 originates from the triplet states, which is typical of type I photoinitiators. As expected, after excitation, the photoinitiator undergo rapid intersystem crossing (ISC) which is an important step for the overall process. In addition to the observed change in the orbital angular momentum, the smallest energy gap was found to be between S_1 and T_1.

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Clarifying the Nature of the Chlorine Surface σ–hole in Chloromethane

Pradeep R. Varadwaj, Arpita Varadwaj, Bih-Yaw Jin
Department of Chemistry, National Taiwan University, Taipei, 10617, Taiwan
Email: pradeep@t.okayama-u.ac.jp ; byjin@ntu.edu.tw

Halogen bonding has attracted recent interest owning to its growing potential in the design of multifunctional halogenated-materials [1]-[2]. Even so, there are still a number of fundamental issues, which are essentially needed to be clarified. To give an example, it has been suggested in many occasions that the chlorine in Chloromethane ($H_3C–Cl$) has no σ-hole on the outermost extension of the C–Cl bond; this therefore cannot halogen bond with the negative site on other molecules [3]-[4]. In this presentation, we would resolve this controversy using first principles calculations by showing that there is indeed a σ–hole on the chlorine surface (cf. Figure 1), which is small and positive, unveiled using the molecular electrostatic surface potential analysis. This specific nature the chlorine in $H_3C–Cl$ can allow it to form halogen bond with several nitrogen donors on the participating molecules, such as that with FCN, ClCN, BrCN, CH_3CN, HOCN, HSCN, PCCN, PN, CCl_3CN, SiH_3CN, NCCN, CNCN, and NaCN. The results obtained using the atoms in molecules, noncovalent interaction reduced density gradient, and natural bond orbital analyses tools are to be used to unravel the intermolecular bonding interactions in these complexes.

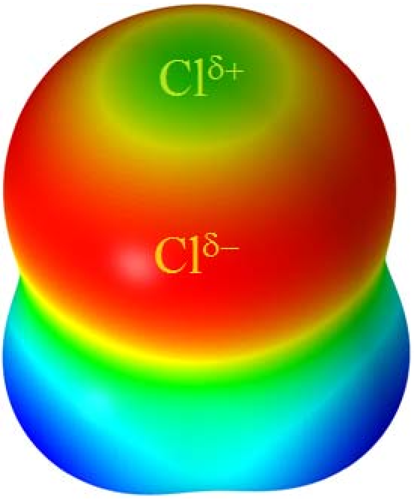

Figure 1: MP2(full)/6–311++G(3d,2p) calculated 0.001 electrons per $bohr^3$ isodensity surface mapped electrostatic potential of the $H_3C–Cl$ molecule. The chlorine is on the top and the $–CH_3$ group is on the bottom. The surfaces painted in red and blue represent the most negative and most positive electrostatic potential.

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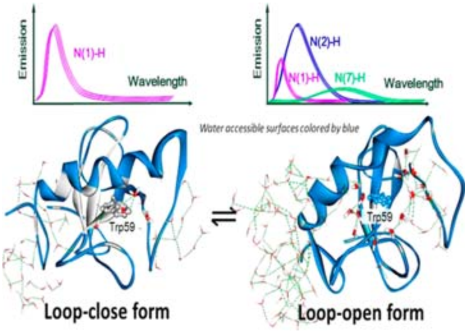
Probing Water Environment of Trp59 in Ribonuclease T1: Insight of the Structure−Water Network Relationship

Shih-Hui Weng(翁詩惠), Cheng-Han Yang (楊承翰) ,Yi-Ching Kuo(郭宜靜),Chi Wei(曲薇),
Hsiao-Ching Yang (楊小青)*
Department of Chemistry, Fu Jen Catholic University, Hsinchuang, Taipei, Taiwan 24205 *Tel: 02-2905-2534 ; E-mail: 068204@mail.fju.edu.tw*

ABSTRACT:

In this study, we used the tryptophan analogue, (2,7-aza)Trp, which exhibits water catalyzed proton transfer isomerization among N(1)-H, N(7)-H, and N(2)-H isomers, to probe the water environment of tryptophan-59 (Trp59) near the connecting loop region of ribonuclease Tl (RNase T1) by replacing the tryptophan with (2,7-aza)Trp. The resulting (2,7-aza)Trp59 triple emission bands and their associated relaxation dynamics, together with relevant data of 7-azatryptophan and molecular dynamics (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, which catalyzes (2,7-aza)Trp59 proton transfer in the excited state, giving both N(1)-H and N(7)-H isomer emissions. The existence of N(2)-H isomer in the loop-open form, supported by the MD simulation, 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. The loop-close form is relatively tight in space, which squeezes water molecules out of the interface of α-helix and β2 strand, joined by the connecting loop region; accordingly, the water-scant environment leads to the sole existence of the N(1)-H isomer emission. MD simulation also 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, providing the structural dynamic features of the connecting loop region in RNase T1.



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Probing Water Microsolvation Dynamics of Heme proteins toward Photochemical Application

Cheng-Han Yang (楊承翰),Tai-An Pan (潘泰安) and Hsiao-Ching Yang (楊小青)*
Department of Chemistry, Fu Jen Catholic University, Hsinchuang, Taipei, Taiwan
24205 *Tel: 02-2905-2534 ; E-mail: 068204@mail.fju.edu.tw*

Scientists have made tremendous endeavors in attempts to gain understanding of the water molecules in proteins via indirect measures, such as molecular dynamics simulation and/or probing the polarity of the local environment. 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 the structurally pending thromboxane A_2 synthase (TXAS), an endoplasmic reticulum 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. In combination with in-depth MD simulation, future quantitative correlation for the ESPT dynamics versus number/orientation of water molecules is feasible, showing different hydration environments between the substrate access channel, aqueduct water channel, and protein surface in, e.g., TXAS. The superb water sensing capability in terms of ESPT and ground-state N_1-H/N_2-H equilibrium thus provides an unprecedented tool for probing the water environment in bio-systems on a structural basis.

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Searching for New GSK3β Kinase Inhibitors: Thermodynamic Integration MD Simulation, Docking Computation, and Kinase Assay

Hsing-Chou Lee (李興洲), Wen-Chi Hsu (許文綺), An-Lun Liu (劉安倫), Hui-Jhen Shih (施惠真), Chia-Jen Hsu (許嘉仁), Ying-Chieh Sun (孫英傑)
Department of Chemistry, National Taiwan Normal University
sun@ntnu.edu.tw; 60242052s@ntnu.edu.tw (A.L. Liu)

Thermodynamic integration molecular dynamics simulation was used to investigate how TI-MD simulation preforms in reproducing relative protein-ligand binding free energy of a pair of analogous GSK3β kinase inhibitors of available experimental data, and to predict the affinity for other analogs. The computation for the pair gave a ΔΔG of 1.0 kcal/mol, which was in reasonably good agreement with the experimental value of -0.1 kcal/mol. The error bar was estimated at 0.5 kcal/mol. Subsequently, we employed the same protocol to proceed with simulations to find analogous inhibitors with a stronger affinity. Four analogs with a substitution at one site inside the binding pocket were the first to be tried, but no significant enhancement in affinity was found. Subsequent simulations for another 7 analogs was focused on substitutions at the benzene ring of another site, which gave two analogs with ΔΔG values of -0.6 and -0.8 kcal/mol, respectively. Both analogs had a -OH group at the meta position and another -OH group at the ortho position at the other side of the benzene ring. To explore further, another 4 analogs with this characteristic were investigated. Three analogs with ΔΔG values of -2.2, -1.7 and -1.2 kcal/mol, respectively, were found. Hydrogen bond analysis suggested that the additional hydrogen bonds of the added –OH groups with Gln185 and/or Asn64 were the main contributors to an enhanced affinity. Effect of displacement of crystal water molecules at binding site will be discussed. The prediction for better inhibitors should interest experimentalists of enzyme and/or cell assays.

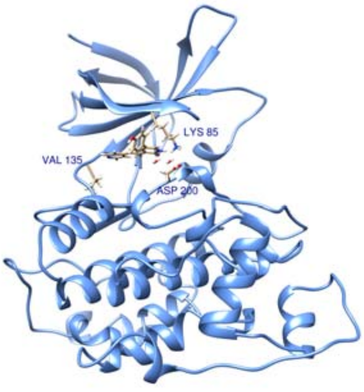

Figure 1: Binding of the reference compound with GSK3β kinase [1]

In addition, progress in using new module in Amber package, pmemd, and experimental measurement for finding new GSK3β kinase inhibitors are reported and discussed. [2]

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Homopharma: A new concept for exploring the molecular binding mechanisms and drug repurposing

Yi-Yuan Chiu[1](邱一原), **Jen-Hu Tseng[1*](曾仁琥)**, Kuan-Hsiu Liu[1](劉冠秀),
Chih-Ta Lin[1](林志達), Kai-Cheng Hsu[1](許凱程), Jinn-Moon Yang[1#](楊進木)
[1]Institute of Bioinformatics and Systems Biology, National Chiao Tung University

Drugs that simultaneously target multiple proteins often improve efficacy, particularly in the treatment of complex diseases such as cancers and central nervous system disorders. Many approaches have been proposed to identify the potential targets of a drug. Recently, we have introduced Space-Related Pharmamotif (SRPmotif) method to recognize the proteins that share similar binding environments. In addition, compounds with similar topology may bind to similar proteins and have similar protein-compound interactions. However, few studies have focused on exploring the relationships between binding environments and protein-compound interactions, which is important for understanding molecular binding mechanisms and helpful to be used in discovering drug repurposing. In this study, we propose a new concept of "Homopharma", combining similar binding environments and protein-compound interaction profiles, to explore the molecular binding mechanisms and drug repurposing. A Homopharma consists of a set of proteins which have the conserved binding environment and a set of compounds that share similar structures and functional groups. These proteins and compounds present conserved interactions and similar physicochemical properties. Therefore, these compounds are often able to inhibit the proteins in a Homopharma. Our experimental results show that the proteins and compounds in a Homopharma often have similar protein-compound interactions, comprising conserved specific residues and functional sites. Based on the Homopharma concept, we selected four flavonoid derivatives and 32 human protein kinases for enzymatic profiling. Among these 128 bioassays, the IC_{50} of 56 and 25 flavonoid-kinase inhibitions are less than 10 μM and 1 μM, respectively. Furthermore, these experimental results suggest that these flavonoids can be used as anticancer compounds, such as oral and colorectal cancer drugs. The experimental results show that the Homopharma is useful for identifying key binding environments of proteins and compounds and discovering new inhibitory effects. We believe that the Homopharma concept can have the potential for understanding molecular binding mechanisms and providing new clues for drug development.

Reference

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Structural Interactomes of Multiple Genomes Reveal Drug-Gene-Pathway-Disease Relationships

Yu-Shu Lo, Sing-Han Huang, Chun-Yu Lin, and Jinn-Moon Yang
Institute of Bioinformatics and Systems Biology, National Chiao Tung University

ABSTRACT

One of crucial steps toward understanding the spatiotemporal dynamics and biological functions of a cellular system is to investigate protein-protein interaction (PPI) networks. Despite the availability of large-scale methods to analyze PPI networks, these methods are often unable to provide the detailed atomic PPI models and the PPI conservation in the networks to connect the relationship between drugs, genes, pathways, and diseases. Here, we have developed a method for enlarging the PPI networks with structural annotation through PPI families and 3D-domain interologs. To our best knowledge, this work is the first to construct structure resolved PPI networks across multiple species, including H. sapiens, M. musculus, and D. rerio. The structural alignment PPI network can describe the binding mechanisms and relationships between the drugs, genes, pathways, and diseases.

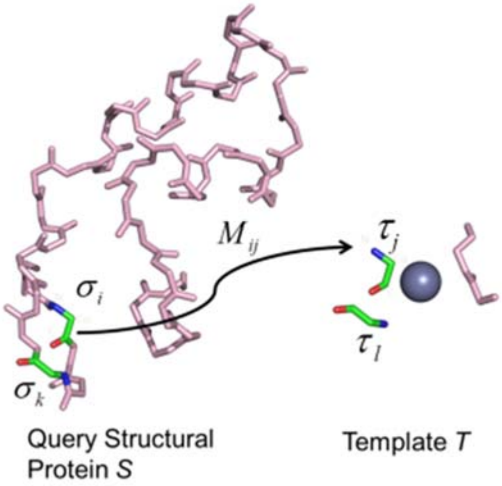
The derived PPIs with atomic residue-based binding models in the derived structure resolved network achieved highly agreement with Gene Ontology similarities. The architectures of these PPI networks of H. sapiens, M. musculus, and D. rerio are scale-free network which is consistent with most of the cellular networks. In addition, our derived networks can reflect consensus proteins and modules which are high conserved appearing in multiple organisms. These consensus proteins are often the essential genes (proteins) and highly related to the diseases recorded in OMIM. Experimental results also indicate that the mutations of interacting residues on the PPIs often related to diseases and its corresponding pathways.

MIB: a Metal Ion–Binding sites prediction tool

Jyn-Han Li (李居翰), Chih-Hao Lu (陸志豪)

Graduate Institute of Basic Medical Science, China Medical University, Taiwan
zxcyzero@hotmail.com

The structure of a protein determines its function and its interactions with other factors. Regions of proteins that interact with ligands, substrates, and other proteins, tend to be conserved both in sequence and structure, and the residues involved are usually in close spatial proximity. More than 90,000 protein structures are currently found in the Protein Data Bank, and approximately one-third contain metal ions which are essential for function. Identifying and characterizing metal ion–binding sites experimentally is time-consuming and costly. For the work reported herein, we developed a method that uses sequence and structural information to predict the metal ion–binding residues. Thirteen kinds of metal ions (Ca^{2+}, Cu^{2+}, Fe^{3+}, Mg^{2+}, Mn^{2+}, Zn^{2+}, Na^{+}, K^{+}, Cd^{2+}, Fe^{2+} ,Ni^{2+}, Hg^{2+} and Co^{2+}) binding residues had been collected and constructed as binding templates, which are metal binding residues within 3.5Å around the metal ions. The structural comparison between query proteins and templates was carried out by using the fragment transformation method. Our prediction tool is at http://140.128.63.8/MIB/.



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