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^{2}CoMSA)

暨

2017 年理論計算化學小組九月研討會
Theoretical and Computational Chemistry September Conference 2017

Program

September 6, 2017

B07 room, Dept. of Chemistry, NTHU

09:40-10:00　registration opens

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

Section I （Chair：Chao-Ping Hsu）

NO.01 10:10-10:25　**Ming-Hsiu Hsieh** 謝明修 (National Chiao Tung University)

“ Mechanistic Study of Radical Pathway in N-Hetrocyclic Carbene(NHC) catalyzed Benzoin Condensation”

NO.02 10:25-10:40　**Bing-Cheng Ji** 紀秉承 (National Taiwan University of Science and Technology)

“ DFT Study of Methanol Decomposition on Ru-Pt clusters supported on Boron and Nitrogen Co-doped Graphene Surface”

NO.03 10:40-10:55　**Shi-En Fu** 傅識恩 (National Taiwan University of Science and Technology)

“ Role of Water on CO oxidation over Boron-Nitrogen sheet supported Gold Clusters (Au_{19}) *-A First Principles study”*

Section II （Chair：Jyh-Chiang Jiang）

NO.04 10:55-11:10　**Cheng-Feng Lan** 藍長風 (Academia Sinica)

“ The anisotropy and temperature dependence in the mobility of rubrene”

NO.05 11:10-11:25　**Chi-You Liu** 劉啟佑 (National Taiwan Normal University)

“ Adsorption Mechanisms of Lithium Polysulfides on Graphene-Based Interlayers in Lithium Sulfur Batteries ”

NO.06 11:25-11:40　**Sin-Mu Jhan** 詹欣穆 (National Taiwan University)

“ Connections Between Current Distributions and Molecular Orbitals in Quantum Transport Through a Single Molecular Junction”

11:40-12:40　Lunch

12:40-13:40 Poster

P01	Bo Li 李波	Remarkable nonlinear optical response of excess electron compounds: Theoretically designed alkali-doped aziridine M-(C_2NH_5)n
P02	Wei-Huan Kao 高偉桓	A calculational study on boron-doped carbon nanotubes as a potential metal-free catalyst for CO oxidation
P03	Ranganathan Krishnan 任剛	First-principles investigation of CO oxidation on N- and B-doped Penta-graphene sheet
P04	Chun-Hao Huang 黃俊皓	Room-temperature phosphorescence from small organic systems containing thiocarbonyl moiety
P05	Gou-Tao Huang 黃國韜	Catalytic roles of Histidine and Arginine in Pyruvate Class II Aldolase
P06	Guan-Ying Du 杜冠瑩	Electrolyte Directed Sulfur Reductions in Metal-Sulfur Batteries
P07	Ming-Yi Huang 黃明怡	Determine the Unknown Structure of Thromboxane Synthase by Molecular Dynamics Simulation Combined with Small-Angle X-ray Scattering
P08	Ying-Ting Lin 林映廷	Theoretical investigation of potential synthetic routes of C_{60} based on molecular Dürer's nets derived from its 158 irreducible resonance structures
P09	Ta-Wei Yang 楊大緯	A Computational Study on Magic-Size $(CdSe)_{13}$ Clusters with TDDFT Calculations

Section III （Chair：Jen-Shiang Yu）

NO.07 13:40-13:55 **Yi-Chen Chen** 陳奕丞 (Academia Sinica)

" Cyclic lin-42 signal and its stochastic consequence dominate the temporal heterogeneity of cell migration in C. elegans"

NO.08 13:55-14:10 **Ho-Wei Wu** 吳和為 (National Taiwan University)

" The attenuation effects of upstream open reading frames on translation variation"

14:10-14:20 Coffee Break

Section IV （Chair：Yuan-Chung Cheng）

NO.09 14:20-14:35 **Karl Kue** 陳學仁 (Academia Sinica)

“ A Hamiltonian-Independent Generalization of the Fragment Difference Scheme”

NO.10 14:35-14:50 **Chen-Wen Wang** 王辰文 (National Chiao Tung University)

“ Franck-Condon simulation with damped harmonic oscillators: solvent effects for molecular electronic spectroscopy of carbazole”

Section V （Chair：Chia-Chun Chou）

NO.11 14:50-15:05 **Yao-Wen Chang** 張耀文 (National Taiwan University)

“ Polarized excitons and optical activity in single-wall carbon nanotubes”

NO.12 15:05-15:20 **Cheng-chau Chiu** 邱政超 (Academia Sinica)

“ An Attempt to Understand the Trends in the Electronic Structure of MX_2 *3d Transition Metal Dihalide Monolayers”*

15:20-15:35 Coffee Break

15:35-16:00 Closing (Awards) Ceremony （Chair：Chia-Chun Chou）

Oral

Mechanistic Study of Radical Pathway in N-Heterocyclic Carbene (NHC) catalyzed Benzoin Condensation

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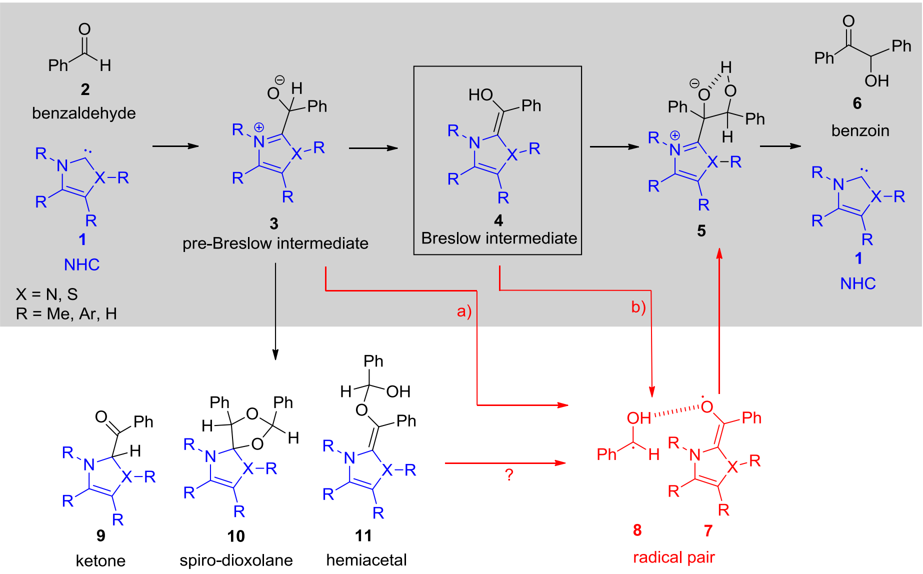
N-heterocyclic carbenes (NHCs) are widely used as organocatalysts in various organic reactions, including benzoin condensation. NHC-catalyzed benzoin condensation is known to proceed *via* two key species, the zwitterionic adduct **3** (pre-Breslow intermediate) formed by the attack of NHC on benzaldehyde and the Breslow intermediate **4**.[1] Recently, the radical-mediated pathway has been suggested as a possible route to benzoin products.[2] In our study, four pathways in Scheme 1 from **3**, **4**, **9** and **11** to form the radical pair **[7 8]** are investigated by DFT calculations. Computational results show that the radical pair is the most likely produced through the hydrogen atom transfer from the Breslow intermediate to benzaldehyde. However, the barriers for the radical formation are higher than that for the non-radical mechanism, which suggests that the radical channel is potentially accessible at high temperature, and could compete with the non-radical route. Hydrogen bond interactions due to protic solvent molecules do not tend to alter the mechanistic preference between the radical and non-radical pathways.



Scheme 1: Catalytic cycle of NHC-catalyzed benzoin condensation. Non-radical pathway is specified in shadow background color.

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DFT Study of Methanol Decomposition on Ru-Pt clusters supported on Boron and Nitrogen Co-doped Graphene Surface

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Over the past few decades, there has been a great attention in finding alternative clean energy resources due to the decrease in fossil fuels. Among them, Hydrogen is considered as a clean and high efficient energy carrier because of its abundant availability and environmental friendliness. [1] At present, a number of different methods are used to produce the hydrogen. In addition, hydrogen production from renewable sources such as biomass and natural gas is also considered. Among the various natural gases, methanol has been regarded as an excellent H_2-containing source because of its biodegradability. [2] The decomposition of methanol over metal catalyst has been suggested as an efficient way to generate hydrogen, however, the use of catalyst has some shortcomings such as poisoning of catalyst sites. Recently, graphene has been demonstrated as a very effective support for electro catalysts for methanol and hydrogen fuel cells due to its less CO poisoning. [3] To further improve the catalytic activity of graphene supported material, here we considered Boron-nitrogen co-doped graphene (BNG) support for Ru-Pt clusters and investigated the methanol decomposition using density functional theory calculations. The calculated adsorption energies for methanol on different possible sites of Ru-Pt / BNG surface are -0.61 eV to -0.99 eV, which are larger than methanol adsorbed on Pt(111) and Ru(001) surfaces. We considered two possible methanol decomposition pathways including dehydrogenation via the O-H bond breaking to form methoxide (CH_3O) and the C-H bond breaking to form hydroxymethyl (CH_2OH) as an initial steps. We also considered the dehydrogenation reactions from the initial steps for the hydrogen production. We found that the calculated reaction barriers for the methanol decomposition is significantly lower than the previous studies of pure and doped metal surfaces. Our results indicate that one-layer Ru-Pt clusters supported BNG surface is an economical catalyst for the hydrogen production via methanol decomposition compared to pure Pt surface.

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Role of Water on CO oxidation over Boron-Nitrogen sheet supported Gold Clusters (Au_{19}) -A First Principles study

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Carbon monoxide (CO) is a highly toxic gas for human because of its high affinity with hemoglobin, and it causes many illnesses, suffocation, and sudden death. [1] Therefore, the elimination of CO is attracted practical importance to control the environment. Among the other methods, the catalytic oxidation of CO to CO_2 over a heterogeneous catalyst surface is the suitable method in CO elimination. Since from the pioneering work by Hartuta et al., [2] on CO oxidation to CO_2 using gold nanoparticles as catalysts on has been a topic of great interest. Previously, many theoretical and experimental studies explored the catalytic activity of Au clusters supported on the pure metals and metal oxide surfaces. To improve the CO oxidation further, here we considered Au_{19} clusters supported on the boron-nitrogen sheet (BN) and investigated its catalytic activity towards CO oxidation using First principle calculations. Further, we also explored the presence of water on the CO oxidation on Au clusters supported on the boron-nitrogen sheet. Our results indicate that Au_{19} clusters stably adsorbed on BN surface and it is more active because of the significant charge transfer from the BN surface. We found that the IR spectrum of adsorbed CO on Au_{19}/BN surface is blue shifted with increasing the moisture content, which is in agreement with the previous experimental study. [3] By exploring the all possible CO oxidation pathways, we found that the reaction barrier for CO oxidation on the Au_{19}/BN surface is only 0.25eV, which is significantly lower than the previously studied materials. The present theoretical study suggests that Au_{19} clusters supported on BN surface could be a promising catalyst for CO oxidation at very low-temperature conditions.

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The anisotropy and temperature dependence in the mobility of rubrene

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The mobility in molecular crystals exhibits anisotropy and power-law temperature dependence, which has not been reproduced simultaneously theoretically. In this work, we developed an analytic expression to account for the anisotropic mobility observed in molecular crystals. The charge mobility is related to the friction coefficient Drude model, and the latter is expressed in terms of force-force correlation function through the fluctuation-dissipation theorem, calculated with a polaron model Hamiltonian. We found that the anisotropy of mobility calculated is similar to experimental observations: at 300 K the ratio of mobility of the fast-axis over slow-axis, μ_b/μ_a, was found to be about 3, while our model yields a ratio of 8.90. Moreover, the temperature dependence of mobility follows the power law observed, T^{-2} (150~300K), which is close to the T^{-2} observed. With most parameters determined by first-principle calculation, there was only two adjustable parameters, and our model offers a way to predict charge mobilities of molecular crystals.

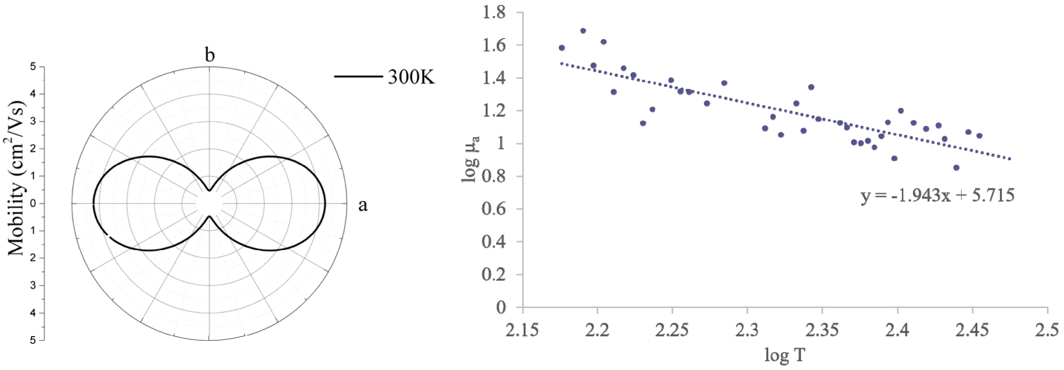

Figure 1 (left) Angular dependence of mobility for rubrene crystal. a and b axis are when the imposed electric field and current observed parallel to the crystal axes a and b, respectively. (right) The temperature-dependence of mobility of rubrene. Shown are mobility along a axis as the left. μ_a is mobility in cm^2/Vs, T is temperature in Kelvin.

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Adsorption Mechanisms of Lithium Polysulfides on Graphene-Based Interlayers in Lithium Sulfur Batteries

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One of the most critical problems in lithium-sulfur (Li-S) batteries is the shuttle effect. The transfer of soluble lithium polysulfides (LiPSs) from the sulfur cathode to the lithium anode leads to a degradation in Li-S battery capacity and life cycles. Recent studies reveal that the carbon-based interlayer materials introduced between the cathode and anode can effectively improve the shuttle effect problem and increase the battery life cycles. In this work, different types of the N-doped, S-doped, and N, S co-doped graphene surfaces are investigated by theoretical calculations. We find that a strong interaction may exist between some of the heteroatom-doped graphene surfaces and lithium ions, and that the adsorption of LiPSs may proceed via one of the three mechanisms, the dissociative, the destructive, and the intact adsorptions. Detailed structural and electronic analyses indicate that the Li-trapped N, S co-doped graphene interlayers (NSG1 and NSG2) could efficiently reduce the shuttle effect through the intact adsorption mechanism. Our results provide a plausible explanation on the observed better performance of the N, S co-doped graphene interlayers in Li-S batteries.

Connections Between Current Distributions and Molecular Orbitals in Quantum Transport Through a Single Molecular Junction

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Connections between the current distribution within a single molecular junction and molecular orbitals are examined in this paper. By using the first-order perturbation theory and nonequilibrium Green's function techniques in the framework of Hückel theory, we derive a simplified local transmittance formula from the local current formula. The formula shows that the local transmittances are closely related to the off-diagonal elements of transition density matrices. Moreover, a few simple molecular junctions consisting of single- and multi-ring conjugated systems illustrate the connections between the off-diagonal elements of transition density matrices and the local transmittances. We find that the distribution of local currents inside the molecular junctions can be faithfully described through consideration of only the transition density matrices of degenerate or nearly-degenerate molecular orbitals.

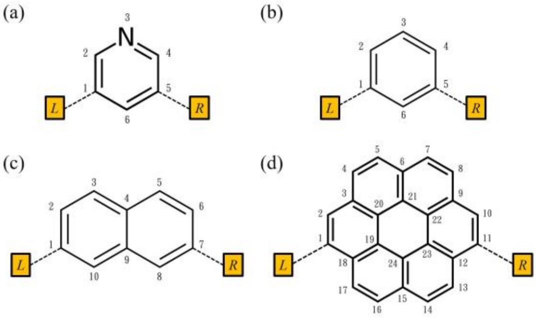

Figure 1

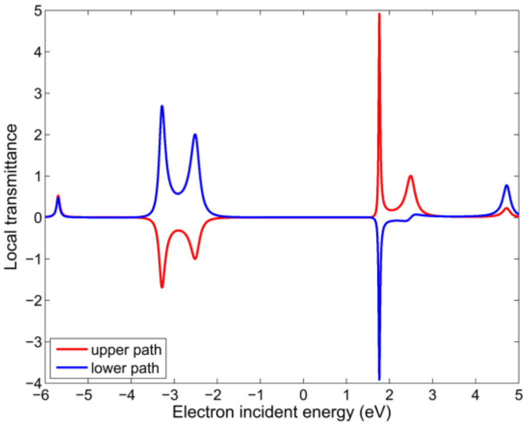

Figure 2

Figure 1: Schematic diagrams of (a) pyridine, (b) benzene, (c) naphthalene, and (d) coronene molecular junctions. The yellow blocks represent the left and right electrodes.

Figure 2: Local transmittances of the pyridine molecular junction as a function of electron incident energy. The upper path is from atom 1 to 2 to 3 to 4 to 5. The lower path is from atom 1 to 6 to 5.

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Cyclic *lin-42* signal and its stochastic consequence dominate the temporal heterogeneity of cell migration in *C. elegans*

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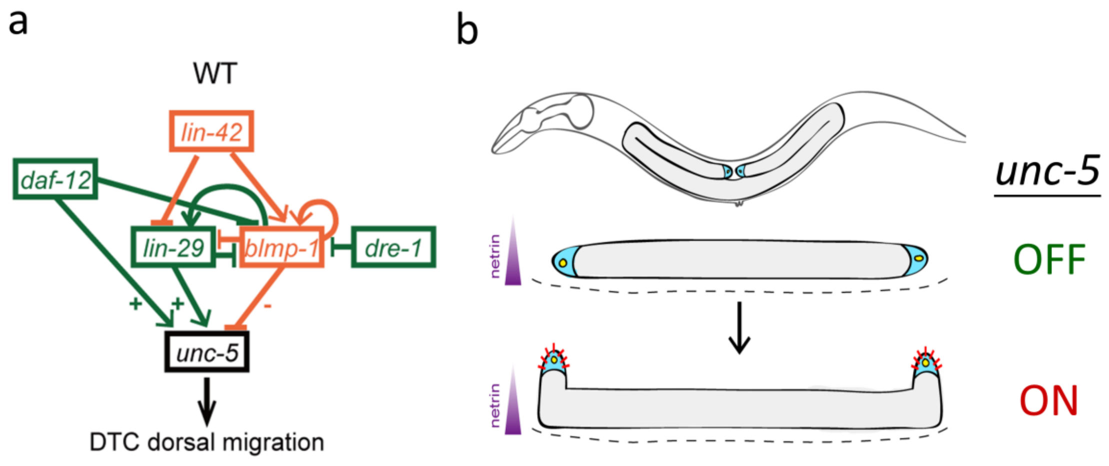
Gene expression noise is correlated with variability in cell fate determination. How noise leads to phenotypic variations during animal development is still not clear. Combined together with computational and experimental approaches, we studied the gene expression noise and phenotypic variations in gonadogenesis. In *C. elegans*, the morphology of hermaphroditic gonad is determined by the migration path of two distal tip cells (DTCs). We determined a genetic network including the cyclic expressing, period-like *lin-42* for spatiotemporal control of DTC dorsal migration. Feedback controls in the genetic network regulate the temporal expression, as well as the expression level of the guidance receptor UNC-5. UNC-5 expression exceeding the threshold ensures timely distal tip cell migration. In the mutant with heterogeneous phenotypes, UNC-5 is produced near the threshold under the cyclic control of *lin-42*. Shifting the threshold and suppressing upstream *lin-42* noise both reduce heterogeneity in this mutant. Our work demonstrates how the cyclical input signals contribute to temporal heterogeneity in cell migration.



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The attenuation effects of upstream open reading frames on translation variation

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The translational regulation can play an important role in gene expression. Our previous studies in photomorphogenic *Arabidopsis* revealed upstream open reading frame (uORF) in 5’ leader sequence can decrease translation efficiency of its main coding sequence on the same transcript[1]. The prevalent and evolutionarily conserved presence of uORFs triggers an intriguing question: whether uORFs play other regulatory roles in addition to translational repression. Through the gene expression processes, the transcripts variation would be inherited into protein via translation, and thus the fluctuation of transcripts can propagate to introduce additional variation into the protein production[2]. We hypothesize the uORF-mediated translational regulations might not only in the repression of translation efficiency, but also in the attenuation of transcripts to be engaged in translation in a *cis*-acting manner. By doing so, uORFs could buffer transcripts variations for steady-state protein production. To investigate these phenomena, a mathematical model with or without uORF was built to compare its function on translational regulation. To get a glimpse, the stochastic simulation approach demonstrated the protein abundance trajectory in uORF-regulated scenario was more smooth and stable than one without uORF-mediated regulation under the same protein mean value. Furthermore, the exact protein variance in the model was calculated mathematically with linear noise approximation. Given biologically reasonable parameters for uORF regulation, the protein variances were always lower than one without uORF-mediated regulation. The translation of main coding sequence can be under surveillance by the uORF(s) in *cis* on the same transcript without introducing extrinsic variation. Therefore, the uORF serves as a coupled incoherent feedforward autoregulation that sequentially attenuates translation in the main coding sequence. In conclusion, the uORF-mediated attenuation can fine-tune transcripts to be actively engaged in translation, which might prevent sudden fluctuation in protein expression levels.

References

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A Hamiltonian-Independent Generalization of the Fragment Difference Scheme

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The fragment excitation difference (FED) scheme is a useful method for calculating the complete diabatic couplings of various energy transfer systems, especially non-charge transfer systems. The current implementation of FED is limited to single-excitation methods due to the ambiguities in the treatment of the transition density matrix which is needed for the off-diagonal values of the FED matrix. We have developed a generalized FED scheme called θ-optimized FED (θ-FED) scheme which does not require the transition density matrices. We calculated both singlet and triplet excitation energy transfer couplings of naphthalene using the θ-FED with single-excitation and multi-excitation methods—our calculations include up to triple excitations. Comparison of θ-FED couplings with FED couplings shows that the two methods are equivalent and that the θ-FED scheme is a valid approach to calculate FED couplings of wave functions obtained from multi-excitation methods. This approach allows for finding diabatic states, and the corresponding couplings, of a much broader set of Hamiltonians.

Franck-Condon simulation with damped harmonic oscillators: solvent effects for molecular electronic spectroscopy of carbazole

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CZ(carbazole) has intrinsic chromophoric properties that plays a vital role in polymeric systems[1-3] and could be widely brought into application in many fields. Such characteristics intrigue our interest to study solvents effects in molecular vibronic spectra. All the work are based on well-developed Franck-Condon approach with damped harmonic oscillators for interpreting solvent-enhanced absorption/fluorescence spectra of CZ.

In this study, we first provide optimized electronic structure of CZ for both ground(S_0) and first excited state(S_1) at the level of (TD)CAM-B3LYP plus polarizable continuum model(PCM) in *n*-hexane and acetonitrile solvents, respectively. These both optimized structures are then treated by Franck-Condon simulations with the use of damped harmonic oscillators to obtain vibronic molecular spectra. Finally, nuclear vibrations should be considered. These related work has been practically done to rubrene[4] and perylene molecule[5]. Since each hydrogen in CZ is subjected to different environment in solution and thus raises the complexity for scaling, we scrupulously change scaling parameter(ξ) to each atom in CZ. In general, we find totally 20 active modes, and three of which are in particular more active to the scaling parameter changes, this also leads to significant enhancement of the second band in either absorption or fluorescence spectra. Our present modeling work are in good agreement with experiment, ensuring us a better understanding to the physical insight for CZ. We give detailed results and analysis with corresponding modes contributed to the spectra in this presentation.

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Polarized excitons and optical activity in single-wall carbon nanotubes

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The polarized transitions and optical activity of single-wall carbon nanotubes (SWNTs) are studied theoretically by Pariser-Parr-Pople (PPP) Hamiltonian and excitonic theory. Based on the intrinsic helical and rotational symmetries, the single-electron energy and properties of a SWNT with arbitrary chirality can be characterized by a helical band structure, which can be solved analytically without considering Coulomb interaction. The dipole-moment matrix elements, magnetic-moment matrix elements, and the selection rules can also be found under the scheme. With the Coulomb interaction included, the absorption and circular dichroism (CD) spectra of SWNTs are calculated by Hartree-Fock approximation and singly-excited configuration interaction. The features of parallel-polarized and cross-polarized excitons in the spectra are then studied. The results are well comparable with the reported experimental spectra. The effects of electron-hole asymmetry and axial magnetic field interaction on the polarized excitons are also discussed. It is found that, the selection rule of cross-polarized transition not only reflects the intrinsic symmetries of SWNTs but also indicates the handedness of the exciton absorption, thus it can be used to analyze the Faraday rotation in the CD spectrum.

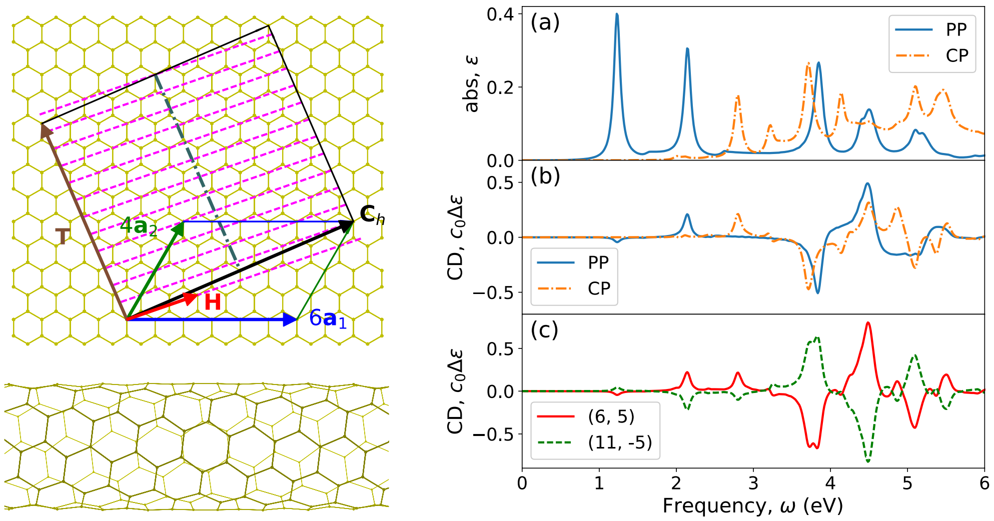

Figure 1: Left: Unrolled and rolled-up (6,4)-SWNT; Right: absorption and CD spectra of (6,5)-SWNT.

References

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An Attempt to Understand the Trends in the Electronic Structure of MX_2 3*d* Transition Metal Dihalide Monolayers

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Due to their wide possibilities of applications, monolayers formed by transition metal dichalcogenides, like MoS_2 have been in the focus of recent research. At variance, the interest in the isostructural transition metal dihalide monolayers is yet comparatively low. Only a few studies have been conducted to explore such species in a systematic way. [1,2]

In this study, [3] we use periodic DFT methods at both LDA and GGA level to investigate, which combinations of 3*d*-transition metal and halide anion can form stable structures that may eventually be synthesized, and try to predict their electronic properties.

A somewhat surprising finding is that the valence isoelectronicity principle seems to only hold partially here: MX_2 monolayers formed by the same metal but different halide anions seem to have different ground state electronic structures with differing magnetic moments. In addition, we see that there are some differences between the electronic structures predicted by LDA and GGA calculations. Both findings are associated with differences in the relative stability between high spin and low spin states. We will try to illustrate that, despite the differences between the LDA and GGA data, the results obtained with the two types of functionals follow the same trend.

In addition to the electronic structure of the monolayers, we will also discuss, at the example of the hydrogen adsorption, the trends in the reactivity of such structures.

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Poster

Remarkable nonlinear optical response of excess electron compounds: Theoretically designed alkali-doped aziridine M-$(C_2NH_5)_n$

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Previous reports have pointed out electride can serve as candidates of nonlinear optical(NLO) materials with remarkable NLO response[1-4]. We theoretically designed a series of new electride molecules with excellent NLO response by CAM-B3LYP method with 6-311+G(3df) for K and aug-cc-pVTZ for other atoms. The static first hyperpolarizability values(β_0) of M-$(C_2NH_5)_n$(M=Li, Na and K; n=1-4) are found very large with peak value 3.3×10^6(a.u.). There are three large values for β_0 appeared at n=4 as 320605(Li), 3329145(Na), 1317491(K) are 10 to 100 times larger than the counterpart of M@Calix[4]pyrrole as 22435 (M=Li), 26614 (M=Na) and 27058 (M=K) (the values are based on the present same calculation for M@Calix[4]pyrrole). Time-dependent CAM-B3LYP calculation demonstrate that those electride molecules exhibit high charge transfer. Furthermore, first hyperpolarizability density analysis show that electron spatial contribution to β_0 values mainly come from surrounding of alkali metal and it conforms why β_{zzz} values are largely positive and negative value. The present systematically investigation of a series of typical electride molecules M-$(C_2NH_5)_n$ as an alkali-doped organic complexes can provide potential application for high-performance novel NLO materials.

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A calculational study on boron-doped carbon nanotubes as a potential metal-free catalyst for CO oxidation

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By means of density functional theory (DFT) calculation, we used the carbon nanotubes with different content of doped boron as potential metal-free catalysts for the CO oxidation. In order to find the possible active sites for CO oxidation, we investigated the O_2 adsorption behavior on different position of 1 and 2 B-doped carbon nanotubes and find the most stable structures of adsorbed O_2 are flat on C-B site of both nanotubes with the adsorption energies of -0.85 and -1.29 eV, respectively.

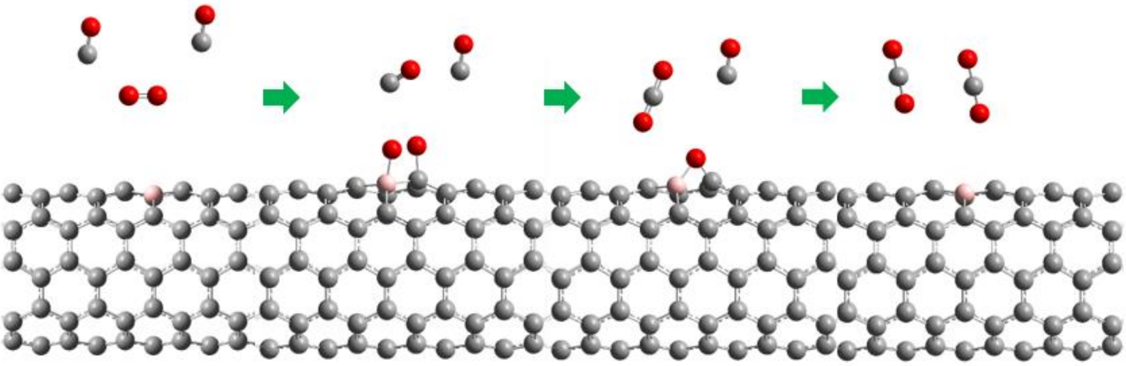

Figure 1: The reaction process on B-doped carbon nanotubes.

Then we investigated the catalytic reaction paths of CO oxidation, divided into two parts: (1) $CO + O_2^* \rightarrow CO_2 + O^*$, where the activation energy required for B-doped and BB-doped catalysts are 0.34 eV and 0.42 eV, respectively; (2) $O^* + CO \rightarrow CO_2$: the activation energy required for BB-doped is 0.14 eV. The reaction is through the Eley-Rideal mechanism (ER) to produce carbon dioxide. After two CO oxidation processes, the carbon nanotubes can be recovered to their original structures and recycled. Finally, we compare the catalytic ability of the doped surface under different boron content.

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Room-temperature phosphorescence from small organic systems containing thiocarbonyl moiety

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Abstract

Small organic molecules based on the unnatural DNA base pair d**TPT3** are designed and synthesized, among which compounds bearing the thiocarbonyl group, compared with their carbonyl counterparts, show a much larger SOC integral between $S_1(^1n\pi^*)$ and $T_1(^3\pi\pi^*)$ states due to proper energy level alignment and heavy sulfur atom effect, resulting in appearance of both fluorescence and phosphorescence in solution and solid at room temperature

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Catalytic roles of Histidine and Arginine in Pyruvate Class II Aldolase

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The retro-aldol reaction catalyzed by pyruvate class II aldolase is investigated with QM/MM metadynamics; this enzyme converts the substrate of 4-hydroxy-2-ketoacid into pyruvate enolate and aldehyde through the aldol cleavage. The simulation shows that the initial deprotonation of the substrate (**preR** → **R1** → **R2**, shown in Figure 1) is completed by the two residue bases of His45 and Arg70, and the metal-bound water molecule acts as a medium during the proton transfer. The aldol cleavage leading to aldehyde and pyruvate enolate (**R1** → **P1**) is the rate-determining step, and the calculated barrier of about 14 kcal mol^{-1} agrees reasonably with experimental data. The catalytic roles of Arg70 are to protect the alkoxide group from being protonated, and to stabilize the enolate oxyanion of the product. The solvent isotope effect observed in experiments is possibly because the hydrogen proton of the metal-bound water of Arg70 is replaced with deuterium.

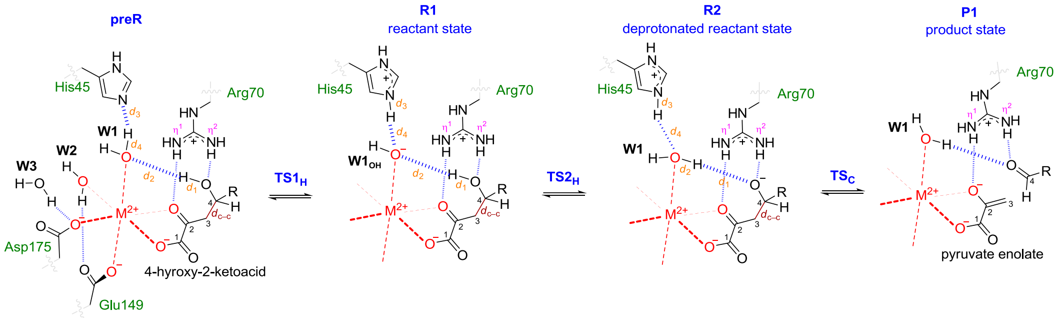

Figure 1: Mechanism of aldol cleavage.

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First-principles investigation of CO oxidation on N- and B-doped Penta-graphene sheet

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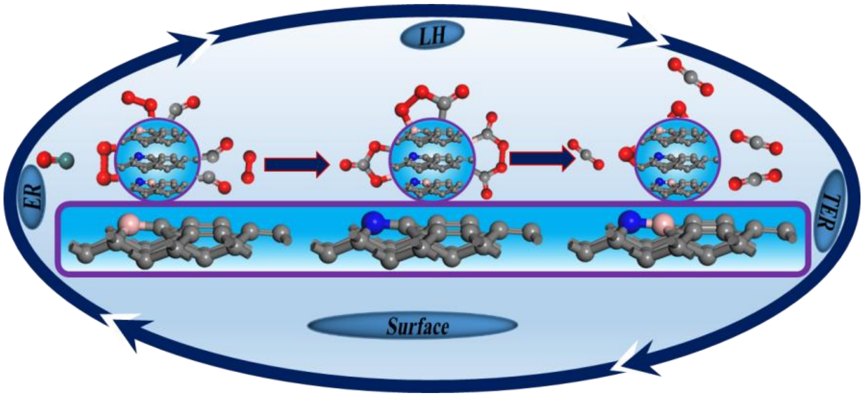
ABSTRACT:

We report a systematic study of carbon monoxide (CO) oxidation reaction over N- and B-doped penta-graphene (NBPG) surface by using the first principle density functional theory (DFT) calculations. This work is to investigate the possibility of synergized O_2 activation by CO for CO oxidation on NBPG. CO oxidation takes place via a two-step process with O_2 dissociation; (i) $CO + O_2 \rightarrow CO_2 + O$ and $CO + O \rightarrow CO_2$ (ii) $CO + O_2 \rightarrow OOCO \rightarrow CO_2 + O$ reactions and a new mechanism of (iii) $2CO + O_2 \rightarrow OCO - OCO \rightarrow 2CO_2$. Considering the three kind of mechanism involves for CO oxidation process, such that; Eley–Rideal (ER), Langmuir–Hinshelwood (LH) mechanisms and Tri-molecular Eley–Rideal (TER) mechanism proposed recently. Given the relatively small and enough of reaction barriers of the rate-limiting steps for the ER, LH and TER mechanism, these three mechanisms are able to occur at low temperature. The current study may provide valuable clues for developing low-cost and higher catalytic carbon-based materials, and then open a new avenue for CO oxidations.



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Electrolyte Directed Sulfur Reductions in Metal-Sulfur Batteries

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Fundamental understanding of solvent's effect in lithium-sulfur (Li-S) batteries is crucial for improving the battery performance. Previous UV-Vis experiments indicate that the $S_3^{\cdot -}$ radical or the S_4^{2-} intermediates may be selectively stabilized by solvents with high or low donor numbers, respectively, leading to different reaction rates of polysulfides in Li-S batteries.[1] We perform extensive computational investigations on a series of sulfur and polysulfide bond breaking and reduction reactions. The reactions of polysulfides with or without explicit lithium ion coupling are both considered in five solvent systems ranging from low to high dielectric constants and donor numbers. To account for the effect of the empirical parameter, the donor number of the solvents, we also compute the successive binding energies of lithium, sodium or potassium ions with explicit solvent molecules. We find that the influence of the solvent system may be indirectly exerted on the polysulfide reaction pathways via the formation of the solvent-cation complexes. Our results, which are consistent with the experimental observations, emphasize how the electrolyte system plays a leading role in Li-S reaction pathways.

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Determine the Unknown Structure of Thromboxane Synthase by Molecular Dynamics Simulation Combined with Small-Angle X-ray Scattering

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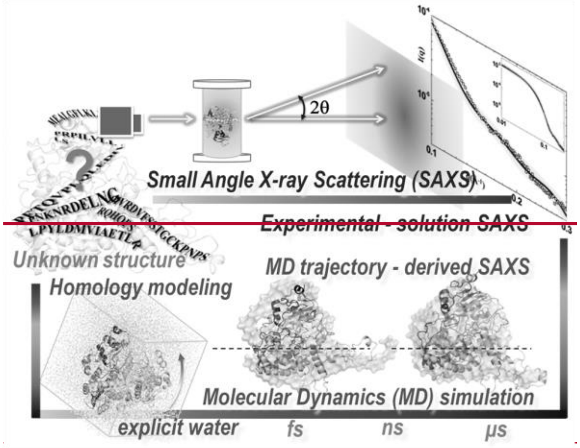
A combination of molecular dynamics (MD) simulations and small-angle X-ray scattering (SAXS) has emerged as the approach of choice for studying protein structures and dynamics in solution. This approach has potential applications for membrane proteins that neither are soluble nor form three-dimensional crystals easily. In the present study, we explore the water-coupled dynamic structures of thromboxane synthase (TXAS) and prostacyclin synthase (PGIS) from scanning SAXS/HPCL/UV-vis measurements combined with MD trajectory ensemble analyses. Both protein are heme-containing proteins and belong to the cytochrome P450s (CYP450s) family. They are counter proteins in playing crucial roles in cardiovascular homeostasis. Up to date, PGIS have the x-ray structures but the structural information about TXAS is still limited with the lack of X-ray crystallographic structure. The use of homology modeling of the TXAS structure with ns-μs explicit water solvation MD simulations allows much more accurate estimation of the configuration space with loop motion and origin of the protein behaviors in solution. In contrast to the stability of the conserved PGIS structure in solution, the pronounced TXAS flexibility has been revealed to have intrinsically unstructured loop regions in connection with the characteristic P450 structural elements. The MD simulation-derived and experimental-solution SAXS results are in excellent agreement. The significant protein internal motions, whole-molecule structures, and potential problems with protein folding, crystallization, and functionality are examined.



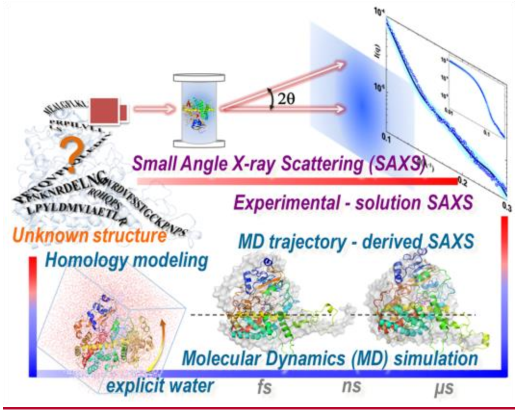


Figure. Homology Modeling and Molecular Dynamics Simulation Combined with X-ray Solution Scattering Defining Protein Structures of Thromboxane and Prostacyclin Synthases.

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Theoretical investigation of potential synthetic routes of C_{60} based on molecular Dürer’s nets derived from its 158 irreducible resonance structures

Since the discovery of C_{60} in 1985, many attempts have been made in the synthesis of this class of beautiful molecules through chemical means. But most of them have been unsuccessful, except the one claimed by L. Scott in 2004 through the photochemical reactions with a yield less than 1% by a precursor, $C_{60}H_{30}$, corresponding to an unfolded three-fold symmetric fullerene with fifteen single bonds breaking. Here, we wish to point out that this precursor can be considered as a particular form of Dürer’s polyhedral net, which will be called molecular Dürer’s net, lying flat on a plane and can be folded back to become the original C_{60}. Moreover, many chemically sensible fullerene nets that could become potential precursors for the chemical synthesis of C_{60} can be deduced from C_{60}‘s 158 irreducible resonance structures. The thirty double bonds in most of these resonance structures form different kinds of interesting labyrinth patterns on a fullerene polyhedron. Systematically removing some of these double bonds, the remaining structures then form unfolded molecular Dürer’s nets with the chemical formula $C_{60}H_{60}$ or $C_{60}H_{30}$ by adding suitable number of hydrogen atoms to complete the incomplete valences. We believe that these fullerene nets derived from irreducible resonance structures are potentially sensible precursors which can be used as a guide of the total synthesis of C_{60} for chemists.

A Computational Study on Magic-Size $(CdSe)_{13}$ Clusters with TDDFT Calculations

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Detailed structures of (CdSe)n nanoclusters are difficult to be characterized experimentally. We use the DFT calculations to clarify the exact geometric shape of (CdSe)n nanoclusters. Three possible structures of bare $(CdSe)_{13}$ isomers, i.e. the cage-core, the cage, and the tubular geometries, as well as the ligated isomers, $(CdSe)_{13}L_{13}$, ($L=MeNH_2$, $EtNH_2$), are investigated in this work.[1] Surprisingly, the tubular structure is found to be greatly stabilized upon ligand attachment and may become even more stabilized than the previously assumed cage-core geometry.[2, 3] A dimerization between two ligated tubular $(CdSe)_{13}L_{13}$ clusters is also considered based on the strong dipole-dipole interactions between two tubular monomers. Overall, the theoretically estimated size and the absorption spectrum of the dimerized tubular CdSe clusters show a good agreement with the experimental SXAFS and optoelectronic measurements.

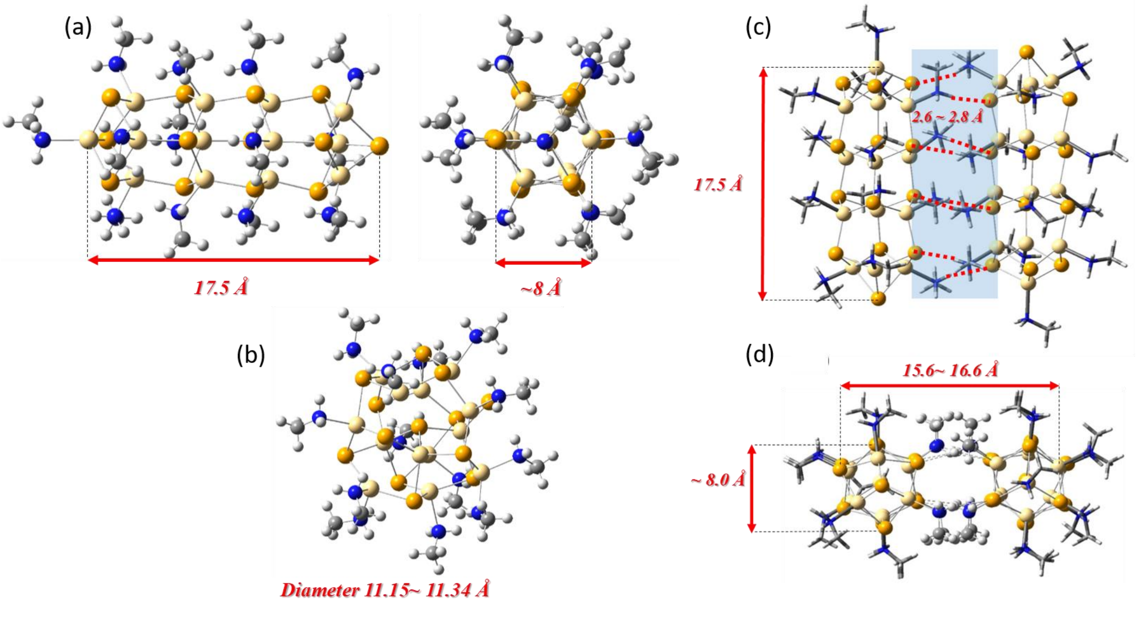

Figure 1: The (a) tubular and (d) cage-core of $MeNH_2$ protected structures. The (c) top view and (d) side view of $MeNH_2$ protected tubular $[(CdSe)_{13}]_2$ dimer structure. The average bond length of the Se...H_N hydrogen bonds between neighboring tubes is around 2.6-2.8 Å.

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