

JST Basic Research Programs
C R E S T
(Core Research for Evolutional Science and Technology)

Annual Report for Research Work in the fiscal year 2006

Research Area :

High Performance Computing for Multi-scale and Multi-physics Phenomena

Research Theme

Simulation of Complex Molecular Systems with Hybrid Methods

Name of Research Director, Belonging and Title:

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Fukui Institute for Fundamental Chemistry, Kyoto University, Research Leader

§1. Outline of Research Work

The aim of the present research is 1. to develop further the hybrid theoretical methods (such as ONIOM or RISM-SCF) already proposed by the principle investigator and his collaborators, 2. to demonstrate that such hybrid methods can be used for simulations of structures, reactions and dynamics and 3. to solve some of the important problems in each field. In the present first year, concerning the simulation of nanomaterials, we initiated quantum chemical molecular dynamics (QM/MD) simulations of carbon nano structures using the density functional tight binding (DFTB) method. As to the simulations of reactions in solution phase, we studied 1. new development of RISM-SCF, 2. mechanism and dynamics of solution reactions and 3. determination of reaction coordinate on free energy surface of complex molecular systems using QM/MM method. Concerning the application of multi-level simulations to enzymatic reactions, we initiated studies of reaction mechanisms using the ONIOM QM/MM optimization. The research is making progress as planned, and preparation for increase of manpower in the next year is nearly complete.

§2. Content of Research Work

In the area of **simulation of nanomaterials** we initiated our research efforts on quantum chemical molecular dynamics (QM/MD) computations of carbon nanostructure formation based on density functional tight binding (DFTB). Specifically

- A) carbon nanotube formation during vacuum heating on the C-face of SiC crystals.
- B) single-walled carbon nanotube (SWCNT) synthesis on Fe/Co/Ni catalysts using C_2 as carbon feedstock material to simulate laser evaporation and carbon arc processes,
- C) fullerene self-assembly during combustion of benzene,
- D) Sc- and Ti-metallofullerene formation in analogy to previous simulations which explained the formation mechanism of C_{60} and higher fullerenes from hot C_2 vapor,
- E) Nanodiamond to fullerene and carbon onion transformations at high temperatures.

Further, we have begun to explore the following areas of nanocarbon materials simulations:

- F) investigation of excited states potential energy surfaces of $Er_2@C_{82}$ and $Er_2C_2@C_{82}$ using TDDFT to understand differences in photoemission profiles,
- G) the molecular and electronic structure of the remarkably stable $Gd@C_{82}$ dimer using regular DFT methods,
- H) the thermodynamic stability of $Fe@C_{82}$ in comparison to $Sc@C_{82}$ using regular DFT methods, and DFTB-based QM/MD simulations of Fe/C_2 mixtures to investigate the early stages of Fe particle aggregation
- I) the origin of handedness preference in double-walled carbon nanotubes using dispersion-augmented DFTB-D
- J) the geometries, thermodynamic stabilities, and high-temperature behavior of linear polyynes $C_{10}H_2$,

$C_{12}H_2$, and $C_{14}H_2$ in SWCNTs of various diameters, as well as the Raman spectra, using dispersion-augmented DFTB-D

K) the computation of Raman spectra of finite-size SWCNTs and graphene sheets with increasing molecular sizes, using our DFTB analytical second derivatives.

Under A) we have submitted a paper explaining the growth of carbon nanotubes and. We explained the following experimental observations: 1. CNT caps only nucleate on the C-face due to the two antagonistic forces attempting to form a balance: formation of strong C-C bonds between top-layer graphene and dangling C surface valences on one hand, and the resistance of the planar sp^2 graphene sheet to take non-planar sp^3 hybridization, 2. Si atom removal leads to unstable carbon species with dangling bonds which makes stable connections with existing carbon material on the surface, thereby continuing to grow existing caps into tubes, 3. Dangling C atoms on the Si-face are protected by the Si atoms as opposed to the C-face, and rather tend to form graphene layers among themselves. Figure shows a sequence during "Si atom random removal".

QuickTime™ and a
TIFF (LZW) decompressor
are needed to see this picture.

QM/MD snapshots of formation of a carbon nanotube on the SiC C-face under random Si removal

Concerning **simulations of solution phase reactions**, we mainly carried out researches on (1) the developments and implementations of RISM-SCF method, (2) free energy surfaces and dynamics of chemical reactions in solution, and (3) transition state determination of enzymatic reactions on the free energy surfaces. In the subject (1), we implemented an efficient 3-dimensional RISM-SCF method by introducing a new algorithm for calculating the solute-solvent electrostatic interaction and solving the 3D-RISM equation. This method was applied to calculate the solvatochromic shifts of acetone, benzonitrile and nitrobenzene in aqueous solution. We also developed the analytical free energy gradient method for RISM-SCF/MP2 method, and applied it to study the equilibrium of Grignard reagent in ether solvent, in which the dynamic electron correlation is important. In the second subject (2), we studied the mechanism of radiationless decay of excited 9H-adenine in polar solvents. We located the minimum free energy conical intersection points among the ground, $n\pi^*$, two $\pi\pi^*$ and $\pi\sigma^*$ excited states. Based on these calculated results, we gave an interpretation of experimental results that the excited state 9H-adenine decays in sub-ps time scale in aqueous solution though its decay time is ps order in the gas phase. In the subject (3), we introduced new linear response free energy (LRFE) functionals based on QM/MM methodology. MD calculations were carried out to obtain the reaction paths for Menshutkin type and Claisen rearrangement reactions in aqueous solutions and the results were compared with those by more reliable free energy perturbation calculations. We found that the modified LRFE method is

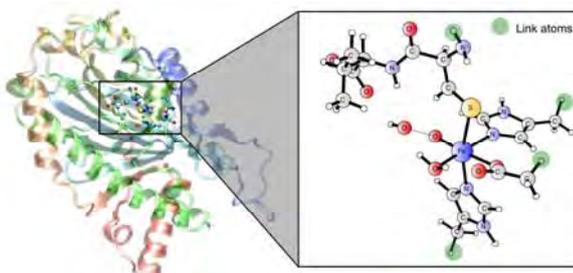
promising to provide reliable free energy surfaces. We further applied this method to locate the transition state for chorismate-prephenate Claisen rearrangement in chorismate mutase. The calculated activation barrier height was in good agreement with the experimental estimate. Comparing the results in aqueous solution, we discussed the origin of catalytic activity in this enzymatic reaction.

As to **the application of multi-level simulation to enzymatic reactions**, we initiated the ONIOM QM/MM optimization studies of reaction mechanisms of the following three systems. All these involve formally spin-forbidden reactions between oxygen and a closed-shell molecule. Aerobic organisms have developed a machinery of enzymes that efficiently catalyze and control these reactions, and their theoretical understanding is urgently needed.

(1) Firefly luciferase catalyses the highly efficient reaction between luciferin and O₂. Although initially a ground-state reaction, the final result is an excited species that emits the characteristic firefly light. ONIOM models are used to understand both how luciferase activates O₂ without the use of a metal center, and how it manages to efficiently convert chemical energy into light energy.

(2) Indoleamine 2,3-dioxygenase (IDO) and tryptophan 2,3-dioxygenase (TDO) catalyze the cleavage of the pyrrole ring of L-tryptophan and incorporate two oxygen atoms from the oxygen molecule. Density functional theory calculations with the B3LYP functional do not support the concerted ene-type addition and Criegee rearrangement previously proposed. An alternative mechanistic pathway is suggested from the calculations.

(3) Isopenicillin N synthase (IPNS) is a non-heme iron enzyme that uses dioxygen to catalyze a critical step in the biosynthesis of antibiotics. A mechanism for this enzymatic reaction is proposed based on active-site DFT models and ONIOM (B3LYP/Amber)



calculations. The most important effect of the surrounding protein is that it stabilizes dioxygen binding (see figure) by 8-10 kcal/mol, an effect that is critical for the reactivity of these enzymes.

The improvement and further development of the ONIOM method and code as well as **preparation for ONIOM molecular dynamics simulations** is also making progress.

§3. Research Structure

(1) "Kyoto University" Group

① Research Participants

	Name	Affiliation	Title	Period
○	Keiji Morokuma	Fukui Institute for Fundamental Chemistry,	Research Leader	2006.10~

		Kyoto University		
	Stephan Irle	Institute for Advanced Research, Nagoya University	Associate Professor (tenure track)	2006.10~
	Marcus Lundberg	Fukui Institute for Fundamental Chemistry, Kyoto University	Postdoctoral Research Fellow (FIFC)	2006.10~
	Shigeki Kato	Faculty of Science, Kyoto University	Professor	2006.10~
	Shigehiko Hayashi	Faculty of Science, Kyoto University	Associate Professor	2006.10~
	Takeshi Yamamoto	Faculty of Science, Kyoto University	Assistant Professor	2006.10~
*	Tsutimu Kawatsu	Fukui Institute for Fundamental Chemistry, Kyoto University	Postdoctoral Research Fellow (CREST)	2006.11~
*	Yasuhito Ohta	Fukui Institute for Fundamental Chemistry, Kyoto University	Postdoctoral Research Fellow (CREST)	2006.12~
	Oscar Chung	Fukui Institute for Fundamental Chemistry, Kyoto University	Postdoctoral Research Fellow (FIFC)	2006.12~
	Biswajit Saha	Fukui Institute for Fundamental Chemistry, Kyoto University	Postdoctoral Research Fellow (FIFC)	2006.12~
*	Yoshiko Okamoto	Fukui Institute for Fundamental Chemistry, Kyoto University	Research Assistant (CREST)	2006.12~
*	Daiki Ishida	Fukui Institute for Fundamental Chemistry, Kyoto University	Technical Assistant (CREST)	2006.12~
*	Momotaro Takeda	Fukui Institute for Fundamental Chemistry, Kyoto University	Technical Assistant (CREST)	2007.1~

② Research Subjects

A1. Development of approximate electronic theory for multilayer ONIOM method.

C1. Development of 3D RISM-SCF method

C4. Development of polarizable force field

D1. Simulation of dynamics of formation of carbon nanotubes, nanopods, fullerenes and metallofullerenes

E1. Transition state theories for enzymatic reactions

E2. Simulation of dynamics of protein functioning

E3. Elucidation of mechanisms of reaction of metalloenzymes

F1. Crossing search and dynamics on free energy crossing in solution

§4. Publication of Research Results

(4-1) Publication of Scientific Papers (The original Work)

① Number of Publications (0 Domestic, 3 International)

② Detailed Information

N. Minezawa and S. Kato, An efficient implementation of three-dimensional reference interaction site model self-consistent-field method: Application to solvatochromic shift calculations, *J. Chem. Phys.*, 126, 054511/1-15 (2007).

S. Yamazaki and S. Kato, Solvent effect on conical intersections in excited state 9H-adenine: Radiationless decay mechanism in polar solvent, *J. Am. Chem. Soc.*, 129, 2901-2909 (2007).

T. Mori and S. Kato, Analytical RISM-MP2 free energy gradient method: Application to the Schlenk equilibrium of Grignard reagent, *Chem. Phys. Lett.*, 437, 159-163 (2007).

(4-2) Patent Application

None