論　文　の　要　約

論文題目：Theoretical investigation of complex molecular systems:
Structures, chemical reactions and spectroscopy
(複雑分子系の理論的研究：構造、化学反応、分光測定の理解に向けて)

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This thesis presents the application of quantum chemistry to study the complex molecular systems and properties. The investigations of complex systems, e.g. those with the many degrees of freedom, are still a great challenge for the computational chemists. Furthermore, the interests to the "nano" and "bio" systems are increasing greatly nowadays. Although the CPU power and speed are developing rapidly during these days, the common quantum mechanics (QM) methods are still too expensive to be employed for those systems. Recently, there are many approximations are available to be applied, for example to study the chemical reactions in the solvents; the accuracy of the methods is another important issue. Therefore, the theoreticians have great challenges to carry out the reliable approaches to handle these "very complicated" molecular systems. Chapter 1 explains briefly the motivations, systems of interest, and the methods employed in these studies. More explanations of the theoretical background are given in the chapter 2.

In chapter 3, we reported our investigations on glucose anomers and the effects of solvation to its thermodynamics stability. We have successfully applied the combination between the QM and statistical mechanics, called RISM-SCF-SEDD, to employ the structural, properties, and energetics analysis in several solvents including the non-conventional solvent, such as ionic liquids (ILs). The preferences of α- and ß-glucose in gas phase and many solvents are well reproduced. In the case of strongly interacting solvents, such as DMSO and ionic liquids, the solvation structures around the anomeric sites clearly show that the short-range interactions between solute and solvents determine the stability of one anomer than the other. The long-ranges interactions are more important in the case of solvation in acetone, acetonitrile, and H_2O.

Besides the conformational analysis of glucose, further chemical reactions have been reported. Due to the demand of the use of biomass as the feedstock of chemicals production, the reaction of glucose and fructose to 5-hydroxymethylfurfural (HMF) is gaining much interest, recently. Furthermore, ILs have shown great potentials as the solvents to process not only glucose, but also biomass directly, in more robust conditions. Therefore, this reaction is considered as 'green process'. In this study, we focused on the acidic catalytic reactions of glucose and fructose to HMF in water and ILs. Two main mechanisms were proposed, open ring mechanism and cyclic mechanism. Our calculations suggested the cyclic mechanism and the open ring mechanism are more favorable in the water and ILs, respectively. Moreover, we were able to explain the solvent effects by the decomposition of free energy and solvation structures that produced by RISM-SCF-SEDD method. The intermolecular

interactions between solute and solvent molecules are greatly effect the stability of the transition states. Furthermore, the overall energy barrier in ILs is 32.4 kcal/mol, which allows the chemical reactions in ILs to be occurred in the lower temperatures and pressures. More details are given in the chapter 4.

Chapter 5 demonstrates the theoretical study on the carbon nano materials (CNM). In this work, we employed the semiempirical methods, called density functional tight binding (DFTB). With the low computational cost, DFTB method allows us to deal with the large number of atoms (~1,200 atoms in our case) with the comparable accuracy to a low-level density functional theory (DFT) calculation. Our interest was directed to the low frequencies Raman properties of CNM, especially the radial breathing mode. The evolution of low frequency breathing mode for finite-size systems of hydrogen-terminated CNMs have shown that there is the size and dimensional dependencies to the position of the breathing mode's frequencies. The radial breathing modes follow the $\omega = aN_{\mathrm{C}}^{-\frac{1}{D}}$ formula where N_{C} is the number of atoms and D is the dimension of the system. Furthermore, this correlation can be used to predict the frequency of breathing mode on the random CNM structures.

Finally, chapter 6 summarizes the findings from chapter 3 to 5 briefly. It includes the author's comments about the present studies and the further prospect of research.