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Theoretical Modeling of Fundamental Chemical Phenomena at Surface and Interface

(表面や界面で起こる基礎的な化学現象に関する理論的モデル化)

Interfacial electron transfer and the associated chemical bond formation form the basis of many research fields, including organic electronic devices, catalytic reactions, and photochemical reactions. A comprehensive atomistic analysis of the impact of individual components of adsorbate-surface systems on interfacial electron transfer can pave the way for interfaces with diverse chemical functions. To obtain such insights, this dissertation addresses computational and theoretical modeling of chemical bonding at the organic molecule-metal interfaces and (photo)chemical reactions occurring at surface systems.

Chapter 1 provides an overview of chemical phenomena on surfaces, focusing on self-assembled monolayers adsorbed on metal electrode surfaces. Experimental characterization and theoretical modeling of adsorbent-surface interactions are presented. Then, in Chapter 2, the theoretical method used in this dissertation is presented, with a particular focus on the specific implementation of plane wave method, natural bond orbital (NBO) algorithm and anharmonic vibrational spectra on surface systems. The artificial force induced reaction method implemented in the global reaction route mapping is also concisely introduced.

In Chapter 3, one of the typical cases of self-assembled monolayers (SAMs), aryl isocyanide molecule adsorbed on Pt(111) surface, was used as a model to systematically analyze the substituent effects of organic molecules on the nature and formation mechanism of chemical bonds induced by metal-SAMs interaction. In order to study the effect of electron-donating and electron-withdrawing substituents, various para-substituents with different Hammett parameters were introduced. The electronic localization in the NC and Pt-C bonds of the adsorbent molecules is thought to be affected by the induction and resonance effects through the aromatic rings. By applying the NBO analysis method extended to periodic systems, I calculated the NBO occupation numbers in the orbitals involved in electron transfer across the interface and bond formation. The mechanism of molecule-surface binding was revealed by quantitative analysis of the strength of donation and backdonation. The bond order, which is a measure of bond strength, was used in the analysis. The bond order and NC stretching frequency were plotted as a function of Hammett parameter, and the correspondence was found to be valid for both adsorbed and free molecules. The proposed bond order model indicator in this chapter can be easily extended to other adsorbate-surface cases.

In Chapter 4, the metal substrate effect was further investigated using aryl isocyanide SAMs adsorbed on two noble metals, Au(111) and Ag(111) surfaces. Both experimental vibrational sum frequency generation

(VSFG) spectroscopy and vibrational spectra predicted by density functional perturbation theory (DFPT) show that the NC stretching frequencies of Au and Ag are blue-shifted compared to those of free molecules, and this blue-shift is larger when Au is used as a substrate. The NBO analysis extended to periodic systems shows that molecules on Au surfaces have stronger σ -donation and π^* -backdonation than those on Ag surfaces. The blueshift of the NC stretching frequency after adsorption compared to the isolated molecule may be due to the greater involvement of σ -donation than π^* -backdonation in the frequency change for both Au and Ag. More importantly, due to the strong σ -donation of Au, the frequency is even more blue-shifted than that of Ag, resulting in a very high stretching frequency of the NC bond in Au. This result embodies the effect of the metal substrate on the electron transfer at the interface region. Furthermore, theoretical methods based on the plane-wave density functional theory yielded results that are in quantitative agreement with experiment for a specific class of SAMs.

In Chapter 5, I focus on the catalytic reactions that occur on the surface of carbon-doped hexagonal boron nitride (h-BN). Earlier studies have demonstrated that doping a single C atom onto an inert h-BN surface is enough to catalyze it and have the ability to activate O_2 molecules. In this chapter, such activation by dopants is used to induce two typical catalytic oxidation reactions, CO oxidation and C_2H_4 epoxidation. The energy profiles of these reactions were calculated for various active sites with different distances from the doped C atoms, and the reaction activities were investigated. The energy profile of the reaction was shown to be less affected by increasing the distance from the doped C atom. Since catalytic activity was observed in a relatively wide region of BN centered on the doped C atoms, the potential catalytic ability of h-BN monolayer could be examined.

In Chapter 6, I attempt to elucidate the reaction mechanism of the photochemical reaction on surfaces, which are difficult to handle using conventional quantum chemical calculation methods. The target reaction is the direct photoexcitation of the phenol molecules adsorbed on anatase $TiO_2(001)$ surface. First, the electronic structure of the neutral phenol adsorbed on the anatase surface was investigated by periodic DFT calculations. According to the density of states, the high energy levels in the valence band and the low energy levels in the conduction band are attributed to O 2p states and Ti 3d levels, respectively, and combined with wavefunctions of phenol near the valence band maximum and conduction band minimum, we verified that the photoirradiation causes electron transfer from the adsorbed phenol to the surface. Reaction paths of phenol cation radicals with oxygen molecule and neutral species with oxygen molecule were investigated by the multicomponent artificial force induced reaction method. We found there is no reaction induced between neutral phenol and O_2 molecule, while 13 reaction paths have been found for the cationic phenol and O_2 . The role of the surface will be examined based on the mechanistic insights provided by reaction pathways between cationic radicals and O_2 .

Finally, in Chapter 7, I conclude this dissertation by summarizing the major findings and discussing a broader perspective for the theoretical modeling of molecules adsorbed on surfaces. In this dissertation, I discuss in detail the bond strength index based on periodic DFT calculations for surface-molecule systems and cover the theoretical methods for describing electron transfer at interfaces. This dissertation clarifies the critical role of substituents and substrates in electron transfer, thereby strengthening fundamental design efforts for atomic scale control of molecule-surface interactions and the development of efficient molecular electronic devices.