Usage Report for Fiscal Year 2016

Theoretical study of interaction between tunneling electrons and individual molecules at surfaces

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1. Background and purpose of the project, relationship of the project with other projects

During the past decade, computer simulations based on a quantum mechanics have developed an increasingly important impact on solid-state physics and chemistry s well as on materials science. In field of material science, the surface chemistry is fundamentally important in many areas, such as molecular electronics, heterogeneous catalyst, fuel cell, etc. The adsorption of molecules onto a surface is a necessary prerequisite to any surface mediated chemical process. Understanding the bonding nature between the molecule and the surface on the basis of the electronic structure is therefore one of the most important issues in this field. The computational methods like density functional theory (DFT) have played a prominent role to elucidate the interaction between the molecule and the surface. Combination of DFT calculation and the method based on quantum many-body theory also provides a powerful approach to describe magnetism and dynamics on the surface with a high accuracy and efficiency. In addition, the computational method can be useful to study the details of energy transport and conversion among photon and electrons mediated with adsorbate at solid surfaces in the nanoscale regime. From the theoretical investigation of the adsorbed molecule on surface in combination with scanning tunneling microscopy and spectroscopy (STM/STS) experiment, we could expect the following research goals; 1) the deep understanding of the chemical/physical properties of an adsorbate on the surface not only in ground state but also in excited state, 2) the fine control of the chemistry on the surface. The overall purpose of our theoretical work is closely related with research goal - describing the details of energy transport and conversion at solid surfaces and interfaces in the nanoscale regime - of our laboratory, Surface and Interface Science laboratory.

2. Specific usage status of the system and calculation method

We have been studying the molecular adsorption on the well-defined metal surface using computational method in combination with experimental method. In our studies, first-principles simulations have been carried out using the Vienna Ab-initio Simulation Package (VASP) code and Quantum Espresso code in the density functional level of theory. The pure DFT methods have been mostly used and the inner electrons are replaced by projector augmented wave pseudopotentials (PAW). The climbing image nudged elastic band method (CI-NEB) is used to determine the transition states that are confirmed by imaginary frequency modes. In most of cases, STM image simulations are performed using Tersoff-Hamann approach. The computational results are compared with the available experimental result obtained from STM in our group. For the gas phase molecules, the Gaussian09 program with atomic-orbital basis set is also effectively utilized to obtain stable geometries and corresponding electronic structures.

We also have been studying the many-body phenomena in molecular adsorption system, in particular the Kondo effect. The characteristic electronic state resulting from the Kondo effect, so-called Kondo singlet state appears as a sharp peak structure (Kondo peak) at the Fermi level (E_F) in STS. In order to simulate the Kondo peak, we build numerical renormalization group (NRG) code and the STS simulation code based on the Keldysh Green's function method.

Electron-transport and luminescence properties of systems, that consist of a single molecule, substrate and the STM tip, are also our main research target. DFT and time-dependent DFT (TD-DFT) calculations are used to investigate the basic properties of components, i.e., the adsorption nature of molecules and dielectric properties of the substrate as well as the excited electronic states of molecules with a high accuracy and efficiency. Based on the obtained results, we construct an effective model and investigate electron dynamics in transport and luminescence processes using the Keldysh Green's function method.

3. Result

(1) Magnetism of nanostructure on solid surface [*Phys. Rev. B* 94, 205402 (2016)]

Magnetism of nanostructure on surface has been attracted much attention due to their potential application to the ultra-high density magnetic storage. Here we focus on magnetic molecules on surface. The characteristics of molecule, flexibility, variety of chemical composition, high-symmetric ligand field, and controllability of the interaction between molecules and surfaces makes these systems unique magnetic materials.

Among various magnetic molecules, we focus on transition metal phthalocyanines (Pcs) such as CoPc, MnPc, and FePc. They have attracted much attention as typical magnetic molecules for the building block of molecular spintronics devices, and numerous studies have been carried out both experimentally and theoretically in these last few decades. However, the ground state electronic configurations and the magnetism of these molecules, in particular FePc, are still under debate because it is not easy to properly describe the electron correlation and spin-orbit interaction (SOI) at the transition metal ion.

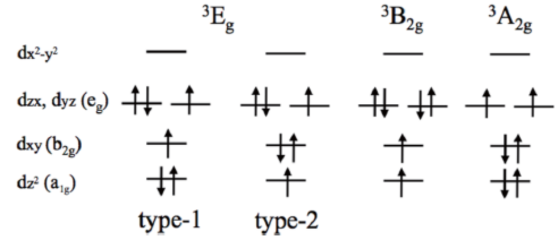

Fig. 1 Electronic configurations of FePc. The Fe 3d orbitals are split by ligand field of the D_{4h} symmetry. The dzx and dyz orbitals are degenerate. The arrows indicate up and down spins. There are two different electron configurations for the ^{3}Eg state; one is called as type 1 and the other type 2.

It is widely accepted that the spin ground state of FePc is triplet (S = 1), however, the previous reports show contradiction in the electronic configuration. In the previous experimental studies, the different electronic configurations are proposed as the ground states ^{3}Eg and $^3B_{2g}$ [see the electronic configurations in Fig. 1]. Theoretical calculations based on the density functional theory (DFT) have also presented different conclusions. The ground state electronic configuration depends strongly on the computational details, and ^{3}Eg, $^3B_{2g}$, and $^3A_{2g}$ ground states are proposed independently.

Recently, the in-plane magnetic anisotropy with a large unquenched orbital magnetic moment in FePc has been found by using the x-ray magnetic circular dichroism (XMCD) and Mossbauer spectroscopy. The magnetic feature cannot be rationalized by assuming that the ground state is described solely as one of the configurations ^3Eg, $^3B_{2g}$, or $^3A_{2g}$. The unquenched orbital moment requires orbital degeneracy, and thus the orbital singlet $^3B_{2g}$ and $^3A_{2g}$ states are ruled out. Although the ^3Eg ground state fulfills this condition, the SOI in the ^3Eg state leads to the easy-axis magnetic anisotropy, which contradicts the in-plane magnetic anisotropy. A plausible origin of such a complex feature is a mixed ground state. Recent x-ray absorption spectroscopy (XAS) work on a monolayer FePc on Au(111) has reported that the ground state of a mixed $^3B_{2g}$-^3E_g character reproduces the XAS spectrum more faithfully. Since the energies of the $^3B_{2g}$ and ^3E_g states are close to each other, as shown in the previous DFT paper, the hybridization of these two states through the SOI is highly possible. Theoretically, the multiplet calculation supports the mixed ground state.

We develop a model Hamiltonian approach based on the mixed ground state. This approach enables us to treat the effect of the ligand-field modification and the d-orbital deformation by adsorption in a simple and efficient manner. The parameters in our model are the energy difference between the ^3Eg and $^3B_{2g}$ states and the weights of d orbitals in the respective eigenstates formed by the hybridization of atomic d orbitals with the ligands, including the substrate (d-orbital deformation parameters). We estimate the d-orbital deformation parameters in FePc on Au(111) as an interesting example, and show the clear influence of the adsorption on the magnetic anisotropy through changing the mixed nature in the ground state. Our model is the simplest one treating the 1st order effect of the SOI and mixed ground state that are not included in the spin Hamiltonian.

From the model Hamiltonian we constructed, we found that whether the FePc molecule takes the in-plane or out-of-plane magnetic anisotropy depends on the parameters, α_{mol}, β_{mol} and Δ. $\mathrm{i}\alpha_{mol} = < \mathrm{E}_\mu | l_x | \mathrm{B}_2 >$ and $\mathrm{i}\beta_{mol} = < \mathrm{E}_\mu | l_z | \mathrm{E}_\nu >$, where $|\mathrm{B}_2>$, $|\mathrm{E}_\mu>$, $|\mathrm{E}_\nu>$ mean the molecular orbitals classified to the respective irreducible representation. Δ is the energy difference between the ^3E_g and $^3B_{2g}$ state. Fig. 2 shows the calculated results plotted in the β_{mol}-Δ plane for α_{mol} = 1.7, 1.3, 0.8 and 0.5. The positive (negative) value of the difference in M_S+M_L represents the in-plane (out-of-plane) magnetic anisotropy. When α_{mol} = 1.7 (the atomic limit), the region exhibiting the in-plane anisotropy extends across the β_{mol}-Δ plane except in the regions around the upper left and right corners. Strong out-of-plane anisotropy lies around the upper left corner and the region around the upper right corner shows weak out-of-plane anisotropy. Strong in-plane anisotropy is observed below the boundary between the in-plane and out-of-plane anisotropies around the upper left corner.

As α_{mol} decreases, which corresponds to the presence of the hybridization with metal substrate, the regions exhibiting the out-of-plane anisotropy extend gradually as shown in Figs. 2(b) - (d). When α_{mol} = 0.5 the out-of-plane anisotropy almost covers the upper region in the β_{mol}-Δ plane except for the region with $|\beta_{mol}| < 0.3$ as shown in Fig. 2(d). $\Delta \sim 0$ separates the regions exhibiting the in-plane and out-of-plane anisotropies; the regions of $\Delta > 0$ and $\Delta < 0$ show the out-of-plane and in-plane anisotropies, respectively. When $\Delta < 0$, the in-plane anisotropy is observed in the wide range of β_{mol}. Even for the α_{mol} = 0.8, the in-plane anisotropy appears in the regions of $\Delta \sim 0$ with $\beta_{mol} \sim -0.5$ (type-1) and $\Delta < 0$ with $\beta_{mol} \sim 0.5$ (type-2).

The reduction of Δ causes the increase of the contribution from the $^3B_2$ state to the ground state. Therefore, the in-plane magnetic anisotropy for FePc on Au(111) stems from the variation of the ratio of ^3E to $^3B_2$ states in the mixed nature of the ground state.

This is in contrast to the bulk FePc in which the type of ^{3}E state determines the anisotropy.

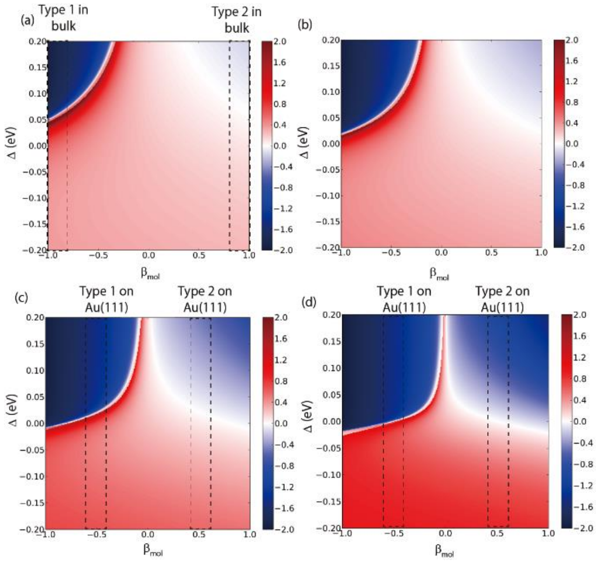

Fig. 2 $\beta_{mol} - \Delta$ plane plot of the in-plane / out-of-plane magnetic anisotropy with (a) $\alpha_{\mathrm{mol}} = 1.7$, (b) 1.3, (c) 0.8 and (d) 0.5. The plotted value is the difference of the total magnetic moment under in-plane and out-of-plane magnetic field with 5T, $(M_S+M_L)_{\text{in-plane}} - (M_S+M_L)_{\text{out-of-plane}}$.

These features different from the bulk would commonly appear in FePc adsorbed on solid surfaces in which the deformation of 3d orbitals due to the molecule-substrate coupling is non-negligible. Our simple model would provide an efficient way to systematic understanding of the different magnetic anisotropy of molecules on various substrates.

(2) Effects of molecule-insulator interaction of geometric property of single π-conjugated molecule on ultrathin insulating films [*Phys. Rev. B* 93, 165419 (2016); *Nature* 538, 364 (2016)]

Physical and chemical properties of a molecule adsorbed on an insulating material have been of great interest in the fundamental science and potential applications for organic devices. A few atomic layers of an insulator grown on a conducting substrate have been widely utilized to analyze the geometric, electronic, optical and magnetic property of isolated molecules with submolecular spatial resolution by means of a scanning tunneling microscope (STM). More than sixty experimental studies investigating the properties of a single molecule on an insulating film have been reported, in which leading-edge researches such as visualization of molecular orbitals, induction of electroluminescence from single molecules, and spin-excitation of single molecule were performed. On the other hand, although some theoretical groups have conducted pioneering works, only a limited number of theoretical analyses from the first principles has been reported. Little is known especially about the interaction between an adsorbed molecule and an insulating film, that can greatly affect the molecular properties. For a metal complex of a π-conjugated molecule adsorbed on an ultrathin insulating film, first-principles study on the details of the adsorption mechanism and/or the molecule-insulator interaction has not yet been reported.

In this study, we conducted detailed and comprehensive analysis for the first time to investigate the effects of molecule-insulator interaction on the adsorption structure and orientation of single molecules. We chose a magnesium phthalocyanine (MgPc) and a metal-free phthalocyanine (H_2Pc) on a bilayer-NaCl film as the representative model system composed of a π-conjugated molecule adsorbed on an ultrathin insulating film. First principles calculations based on density functional theory (DFT) as well as experiments using a low-temperature STM operated under ultrahigh vacuum (UHV) were performed to analyze the nature of the adsorption.

We calculated adsorption energy for MgPc and H_2Pc on different symmetry sites (Cl top, Na top, bridge and hollow) with different angles to determine the most stable structure for MgPc/NaCl and H_2Pc/NaCl systems. The theoretical results show the leading role of van der Waals interaction in adsorption energy of these molecules on the NaCl film. H_2Pc is adsorbed with its center over Na^+ cation, whereas MgPc is adsorbed with Mg cation over Cl$^-$ anion as a formation of Mg-Cl bonding makes Cl-top site energetically preferable (Fig. 3).

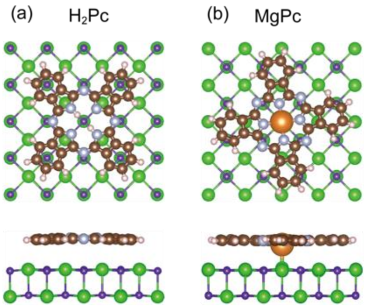

Fig. 3. DFT calculation results of energetically stable adsorption structure of H2Pc and MgPc on bilayer-NaCl films.

Adsorption site and configuration of these molecules are confirmed by experimental analysis. Figure 4(c)-(e) shows high resolution STM images obtained with the STM tip terminated by a CO molecule, which provide clear evidence for determining the adsorption sites and orientations.

The mechanism in determining the adsorption characters of phthalocyanine molecules has been analyzed on the basis of further DFT calculations. For the adsorption of MgPc, a formation of a chemical bond between the Mg and the underlying Cl atoms makes the Cl-top site energetically preferable. Orientation of MaPc is determined to minimize the distance between the benzene rings of the molecule and the Na atoms of the NaCl film. H_2Pc is adsorbed on the Na-top site with the distance from the benzene rings and the aza-bridging N atoms to the Na atoms minimized. Based on the results, we concluded that a small electrostatic interaction between the phthalocyanine and the NaCl film plays an essential role in determining the molecular orientation.

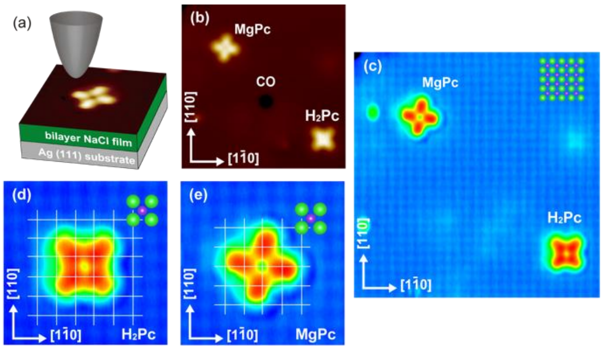

Fig. 4 (a) Schematic of experimental system composed of the STM tip and bilayer-NaCl/Ag(111) with the phthalocyanine positioned between. (b) Constant current topographic image of H2Pc and MgPc on a bilayer NaCl island grown on a Ag(111) surface. (c) High-resolution topographic image of the same area as (b). Green and purple spheres describe the estimated position of the chlorine and sodium ions, respectively. High-resolution topographic image of (d) H2Pc and (e) MgPc obtained with the STM tip terminated by a CO molecule. The grid shows the positions of chlorine anion.

In conclusion, we have investigated the nature of the adsorption of MgPc and H_2Pc on the ultrathin NaCl film. Our findings give a novel insight into the essential physics underlying the adsorption of a π-conjugated molecule on various insulating materials. They would significantly contribute to the development of a wide range of scientific fields including surface science, nanoscale physics, physical chemistry, etc. Also, the present results would contribute to microscopic understanding of the chemical/physical properties of molecules on insulating materials, and hence would facilitate the design of innovative functional materials for organic electronic and optoelectronic devices.

(3) A direct pathway to molecular photodissociation on metal surfaces using visible light [*J. Am. Chem. Soc.* DOI:/10.1021/jacs.6b12680 (2017)]

Molecular photodissociation is a crucial reaction for the effective use of solar energy, a clean and renewable energy resource. However, the photodissociation of small molecules (H_2O, O_2, NO_x, SO_x, etc.) in the gas and liquid phases with visible light is not feasible because of the wide energy gap between the frontier molecular orbitals, such as the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Thus, although photodissociation has been studied extensively, most researchers have focused on irradiation by ultraviolet (UV) light. Molecular adsorption onto solid surfaces can provide a new opportunity for photochemical reactions with visible light, based on reconstructing the interfacial electronic structures due to the molecule-surface interaction. Visible-light-induced photodissociation has attracted significant attention as a novel route to practical solar energy uses.

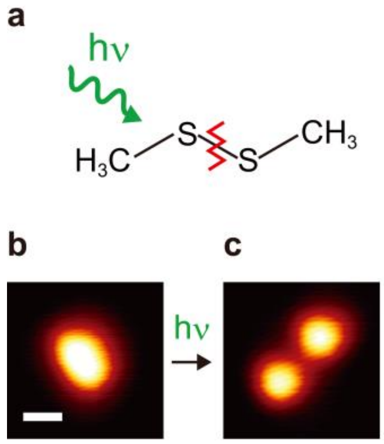

Fig. 5. (a) Structure of a $(CH_3S)_2$ molecule, indicating the photodissociation of the S-S bond. Topographic STM images of $(CH_3S)_2$ molecules on Cu(111) (b) before and (c) after irradiation with 532 nm.

Herein, we report the visible-light-induced photodissociation of dimethyl disulfide, $(CH_3S)_2$, on Cu(111) and Ag(111) surfaces investigated by STM combined with DFT calculations. A quantitative analysis of the STM images revealed that S-S bond dissociation is induced by visible-light irradiation, unlike the gas-phase photodissociation induced by UV light. Moreover, the dissociation yield as a function of the wavelength of incident light indicates that the reaction is not induced by hot electrons generated in the photo-excited metal substrates but by *direct* excitation of the molecules with visible light (Figure 5).

To verify the *direct* excitation mechanism, we carried out periodic DFT calculations. The adsorption structures were optimized on the basis of the atomically-resolved STM images (Figure 6(a) and 6(b)). Two S atoms are located at the ontop sites of adjacent metal atoms, and thus the molecular center is positioned above bridge sites on both surfaces. The adsorption energies of $(CH_3S)_2$ are 1.52 and 1.05 eV for the Cu(111) and Ag(111) substrates, respectively. Accordingly, the optimized distance between S and the nearest Cu atom ($d_{S\text{-}Cu}$ = 2.34 Å) is shorter than $d_{S\text{-}Ag}$ (2.66 Å). The direct interaction between S and the metal atoms underneath results in the elongation of $d_{S\text{-}S}$, which would enhance the reactivity for S-S bond dissociation. Compared to $d_{S\text{-}S}$ of $(CH_3S)_2$ in the gas phase, the $d_{S\text{-}S}$ values on Cu(111) and Ag(111) increase by 0.08 and 0.06 Å, respectively.

The projected density of states (PDOS) and the spatial distribution of MOs for $(CH_3S)_2$ adsorbed on the metal substrates were investigated to examine the detailed electronic structures at the molecule-substrate interfaces. Figures 6(c) and 6(d) show the PDOS of the three p states of the S atoms and the d_{z^2} state of the two metal atoms that are underneath the S atoms and that directly interact with $(CH_3S)_2$ on Cu(111) and Ag(111). On both surfaces, while the occupied molecular states are mainly composed of the S p_z state, the unoccupied states are composed of S p_x and S p_y. On the Cu(111) surface, the main peaks corresponding to the frontier states, i.e., the HOMO- and LUMO-derived MOs, of the $(CH_3S)_2$ molecule are located at ~1.5 eV (peak H-1) below E_F and at ~1.0 eV (L-1) followed by the peak at ~1.4 eV (L-2) above E_F, respectively (Figure 6c). The H-1 aligns well with the d_{z^2} state of the two Cu atoms underneath the S

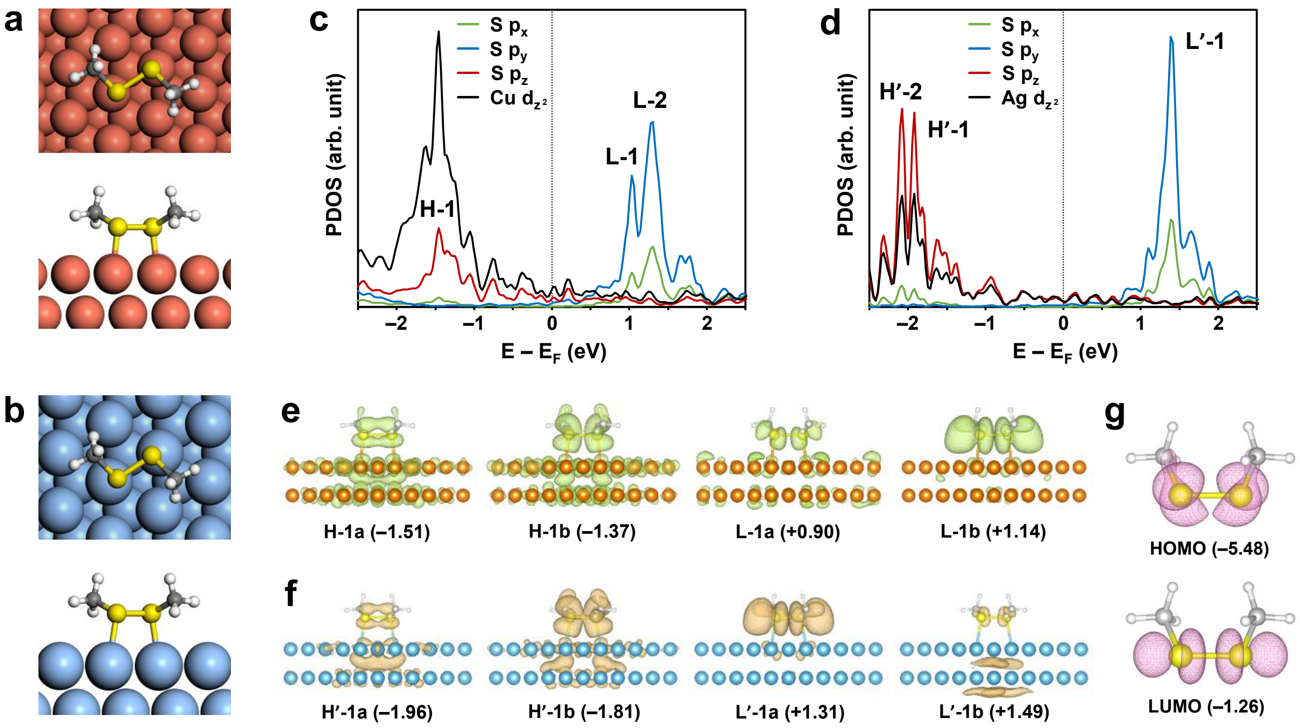

Fig. 6. (a), (b) The adsorption structures of a $(CH_3S)_2$ molecule on (a) Cu(111) and (b) Ag(111) optimized by DFT calculations. The x, y, and z directions are taken as parallel to the surface and perpendicular to the S-S pond, parallel to the surface and to the S-S bond, and perpendicular to the surface, respectively. (c), (d) The calculated PDOS of three p states on S atoms in a $(CH_3S)_2$ molecule and d_{z^2} state of two metal atoms that are underneath the S atoms and directly interact with $(CH_3S)_2$ on (c) Cu(111) and (d) Ag(111). The zero energy corresponds to the Fermi level (E_F). The main DOS peaks for the frontier molecular electronic states are labelled H-1, L-1, and L-2 in panel (c) and H'-1, H'-2, and L'-1 in panel (d). (e), (f) the spatial distribution (isovalue = 0.0005 *e*/bohr^3) of the frontier orbitals nearest to E_F for an isolated $(CH_3S)_2$ molecule on (e) Cu(111) and (f) Ag(111) (magnified images of (e) and (f) including the electronic states for L-2 on Cu(111) and H'-2 on Ag(111) are provided in Figures S8 and S9). (g) The spatial distribution (isovalue = 0.01 *e*/bohr^3) of the HOMO and LUMO orbitals in the gas phase $(CH_3S)_2$.

atoms, but there is no significant distribution of the Cu s, p and d states in the unoccupied region. The charge density plots clearly represent the strong and weak interfacial hybridization between $(CH_3S)_2$ and Cu(111) at H-1 and L-1, respectively (Figure 6(e)). Both the H-1 and L-1 peaks consist of two overlapping electronic states at –1.51 eV (H-1a) and –1.37 eV (H-1b) and at +0.90 eV (L-1a) and +1.14 eV (L-1b). Comparing them with the frontier MOs of $(CH_3S)_2$ in the gas phase (Figure 6(g)), the H-1b and L-1b states have almost the same charge density distributions as the HOMO and LUMO of gas phase $(CH_3S)_2$, respectively. The H-1a state can be characterized by a π-bonding orbital along the S-S bond (π_{SS}), and H-1b is mainly composed of nonbonding lone-pair type orbitals on the S atoms (n_S). Both L-1a and L-1b are derived from the antibonding orbital localized on the S-S bond (σ^*_{SS}) isolated from the Cu(111) substrate. The PDOS (Fig. 6(d)) and the spatial distribution of the charge density (Fig. 6(f)) for the $(CH_3S)_2$ molecule on Ag(111) also exhibit a similar interfacial interaction to that on Cu(111). Two neighboring peaks in the occupied region, approximately –1.9 eV (H'-1) and –2.1 eV (H'-2) and one L'-1 peak in the unoccupied region (~+1.4 eV), are observed. Figures 6(e) and 6(f) show that both H'-1 and L'-1 nearest to E_F are composed of the same kinds of electronic states observed on Cu(111), although the relative stability of L'-1a and L'-1b is opposite to that of the corresponding states, L-1a and L-1b, on Cu(111). Therefore, as with the frontier states on Cu(111), the two states H'-1b and L'-1a on Ag(111) closest in energy to E_F can be characterized by n_S and σ^*_{SS}, respectively. The unoccupied frontier states with σ^*_{SS} character are electronically isolated from the substrate.

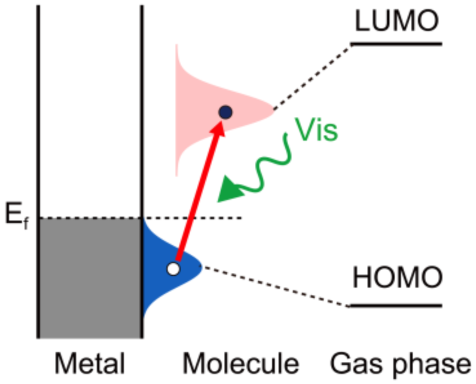

Fig. 7. Excitation mechanism for visible-light-induced photodissociation on metal surfaces. Photodissociation through *direct* excitation between the HOMO- and LUMO-derived MOs. The LUMO-derived MOs have negligible overlap with the metal substrate

The computationally estimated energy gaps between the frontier electronic states for the expected excitation pathways ($n_S \rightarrow \sigma^*_{SS}$), i.e. H-1b → L-1a or L-1b on Cu(111) and H'-1b → L'-1a or L'-1b on Ag(111) are 2.27–2.51 eV (494–546 nm) and 3.12–3.30 eV (376-397 nm) on Cu(111) and on Ag(111), respectively. The numerical discrepancies between the energy gaps evaluated by DFT and the observed threshold energy of photodissociation might result from underestimating the adsorption strength of $(CH_3S)_2$ on coinage-metal substrates, even though we employed a density functional that accounts for dispersive interactions. However, the computational results not only describe well the reduction of the energy gap from the HOMO-LUMO gap of gas-phase $(CH_3S)_2$ but also provide a way to explain the experimental results in which the threshold energy for photodissociation on Cu(111) was found to be lower than that on Ag(111). The reduction of the optical energy gap for an adsorbed molecule has been reported in the UV region. Therefore, our results indicate that the hybridization between the molecules and the metal substrates reduces the energy gap between the frontier electronic states near E_F (Figure 7), thus enabling photodissociation by visible light.

Our results on metal single crystals should apply to all forms of the bulk metal and will therefore be of more general applicability than results that pertain only to metal nanoparticles.

4. Conclusion

We have tried to examine a variety of molecular behaviors on the surface in FY2016. Our theoretical studies combined with experiments in FY2016 provide deep insight into a variety of chemical and physical phenomena on solid surface. We expect that our results can provide new perspective to develop a potential strategy for controlling electronic properties of molecular adsorbates on the surface.

5. Schedule and prospect for the future

(1) Controlling chemical reactivity of ultrathin oxide film

Ultrathin oxide film grown on metal substrate has been a subject of great interest not only as a supporting material for chemically active nanoparticles but also as a catalyst in the field of heterogeneous catalysis, where it provides various ways to control the properties of adsorbates via following factors: (i) charge transfer between adsorbates and oxide-metal interface, which is closely correlated with the electronic affinity (EA) of adsorbate and workfunction reduction, (ii) adhesion between oxide and metal layers with strong polaronic distortion, (iii) film thickness, and (iv) the chemical composition of oxide surface.

Therefore, we will continue our work to find the way for controlling the chemical reactivity using theoretical and experimental studies. In FY2017, we will extend our study into dissociation of CH_3OH and O_2 on MgO/Ag(100) using combined STM and DFT methodology. In particular, regarding the CH_3OH dissociation on MgO/Ag(100), we will try to find a way to selectively dissociate a bond in CH_3OH, e.g., C-H, O-H, and C-O, using an ionic species on MgO film surface which is introduced through charge transfer between the oxide surface and oxide-metal interface. For the for O_2 dissociation on MgO/Ag(100), we should consider an influence from the charge redistribution between the oxide-metal interface and the adsorbate, because of O_2 has much higher EA than that of H_2O molecule. The other branch of our study is clear understanding of the drawing effect at the oxide-metal interface, which can enhance the concentration of dopants at the interface. In addition, we have interests in other ultrathin oxide film systems, such as titania and ceria. We believe that our study provides not only profound insight into the chemical reactivity control of ultrathin oxide film but also an impetus for investigating ultrathin oxide films for a wider range of applications.

(2) Molecular adsorption on solid surface: From single molecule to molecular network

The controllable fabrication of molecular architectures is a topic of great importance not only as a fundamental subject in surface science but also for realizing molecular-scale electronic devices. Computational techniques can provide the underlying mechanisms for the formation of various molecular architectures experimentally observed by STM as well as single molecule adsorption. For the adsorption of single molecules on metal substrate, we suggested the origin of adsorption-induced stability reversal of photochromic DAE on metal surfaces and revealed that the interfacial orbital interaction originated from the weak electronic coupling between the molecular π-state and the electronic states of the Au surface can play a decisive role in constraining adsorption geometry even in the archetypal vdW adsorption system. For one-dimensional (1-D) systems, we have explained (i) the formation mechanism of 1D zipper-type architecture of azobenzene derivatives with the balanced non-bonding interactions, H-bonding and vdW interactions, between adjacent molecules and (ii) the dispersive electronic feature due to the π-orbitals stacking in 1-D molecular lines fabricated on the Si(001)-(2×1)-H. For 2D systems, we contributed to unveil the adsorption geometry of 2D molecular films composed of fluorinated fullerene ($C_{60}F_{36}$), which is strongly related to the distribution of frontier molecular orbitals and thus the n-type character of molecular film. In addition, we recently revealed the novel formation mechanism of supramolecular assembly using photochromic diarylethene derivative, which is the first report on molecular architectures formed by ion-dipole interaction on solid surface. Our results provide not only deeper insight into the molecular adsorption process, but also a general basis for designing the architectures of molecular electronics with desired electronic properties. In FY2017, we will continue the research not only for a variety of molecular assemblies but also isolated molecule on the surfaces as follows: (1) 2-D DNBA molecular assembly and (2) the formation mechanism of van der Waals interface between π-conjugated molecule and novel metal substrate.

(3) Electronic structures of functionalized graphene grown on metal substrate

Functionalization of graphene has attracted great scientific interest not only in controlling the physical properties of graphene, such as opening band gap to achieve semiconducting nature, but also in improving chemical adaptability to integrate graphene as a building block into a variety of functional devices. In particular, we first suggested that the atomic oxidation of graphene grown on a metal substrate results in the formation of graphene enolate, i.e., negatively charged oxygen adsorbed at ontop position on its basal plane, which is strikingly different from the formation of epoxy groups, i.e., adsorption of atomic oxygen at bridge position, on pristine graphene and on graphite. Whereas the enolate is the transition state between two nearest epoxides both on graphene and on graphite, we revealed that improved interfacial interaction between graphene and metal substrate during atomic oxidation plays a crucial role not only in the formation of graphene enolate as a local minimum but also in stabilizing it over the graphene epoxide. In FY2017, we are going to theoretically investigate our very recent experimental finding of well-ordered graphene functionalization, in which the formation of graphene enolate would be one of the main driving forces. Our results are expected to provide not only a novel perspective for a chemical route to functionalize graphene but also a new opportunity for graphene-based applications.

(4) Magnetism of nanostructure on solid surface

Magnetism of nanostructure on surface has been attracted as a fundamental model system of the magnetic device. In FY2017, we focus on I) the interfacial magnetism in metal-phthalocyanine (MPc)/ferromagnetic metal, and II) dynamical magnetic susceptibility in magnetic molecules on metal surface.

I) The magnetism in the MPc on nonmagnetic metal has long been investigated and various interesting phenomena have been reported, e.g., Kondo effect, spin state tuning by molecular adsorption. On the other hand, the unique interfacial magnetism, for example, formation of the unique electronic state so called as spinterface and magnetic hardening when molecule adsorb on ferromagnetic surface. Combining these two direction, we will investigate the magnetism of MPc on ferromagnetic metal surface. In particular, we will evaluate the magnetic anisotropy and its response to the electric field in these systems.

II) For the application of magnetic nanostructure to devices, not only the static properties, but also dynamical ones such as relaxation time are important. The dynamical magnetic susceptibility is one of the physical properties that contains the information of dynamical process. We will extends our own build numerical renormalization group code to the calculation of the dynamical magnetic susceptibility of localized magnetic moment interacting with itinerant electrons. Then, we will evaluate the spectrum of the dynamical magnetic susceptibility of the magnetic atoms/molecules on metal surface and discuss the relation with the Kondo effect.

Finally, we will connect the above investigations with the spin inelastic electron tunneling spectrum obtained by STM.

(5) Electron-phonon coupling in 2D materials

The electron-phonon coupling (EPC) is at the heart of many fundamental physical and chemical phenomena. In FY2017, we focus on I) the effect of the phonon at the interface between graphene and insulating substrate, II) phonon-mediated superconductivity in the intercalated layered materials.

I) The target system is epitaxial graphene grown on SiC(0001) surface. Thermal decomposition of SiC is one of the smart technique of transfer-free wafer scale epitaxial graphene growth. While the measurement of quanum Hall effect in the epitaxial graphene on SiC indicates the high quality and continuous monolayer growth, the mobility is strongly reduced by presence of SiC substrate. The dominant origin is the phonon scattering at the interface between graphene and SiC. However, the information of interfacial phonon in this system still remained to be answered. We plan to calculate the phonon band dispersion, density of states and electron-phonon coupling in this system by using ab-initio calculation. In addition, we will simulate the inelastic electron tunneling spectroscopy in scanning tunneling microscopy measurement in this system.

II) Recently, the superconductivity in alkali metal decorated/intercalated graphene is confirmed experimentally, and these layered materials have attracted more attention as new candidates of the materials for ultrathin superconducting devices.

The possibility of the superconducting transition is not limited to graphene. For example, silicene, Si cousin of graphene, is also predicted to be a BCS type superconductor when electrons are doped. We will carry out material search for the possible candidate of superconductor based on layered materials by using ab-initio calculation of the superconducting transition temperature supported by Wannier interpolation.

(6) Photoelectric conversion in single molecule on surface

Our studies on carrier dynamics in energy conversion processes are extended to the research on photoelectric conversion in single molecule. Luminescence from a single molecule can be induced by the tunneling current of STM. This enables us to investigate the electroluminescence processes of a molecule with submolecular spatial resolution in a well-defined manner. Especially, we focus on electron correlations in electroluminescence processes, e.g., charging of the molecule, formation of single/triplet excitons, radiative and nonradiative decay, and so forth. The key factor in the theoretical analysis is the calculation of (i) excited electronic states of the molecule with a high efficiency and accuracy as well as (ii) nonequilibrium electron dynamics in electroluminescence processes under applied bias. We plan to investigate these points using the method based on first-principles many-body perturbation theory (MBPT) and the nonequilibrium Green's function (NEGF) methods. Our study would make a contribution for understanding the fundamental nature of molecular electroluminescence and in the designing of novel functional materials for organic (opto)electronic devices.

Usage Report for Fiscal Year 2016

Fiscal Year 2016 List of Publications Resulting from the Use of the supercomputer

[Publication]

1. Hiroshi Imada, Kuniyuki Miwa, Miyabi Imai-Imada, Shota Kawahara, Kensuke Kimura, and Yousoo Kim, "Real-space investigation of energy transfer in heterogeneous molecular dimers", *Nature* 538, 364 (Aug. 2016)
2. Kuniyuki Miwa, Hiroshi Imada, Shota Kawahara, and Yousoo Kim, "Effects of molecule-insulator interaction on geometric property of a single phthalocyanine molecule adsorbed on an ultrathin NaCl film", *Phys. Rev. B* 93 (16) 165419 (Apr. 2016).
3. Emi Minamitani, Noriaki Takagi, and Satoshi Watanabe, "Model Hamiltonian approach to the magnetic anisotropy of iron phthalocyanine at solid surfaces" *Phys. Rev. B* 94, 205402 (Nov. 2016)
4. Emiko Kazuma, Jaehoon Jung, Hiromu Ueba, Michael Trenary, and Yousoo Kim, "A direct pathway to molecular photodissociation on metal surfaces using visible light" *J. Am. Chem. Soc.* DOI:/10.1021/jacs.6b12680 (Feb. 2017)

[Oral presentation at an international symposium]

1. Hiroshi Imada, Kuniyuki Miwa, Miyabi Imai-Imada, Shota Kawahara, Kensuke Kimura, Yousoo Kim, "Real-space investigation of intermolecular energy transfer dynamics", The 15th International Workshop on Dynamics, Interactions and Electronic Transitions at Surfaces (DIET15), Shanghai, China (October 2016).
2. Hiroshi Imada, Kuniyuki Miwa, Miyabi Imai-Imada, Shota Kawahara, Kensuke Kimura, Yousoo Kim, "Single-molecule emission and absorption spectroscopy with STM", The 15th International Workshop on Dynamics, Interactions and Electronic Transitions at Surfaces (DIET15), Shanghai, China (October 2016).
3. Yousoo Kim, "Single-molecule optical spectroscopy with STM", The 34th Samahang Pisika ng Pilipinas (SPP) Physics Conference and Annual Meeting, Iloilo, Philippines (August 2016) [Invited].
4. Jaehoon Jung, Tomoko K. Shimizu, Ju-Hyung Kim, Maki Kawai, and Yousoo Kim, "Computational studies on geometric and electronic structures at organic-metal interfaces", The 20th International Vacuum Congress (IVC-20), Busan, Republic of Korea (August 2016).
5. Yousoo Kim, "Single-molecule near-field optical spectroscopy on an ultrathin insulating film with a photon-STM", The 18th International Symposium on the Physics of Semiconductors and Applications, 2016 (ISPSA-2016), Jeju, Korea, (July 2016) [Invited].
6. Yousoo Kim, "Single-molecule chemistry and spectroscopy on insulating films with STM", International Conference on Physics 2016, New Orleans, USA, (June 2016).
7. Jaehoon Jung, Ju-Hyung Kim, and Yousoo Kim, "Energy level alignment between π-conjugated molecule and gold surface", The 11th International Forum on Strategic Technology (IFOST 2016), Novosibirsk, Russia (June 2016).

[Others (Press release, Science lecture for the public)]

1. “Energy jumps back and forth between molecules during transfers” RIKEN Press release, October 4, 2016