Usage Report for Fiscal Year 2017

Project Title:

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

Name:
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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 (EF) 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) Molecular adsorption on solid surface: From single molecule to molecular network, and their optical properties [E. Kazuma, J. Jung, H. Ueba, M. Trenary, and Y. Kim, Science, in revision]

Localized surface plasmon (LSP) resonance of metal nanostructures is a unique way of focusing light near the metal surface beyond the diffraction limit and the generated localized electric field has been utilized for near-field optical spectroscopies. In addition, the LSP facilitates highly efficient conversion of solar energy in photovoltaics and photocatalysts. The plasmon-induced chemical reactions have been explained mainly by an "indirect hot-electron transfer mechanism" (Fig. 1A). Electron-hole pairs are generated in the metal nanostructures by non-radiative decay of the LSP. The generated hot electrons are then transferred to form a transient negative ion (TNI) state of the adsorbed molecule (hot e- → TNI). Recently, plasmon-induced dissociation of O2 and H2 molecules were observed and explained by a mechanism in which the dissociation reactions proceed through vibrational excitation following hot-electron transfer to generate TNI states. Herein, we experimentally found a "direct intramolecular excitation mechanism" (Fig. 1B), on the basis of direct observation of a plasmon-induced chemical reaction of a single molecule for the first time, using STM. In the direct intramolecular excitation mechanism, the LSP resonantly excites electrons from the occupied state to the unoccupied state in the electronic structure of an adsorbate.

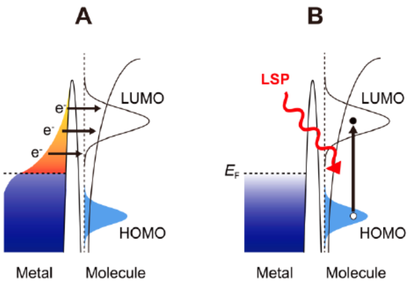

Fig. 1 | Excitation mechanisms for plasmon-induced chemical reactions

In the indirect hot-electron transfer mechanism (Fig. 1A), the Y_{LSP} is determined both by the energy distribution of hot electrons and by the DOS of the LUMOs. If the energy of the LSPs is lower than the threshold energy for direct interband transitions of the metals, both electrons and holes are equitably distributed from zero to the energy of the LSP due to phonon-assisted transitions. In contrast, at higher energies, direct transitions are dominant, and the relative probability density of hot carriers dramatically increases. If the plasmon-induced dissociation of $(CH3S)_2$ is explained by the hot-electron transfer mechanism, the Y_{LSP}-λ spectra would exhibit a step change at the threshold energy of the interband transition at ~3.0 eV and ~2.0 eV for Ag and Cu, respectively, and increase at the higher energies, because the LUMO states are distributed broadly above the EF (Fig. 2).

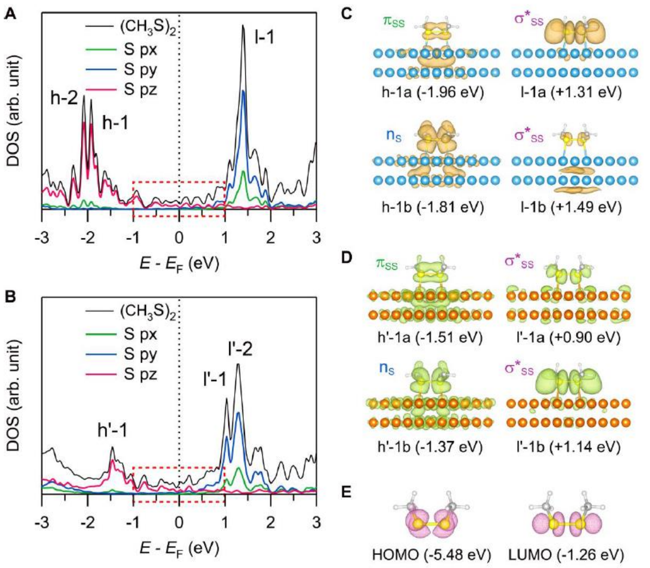

Fig. 2 | Electronic structures and molecular orbitals of $(CH_3S)_2$ molecules on Ag(111) and Cu(111) obtained by DFT calculations.

In addition, the hot electrons generated by the direct transitions of Cu have a broad energy distribution above the E_F and can be transferred into the LUMO states resulting in the excitation of vibrational modes lying along the reaction coordinate. However, the expected spectral change at the threshold energy of the interband transition of the metal is not observed. Moreover, the overall shapes of the Y_{LSP}-λ spectra are observed to reflect not only the shape of the E_{gap}-λ spectra (Fig. 3C) but also the shape of the Y_{photon}-λ spectra, i.e., the energy distribution of the DOS for both HOMO (n_S) and LUMO (σ^*_{SS}) (Fig. 3A, B). We therefore exclude the indirect hot-electron transfer mechanism. We therefore conclude that the LSP efficiently induces and enhances the dissociation reaction through the same reaction pathway as photodissociation ($n_S \rightarrow \sigma^*_{SS}$), based on the direct intramolecular excitation mechanism (Fig. 1B).

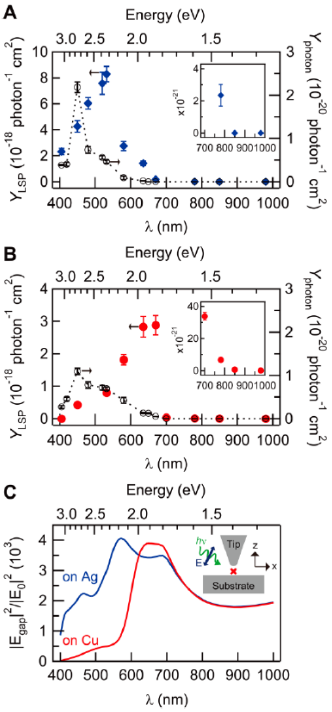

Fig. 3 | Wavelength dependence of the plasmon-induced chemical reaction and of the plasmonic electric field

The Y_{LSP}-λ spectra also have tails extending to longer wavelengths where photodissociation never occurs. This suggests that the LSP also enables direct intramolecular excitation from the MOs in-gap states near the E_F to σ^*_{SS} ($MO_{in\text{-}gap} \rightarrow \sigma^*_{SS}$), as well as the HOMO-LUMO transition ($n_S \rightarrow \sigma^*_{SS}$). The computationally estimated energy gaps between E_F and the edge of the LUMO state are ~1.0 eV and ~0.80 eV on Ag(111) and on Cu(111), respectively (Fig. 2). This explains the experimental results in which the threshold energy of the Y_{LSP} on Ag(111) was found to be higher than that on Cu(111). Therefore, we conclude that dissociation is also induced by direct intramolecular excitation of $MO_{in\text{-}gap} \rightarrow \sigma^*_{SS}$. The DOS of the in-gap states is much smaller than that of the frontier electronic states, and thus the direct excitation of $MO_{in\text{-}gap} \rightarrow \sigma^*_{SS}$ is expected to be a much less efficient process than that of HOMO-LUMO transition ($n_S \rightarrow \sigma^*_{SS}$). However, the LSP generates a strong electric field localized at the interface between the adsorbate and the metal, and therefore it enables dissociation even through inefficient excitation pathways ($MO_{in\text{-}gap} \rightarrow \sigma^*_{SS}$).

(2) Formation mechanism of sea-urchin-shaped hierarchical porous covalent organic framework [S. Kim, C. Park, M. Lee, I. Song, J. Kim, M. Lee, J. Jung, Y. Kim, H. Lim, and H. C. Choi, Adv. Funct. Mater. 27, 1700925 (2017)]

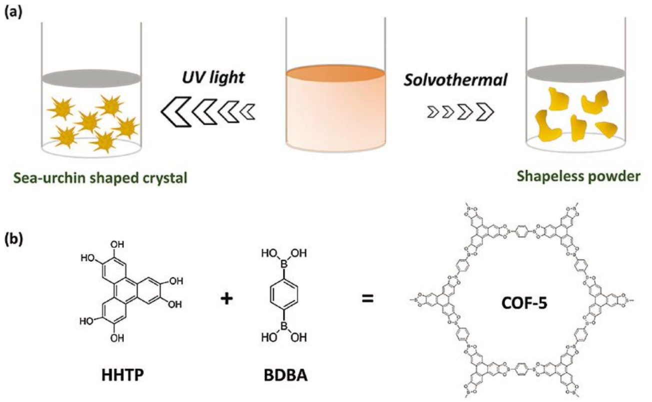

Fig. 4 | Scheme of two different synthesis methods of covalent organic framework-5 (COF-5)

Covalent organic framework (COF) is a secondary building unit of porous, crystalline structure purely linked through covalent bonds among light atoms, such as carbon, nitrogen, boron, and oxygen. Due to their high thermal stability and stable porosity in various chemical environments compared with their precedent family materials, metal organic frameworks (MOFs), COF materials have been widely studied as one of the potential materials in the next generation of upcoming urgent applications, such as gas storage, catalyst, and chemical sensing. We recently experimentally found a good candidate way for the fast, and direct patternable synthesis of COFs which would be a photochemical method. Unlike the shapeless structures mostly obtained by the conventional solvothermal method, COF-5 crystals having homogeneous sea-urchin-shaped morphology with uniform size were obtained (Fig. 4). The sea-urchin-like structure was further characterized by transmission electron microscopy (TEM) (Fig. 5a–c). The stripe patterns were occasionally observed in the "tentacle" structure in the TEM images. Since the interplanar distance is approximately ~2.57 nm, based on the fast Fourier transform (FFT) patterns, the stripe is regarded as repeating (100) planes, which may consist of periodic atomic scale lattice, indicates the [001] direction of COF-5 (Fig. 5d). Therefore, the zone axis of the area where the stripe pattern is assigned as the [010] direction implies that the growth direction of the tentacle-like structure is the [001] direction. These TEM results provide insight into the origin of the unique sea-urchin-like shape of UV-COF-5. We suggest that the growth rate along the out-of-plane direction ([001] direction) is faster than the rate along the in-plane direction during the photochemical process, which can produce the 1D tentacle-like structures in UV-COF-5.

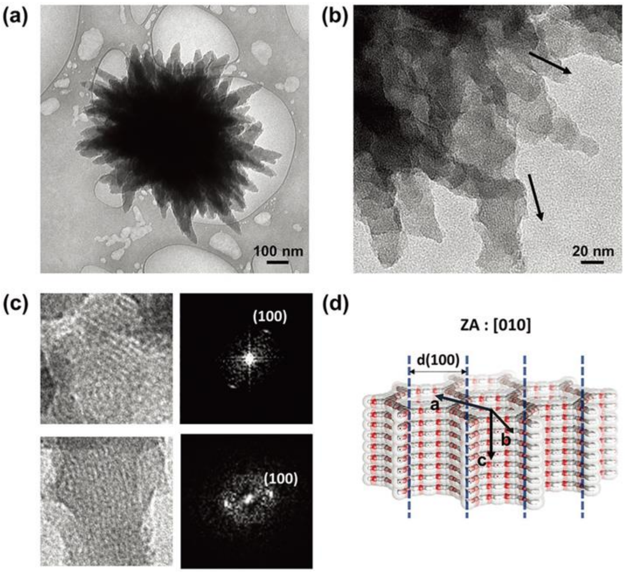

Fig. 5 | Transmission electron microscopy (TEM) images of UV-COF-5 and schematic illustration of periodically stacked UV-COF-5 along the [001] direction.

Theoretical calculations suggest that the orbital coupling between COF-5 layers at the electronically excited states is responsible for the highly enhanced growth rate along the out-of-plane direction, which thus leads to the unique and hierarchical morphology. To effectively describe the interlayer interaction between COF-5 layers, we constructed the single hexagonal COF-5 (hCOF-5) model system (Fig. 6a), which has a planar geometry and consists of six HHTP- and six BDBA-derived moieties. The optimized center-to-center distance between two benzene moieties in a diagonal position is 30.2 Å, which agrees well with the extracted value of 29.36 Å from the XRD patterns of UV–COF-5 or th-COF-5 (Figure 1b). Using the optimized atomic configuration of single hCOF-5, we evaluated the interlayer interaction energies by varying the interlayer distance through single-point calculations (Fig. 6a). The bilayer hCOF-5 model system is most stable with the interaction energy of 3.81 eV at the interlayer distance of 3.5 Å, which is also remarkably coincident with the (001) interplanar distance of 3.46 Å estimated from the corresponding XRD peak. To provide insight into the enhanced growth rate during photochemical synthesis, we examined the molecular electronic structure of the bilayer hCOF-5 with the optimized configuration of single hCOF-5. The distribution and interaction characteristics of the highest occupied molecular orbital (HOMO), HOMO−1, lowest unoccupied molecular orbital (LUMO), and LUMO+1 at the frontier energy region were also investigated (Fig. 6b), which mainly contribute to the excitation from ground state (S_0) to first-excited state (S_1). The time-dependent DFT (TD-DFT) calculation revealed that the first-excitation process is mainly contributed by the transition of HOMO−1 to LUMO (32%) and HOMO to LUMO + 1 (36%). Although the top and bottom hCOF-5 layers interact with each other in a noncovalent fashion, the characteristics of interlayer interaction in occupied and virtual states can provide insights into the large enhancement of growth rate along the [001] direction observed in UV-COF-5. While the HOMO and doubly degenerated HOMO−1 states show fully antibonding characteristics between the two hCOF-5 layers, the LUMO and doubly degenerated LUMO+1 states show bonding characteristics, as shown in Figure 3b. It is worth noting that the bonding characteristics are mainly distributed to the BDDA-derived moieties. Therefore, it can be concluded that the bonding characteristics of virtual states, unlike the antibonding characteristics of the occupied states, lead to the drastically improved growth rate of COF-5 crystals along [001] direction in photochemical synthesis due to the photoexcitation from the occupied states to the virtual states.

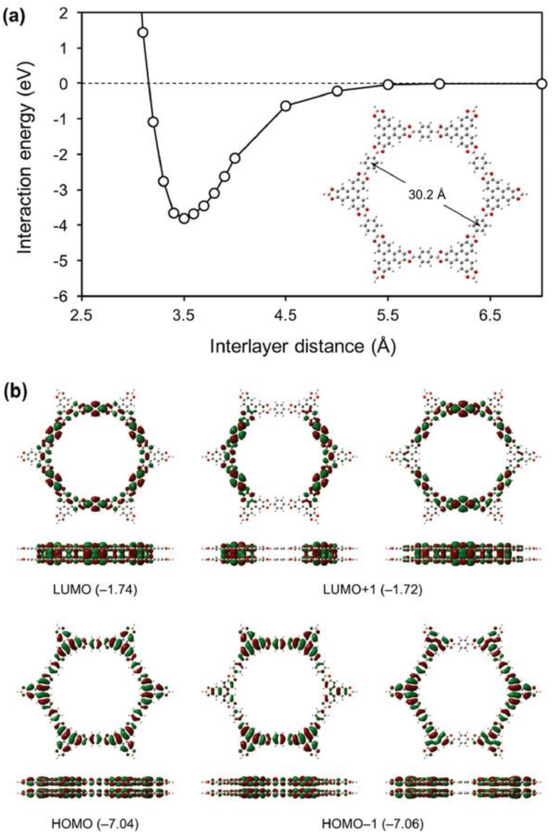

Fig. 6 | (a) Potential energy surfaces for the interlayer interaction between two hCOF-5 model systems. (b) Top- and side-view images of the frontier molecular orbitals, LUMO, LUMO+1, HOMO, and HOMO−1, for the bi-layer hCOF-5 model system.

(3) Electron-phonon coupling in 2D materials [N. H. Shimada, E. Minamitani, S. Watanabe, Appl. Phys. Express, 10, 093101 (2017), E. Minamitani, R. Arafune, T. Frederiksen, T. Komeda et al., Phys. Rev. B, 96, 155431 (2017)]

3-1 Theoretical prediction of phonon-mediated superconductivity with Tc~25K in Li-intercalated h-BN bilayer

Two dimensional (2D) materials have attracted attention as a new class of materials for applications in novel nano devices. The varieties of possible chemical compositions in 2D materials enable us to realize almost every electronic property such as metallic, semimetallic, semiconducting, insulating, and superconducting. We focus on h-BN as a new candidate for 2D superconductor materials. Both bulk and monolayer h-BN have wide energy band gaps of ~5 eV, which tends to make them less suitable as superconductors, compared to other 2D materials. Consequently, they have been paid less attention as candidates for superconductors. However, the metallization of h-BN by alkali-metal intercalation has been predicted theoretically. In addition, Li-intercalated bulk h-BN materials have recently been synthesized. The stronger interlayer interaction in h-BN as compared to that in graphene might be advantageous for enhancing electron–phonon coupling. Considering these factors, in the present study, we carried out ab-initio calculations on superconducting properties of systems comprising of h-BN; specifically, Li-intercalated h-BN bilayer (hBN-Li-hBN). The obtained Tc of 25 K is much higher than the previously reported values of metal decorated/intercalated graphene. We also compared hBN-Li-hBN with Li-intercalated bilayer graphene (G-Li-G) to investigate the origin of the pronounced superconductivity in hBN-Li-hBN. We found that hBN-Li-hBN exhibits higher Tc than G-Li-G; this is because of the formation of characteristic bonds connecting two B atoms in the upper and lower h-BN layers, which results from the weak electronegativity of boron. This finding will provide a new guideline for designing 2D superconductors with high Tc.

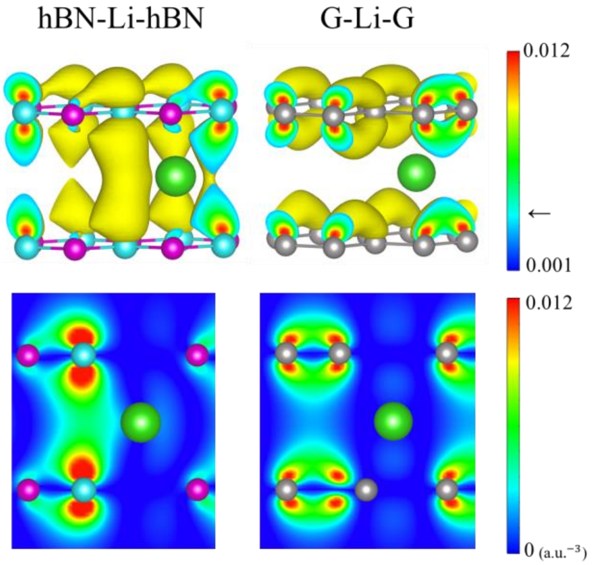

Fig. 7 | Charge density distributions of the eigenstate (specified by blue points in Figure 2) for hBN-Li-hBN and G-Li-G. Charge densities (a.u.^(-3)) are normalized so that the integrated value over a unit cell is 1. They are plotted with the scale given on the right side. In upper panels, the value of 0.03 indicated by arrow in color bar is used for isosurfaces (represented by yellow sheets).

3-2 Atomic-scale characterization of the interfacial phonon in graphene/SiC

Epitaxial graphene on SiC that provides wafer-scale and high-quality graphene sheets on an insulating substrate is a promising material to realize graphene-based nanodevices. The presence of the insulating substrate changes the physical properties of free-standing graphene through the interfacial phonon, e.g., limiting the mobility. Despite such known impacts on the material properties, a complete and microscopic picture is missing.

A characteristic feature of the graphene/SiC interface is the presence of a C buffer layer beneath the graphene layer with a $6\sqrt{3} \times 6\sqrt{3}$ R30 reconstructed structure, hereafter denoted by $6\sqrt{3}$. This superstructure is originated from several types of interfacial Si and buffer-layer C with different local atomic environments, i.e., with covalent Si-C bonds or dangling bonds. Previous ab-initio calculations addressed how the interfacial electronic states are strongly affected by the local atomic environment and how this leads to spatial dependence, which suggests that the phonon properties should also show spatial variation. Local measurements for revealing such correlations between the geometric structure and the phonon properties are key to understanding the interfacial phonon. For this purpose, we use scanning tunneling microscopy (STM) and demonstrate that information about phonons at the interface between graphene and SiC can be extracted from inelastic electron tunneling spectra (IETS). We detect phonon modes with energies of 9 meV and 24 meV, whose intensity change appears in a synchronized manner with the superstructure that appears in the topographic image. Based on density functional theory (DFT) calculations, we identify that the feature at 9 meV is derived from vibrations in graphene and the buffer layer, while the one at 24 meV is derived from the phonon mode associated with the interfacial Si atom possessing a dangling bond. Our combined experimental and theoretical results thus provide a detailed atomic-scale characterization of the interfacial geometric structure and the associated phonon properties.

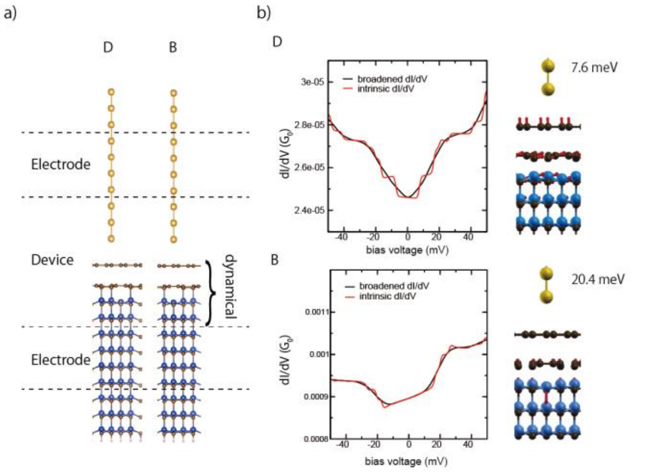

Fig. 8 | (a) Two structure models (D and B) used in the dI/dV calculations. (b) dI/dV simulations in the D and B models. Black lines are dI/dV taking into account the extra broadening from the lock-in measurement technique (Vrms = 5 meV). Red lines are the intrinsic dI/dV results (linewidth only due to a finite temperature of T = 4.2 K). The structural side views show the displacements of the atoms in the active phonon modes that contribute to the narrow (7.6 meV) and wide (20.4 meV) gaps, respectively.

(4) Magnetic molecules on metal surface [R. Hiraoka, E. Minamitani, R. Arafune, N. Tsukahara, S. Watanabe, M. Kawai, and N. Takagi, Nat. Commun., 8, 16012 (2017)]

The Kondo effect, a many-body quantum phenomenon emerging ubiquitously in various condensed matters1-17, arises from the exchange coupling of an impurity spin localized in a host with the conduction electrons. A many-body singlet, Kondo resonance, forms at the Fermi level (E_F) below the Kondo temperature (T_K). Spin-orbit interaction (SOI) at the impurity spin gets entangled with the Kondo effect, resulting the exotic physics. The SOI lifts the degeneracy in spin quantum number S_z into multiple fine structures (denoted as

SOI-splitting), causing magnetic anisotropy (MA). The SOI-splitting is often described as a uniaxial MA term of DS_z^2, where D represents the splitting energy. In half-integer impurity spin with D>0, since the Kramers doublet of $S_z=\pm1/2$ is the ground state, the Kondo resonance forms and coexists with the inelastic steps derived from the SOI-splitting as revealed by scanning tunneling microscopy (STM) studies. In contrast, the SOI competes the Kondo effect in integer impurity spin. For instance, in S=1 system of D>0, the SOI lifts the degeneracy into the $S_z=0$ ground state and the Kramers doublet of $S_z=\pm1$, which hampers the Kondo effect. To reveal the competition, tuning the competing strengths is indispensable. This requires the continuous control of the geometric structure around the impurity in atomic scale that is experimentally challenging.

An iron phthalocyanine (denoted as FePc hereafter) molecule on Au(111) offers a good opportunity to reveal the competition. Bulk FePc molecules take S=1 spin triplet with the in-plane MA derived from the SOI at the Fe^{2+} ion. When attached to Au(111), two unpaired electrons of S=1, one in the dz^2 orbital and the other in the degenerate 3dzx/dyz (dπ) orbitals, are Kondo-screened with the Au electrons to generate two Kondo resonances of high T_K ~100 K and low T_K =2.7 K, respectively. Since the bulk FePc exhibits the in-plane MA, it is expected that the competition between the Kondo effect and the SOI is hidden behind this two-spin and two-channel Kondo system. In addition, the Fe^{2+} ion in the organic cage is movable perpendicularly to the molecular plane as implied from the structural variation of heme protein molecules in which Fe2+ ion in a porphyrin ring moves upon the attachment and detachment of oxygen molecule. Thus, tuning the local structure around the Fe^{2+} ion in FePc brings about a transition between the Kondo- and SOI-dominant regimes.

In this work, we experimentally and theoretically investigate the spectral evolution arising from the competition between the Kondo effect and the SOI in an S=1 Kondo system of FePc on Au(111). By controlling the distance between the Fe^{2+} ion and the Au substrate through approaching a scanning tunneling microscopy (STM) tip to the ion, we tune the Kondo couplings relatively to the SOI, and demonstrate the spectral crossover between the Kondo- and the SOI-dominant regimes.

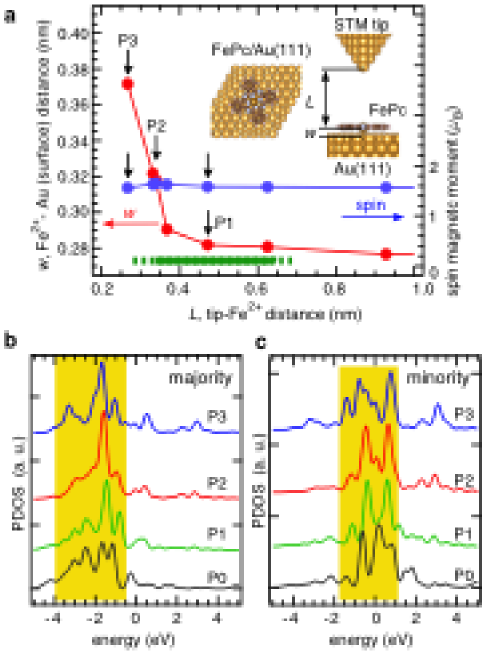

Fig. 9 | Variation of geometric and electronic structures. (a) Variation of distance between the Fe^{2+} ion and the Au atom underneath (defined as w) and the spin magnetic moment in Fe 3d orbitals calculated as a function of the distance between the ion and an apex Au atom of approaching STM tip (defined as L). The inset shows the calculated structure models rendered by VESTA. FePc is located at the on-top site of Au(111). Green horizontal bar indicates the traveling range of tip in the STM experiment. (b, c) Variation of PDOS spectra of dz^2 as a function of tip-molecule configuration (P0-P3). The PDOS of the majority and minority spins are shown in b and c, respectively. P0 represents the configuration without the tip. P1-P3 indicate the tip positions marked in a with small arrows. Highlighted regions show marked differences in the PDOS spectra.

(5) Raman spectra of self-assembled monolayers on gold electrode

We are developing new experimental technique, tip-enhanced Raman spectroscopy (TERS) in liquid environment, to achieve nanoscale Raman signal mapping of organic molecules on metal electrodes with local structural properties. While a gold tip enhances the incident electric filed as much as 100, TERS measurements still reacquires the highly Raman active molecules to be studied because the long accumulation of the Raman signal is hampered by instrumental instability. It is thus prerequisite to systematically study the Raman intensity for the various kinds of organic molecules (self-assembled monolayers (SAMs) on gold electrode). In this study, we have succeeded in obtaining Raman spectra of 24 molecules adosobed on gold dimer, by which we can model the SAMs (Fig. 1(a)). We found that Ph_3SH molecule on the gold dimer is the most Raman active system, and the DFT calculation reproduce the Raman spectra very well (Fig. 1(b)). Now we are trying to develop the TERS technique in liquid environment using the Ph_3SH SAMs on gold.

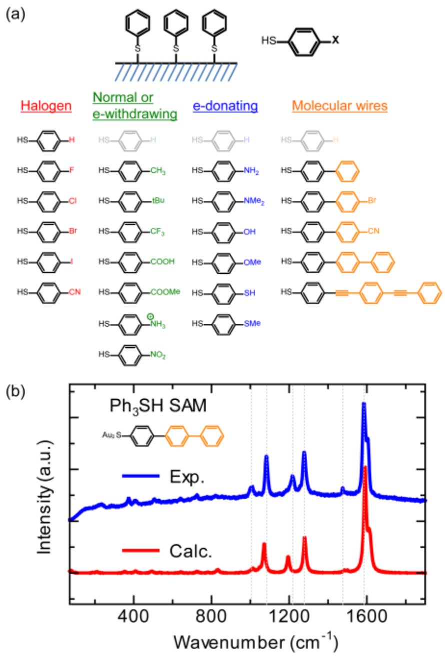

Fig. 10 | (a) Molecules calculated in this study. (b) Experimental and calculated Raman spectra of Ph3SH SAM.

(6) Quantum many-body effects on fluctuation in electrical current for single molecule junction system [K. Miwa, F. Chen, M. Galperin, Sci, Rep. 7, 9735 (2017)]

Transport and optical properties of molecules have been of great interest from the viewpoint of fundamental science and potential applications to organic (opto)electronic devices, e.g., organic light-emitting diodes (OLEDs) and organic field-effect transistors (OFETs). With a recent progress in experimental techniques at nanoscale, it becomes possible to observe a transport and optical characteristics of molecules beyond average flux measurement. Especially, measurements of fluctuation in electrical current and/or photon flux for single molecule junctions were recently reported in the literature. Time-dependent fluctuations due to the discrete nature of electrons and/or photons are known as shot noise that provides additional information not accessible through average flux measurements. Comparing with the average flux, shot noise is also in general more sensitive to the intra-molecular interactions, e.g. Coulomb interactions between electrons occupying molecular orbitals, magnetism, and intra-molecular electron-vibration interactions. Constructing a simulation method of shot noise in electrical current and photon flux for single molecule junctions within the quantum many-body theory will reveal a detailed process of conduction and/or optoelectronic conversion in molecular junctions.

In this financial year, we developed the theoretical technique to calculate the electrical current noise for single molecule junction, taking into account intra-molecule Coulomb interaction. The proposed technique employs the nonequilibrium Green's function method formulated using Hubbard *X*-operators (Hubbard-NEGF technique), and its validity was investigated by simulating the bias-voltage dependence of shot noise and noise spectrum within the generic models for the case of non-, weakly and strongly interacting systems. By comparing with the shot noise and noise spectrum obtained by using other theoretical technique best suited for each of the three parameter regimes (standard NEGF approach, the pseudoparticle NEGF approach, and Quantum master equation approach), we confirmed that Hubbard NEGF technique is valid over the wide range of parameters. [K. Miwa et al., Sci. Rep. 2017]. Our proposed technique thus serves as a useful tool for investigation of noise characteristics for single molecule junctions. Now we're expanding the technique in order to include intra-molecular electron-vibration couplings as well as exciton-photon couplings for simulating not only electrical current noise but also photon flux noise. Based on the developed technique, quantitative simulation of noise characteristics combining first principles calculations will be performed.

４. Conclusion

We have tried to examine a variety of molecular behaviors on the surface in FY2017. Our theoretical studies combined with experiments in FY2017 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 FY2018, 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, and their optical properties

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 that the interfacial electronic structure of individual adsorbate on solid surface is closely related to the chemical reactivity through the excitation with photon and plasmon. 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 FY2018, we will continue the research not only for a variety of molecular assemblies but also isolated molecule on the surfaces as follows: (1) the formation mechanism of van der Waals interface between π-conjugated molecule and novel metal substrate, and (2) optical property of adsorbate on solid surface.

(3) Electronic structures of layered materials, such as graphene and dichalcogenide, and of framework materials, such as MOF and COF

Functionalization of layered materials, such as graphene and dichalcogenide, has attracted great scientific interest not only in controlling their physical properties but also in improving chemical adaptability to integrate them 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 addition, we recently studied the growth mechanism of covalent organic framework (COF) through photo-excitation. In FY2018, we are going to theoretically investigate (1) 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, and (2) the catalytic effect of metal-organic framework (MOF).

(4) Magnetic molecules on metal surface

As we demonstrated in the above section, the magnetism in the molecular adsorption system exhibits unique physical properties. We will also try to investigate the influence of the molecular adsorption in the magnetic properties of substrates. In particular, we will focus on the possibilities of tuning the magnetic anisotropy of ferromagnetic substrate by molecular decollation.

(5) Electron-phonon coupling in 2D materials

As we shown in the above section, now we become possible to estimate electron-phonon coupling in layered materials quantitatively. We will extend our research target to transition metal dichalcogenides and polar semiconductor, where the electron-phonon interaction plays important role for transport and thermal properties.

(6) Raman spectra of self-assembled monolayers on gold electrode

As mentioned in the above section, we have obtained the 24 Raman spectra of self-assembled monolayers using DFT calculation. We will try to perform experiments for next half year, and will perform DFT calculation to find next more attractive targets.

(7) 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. Single molecule luminescence can be induced by the tunneling current of STM, enabling 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 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 calculations 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 2017

Fiscal Year 2017 List of Publications Resulting from the Use of the supercomputer

[Publication]

1. Ryoichi Hiraoka, Emi Minamitani, Ryuichi Arafune, Noriyuki Tsukahara, Satoshi Watanabe, Maki Kawai, and Noriaki Takagi, “Single-molecule quantum dot as a Kindo simulator”, *Nature Communications*, 8, 16012 (Jun 2017)
2. Hiroshi Imada, Kuniyuki Miwa, Miyabi Imai-Imada, Shota Kawahara, Kensuke Kimura, Yousoo Kim, “Single molecule investigation of energy dynamics in a coupled plasmon-exciton system”, *Physical Review Letters* 119, 013901 (Jul. 2017).
3. Kuniyuki Miwa, Feng Chen, Michael Galperin, “Towards Noise Simulation in Interacting Nonequilibrium Systems Strongly Coupled to Baths”, *Scientific Reports* 7, 9735 (Aug. 2017).
4. Soyoung Kim, Chibeom Park, Minkyung Lee, Intek Song, Jungah Kim, Minhui Lee, Jaehoon Jung, Yousoo Kim, Hyunseob Lim, and Hee Cheul Choi, “Rapid photochemical synthesis of sea-urchin-shaped hierarchical porous COF-5 and its lithography-free patterned growth”, *Advanced Functional Materials* 27, 1700925 (Aug. 2017).

[Oral presentation at an international symposium]

1. Hiroshi Imada, “Single molecule investigation of energy absorption, emission, and transfer dynamics with a scanning tunneling microscope”, Nano Korea 2017, Ilsan, Korea, (Jul. 2017) [Invited].
2. Jaehoon Jung and Yousoo Kim, “Computational studies on the interfacial electronic structures on solid surfaces”, ISCPMS 2017, Bali, Indonesia, (Jul. 2017).
3. Kuniyuki Miwa, Hiroshi Imada, Feng Chen, Kensuke Kimura, Miyabi Imai-Imada, Yousoo Kim, and Michael Galperin, “Theory of current fluctuation for single molecule junction with intra-molecule Coulomb interaction and multimode vibronic interactions”, APS March Metting 2018, Los Angeles, USA, (Mar. 2018).
4. Kensuke Kimura, Hiroshi Imada Kuniyuki Miwa, Miyabi Imai-Imada, Shota Kawahara, Jun Takeya, Maki Kawai, Yousoo Kim, “Investigation of the Exciton Formation in a Single Molecule with a Scanning Tunneling Microscope”, APS March Metting 2018, Los Angeles, USA, (Mar. 2018).

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

1. “新原理に基づく単一分子発光・吸収分光を実現”, 理化学研究所報道発表, Jul. 2017.