Calculation of photoelectron angle distribution in the photoexcitation process on the organic molecules adsorbed surface

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In recent years, it has been reported electronic and physical properties of organic molecules which interact with the surface using Wave number space resolved Photoelectron Spectroscopy. We have investigated the copper (Ⅱ) phthalocyanine (CuPc) - monolayer substrate system. Monolayer $TiSe_2$ have two typically phases depending on the temperature. A (1×1) structure (normal phase) is shown at room temperature and a (2×2) superstructure (CDW phase) is realized under the 200 K. Each phase has band gap of 83 meV and 153 meV, respectively [1, 2]. We have adopted this interesting thin film as the substrate and reported the structural changes depending on the temperature in the previous year. In this year, we investigated the electronic state of a (1×1) monolayer $TiSe_2$. Based on these results, we optimized the structure of CuPc adsorbed on $TiSe_2$.

1. Band calculation of TiSe₂ monolayer

We performed density functional theory (DFT) calculations using the Vienna Ab Initio Software Package (VASP) version 5.4.4 [3,4]. The exchange correlation effects were described by the Generalized Gradient Approximation (GGA) within the Perdew-Burke-Ernzerhof (PBE) formalism. We used a unit cell with lattice constants a = b = 3.53 Å, c = 20.0 Å, $\alpha = \beta = 90°$ and $\gamma = 120°$, and plane-wave basis set with the projector augmented wave (PAW) approach with an energy cutoff of 380 eV. The Brillouin zone integration was performed on a Monkhorst-Pack of 18×18×1 grid of k-points. The energy convergence criterion was chosen for the self-consistency cycle was $1×10^{-7}$ eV. To account for Fermi surface broadening, temperature parameter σ for Methfessel-Paxton smearing was applied [5].

We investigated a local Coulomb repulsion of Ti 3d electrons and the effect of the electronic smearing parameter σ on the band gap. We calculated band gaps with different sets of Coulomb repulsion U and σ. Fig. 1(a) show a negative bandgap without considering U and σ. On the other hand, fig. 1(b) and (c) have positive bandgaps close to 0. It is found that both σ and U increase the gap between the top of Se 4p band (Γ, red point) and the bottom of Ti 3d band (M, blue point). However, the rise in σ push up the upper end of the Se4p band above the fermi surface, so Fig. (b) is also excluded. As a result, we find the parameter set

($U = 3.9$ eV and $\sigma = 0.01$ eV) which reproduce experimental result [6]. We used these parameters for optimization of CuPc / TiSe$_2$ structure.
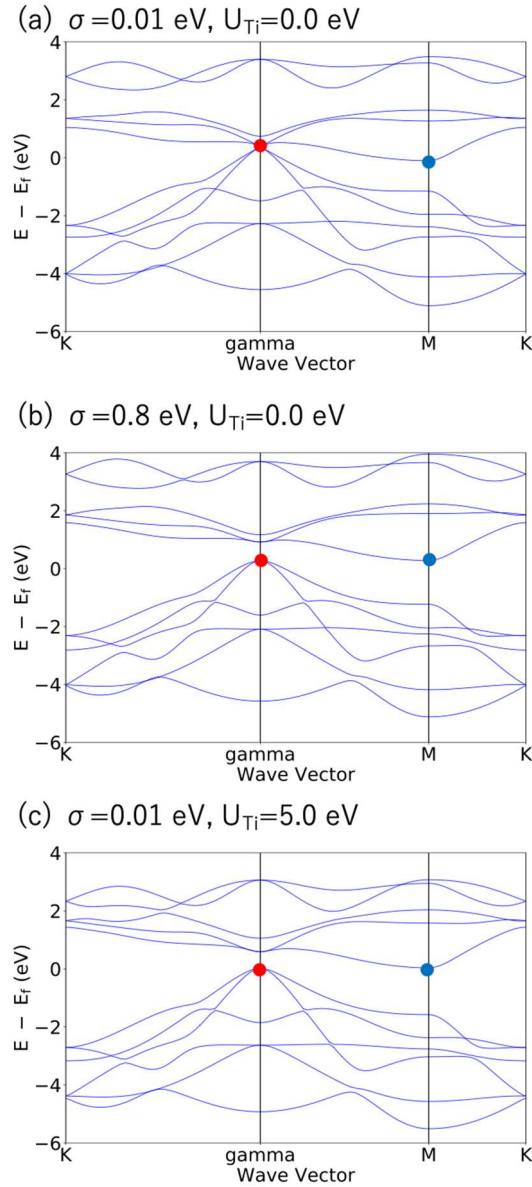
(a) $\sigma = 0.01$ eV, $U_{Ti} = 0.0$ eV

(b) $\sigma = 0.8$ eV, $U_{Ti} = 0.0$ eV

(c) $\sigma = 0.01$ eV, $U_{Ti} = 5.0$ eV

Figure 1 Band dispersion of the (1×1) monolayer TiSe$_2$ with different electronic smearing parameter σ and effective Hubbard parameter U for Ti.

2. Structural optimization of CuPc/TiSe$_2$

We expanded above model for an 8 × 8 structure of the monolayer TiSe$_2$ with lateral dimensions of 693 Å^2. For Cu atom of CuPc, U value was adjusted to 4.0 eV which could reproduce the qualitative orbital ordering of isolated CuPc. In addition, CuPc had an unpaired electron, thus we considered spin polarization. Ionic positions were optimized until the residual force on each ion was less than 1×10^{-2} eV/Å. When starting with a random wave function, it took about 12 hours to converge one electronic state using 5 nodes with total 144 cores. From this structure optimization calculation, it is found that the adsorption distance between molecule and substrate is 3.16 Å, resulting in a flat molecule structure.

We have reached the stage where it is possible to calculate the Wave number space resolved Photoelectron Spectroscopy. We are planning to perform this calculation next year.

References

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