Development of analysis method for molecular crystal surface using wave number space-resolved photoelectron spectroscopy

Kaori Niki

Graduate school of science

Chiba University, Yayoi-cho, Inage-ku, Chiba 263-0022

By using wave number space photoelectron spectroscopy, it has become possible to obtain a photoelectron momentum maps (PMMS) of a molecular thin film in a short time. This allowed us to obtain tomography of the wavefunction. It is suggested that more information can be obtained by analyzing PMMS in detail. We have been analyzing the surface of molecular crystals with the aim of establishing a method for analyzing momentum maps based on the multiple scattering method. For the initial state, we refer to the electronic state of the adsorption system calculated by Vienna Ab initio Simulation Packge (VASP) [1,2]. So far, we have suggested that by PMMS, it may be possible to identify the adsorption position of molecules adsorbed on the substrate surface [3].

In 2020, we expanded the sample to a more complex system. We placed VASP on the Supercomputer of Institute for Solid State Physics and performed two calculations.

1. Structural optimization and multiple scattering calculation of PTCDA / Ag (111).

The initial position of 3,4,9,10-Perylenetetracarboxylic dianhydride (PTCDA) was set to the Short-bridge site on Ag (111), and structural optimization was performed. Since PTCDA does not contain transition elements, the calculation cost is low. Periodic DFT calculations were carried out with VASP code using the projector augmented wave (PAW) method with a plane wave energy cutoff of 400 [eV] and the PBE exchange-correlation functional. The criterion convergence chosen for the SCF cycle was 10^{-8} eV, and optimization were considered converged once the forces on all atoms were lower than 10^{-8} [eV/Å] The slab was 12.1 x 12.1 [Å] large, and 10 [Å] thick (60 Ag atoms, 2PTCDA per unit cell) with a vacuum separation 20 [Å]. The three lowest layers were frozen during optimizations. The Brillouin zone was sampled with a 4x4x1 k-point grid. Electron occupancies were determined according to a Methfessel-Paxton scheme (order1) with an energy smearing of 0.2[eV].

As a result of structural optimization, PTCDA was curved in an arc with respect to the surface. PMMS calculations (using our computer) were performed using these coordinates. The PMMS has changed significantly compared to the results without the substrate. When I did the same calculation on multiple sites, I found that PMMS was different for each site. This indicates

the possibility of obtaining information on the adsorption position from PMMS.

2. Structure optimization and multiple scattering calculation of CuPc and $TiSe_2$

In order to calculate the PMMS of Copper (Ⅱ) phthalocyanine (CuPc) / $TiSe_2$, the structure of CuPc and $TiSe_2$ was optimized. First, we performed structural optimization of CuPc. CuPc has a large number of constituent atoms and contains transition elements with spin. The calculation cost is high and the calculation method is complicated. Highest Occupied Molecular Orbital (HOMO) -1 was not calculated in the correct position when Generalized Gradient Approximation (GGA) was used as a functional. It has been reported that HOMO -1 can be calculated correctly using the hybrid functional according to Heyd et al. (HSE), but the calculation cost is high [4]. We also tried this, but couldn't succeed.

Next, the structure of TiSe2 was optimized. TiSe2 takes the CDW layer at low temperature and undergoes a phase transition to the normal phase at around 200 K [5]. To obtain information about the relationship between σ and temperature during smearing, we calculated the temperature dependence of the charge density wave (CDW) structure and the normal phase. Structural optimization was performed for two layers of TiSe2. The calculation conditions are the same as those described above. The normal layer extended the (1x1) structure to (2x2). For the CDW layer, the coordinates were entered based on the paper [5].

Figure 1 shows the temperature dependence of energy. The horizontal axis is temperature, and the longitudinal axis is energy, white triangles are the CDW layer, and black squares are the normal phase. From this calculation, it was found that 200K at which the phase transition occurs is approximately σ = 0.3. This calculation provided us with a guideline to use σ = 0.1 for low temperature calculations and σ = 0.4 for room temperature calculations in future.

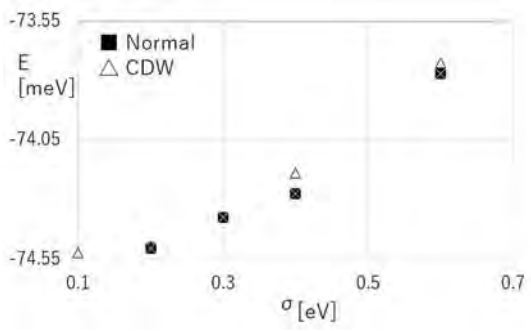

Figure 1. Energy dependence of sigma

Using these calculation results obtained, we plan to calculate the structural optimization and electronic state of the adsorption system in 2021.

References

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