

Coverage Dependence of Energy Levels in Organic Monolayer

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It is reported that the ionization energy (IE) and electron affinity (EA) of organic materials in the solid phase depend on the molecular orientation¹ and mixing ratio of two molecules having different quadrupole moments². In this presentation, we will demonstrate that IE and EA also depend on the surface coverage of an organic molecule below 1 monolayer (ML).

In the earlier studies, only IE is measured by using ultraviolet photoemission spectroscopy (UPS) and discussed alongside theoretical studies¹⁻³. Here, we also precisely examine the EA to elucidate the mechanism based on the experimental data by using low-energy inverse photoemission spectroscopy (LEIPS) which enable us to directly measure the unoccupied states with the precision of 0.1 eV⁴.

For the molecules, copper phthalocyanine (CuPc) and copper hexadecafluorophthalocyanine (F₁₆CuPc) were chosen since the molecules have a similar structure but possess a permanent quadrupole moment with the opposite direction. To obtain films with flat-lying orientation, we used a highly oriented pyrolytic graphite (HOPG) surface as a substrate⁵.

Figure 1 shows the combined UPS and LEIPS spectra. The energies of the HOMO and LUMO peaks corresponds to the IE and EA, respectively. As the surface coverage increases, both HOMO and LUMO peaks shift with the same direction to each other.

This behaviour can be explained by using the polarization effect in solid-state. The polarization effect can be divided into the dynamic interaction *D*, approximated by charge-induced dipole interaction, and the static interaction *S*, approximated by charge-permanent quadrupole interaction³. Since *D* and *S* shows different dependence on the polarity of the charge, *S* and *D* can be connected with EA and IE in the solid (*A_s*, *I_s*) and gas (*A_g*, *I_g*) phases as follows:

$$A_s - I_s = A_g - I_g + 2D$$

$$A_s + I_s = A_g + I_g + 2S$$

Since *A_g* and *I_g* are constants, the coverage dependence of *S* and *D* can be discussed as shown in figure 2. The results clearly indicate that *S* is

more coverage-dependent compared to *D* in the sub-monolayer.

From this experiment, we can conclude that the shift of EA and IE in the sub-monolayer region is predominately contributed by *S*.

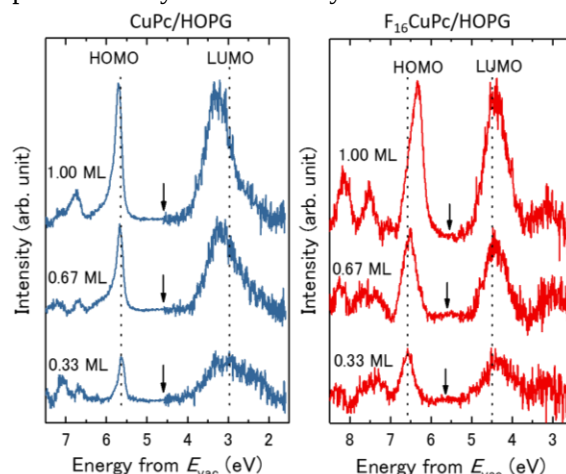


Figure 1. LEIPS (low energy region) and UPS (high energy region) spectra of CuPc and F₁₆CuPc. The arrows indicate the fermi level.

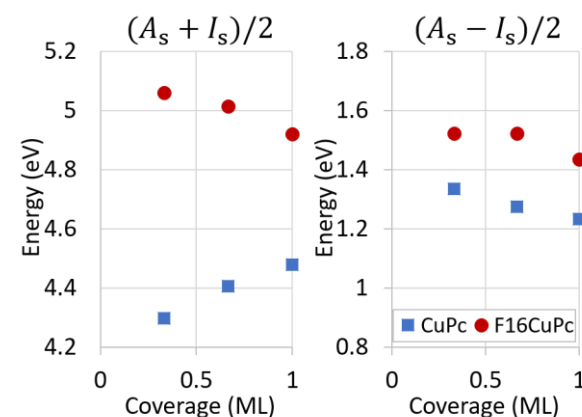


Figure 2. Dynamic and static interaction for both CuPc and F₁₆CuPc.

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