Temperature and Coverage Dependent Quasi-reversible Two-photon Photoemission of 1-phenyl-1-propyne on Cu(111)

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A temperature- and coverage-dependant quasi-reversible change in two-photon photoemission (2PPE) of chemisorbed 1-phenyl-1-propyne (PP) on Cu(111) is reported. For PP on Cu(111) at 300 K probed at a photon energy of 4.13 eV, two broad peaks of comparable intensity show final state energies of 7.25 and 7.75 eV above the Fermi level. The former peak could be assigned to the first image potential state (IS, n = 1) and/or unoccupied molecular orbital (UMO), located at 3.1 eV above the Fermi level. The latter is plausibly attributed to a mix of unoccupied higher-order IS (and/or UMO) and occupied surface state (SS) of Cu(111). With decreasing the temperature, the former 2PPE peak shows a shift in position by about 0.2 eV, and the latter exhibits a dramatic increase in intensity. In the system, intermolecular interactions (and/or order-disorder transition) of PP and substrate lattice temperature may play a significant role in change in photoexcitation lifetime (or excitation cross-section), and the unoccupied molecular orbital (UMO)-metal (IS) charge transfer coupling. Our unique 2PPE results provide a deeper insight for understanding photoexcitation charge transfer with temperature in an organic molecule/metal system.

Key Words : Two-photon photoemission spectroscopy, Image potential state, Surface state, Photoexcitation charge transfer, 1-Phenyl-1-propyne (PP)

Introduction

The aligned energy levels at molecule/metal interfaces and the relevant charge transfer processes are critically important to understand such as performance of molecular electronic devices and surface photochemical reactions.[1-6] For a simple molecular electronic device consisting of a molecule sandwiching between two metal electrodes, a basic operation concept is a charge flow from one to the other electrode through the sandwiched molecule.[1,2] In the device, the electron and hole barrier heights are one of the most important factors determining efficiency. The binding of an anchor functional group such as thiol (-SH) with the metal electrode is directly related with the interfacial energy levels and electronic couplings.[2] For understanding photo-induced charge transfer chemical reactions, an electronic coupling between the unoccupied orbitals of molecules and metal substrates needs to be understood.[1]

Two-photon photoemission spectroscopy (2PPE) has been widely employed to investigate the interfacial energy levels and the electronic couplings at molecules/metal, however, the metal-UMO resonance has been debated because the resonance is absent in most cases.[1,2,7-9] Motivated by this, we further delve into this issue by investigating the 1-phenyl-1-propyne/Cu(111) system by means of 2PPE, ultraviolet photoelectron spectroscopy (UPS) and temperature-programmed desorption (TPD) spectroscopy.

Experimental Section

The experiments were performed in an ultrahigh-vacuum chamber with a base pressure of less than 5×10^{-10} Torr, equipped with a time-of-flight (TOF) mass spectroscopy, X-ray photoelectron spectroscopy (XPS), UPS, Auger electron spectrometer, and a time-of-flight electron energy analyzer for 2PPE spectroscopy. The Cu (111) (13 mm diameter and 2.5 mm thick, MaTecK) single crystal was cleaned by several cycles of Ar+ ion sputtering and annealing until no contaminant was detected by XPS or Auger electron spectroscopy (AES). The 1-phenyl-1-propyne (Acros, 98%) was degassed by several freeze-pump-thaw cycles using liquid nitrogen. The molecule was dosed on the Cu(111) surface at 100 K or a selected temperature using a leak valve. Time-of-flight (TOF) temperature programmed desorption (TPD) spectra were taken at a temperature ramp rate of 2 K/s. For 2PPE, we utilized a tunable Spectra-Physics MOPO/FDO-900 laser system pumped by a Quanta-Ray 170-10 Nd-YAG laser, and the photon pulses (7 ns) were incident at 45°.[10]

Results and Discussion

On the basis of temperature programmed desorption (TPD)

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profiles of 1-phenyl-1-propyne on Cu(111) dosed at 100, 300 and 340 K, 1-phenyl-1-propyne (PP) molecularly adsorbs and desorbs without detectable dissociation.[11] For the first-layer chemisorbed PP, a minor and a major peak are observed at 320 and 390 K, respectively, with an integrated intensity ratio of 0.15.[11] The major peak has been assigned to a cross-bridged -C=C- geometry, where the *sp* hybridization of carbon of acetylene group changes to *sp*². The minor peak has been assigned to vertically aligned vinilyidene-type structure.

Figure 1 shows the 2PPE spectra of 1.0 ML PP on Cu(111) dosed at 300 K, measured with decreasing the substrate temperature. In the spectra, three major photoemission characteristics are revealed. First, in the 2PPE spectra taken at 300 K, two broad peaks are clearly seen above 7 eV; one peak at ~7.25 eV varies linearly with photon energy while the other peak at ~7.8 eV exhibits a linear fit slope of slope= 1.5 ± 0.25. The details of the slopes and the peak assignment are described in elsewhere.[11] Briefly, in 2PPE process, if the variation is 1 the photoemission peak is due to a photo-ionization from an unoccupied state, corresponding to the former peak. The former peak (slope=1) is then assigned to an unoccupied state.[1,2] The peak could be due to the first image potential state (IS, n=1). Considering the probe photon energy of 4.13 eV, the unoccupied state is located at ~1.0 eV below the vacuum level (or 3.1 eV above the Fermi level). This value is fairly close to the value of IS (n=1) for clean

Cu(111) reported in the literature.[12,13] For 1 ML naphthalene/ Cu(111), Wang *et al.*, found an unoccupied state located at 1.1 eV below the vacuum level (or 3.1 eV above the Fermi level).[14] This is in very good agreement with our result. They showed that the unoccupied state behaves like an image state. In this paper, we will tentatively assign the unoccupied state peak to IS (n=1) and/ or unoccupied molecular orbital (UMO). For the latter peak, unfortunately, the peak could not be well-resolved using our experimental (photon energy) setup. The slope of 1.5 is neither solely due to an unoccupied state nor an occupied state. The direct two-photon photo-emission from an occupied state exhibits a slope of 2. This could suggest that the slope of 1.5 is a mixed state originated from both unoccupied (slope=1) and occupied (slope=2) states. We attribute the slope=2 to Cu surface state (SS). The slope=1 could be due to higher-lying image potential state (IS),[11] UMO, or a mixed IS/UMO state. In addition to the two broad peaks, the peak at ~6.1 eV shows a slope of 2 with photon energy, and is assigned to the highest occupied molecular orbital (HOMO) and Cu *d*-band.[10]

The second main observation in Figure 1 is that as the temperature is lowered the intensity of the latter peak (IS/ UMO+SS) dramatically increases accompanying the narrowness of the peak. While the HOMO/*d*-band and the IS(n=1)/ UMO peaks show slight decreases in intensity, as seen in Figure 1. The former IS(n=1)/UMO peak shows a shift to the higher kinetic energy side, a decrease in intensity, and a
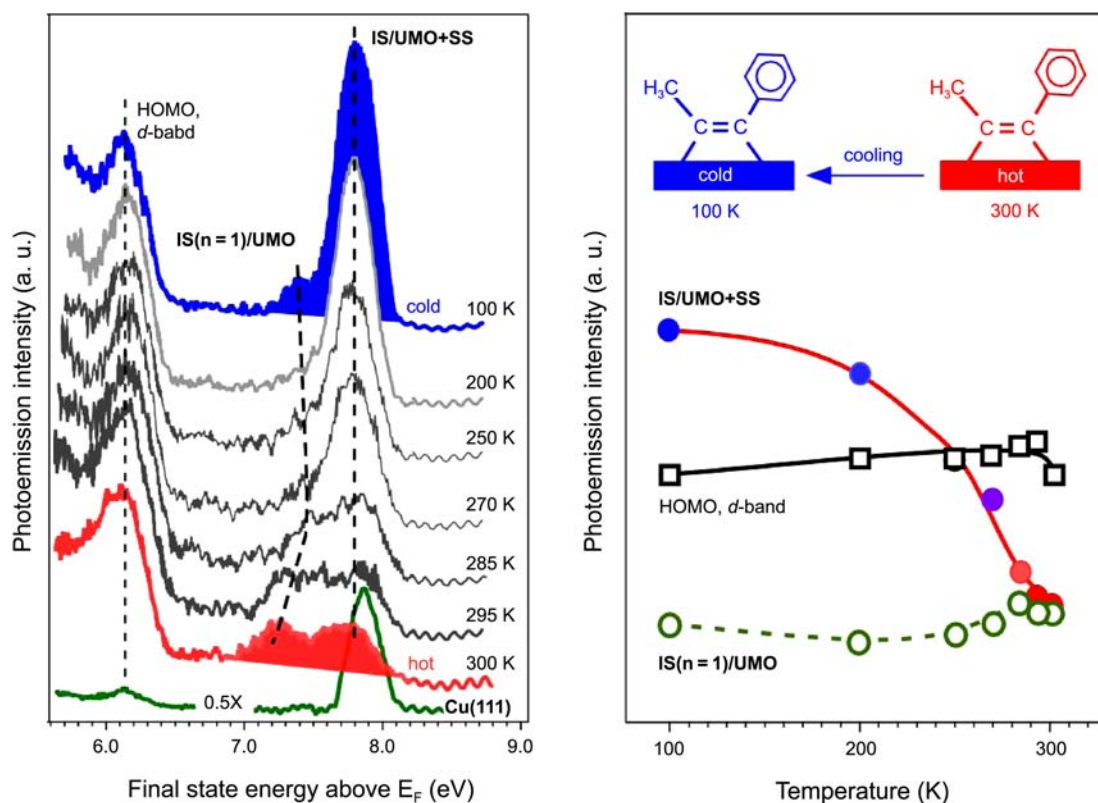

Figure 1. 2PPE spectra taken with lowering temperature from 300 to 100 K for 1.0 ML PP in Cu(111) dosed at 300 K, at a pump-probe photon energy of 4.13 eV, including the 2PPE of bare Cu(111) at 300 K. IS=image potential state; UMO=unoccupied molecular orbital; SS=surface state. The laser power was fixed during the measurements. Right figure shows the changes in the peak intensities with temperature.

narrowness of the peak. In the 270-200 K region, the IS(n=1)/UMO peak is not clearly revealed, which has been reproducibly observed. It appears that the former and the latter peaks merge to a single peak. The IS(n=1)/UMO peak may be shifted further and buried in the IS/UMO+SS peak. In the temperature below 200 K, the IS(n=1)/UMO peak obviously reappears, and looks re-separated from the IS/UMO+SS peak. Upon cooling to 100 K, the state is positioned at ~0.85 eV below the vacuum level, 0.15 eV shift towards the vacuum level. We assume that a change in Cu lattice with temperature could lead the changes in spectral shape and position.[15] We also do not exclude a wave function mixing between the metal and PP involving the photoemission from UMO. For physisorbed molecules such as benzene and naphthalene on metal substrates, the electronic coupling between metal and UMO is weak, and the UMO peak is commonly not seen in the 2PPE spectra.[1,2,7] It should be emphasized here that the 2PPE of bare Cu(111) shows no critical change in intensity with temperature. Therefore, the observed reversible changes must involve chemisorbed PP molecules on Cu(111).

The third is that the 2PPE spectra quasi-reversibly change with temperature as seen in Figure 2(a). The enhanced IS/UMO+SS peak attenuates upon re-heating to 260 and 300 K, and re-grows by re-cooling to 100 K. And, the IS(n=1)/UMO peak oppositely shows the same phenomenon. For

multilayer PP on Cu(111) at 100 K, the 2PPE spectrum is very similar to that taken at 300 K. To check the effect of the vertically aligned minor chemisorbed PP[11] on the photoemission intensity with temperature, we dosed PP on Cu(111) at 340 K to remove the minor PP, and took 2PPE spectra with decreasing temperature. As mentioned above, the desorption temperature of the minor PP is at 320 K, and the surface coverage of PP is about 0.8 ML after dosing at 340 K. The 2PPE spectra in Figure 2(b) also show the very similar change in intensity as the spectra in Figure 1. The intensity of the latter peak (IS/UMO+SS) at 100 K is enhanced by 10×, compared to that at 340 K. The IS(n=1)/UMO peak almost disappears at 290 and 270 K, but reappears at lower temperatures (160 and 100 K). From the result, we conclude that the vertically aligned PP is not importantly involved in the enhancement of IS/UMO+SS peak, and the shift in IS(n=1)/UMO peak. To check the influence of PP coverage on the photoemission intensity, we further reduced the coverage of PP on Cu(111) by dosing at a higher temperature of 380 K, corresponding to a coverage of about 0.5 ML. Interestingly, the 2PPE spectra show no critical change with decreasing temperature to 100 K (Figure 2(c)). In addition, the latter IS/UMO+SS peak becomes weaker than the former IS(n=1)/UMO peak. This indicates that the 2PPE of PP/Cu(111) is a coverage-dependant. In other words, intermolecular interactions may play an impor-
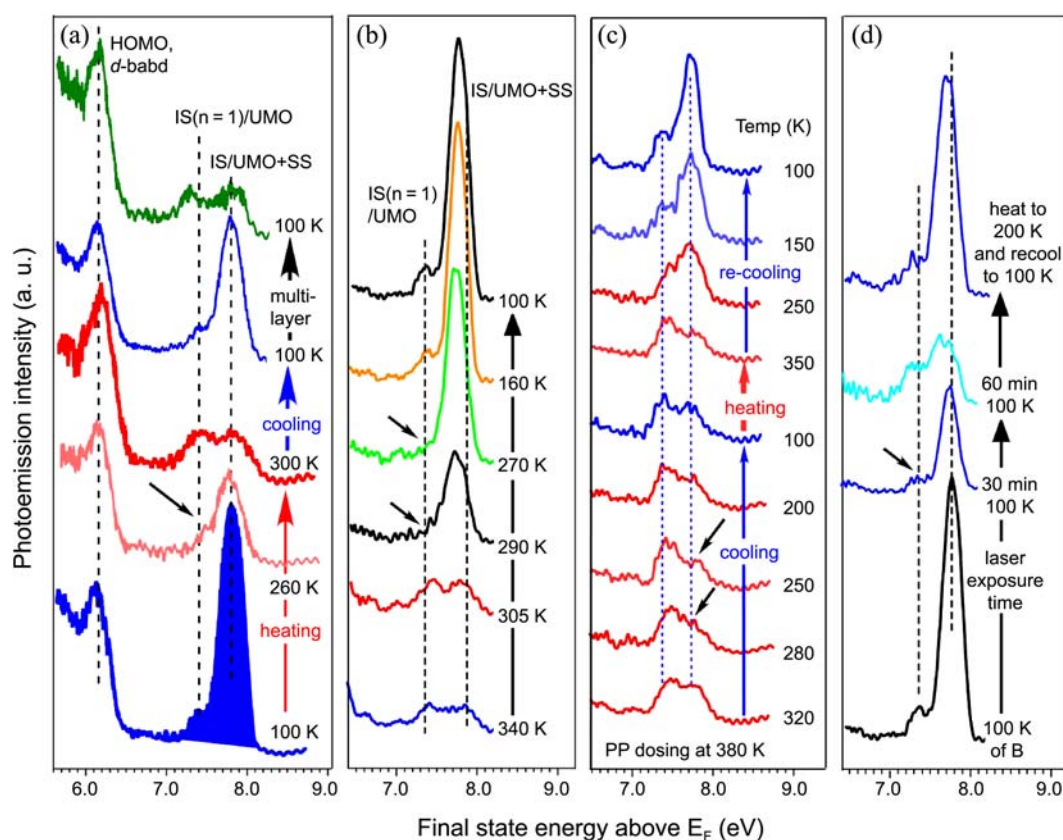
Figure 2. (a) 2PPE spectra upon reheating to 260 and 300 K, and cooling back to 100 K. 2PPE spectrum upon further dosing to form multilayer. (b) 2PPE spectra for PP dosed at 340 K with decreasing temperature. (c) 2PPE spectra of PP on Cu(111) dosed at 380 K with cooling, heating and recooling the substrate. (d) 2PPE spectra (at 100 K) after exposing the incident laser for 30 and 60 min, and after reheating to 200 K followed by cooling to 100 K.
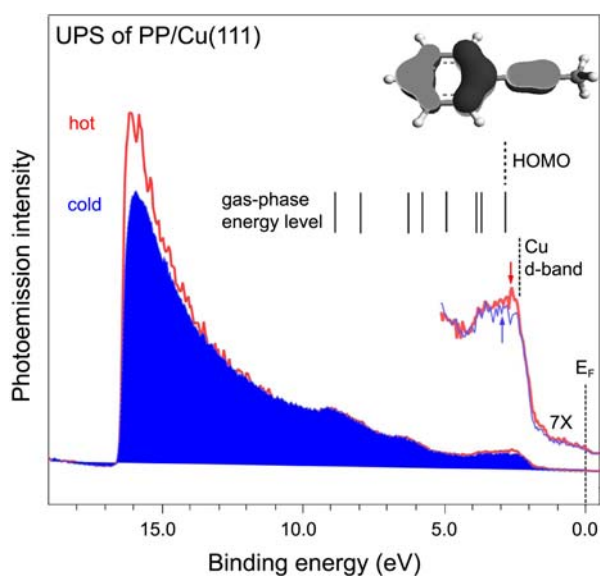
Figure 3. UPS spectra (He **I**, $\hbar\omega$ = 21.2 eV) of 1.0 ML PP on Cu(111) dosed at 300 K, taken at 300 (hot) and 100 K (cold). Upper right shows the corresponding spectra after 7×. Binding energy is referenced to the Fermi level (E_F = 0.0 eV). Theoretically calculated gas-phase energy levels and HOMO of PP are displayed for reference.[11]

tant role in change in the 2PPE with temperature. The intensity of the latter peak at 100 K could be more or less enhanced, but not as much as the peak in Figure 2(b), by re-heating to 350 K followed by re-cooling to 100 K. The 2PPE is also influenced by laser irradiation. The IS/UMO+SS peak intensity deteriorates with increasing laser exposure time (Figure 2(d)), but the intensity could be recovered by reheating and cooling. In Figure 2(d), the peak intensity is recovered after reheating to 200 K followed by cooling to 100 K.

Figure 3 shows the ultraviolet one-photon photoemission spectra taken at 300 and 100 K for the fully saturated 1.0 ML PP on Cu(111). For the 1.0 ML PP on Cu(111), the work function is lowered by 0.85 eV, referenced to the work function (Φ = 4.95 eV) of bare Cu(111).[11] Unlike the 2PPE profiles, there is no notable change in photoemission peak profiles with temperature. In addition, the exactly same low energy secondary electron cutoff indicates no change in work function (or no change in molecular dipole alignment) with temperature. Because of the same broad peak positions (BE = 0 to 10 eV) and no change in work function, we ruled out the scenario of changing from the state of chemisorption to that of physisorption with lowering temperature.[8] One may argue that although the change in UPS is not significant as 2PPE, there is a slight spectral change (marked by arrows) in the HOMO position between 0.0 and 5.0 eV (7× expanded spectra). This could be related with a slight change in chemical interaction between PP and Cu *d*-band,[12] consequently leading a dramatic change in 2PPE.

Then, why does the dramatic change in 2PPE peak occur without disturbing the main chemical bonding? The dramatic enhancement could be due to a resonance excitation between

the surface and image potential states. When a photon energy ($\hbar\omega$) tunes to the energy gap the transition probability from the SS to the IS increases considerably, leading to an overlap and a drastic enhancement of the photoemission peak.[16] However, this may not be the major reason because the IS/UMO+SS peak probed at lower photon energies (e.g., 3.76 eV, an off-resonance condition) is also dramatically enhanced by about the same fold increase, compared to the spectra taken at 300 K. In addition, if the resonance excitation is the major reason, the 2PPE enhancement should also occur irrespective of temperature and coverage. But this is not consistent with our results. Image state lifetime and dephasing rate influenced by lattice temperature are plausibly considered.[15,17] For clean Cu(111), Wolf and coworkers first observed that IS and SS peaks shift with temperature.[15] They explained the temperature dependent 2PPE by lifetime and dephasing rate. The former IS(n=1)/UMO peak in Figure 1 could be explained by this.

For an organic molecule on metal substrate, the 2PPE intensity (especially the latter IS/UMO+SS peak) more drastically changes with temperature, and our 2PPE is the first observation. Then, plausible scenarios can be suggested on the basis our results as discussed above: intermolecular interactions (or order-disorder transition [18]) of adsorbate and the Cu lattice temperature could change the 2PPE[1] without disturbing the interface dipole and the main chemical bonding. Schöll *et al*. have shown that the interfacial bonding between an organic molecule and metal could be changed with temperature by order-disorder transition.[18] Consequently, with decreasing temperature, the binding energies of occupied and unoccupied states vary to change UMO-metal (IS) charge transfer coupling (or excitation cross-section and photoexcitation lifetime), leading to enhancing the 2PPE intensity.

Summary

In summary, for an organic molecule/metal system we have first observed that the 2PPE characteristics of 1-phenyl-1-propyne on Cu(111) quasi-reversibly changes with temperature, without a change in PP-Cu(111) chemical bonding. The change in UPS spectrum with temperature is not significant as the corresponding 2PPE spectrum. For bare Cu(111), no significant change in 2PPE was found with temperature using our experimental setup. Therefore, the PP molecules are must be involved in the temperature- and coverage-dependant quasi-reversible change in 2PPE. In the 2PPE spectrum, two broad peaks with final state energies of 7.25 and 7.75 eV above the Fermi level are seen. The former peak is assigned to unoccupied IS(n=1)/UMO state located at ~1.0 eV below the vacuum level (or 3.1 eV above the Fermi level). The latter peak is attributed to a mix of unoccupied IS/UMO and occupied SS states. With lowering the temperature, the IS(n=1)/UMO peak shifts towards the vacuum level, and latter peak shows a dramatic increase in intensity. We have explained the 2PPE results by changes in photoexcitation lifetime (excitation cross-section), dephas-

ing rates, and the unoccupied molecular orbital (UMO)-metal (IS) charge transfer coupling which are plausibly influenced by the intermolecular interactions (or order-disorder transition) of adsorbate and Cu lattice temperature. Although some are still under question, and requires more supporting experimental evidences, our unique temperature- and coverage-dependent 2PPE results provide a new insight for deeper understanding of photoexcitation charge transfer process between an adsorbate organic molecule and a metal surface.

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