PHYSICAL REVIEW B **80**, 113310 (2009)

Vibrationally resolved two-photon photoemission spectroscopy for lead phthalocyanine film on graphite

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(Received 9 July 2009; revised manuscript received 11 August 2009; published 30 September 2009)

Vibronic structure has been resolved in two-photon photoemission (2PPE) from the highest occupied molecular orbital (HOMO)-derived level of lead phthalocyanine film formed on graphite. The 2PPE from the HOMO-derived level was enhanced by the resonance with the third lowest unoccupied molecular orbital (LUMO+2)-derived level. At photon energies below and well above the resonance, the intensity of the vibronic structure was similar to that of one-photon photoemission. On the other hand, the vibronic structure was significantly weak at photon energies slightly above (<0.4 eV) the resonance. The decrease in the vibronic structure was attributed to the nuclear motion of molecule in the intermediate state associated with LUMO +2.

DOI: 10.1103/PhysRevB.80.113310 PACS number(s): 73.20.−r, 68.35.Ja, 79.60.Dp

The interaction of electron and hole with phonon is a key for electric conduction in solids as well as at interfaces. As for carrier transportation in organic semiconductors, the role of vibronic coupling has been discussed.[1,2] The hole-vibrational coupling at interfaces between organic molecular films and substrates has recently been resolved in photoemission spectroscopy and was discussed in relation to the hole-hopping mobility and the reorganization energy.[3,4] Experimental detection of the nuclear motion of molecule triggered by injection of electron into an unoccupied state is the next step to be explored for deeper understanding of electron transportation at the interface between inorganic substrate and organic film. Nuclear wave-packet motion of adsorbed atoms in an unoccupied state was reported as the real-time observation of a surface photochemical reaction.[5] On the other hand, vibration of molecule in an electronic excited state can be resolved only for thick films and is hardly resolved for the first adsorbed layer because lifetime of the excited state becomes too short by interaction with the substrate.[6] Two-photon photoemission (2PPE) spectroscopy gives spectroscopic and dynamic information on both occupied and unoccupied energy levels. Vibrational structure in 2PPE spectroscopy for adsorbed molecules will provide rich information on carrier dynamics at surfaces and interfaces, though vibrational resolution in 2PPE for adsorbed molecules was not very clear so far.[7] Here, we report vibrationally resolved features in 2PPE spectra for lead phthalocyanine (PbPc) films formed on highly oriented pyrolytic graphite (HOPG).

In our former 2PPE work for PbPc/HOPG, we have identified molecule-derived levels due to the next highest occupied molecular orbital (HOMO-1), HOMO, the lowest unoccupied molecular orbital (LUMO), LUMO+1, LUMO+2 as well as the first image potential state (IPS). Resonant excitation from the HOMO level to the LUMO+2 level was observed.[8] In this Brief Report, we examined the detailed spectral profiles of the HOMO- and LUMO+2-derived peaks at photon energies below and above the resonance. The vibrational satellite of the HOMO peak was found to be dependent on the excitation photon energy. The dependence was attributed to the nuclear motion of the molecule in the LUMO+2-related intermediate state.

The 2PPE experiments were performed in an ultrahigh vacuum (UHV) chamber. The light source was the p-polarized third harmonic output of a titanium sapphire laser operated at a pulse duration of 100 fs and a repetition rate of 80 MHz. The light was focused by a concave mirror of 350 mm focal length onto the sample surface at an incidence angle of 60°. Photoelectrons emitted to the surface normal were detected with a hemispherical energy analyzer (VG-CLAM4 with nine channeltrons) of 20 meV energy resolution. The acceptance angle of the analyzer was limited to be $\pm 1°$ with a specially modified electron entrance lens. HOPG substrate was cleaved in air and cleaned by heating at 673 K for 50 h in UHV. The cleanliness was confirmed by the work function (4.45 eV) and the peak width of the IPS feature (140 meV) measured with 2PPE spectroscopy for the bare HOPG. Note that focusing of the light to a sub-μm spot as in Ref. 8 was not employed here. The spot size of the light in this experiment was estimated to be about 80 μm. The large spot size was advantageous to increase the photoemission intensity while suppressing the broadening of spectrum due to the space-charge effect.[9] Then the uniformity of the films was a key of this experiment. Our microspot-2PPE (Ref. 8) and photoemission electron microscopy[10] experiments showed that well-ordered films of 1 monolayer (ML) thickness were prepared by annealing PbPc films of 0.4 nm thickness (reading of a quartz microbalance) at 373 K for 1 h. Formation of uniform films of sub-ML or >1 ML thickness was not successful[8] and only the 1 ML films were used in this experiment.

The 2PPE spectrum for the PbPc film at the room temperature measured with photon energy of 4.59 eV is shown in the top of Fig. 1. The lower horizontal axis is the initial energy (final energy $-2h\nu$, where $h\nu$ is the photon energy) with respect to the Fermi level (E_F), the upper one, the intermediate energy defined as (final energy $-1h\nu$). The one-photon photoemission (1PPE) result measured at 90 K with a He-I light source was plotted on the initial energy scale at the bottom. The 1PPE spectrum reproduced that of Ref. 11. The 1PPE feature at −1.33 eV initial energy was assigned to originate from the HOMO-derived level. Molecules in the film were lying flat on the substrate directing Pb atoms to

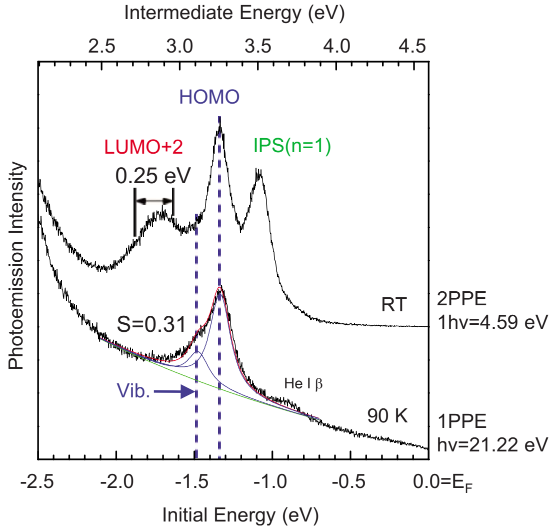

FIG. 1. (Color online) 1PPE (bottom) and 2PPE (top) spectra for the well-annealed 1 ML PbPc film on HOPG. Sample temperatures were 90 K and room temperature for 1PPE and 2PPE, respectively. The temperature difference caused no significant effects. The upper horizontal axis, valid only for 2PPE, is the intermediate energy above E_F. The main HOMO peaks were at -1.33 eV for both spectra. The LUMO+2 and IPS ($n=1$) peaks were observed in the 2PPE result. The width of the LUMO+2 feature was about 0.25 eV. The HOMO feature of the 1PPE spectrum was deconvoluted into two vibronic components [blue (gray) curves] separated by 140 meV. The fitted curve was shown by red (dark gray) line. The peak width was 157 meV and the S value (see text) was 0.31. The vibronic structure of the 2PPE result is significantly weaker than that of 1PPE. The hump at -0.9 eV is due to the HOMO-1 (-2.78 eV) feature excited by He Iβ.

vacuum side.[11] The HOMO-derived feature was deconvoluted with two Voigt functions of 157 meV full width at half maximum (FWHM), as shown by thin [blue (gray)] curves. The FWHMs of the fitted functions were 50 and 140 meV for Gaussian and Lorentzian, respectively. The small component at -1.47 eV was attributed to the vibronic structure in the final state.[3,4,11] The structure should be composed of several vibrational modes[3] though detail was not reported. Higher vibronic structures and an additional component at right-hand side of the main HOMO peak reported in Ref. 11 were not involved in the present fitting. In the 2PPE result, three clear peaks appeared. The peak at -1.33 eV initial energy was in agreement with the 1PPE result and was assigned to direct two-photon photoemission from the HOMO level. Note that the vibronic structure of the HOMO feature is only faintly visible in the 2PPE result. Because of the weak vibronic feature, it seems as if the HOMO-derived 2PPE peak was sharper than that of 1PPE. In reality, the width of the main HOMO peaks in 2PPE measured at 90 K (see Fig. 2) was about 155 meV and there was no difference from the 1PPE result. The peaks at $+2.87$ and $+3.52$ eV intermediate energies were absent in the 1PPE result. These were due to the LUMO+2-derived unoccupied state and the IPS ($n=1$) formed on the PbPc films, respectively.[8]

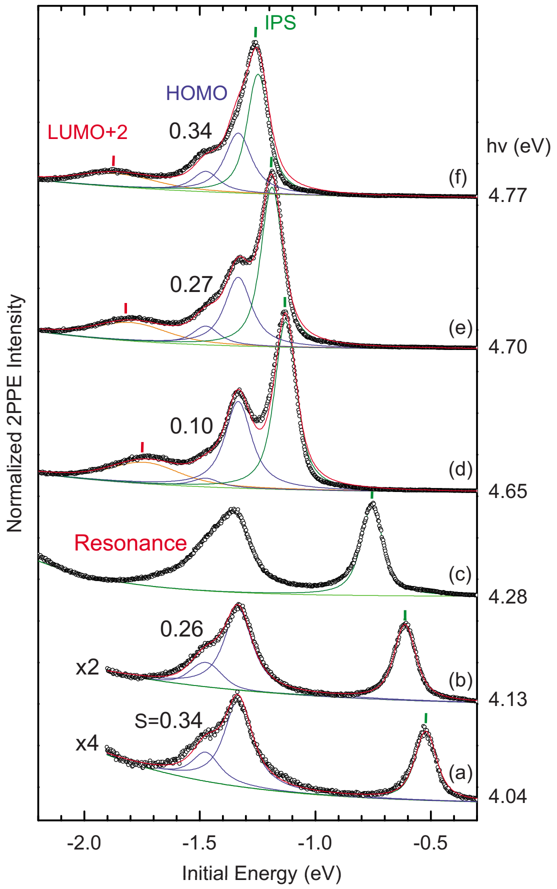

FIG. 2. (Color online) 2PPE spectra (open circles) for the 1 ML PbPc film measured with photon energies below and above the HOMO-LUMO+2 resonance were plotted on the initial energy scale. The photon energies were shown on the right-hand side. The lower two spectra were expanded by the indicated factors. The spectra were deconvoluted with Voigt functions for IPS peak [green (gray)], HOMO peak with the vibronic structure [blue (dark gray)], and the LUMO+2 peak [orange (light gray)]. The red (dark gray) lines overlapped with the experimental points were the fitted curves. The spectrum (c) was not deconvoluted. The S values were shown at the left side of the HOMO peaks. The S value for (d) was significantly smaller than those for other spectra.

In order to see the origin of the weak vibronic structure, 2PPE spectra measured at 90 K with different photon energies were shown in Fig. 2. The sample was prepared in another experimental run. Except for sharpening of spectral features at the low temperature, no significant temperature dependence of the vibronic structure was identified. The peaks due to LUMO+2 and IPS shifted with the photon energy in the initial energy scale while the peaks due to HOMO aligned at the fixed initial energy. The shifts of peak positions were accurately in accordance with the 2PPE processes: With the increase in the photon energy by $\Delta h\nu$, the occupied state feature shifts with $2\Delta h\nu$, and the unoccupied feature with $1\Delta h\nu$.[8] The details of these unoccupied features will be discussed elsewhere and we focus our attention on the HOMO feature. The HOMO peak and the LUMO+2 peak overlapped at the photon energy of 4.28 eV, where the pump photon was closely resonant with the energy separation between the HOMO- and LUMO+2-derived levels.[8] Disregarding (c) and (d), the HOMO peaks for (a), (b), (e), and (f) were accompanied by clear shoulders at -1.47 eV in a similar way as in the 1PPE result. The shoulder was seen at around half height of the main HOMO peak, indicating that the intensities of the vibronic structures in these 2PPE spectra were similar to that of 1PPE. On the other hand, the vibronic structure in (d) was weakly seen at the valley between the peaks due to HOMO and LUMO+2. The 2PPE results in (d) and Fig. 1 indicates that the photon energy slightly above the resonance caused something in the photoemission process to decrease the vibronic structure.

As a quantitative analysis, the HOMO feature was deconvoluted into components of 0–0 and 0–1 vibrational transitions, as shown by smooth lines [blue (dark gray)] in Fig. 2. The intensity ratio S of the components, defined as $S=I(0\text{-}1)/I(0\text{-}0)$, was determined from the deconvolution. The spectrum (c) at the photon energy of 4.28 eV was not deconvoluted because of the heavy overlapping of the LUMO+2 and HOMO features. Except for (d), the S values were 0.34, 0.26, 0.27, and 0.34 for spectra (a), (b), (e), and (f), respectively. The error of the S value caused by the overlapping of the spectral features was less than ±0.05. The S value of about 0.3 is very close to the value of 0.31 for the 1PPE result (see Fig. 1) and 0.33 reported in Ref. 12. The similarity of the S value is reasonable because coherent two-photon excitation results in the same final state as 1PPE. Slightly smaller S values of 0.26 and 0.27 for (b) and (e) may have some meaning but we cannot discuss them because of the limited certainty. In contrast to these cases, the S value at 4.65 eV photon energy (d) was 0.10, significantly smaller than that of the 1PPE value or other 2PPE results. Decrease in the S value was always found at photon energies slightly higher (<0.4 eV) than the resonance.

The enhancement of the HOMO peak at the resonance is seen by traces (a)–(c) in Fig. 2. The HOMO peak enhancement and the appearance of the LUMO+2 peak indicate the formation of the real intermediate state at the photon energies higher than 4.28 eV. The molecule in the LUMO+2-related intermediate state should be in several vibrational states of different vibrational modes. As schematically shown in Fig. 3, when nuclei in the molecule move along relevant normal coordinates before suffering any relaxation process, the second photon leads to the HOMO peak of modified vibrational distribution. The vibrational potential curves in Fig. 3 were drawn by considering the electronic structure of a free molecule. Molecular structure of the excited state in which the bonding electron in HOMO is excited to antibonding LUMO+2 is rather similar to that of the molecular cation in which the bonding HOMO electron is removed. The equilibrium distance of the ground-state molecule is shorter than those of the excited state and the cation. The smaller S value, that is, smaller vibrational excitation by photoemission corresponds to elongation of the bond lengths in the intermediate state associated with LUMO+2. Assuming the molecular vibrational energy in the intermediate state to be 140 meV similar to the ionic state, the time of the molecular vibration cycle is estimated to be about 30 fs. The time for the nuclear motion in the state should be a fraction of the vibrational cycle, that is, a few fs. The width of the LUMO+2 feature in Fig. 1 was about 0.25 eV. The width indicates that the lifetime of the intermediate state produced by 4.59 (Fig. 1) and 4.65 [Fig. 2(d)] eV photon is longer than a few fs. The lifetime is sufficient for the nuclear motion. The energy window of 0.4 eV for the small S value may be related to the sum of the widths of the occupied and unoccupied levels. The photon energies are within tail part of the resonance.

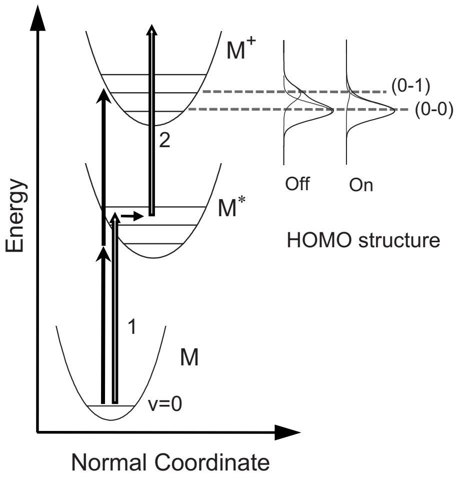

FIG. 3. Vibrational potential curves against a normal-mode coordinate are schematically shown. The curves for the ground, neutral excited, and ionic states are denoted by M, M^*, and M^+, respectively. At off-resonant condition (black arrows), the vibrational distribution of the ion is mainly determined by the Franck-Condon factor between M and M^+. At photon energy just above the resonance (open arrow 1), the M^* molecules should be in several vibrational states of different vibrational modes. When nuclei move (horizontal arrow) along the normal coordinate before suffering any relaxation processes, the second photon (open arrow 2) leads to M^+ of a modified vibrational distribution. The change in the S value is a result of the nuclear motion in M^*. The right-hand curves schematically show the HOMO features at off- and on-resonant conditions.

Even at photon energies far above the resonance [(e) and (f)], the LUMO+2-derived intermediate state was populated through some relaxation process. The off-resonantly populated intermediate state does not affect the vibronic structure. This is deduced from the width of the LUMO+2 feature. The width of the LUMO+2 feature increased as the photon energy exceeded the resonance and became about 0.4 eV at photon energy of 4.77 eV. The main origin of the broadening is tentatively considered to be related with the hole scattering effect in the intermediate state[13] rather than a final-state effect because the change of the final-state energy in the photon energy range is small ($4.77-4.59=0.18$ eV). The broadened LUMO+2 feature suggests that the lifetime of the intermediate state is less than few fs. Then nuclei cannot move within the lifetime.

At photon energy below the resonance, the LUMO+2 feature was not observed. Considering the widths of the relevant energy levels and the dephasing processes discussed in 2PPE process,[14,15] it seems the feature should appear even at photon energies below the resonance. This is in contradiction to the observation. The 2PPE intensity variation around the resonant photon energy is the unresolved question.[16] Anyway, the intermediate state was not excited at the low photon energy. Thus the S values for (a) and (b) are similar to that of 1PPE. Time-resolved pump-probe experiment was performed by compressing the UV laser-pulse width to 60 fs. The lifetimes of the HOMO and the LUMO+2 peaks were shorter than our time resolution of 30 fs, in consistency with the very rapid process discussed above. In order to consider a contribution of higher order processes, we measured 2PPE spectra at 4.59 eV photon energy by changing the laser power from 3 to 16 mW. No significant change of the S value was detected.

At the photon energy of 4.8 eV, the intermediate state from the HOMO level becomes close to the resonance with IPS.[8] It is interesting that the S value at 4.77 eV photon energy was not affected by the resonance. The molecular vibration may not couple with the two-dimentional free-electron orbital of IPS. This may be reasonable for in-plane molecular vibrations but it is speculative that out-of-plane vibrations and molecule-substrate vibrations may couple with the IPS orbital. Rather drastic change in the electronic structure by the molecule-substrate distance is known for several organic films.[17] Analysis of vibronic structure around the resonance with IPS may be informative for such systems.

Though wave-packet motions in electronic excited states have been extensively studied in gas and liquid phases,[18,19] such motions are difficult to be detected for adsorbed molecules because lifetimes of electronic excited states are typically shorter than vibrational cycle. The motion of adsorbed atom along a repulsive potential of an excited state was observed in photodesorption of Cs from Cu(111) and coherent control of the photodesorption was demonstrated.[5,20] Similarly, vibronic structure in 2PPE spectroscopy will be fruitful to know very fast dynamics within few fs occurring at interfaces between organic molecule and inorganic substrate.

This work was partly supported by Grant-in-Aid for Scientific Research on Priority Areas from MEXT (Grant No. 17069012). The authors are grateful to N. Ueno of Chiba University for supply of PbPc sample, preparation methods of uniform films, and detailed information on his recent works. Global COE Program at Osaka University is acknowledged for partial support to M.S.

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