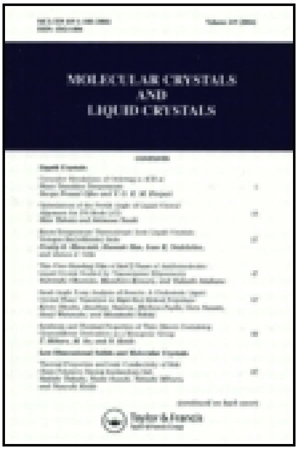

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Hole-Vibration Coupling in the Uppermost Valence Band Photoemission of Pentacene Monolayer on Graphite

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The hole-vibration coupling of the highest occupied state in pentacene thin films on graphite was studied by high-resolution ultraviolet photoemission spectroscopy. It was found that vibration satellites in the film are more intense than that in the gas phase and the vibrational energy in the film is slightly lower than that in the gas phase. This demonstrates that the reorganization energy (hole mobility) in the pentacene thin film is slightly larger (smaller) than that expected from the photoemission spectrum of free pentacene molecules.

Keywords: electronic structure; high-resolution ultraviolet photoemission spectroscopy (UPS); hole-vibration coupling; pentacene

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INTRODUCTION

Since the discovery of electrical conduction in organic solids [1], extensive researches have been performed so far. Among these, theoretical work has shown that the hole-vibration coupling of the highest occupied molecular orbital (HOMO) plays a crucial role in the hopping hole transport in organic solids [2]. Furthermore, the electron-phonon coupling is predicted to be a key parameter in the superconductivity [3]. Although many groups have studied the charge-vibration coupling [2,3], a lack of direct experimental data on the charge-vibration coupling in the solid state has hindered to obtain deeper insights of the charge mobility of organic solids.

A vibrational fine structure in ultraviolet photoemission spectroscopy (UPS) spectra has been reported for the condensed O_2 [4] and N_2 [5]. For thin films of large molecules, on the other hand, the vibrational satellites have recently been observed in the HOMO-band UPS of the monolayers of C_{60} [6] and metal-phthalocyanines [7] on highly oriented pyrolytic graphite (HOPG) surfaces. These observations demonstrated that the hole-vibration coupling in solid states can be studied directly with UPS even for large organic molecules.

In this work, we succeeded to resolve the hole-vibration coupling in the UPS-HOMO band for a pentacene monolayer on HOPG, in which molecules orient with a molecular plane parallel to the substrate surface [8]. We found a clear difference in the hole-vibration coupling between the thin-film and the gas-phase pentacene.

EXPERIMENTAL

High-resolution UPS spectra with polarized HeI radiation were obtained using a VG-CLAM4 analyzer with a multichannel detector and an Omicron-HIS13 VUV source with a rotatable linear polarizer. The total energy resolution was less than 20 meV, as determined from the Fermi edge of an evaporated Au film. All spectra were measured with a −5 V bias applied to the sample to observe the vacuum level (VL).

A ZYA-HOPG substrate was cleaved in air just before loading into the UHV chamber, and cleaned by heating *in situ* at 673 K for 15 h. The cleanliness of the substrate surface was confirmed by measuring the VL using UPS. Pentacene was purified by three-cycle sublimation in an Ar gas stream of 13 Pa and deposited *in situ* onto the HOPG substrate at a rate of 0.1 nm/min. The well-oriented monolayer was prepared by heating a 0.5-nm-thick film at 380 K for 6 h, confirmed by a narrowing of the HOMO linewidth from 300 to 230 meV at 298 K and a shift of 80 meV to the lower side of the binding energy (E_B). Further annealing or aging of the film did not cause any changes in the UPS spectra, indicating that the well-oriented monolayer could be realized [8].

RESULTS AND DISCUSSION

Figure 1 shows the normal-emission UPS spectra of the pentacene/HOPG measured at 298 and 49 K with p-polarized HeI radiation, compared with the gas-phase UPS spectrum [2a,b]. The E_B is measured from the Fermi level of the substrate (E_F^{sub}), and the gas-phase spectrum is shifted to align the HOMO peak to that of the 298-K spectrum. The relative E_Bs of the valence-band peaks in the 298-K spectrum agree well with those in the gas phase, which is the reflection of the persistence of molecular characteristics in the film. The VL of the 298-K film is increased by 10 meV from that of the substrate indicating the existence of a weak dipole layer where the film is slightly charged by electrons. Upon cooling the film to 49 K, the VL is increased further by 10 meV. For the HOMO, the 298-K spectrum

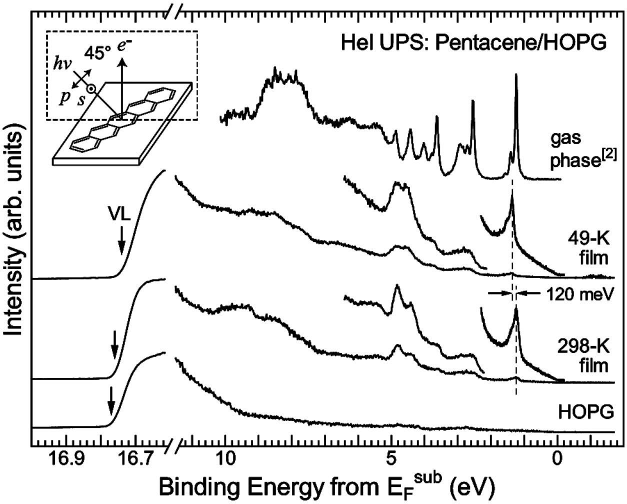

FIGURE 1 The normal-emission UPS spectra for the pentacene/HOPG measured at 298 and 49 K with p-polarized HeI radiation compared with gas-phase spectrum [2a,b]. The gas-phase spectrum is shifted to align the HOMO peak to that of the 298-K spectrum.

represents an asymmetric lineshape caused by a vibrational progression towards the high-E_B side, which is independent of the polarization of HeI radiation [9]. Upon cooling, the HOMO is shifted to the high-E_B side by 120 meV and the vibrational progression resolves more clearly. When the film is heated to 298 K, all UPS features recover to that of the original 298-K film indicating a fully reversible temperature dependence of the electronic structure. This may originate from a change in the film structure due to a temperature dependent pentacene-HOPG interaction.

Figure 2 shows the angle-integrated HOMO-band UPS spectra of the gas phase (●) [2a,b] and the 49-K film (○), where the 49-K spectra

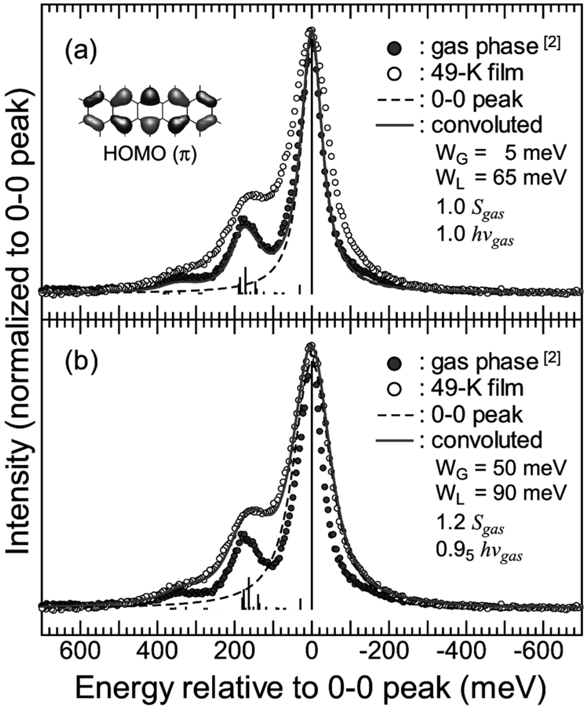

FIGURE 2 The angle-integrated thin-film and gas-phase UPS spectra with the best-fit convoluted curves with 18 A_g vibrational modes (a) for the gas-phase spectrum [2b] using Voigt functions of $W_G = 5$ meV and $W_L = 65$ meV with S_{gas} and $h\nu_{gas}$ and (b) for the thin-film spectrum using the Voigt functions of $W_G = 60$ meV and $W_L = 90$ meV with 1.2 S_{gas} and 0.95 $h\nu_{gas}$. The vertical bars represent intensities of 0-0, 0-1 and 0-2 vibrational transitions used in the convolutions.

are shown after the background subtraction. One can see that the HOMO of the 49-K film is clearly resolved into at least three components as in the gas phase. Note that the intensities of the vibration satellites in the 49-K film are more intense than those in the gas phase, and that the progression with an energy in the film ($h\nu_{film} = 158\,\text{meV}$) is slightly lower than in the gas phase ($h\nu_{gas} = 167\,\text{meV}$). That is, $h\nu_{film} = 0.95\ h\nu_{gas}$.

Brédas and coworkers pointed out the contribution of several vibrational modes to the hole-vibration coupling in gas-phase molecules whose intensities satisfy the linear coupling model [2b]. If transitions only from the vibrational ground state are considered, intensities of the vibration satellites are given by a Poisson distribution, $I_n = S^n e^{-S}/n!$, where I_n is the intensity of the nth vibrational excitation in the electronic final state and S is the Huang-Rhys factor for the vibration mode concerned. According to the work of Brédas *et al.* [2b], we convoluted both the gas and the film spectra using Voigt functions, in which the vibration satellites by 0-0, 0-1, and 0-2 transitions for 18 totally symmetric (A_g) vibrational modes are included. The best-fit results for the gas and the film are compared in Figure 2(a) and (b), respectively. For the convolution of the gas-phase spectrum we used Voigt functions of $W_G = 5\,\text{meV}$ meV and $W_L = 65\,\text{meV}$ for the vibration satellites given by the gas-phase Huang-Rhys factor (S_{gas}) and $h\nu_{gas}$, which were obtained by Brédas *et al.* [2b]. The best agreement with the 49-K-film spectrum is obtained for $S_{film} = 1.2\ S_{gas}$ used for each A_g vibrational mode, in which all of $h\nu_{gas}$ are contracted by 0.95, with $W_G = 50\,\text{meV}$ and $W_L = 90\,\text{meV}$ for Voigt functions.

The sum of intra- (charge-vibration coupling) and inter-molecular (coupling to lattice phonons and electronic polarization) relaxation energies is in general expressed by the reorganization energy (λ) which is a key parameter in discussing the charge mobility [2a,b], e.g., a smaller λ is required for a higher charge mobility. The intramolecular λ has been determined by the analysis of gas-phase UPS spectra and estimated to be $\lambda_{gas} \approx 2\Sigma S_i h\nu_i$ [2b]. If we apply this to the pentacene/HOPG, λ_{film} is obtained to be $\lambda_{film} = 109\,\text{meV} = 1.14\ \lambda_{gas}$ at 49 K. This difference may originate from the intermolecular and/or substrate effects in the film and indicates that the hole mobility in the pentacene thin film is slightly smaller than that expected theoretically using the gas-phase spectrum.

The present success ensures the effectiveness of the methodology for the study of the hole-vibration coupling in semiconductors and superconductors of large organic molecules that are not obtainable from a gas-phase spectrum.

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