

## Hole-vibration coupling of the highest occupied state in pentacene thin films

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The hole-vibration coupling of the highest occupied state in pentacene thin films on graphite is studied by high-resolution ultraviolet photoelectron spectroscopy. Vibration satellites in the film show a take-off-angle dependence, indicating that the Franck-Condon principle is not strictly satisfied in this system. They are more intense than 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 in pentacene thin films is slightly larger than that estimated from the photoelectron spectrum of free pentacene molecules. Furthermore, it is pointed out that the electron hopping in the low-temperature film may occur in the femtosecond scale before the electronic polarization of the surrounding medium is completed.

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The recent success in realizing organic devices has accelerated comprehensive research on electronic processes in organic solids.<sup>1</sup> The charge-vibration interaction plays a crucial role in the hopping charge transport (i.e., charge mobility) in organic solids. In order to understand the hole transport mechanism in organic solids including pentacene, a high hole mobility material,<sup>2-4</sup> the hole-vibration coupling of the highest occupied molecular orbital (HOMO) has been studied theoretically. Furthermore, the electron-phonon coupling is predicted to be a key parameter in superconductivity.<sup>5-7</sup> These studies have been performed to interpret gas-phase ultraviolet photoelectron spectroscopy (UPS) spectra, which provides the intramolecular contributions to the charge transport.<sup>2-5</sup> However, charge-vibration coupling in the solid state has remained elusive to date. Charge injection into a molecule or the ionization of a molecule in organic solids is accompanied by intermolecular electronic polarization simultaneous with the intramolecular geometry relaxation associated with the charge-vibration coupling. For a deeper understanding of the charge transport properties of organic solids, a more pertinent approach to resolving this topic is required.

The UPS-HOMO peak of organic solids has typically been observed with a full-width at half-maximum (FWHM) of about 400 meV. The HOMO linewidth of organic solids is believed to be mainly dominated by the site dependence of electronic polarization,<sup>8</sup> the energy-band dispersion,<sup>9</sup> and the progressions of vibrational modes.<sup>10</sup> In the case of molecular thin films, a vibrational fine structure in UPS spectra has been reported for condensed O<sub>2</sub> (Refs. 11 and 12) and N<sub>2</sub>.<sup>13,14</sup> For thin films of large molecules, such a structure has recently been observed for C<sub>60</sub> (Ref. 15) and phthalocyanine<sup>16-18</sup> monolayers on highly oriented pyrolytic graphite (HOPG). From these works one could demonstrate that the HOMO hole-vibration coupling can be studied directly even for organic solids of large molecules, providing details on the origin of the UPS lineshape of organic thin films.

In this work, high-resolution UPS spectra were obtained for the pentacene/HOPG system, in which molecules orient

with a molecular plane parallel to the substrate surface.<sup>19</sup> Thus, the pentacene-HOPG interaction can be a model of the intermolecular  $\pi$ - $\pi$  interaction in a pentacene crystal. 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 angle between the incident photon and the emitted photoelectron direction was fixed at 45°, and the acceptance angle of the photoelectron was 12°. The total energy resolution was less than 20 meV, as determined from the Fermi edge of an evaporated Au film. All UPS spectra were measured with a -5 V bias applied to the sample to observe the work function ( $\phi$ ). 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  $\phi$  using UPS. Pentacene was purified by three-cycle sublimation in an Ar gas stream of 13 Pa and deposited onto a HOPG substrate at a rate of 0.1 nm/min. In order to eliminate spectral broadening of the HOMO peak due to the site dependence of electronic polarization,<sup>8</sup> 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 peak from 300 to 230 meV at 298 K and a shift of 80 meV to the lower side of the binding energy ( $E_B$ ).<sup>20</sup> 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.

Figure 1(a) shows the normal emission UPS spectra of the pentacene/HOPG measured at 298 and 49 K, compared with the gas-phase UPS spectrum.<sup>2</sup>  $E_B$  is measured from the Fermi level of the substrate, and the gas-phase spectrum is shifted to align the HOMO peak to that of the 298 K spectrum. The relative  $E_B$ 's of the valence-band peaks in the 298 K spectrum correspond well with those in the gas phase, and the 298 K spectrum representing an asymmetric shape caused by a vibrational progression towards the higher  $E_B$ . This is the reflection of the persistence of molecular characteristic in the film. On the other hand, the  $\phi$  of the 298 K

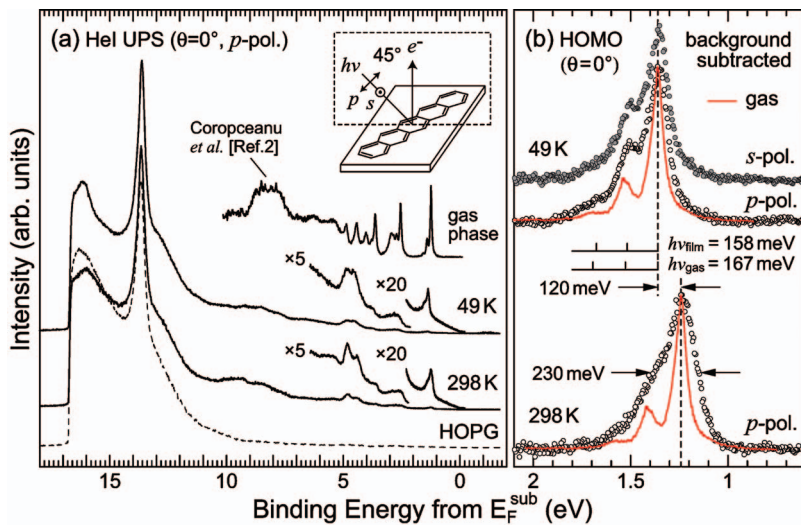


FIG. 1. (Color) (a) The normal emission UPS spectra for the pentacene/HOPG measured at 298 and 49 K with  $p$ -polarized HeI radiation, compared with the gas-phase spectrum (Ref. 2). The gas-phase spectrum is shifted to align the HOMO-peak position to that of the 298 K spectrum. (b) Fine structures of the HOMO peak of the pentacene monolayer at normal emission obtained with  $p$ ( $\circ$ )- and  $s$ ( $\bullet$ )-polarized HeI radiation after background subtraction. The gas-phase spectrum (solid line) is shown for comparison.

film is increased by 10 meV from that of HOPG. This indicates the existence of a weak dipole layer where the film is slightly charged by electrons. Upon cooling the film to 49 K, the UPS feature changes slightly. In particular, the HOMO is shifted to the high- $E_B$  side by 120 meV, and the  $\phi$  is increased further by 10 meV. When the film is heated to 298 K, the UPS feature recovers to that of the original 298 K film, indicating a fully reversible temperature dependence of the electronic structure. Although we cannot specify a definite origin of the temperature dependence of the spectra, it may originate from a change in the film structure accompanied by a different pentacene-HOPG interaction causing a change in the electronic polarization.

In Fig. 1(b), the thin-film spectra measured at 298 and 49 K in the HOMO region are compared with the gas-phase spectrum<sup>2,3</sup> after subtracting the background photoelectrons. At 49 K, the HOMO is clearly resolved into at least three components as it is in the gas phase. The HOMO lineshape is independent of the polarization of HeI radiation. For these films, it was confirmed that the lineshape and the  $E_B$  position

of the HOMO exhibit no time dependence, indicating that the system is in thermodynamic equilibrium and free from radiation damages. It can be concluded that the observed fine structure originates from the hole-vibration coupling in the pentacene thin film. 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 ( $h\nu_{\text{film}}=158$  meV) is slightly lower than in the gas phase ( $h\nu_{\text{gas}}=167$  meV).<sup>2</sup> That is,  $h\nu_{\text{film}}=0.95h\nu_{\text{gas}}$ . We found that such a fine structure shows no coverage dependence during the monolayer formation since the intermolecular interaction along the surface lateral is dominated by the negligibly weak  $\sigma$ - $\sigma$  interaction. These indicate that the hole-vibration coupling in pentacene thin films is different from that in free molecules owing to the solid-state effect.

Figures 2(a) and 2(b) show the take-off-angle ( $\theta$ ) dependence of the HOMO-band UPS spectra on the pentacene/HOPG at 298 and 49 K, where the intensity is normalized to the main peak. At both temperatures, the vibration intensities depend on  $\theta$ . The observed spectra are deconvoluted using

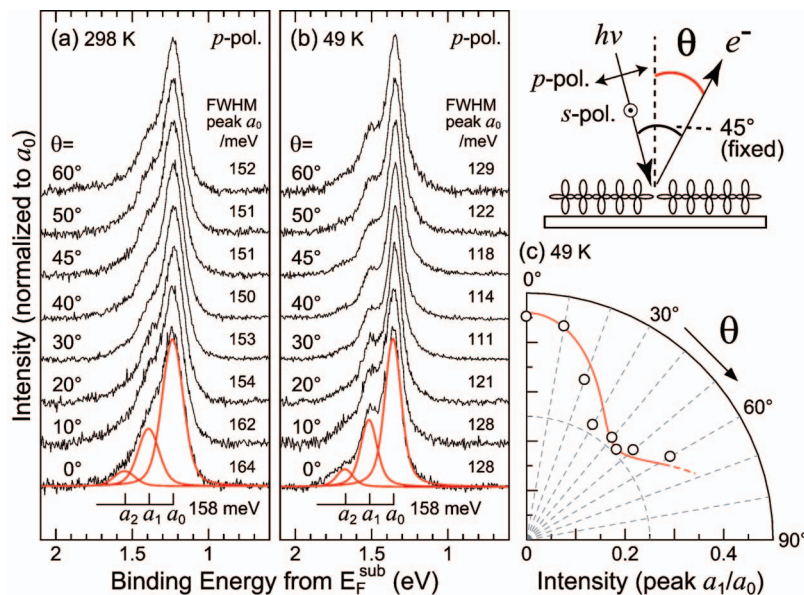


FIG. 2. (Color) The take-off angle ( $\theta$ ) dependence of the UPS spectra for the pentacene/HOPG at (a) 298 and (b) 49 K after background subtraction. (c) The  $\theta$  dependence of the intensity ratio  $a_1/a_0$  at 49 K.

Voigt functions (thick curves), which consist of Gaussian and Lorentzian components, by considering coupling with a single vibrational mode of  $h\nu_{film}=158$  meV. In this fitting, the FWHM of Gaussian and Lorentzian components ( $W_G$  and  $W_L$ ) and their intensities are obtained by the least-squares method. The  $\theta$  dependence of the intensity ratio  $a_1/a_0$  in the 49 K film as obtained by the fitting [Fig. 2(c)] shows a maximum at  $\theta=0^\circ$  and a minimum at  $\theta=45^\circ$ , which is obviously absent in gas-phase spectra with a random spatial orientation of the molecules. Such a  $\theta$  dependence suggests that the Franck-Condon principle is not strictly satisfied in the photoionization process in the pentacene/HOPG. In addition, the FWHM of the vibration satellites depends on  $\theta$  as well, probably due to the contribution of several vibrational modes and the vibrational-mode-dependent  $\theta$  distribution of photoelectrons.

Brédas and co-workers pointed out the contribution of several vibrational modes to the hole-vibration coupling in gas-phase molecules.<sup>3,4</sup> The vibrational fine structure of the gas-phase pentacene was well reproduced using 18 totally symmetric ( $A_g$ ) vibrational modes whose intensities satisfy the linear coupling model.<sup>3</sup> If transitions only from the vibrational ground state are considered, the vibration satellites are given by a Poisson distribution,  $I_n = S^n e^{-S}/n!$ , where  $I_n$  is the intensity of the  $n$ th vibrational mode in the electronic final state and  $S$  is the Huang-Rhys factor for the vibrational mode.<sup>3</sup>

In order to label the difference in the hole-vibration coupling between the two phases, the  $\theta$ -integrated ( $=0-66^\circ$ ) thin-film spectra ( $\circ$ ) and the gas-phase spectrum ( $\bullet$ ) are compared with convoluted curves using 18  $A_g$  vibrational modes (Fig. 3). The energy scale is relative to the 0-0 transition peak (dashed curve). Here, the thin-film spectra are also integrated for the azimuthal angle around the surface normal by the azimuthal disorder of the single-crystal domains in the HOPG surface. The convolutions were performed using Voigt functions, in which the vibration satellite is given by 0-0, 0-1, and 0-2 transitions as represented by the Poisson distribution. First, we used  $W_G=5$  meV and  $W_L=65$  meV for Voigt functions with the vibration intensities given by the gas-phase Huang-Rhys factor ( $S_{gas}$ ) and the gas-phase vibrational energies ( $h\nu'_{gas}$ ), which were used in the analysis of the gas-phase spectrum.<sup>3</sup> The convoluted curve in Fig. 3(a) is in excellent agreement with the gas-phase spectrum as reported previously.<sup>3</sup> In Fig. 3(a), however, there is marked disagreement between the convoluted curve and the 49 K spectrum both in the satellite intensities and the linewidth. In Fig. 3(b), we changed the width to  $W_G=50$  meV and  $W_L=90$  meV while keeping  $S_{gas}$  and  $h\nu'_{gas}$  unchanged. The convoluted curve in Fig. 3(b) reproduces the tail appearing at the low- $E_B$  side of the 0-0 peak, while the vibration intensity of the convoluted curve is clearly lower than that of the 49 K spectrum. In Fig. 3(c), a better agreement between the 49 K and the convoluted spectrum is obtained for  $S_{film}=1.2S_{gas}$  used for each  $A_g$  vibrational mode, in which  $h\nu'_{gas}$ 's are contracted by 0.95 as obtained from Fig. 1(b). Furthermore, the 298 K spectrum is well reproduced by Voigt functions with  $S_{film}=1.3S_{gas}$  and  $h\nu'_{film}=0.95h\nu'_{gas}$ . Best agreement is achieved with

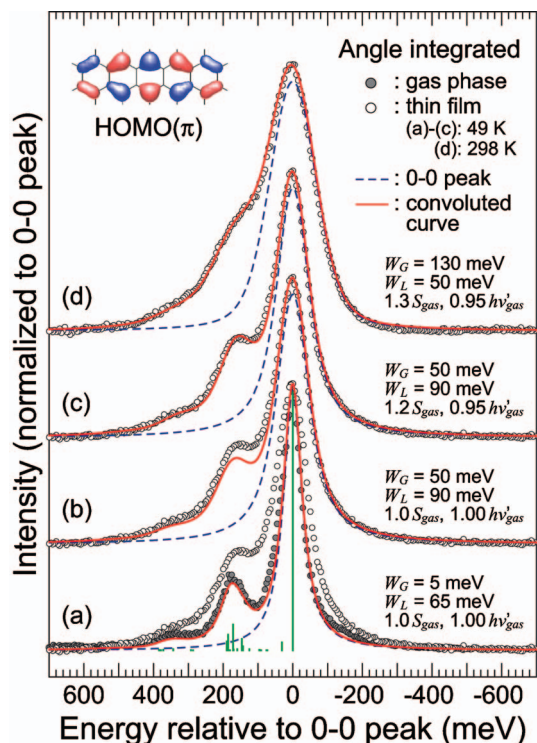


FIG. 3. (Color) The angle-integrated thin-film UPS spectra ( $\circ$ ), compared with convoluted curves of 18  $A_g$  vibrational modes (solid curves). The energy is relative to the 0-0 transition peak (dashed curve): (a) convolution by Voigt functions ( $W_G=5$  meV,  $W_L=65$  meV) with  $S_{gas}$  and  $h\nu'_{gas}$ , compared with the gas-phase ( $\bullet$ ) and the 49 K spectra, where the 0-0, 0-1, and 0-2 transition intensities are indicated by vertical bars. The convoluted curve in (a) agrees only with the gas-phase spectrum. (b) Convolution using  $W_G=50$  meV and  $W_L=90$  meV does not agree with the 49 K spectrum in the vibration intensity although a tail on the low-energy side of the 0-0 peak is well reproduced. The 49 K (c) and 298 K (d) spectra are well reproduced assuming values of  $1.2 S_{gas}$  and  $1.3 S_{gas}$ , respectively, with  $0.95 h\nu'_{gas}$ . Voigt components of  $W_G=50$  meV and  $W_L=90$  meV for the 49 K film (c), and  $W_G=130$  meV and  $W_L=50$  meV for the 298 K film (d) are obtained.

$W_G=50$  meV and  $W_L=90$  meV for the 49 K film [Fig. 3(c)] and  $W_G=130$  meV and  $W_L=50$  meV for the 298 K film [Fig. 3(d)]. Note that the intensity ratio  $a_1/a_0$  still increases for  $\theta > 60^\circ$  [see Fig. 2(c)]. This suggests that the vibration satellites integrated for the full  $\theta$  range may be more intense than that shown in Fig. 3, leading to  $S_{film}$ 's larger than  $1.2 S_{gas}$  for the 49 K film and  $1.3 S_{gas}$  for the 298 K film.

The sum of intramolecular (charge-vibration coupling) and intermolecular (coupling to lattice phonons and electronic polarization) relaxation energies is generally expressed by the reorganization energy ( $\lambda$ ) which is a key parameter in determining the charge mobility.<sup>2,3</sup> For a higher charge mobility, a smaller  $\lambda$  is required. The intra- and intermolecular contributions have been considered separately in the case of organic solids which have been justified by the presence of the only weak van der Waals interaction.<sup>21</sup> The intramolecular  $\lambda$  has been thus determined by the analysis of the gas-phase UPS spectrum, and estimated to be  $\lambda_{gas} \approx 2 \sum S_i h\nu'_i$ .<sup>3</sup> If

we apply this to the pentacene/HOPG,  $\lambda_{film}$  is obtained to be  $\lambda_{film}=109$  meV  $=1.14\lambda_{gas}$  at 49 K and  $\lambda_{film}=118$  meV  $=1.23\lambda_{gas}$  at 298 K. These differences may originate from the presence of the intermolecular relaxation in the film. Thus, the data indicates that the hole mobility at the interface and in the bulk of oligoacene crystal is slightly smaller than that expected from the gas-phase spectrum.

Finally, we briefly discuss the origins of the Lorentzian contributions in the gas-phase ( $W_L=65$  meV), 298 K ( $W_L=50$  meV), and 49 K spectra ( $W_L=90$  meV), which are necessary to reproduce the tail of the HOMO peak towards the low- $E_B$  side. The origin of Lorentzian contributions to the UPS lineshape at the low- $E_B$  side could be thermal excitations of vibrations in the initial state of photoionization (energy gain) and the finite hole lifetime.<sup>22</sup> When one considers the thermal energies of the samples in the measurements (43.6 meV for the gas phase,<sup>2,3</sup> 25.6 meV for the 298 K film, and 4.2 meV for the 49 K film), the gas phase and the 298 K spectra might reflect an energy gain. For the 49 K film, the energy gain is much smaller. It can thus be considered that the important origin of the large low- $E_B$  tailing at low temperature is the HOMO-hole lifetime, which is dominated by electron hopping from the substrate to the molecule in the case of the flat-lying organic monolayer on HOPG.<sup>16</sup> The change in  $W_L$  between the 298 K and the 49 K films may originate from change in the molecule-substrate interaction.

Using an equation describing the lifetime effect in the breakdown of the sudden approximation for photoemission,<sup>22</sup> the hole lifetime for reproducing the low- $E_B$  tailing in the 49 K spectrum is estimated to be 2.0 fs, which will be discussed in detail elsewhere. At this time scale, the electronic polarization in the solid state is still time dependent,<sup>23</sup> oscillating around the final static value. Charge hopping may occur before the electronic polarization of the surrounding medium is completed.

In summary, we have succeeded in resolving the hole-vibration coupling in the pentacene/HOPG and obtained a  $\lambda$  in the film slightly larger than that in free molecules. The present success ensures the effectiveness of the methodology for the study of the hole-vibration coupling of large organic semiconductors/superconductors that are not obtainable from a gas-phase spectrum.

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