

Fingerprinting weak electronic interaction at a van der Waals interface: Fano signatures in a pentacene monolayer on graphite

Yuri Hasegawa^{1,*}, Takuma Yamaguchi,² Matthias Meissner¹, Takahiro Ueba¹, Fabio Bussolotti,¹ Shin-ichiro Ideta^{3,†}, Kiyohisa Tanaka,^{2,3} Susumu Yanagisawa⁴, and Satoshi Kera^{1,2,3,‡}

¹Department of Photo-Molecular Science, Institute for Molecular Science, Okazaki 444-8585, Japan

²SOKENDAI (The Graduate University for Advanced Studies), Okazaki 444-8585, Japan

³UVSOR Synchrotron Facility, Institute for Molecular Science, Okazaki 444-8585, Japan

⁴Department of Physics and Earth Sciences, Faculty of Science, University of the Ryukyus, Nishihara, Okinawa 903-0213, Japan



(Received 28 October 2024; revised 7 May 2025; accepted 13 June 2025; published 1 August 2025)

We investigated the influence of van der Waals interactions on the electronic structure at the interface between a pentacene monolayer and a graphite surface. Upon cooling below 130 K, the pentacene molecules form a densely packed monolayer characterized by newly developed dispersive bands. These bands, observed using low-energy angle-resolved photoelectron spectroscopy with photon energy varying from 7.2 to 8.5 eV, exhibit constant final-state characteristics that overlap with nondispersive molecular-orbital states. This overlap results in variations in photoemission intensity—both enhancement and suppressions—indicative of Fano resonance. Such resonance arises from the interaction between a discrete molecular state and a continuum state. The Fano profile analysis of spectral fine features reveals the wave-function connection by the broader spread in unoccupied states at the physisorbed interface.

DOI: [10.1103/2k7h-h8jm](https://doi.org/10.1103/2k7h-h8jm)

I. INTRODUCTION

Understanding how organic molecules interact with inorganic surfaces is essential for elucidating the formation of interfacial electronic states. Although the influence of strong chemical interactions, such as molecular-orbital hybridization with metal substrates, has been extensively studied, the effects of weak interactions—particularly van der Waals (vdW) forces—on electronic states remains insufficiently explored, partly due to prevailing oversimplifications. Nevertheless, revealing the diverse properties of molecular materials requires a detailed understanding of electronic coupling, even in weakly bound systems [1–3].

We have demonstrated that weak interfacial interactions mediated by vdW forces influence the electronic state [4–6]. A notable example is the pentacene (PEN) molecule on a graphite substrate, a classic physisorption system. Yamane *et al.* investigated the electronic structure of the PEN monolayer (ML) on graphite using angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) [7]. They observed

differences in the spectral features of the highest occupied molecular orbital (HOMO) compared with those of an isolated gaseous molecule indicating an increase in charge reorganization energy in the solid state. Furthermore, Paramonov *et al.* simulated the photoemission spectrum while accounting for interfacial interactions and found a good agreement with the experimental data, highlighting the role of weak interfacial interactions in the delocalization of discrete states and in hole-vibration coupling [8]. Their findings indicate a highly localized charge within the ML, along with a weak 40-meV dispersion for the HOMO band, consistent with theoretical prediction. Additional important observations include (i) the dependence of photoelectron-emission angle on the vibronic progression, which deviates from the Franck-Condon (FC) principle [5,7] and (ii) a pronounced density of states (DOS) around the normal emission in ARUPS, which is absent in photoemission orbital tomography simulations of an isolated molecule [9,10]. These results collectively underscore the need for a detailed understanding of the ARUPS fine structure to fully comprehend the electronic characteristics of weakly interacting molecular systems beyond simplistic approximations.

Although changes in the occupied states of physisorption systems are typically minimal, unoccupied states can substantially influence the spectral features due to their broader spatial distribution and electron cloud overlap. While experimental access to band mapping of unoccupied states remains limited, two-photon photoemission spectroscopy and vdW-corrected density functional theory have revealed their essential role in the formation of interfacial states [11–13]. ARUPS is generally used to investigate the band structure of the occupied states. However, unoccupied states can

*Present address: Institute of Pure and Applied Sciences, University of Tsukuba, Tsukuba 305-8573, Japan.

†Present address: Hiroshima Research Institute for Synchrotron Radiation Science (HiSOR), Hiroshima University, Hiroshima 739-0046, Japan.

‡Contact author: kera@ims.ac.jp

be accessed using angle-resolved secondary-photoelectron spectroscopy [14,15], which corresponds well with observations from very-low-energy electron-diffraction (LEED) experiments [16]. In ARUPS measurements, spectra in the low-kinetic-energy region can contain information about the photoemission final states. In this region, secondary electrons are populated and can couple with the conduction band (CB) above the vacuum level (E_v) before being emitted to the vacuum. These interactions appear in the spectra as constant kinetic-energy features which are attributed to the CB and referred as constant final-state (CFS) spectra. This effect can be identified by scanning the photon energy and observing spectral features that shift with the excitation energy, in contrast with valence-band (VB) features.

In this study, we investigated a PEN ML on graphite substrates—specifically, single crystalline graphite (SCG) and highly oriented pyrolytic graphite (HOPG)—using low-energy ARUPS (LE-ARUPS) with a synchrotron radiation source, to clarify the influence of vdW interactions on the electronic properties. The observed dispersive band exhibited constant kinetic-energy features with intensity modulations that correlated with excitation energy, indicating the presence of Fano resonance. Fano resonance occurs when a discrete state interferes with a continuum state, producing a characteristic asymmetric spectral shape known as the Fano profile [17,18]. Although previous studies have reported on photoelectron emissions resulting from core excitation and subsequent Auger decay processes [19–22], as well as valence excitation of metal atoms embedded in a rare-gas superstructure on the surfaces [23], complex molecular-orbital systems have not yet been studied in this context. The continuum state at the PEN/graphite interface likely originates from a newly formed CB at the weakly bound interface, suggesting that weak interactions significantly contribute to wave-function hybridization in the CB. We propose a concept framework to assess the influence of weak interactions on electronic states through Fano profile analysis.

II. EXPERIMENT

All the experiments were performed at ultrahigh-vacuum (UHV) conditions. HOPG and SCG were cleaved using Scotch tape before being introduced to the UHV chamber. A clean surface was achieved by annealing at 870 K. A molecular layer of PEN was deposited onto the substrate at room temperature using a custom-built UHV chamber designed for organic molecular layer deposition. The deposition rate of PEN, monitored using a quartz microbalance, was set to be 0.1–0.5 Å/min. The LEED pattern was measured using a highly sensitive microchannel plate (OCI). The electronic state was measured by LE-ARUPS using p-polarized light at BL7U in the UVSOR Synchrotron Facility [24], IMS. The excitation energy varied from 7.2 to 8.5, and 21 eV. The total energy resolution was 92, 28, and 10 meV at room temperature, 165, and 14 K, respectively, confirmed from the Fermi edge of a reference Au sample. The experiments were carried out over several beam times: some low-temperature data were obtained at slightly different temperatures. However, since each low-temperature dataset was recorded below the

transition temperature, they are consistent for Fano resonance analysis and valid for qualitative discussion.

First-principles electronic-structure calculations were conducted using specialized program codes to clarify the electronic nature of the PEN-graphite interaction [25–28]. The valence wave functions were expanded using plane waves with an energy cutoff of 750 eV, and projector augmented wave potentials were employed to describe the ionic core [29]. The graphene substrates were used with the two-dimensional unit cells of $a = b = 16.16$ Å, $\beta = 120^\circ$ (structure A) and $a = 17.2$ Å, $b = 6.5$ Å, $\beta = 79.1^\circ$ (structure D), which consisted of one and two adsorbate molecules, respectively. The k -point meshes of 2×2 and 2×4 were used to sample the two-dimensional BZ. The periodic slab model with the vacuum layer of 2 nm thickness was used to avoid the artificial interaction along the normal of the slab. The atomic geometries were allowed to relax until all the interatomic forces fell below 0.02 eV/Å. The van der Waals density functional (vdW-DF) was used to describe the intermolecular and molecule-substrate van der Waals forces [30]. The one-electron wave function was obtained with the STATE program code [31]. The wave function and the band structures were calculated with the GGA-PBE level of theory [32].

III. RESULT AND DISCUSSION

We first investigated the temperature-dependent structural transition of PEN in the sub-ML regime deposited on SCG. The LEED images in Fig. 1 illustrate this transition upon cooling. At 170 K [Fig. 1(a)], a filled hexagonal pattern indicates the molecular alignment relative to the graphite surface, as well as the mean intermolecular distance and dense packing with small grain sizes, a configuration commonly referred to as two-dimensional (2D) gas phase [33]. We designate this 2D gas phase as the higher-temperature (HT) phase. In contrast, a distinct sixfold symmetry appears at 72 K [Fig. 1(b)] with the transition temperature around 130 K. In the crystalline low temperature (LT) phase, a distinct pattern emerges depending on the coverage; structure A is observed at a nominal coverage of 3 Å, as shown in Fig. 1(b). The LEED pattern of structure A is simulated to using lattice parameters of $a = b = 16.1$ Å, and $\beta = 60^\circ$ [Figs. 1(c) and 1(d)] demonstrating commensurate packing within experimental accuracy. Additional ML structures are presented in Fig. S1 (see Supplemental Material [34]). Structure B appears at a higher coverage of 4 Å [Fig. S1(a)] partially coexisting with structure A, in contrast with previously identified structures C and D [8,35].

As the sample is cooled, changes in the electronic structure are observed via UPS measurements at an excitation energy of 21 eV [Fig. 1(e)]. In the HT phase, an asymmetric spectral feature appears, characterized by a sharp HOMO peak (00) at 1.20 eV, accompanied by vibronic satellite peaks at higher binding energy, (01) and (02), spaced approximately 0.16 eV apart. These spectral features arise from hole-vibration coupling triggered by photoionization, as illustrated in Fig. 1(f). Here, (0*m*) denotes FC transition from the ground electronic state to an excited vibrational state, where *m* represents a vibrational quantum number. The energy separation corresponds to the C-C stretching mode, as commonly observed in many conjugated molecules. In the LT phase, the spectral line

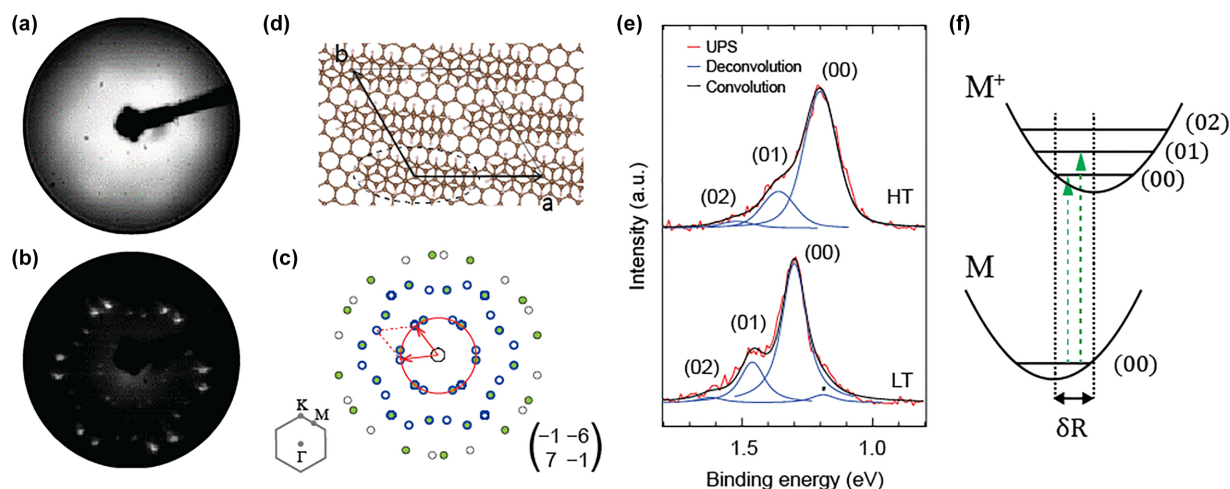


FIG. 1. LEED pattern of PEN/SCG taken at (a) HT (170 K) and (b) LT (72 K) phases with an electron-beam energy of 18 eV. (c) Simulated diffraction pattern considering rotational 3-fold and mirror domains and (d) schematic images of real-space unit cell of structure A. (e) ARPES spectra of PEN/HOPG recorded at HT (278 K) and LT (50 K) phases around the K point. The spectrum at 50 K (278 K) is reproduced using the Voigt function, with 48 meV (119 meV) Gaussian components and 91 meV (54 meV) Lorentzian components, respectively. A small peak at 1.2 eV marked by “*” indicates the residual HT phase. (f) Schematic image of transition from the neutral molecule (M) in the ground state to the cation molecule (M^+) in the excited state governed by the FC principle. Change of atomic bonding distance is denoted as δR .

sharpens and shifts toward higher binding energies, indicating relaxation energy associated with the electrostatic potential generated by the molecular quadrupole effect [36]. The spectral profile closely resembles that of gas-phase PEN; however, the reorganization energy exhibits slight variations due to the influence of the substrates and neighboring molecules, as supported by the theoretical models [8]. In the calculated band structures, the discrete HOMO-derived states are nearly identical to those of gas-phase PEN, suggesting that the electronic structure of PEN is only weakly influenced by the substrate, consistent with characteristics of a physisorbed interface (shown in Fig. S2).

Next, the photon energy dependence of the LE-ARUPS spectra of PEN ML on HOPG was investigated. Unexpected HOMO features, which differ significantly from those observed in conventional ARUPS using HeI or HeII light sources, exhibit pronounced photon energy dependence around the normal emission in the physisorbed system, as shown in Fig. 2. Despite the nearly flat-lying orientation of PEN on the surface, a high intensity at the normal emission is evident in the HOMO feature for both phases. This phenomenon is notably absent in planar-conjugated molecules as demonstrated by both ARUPS measurement and the theoretical models of photoemission angular distribution for isolated molecules [9,10], suggesting that adsorption-induced new states emerge even in the weakly interacting physisorption systems. Although the optimized structure of a slightly inclined PEN, by approximately 10° , could generate faint photoemission intensity at normal emission, it is insufficient to account for the experimentally observed intensity (see Fig. S3).

For the LT phase at $h\nu = 8.5$ eV, the spectral shape of the HOMO, which reflects FC factor as the relative intensity between the HOMO (00) peak and the (01) or (02) satellite peaks, exhibits significant deviations from the one observed under conventional HeI and HeII excitations. Moreover,

spectra acquired at lower excitation energies for both the LT and HT, suggest that the HOMO intensity deviates from the expected FC principle. To investigate the differences between the LT and HT phases, we plotted the relative intensity of the (00) to (01) peaks as a function of photon energy [Fig. 2(c)].

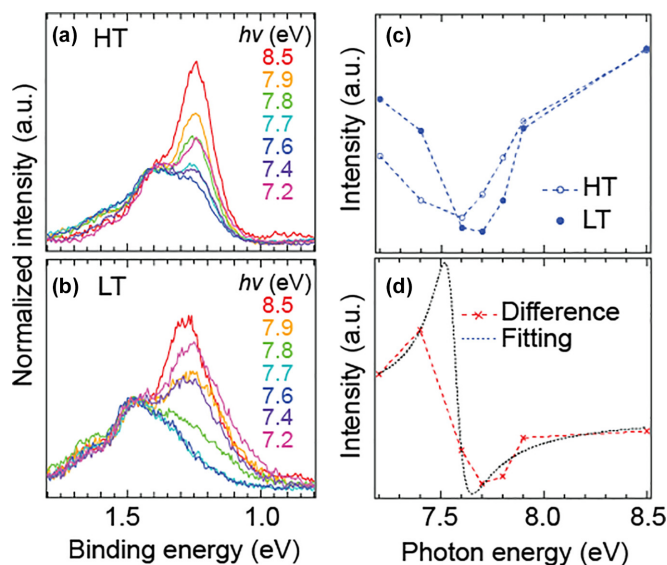


FIG. 2. Photon energy dependence of LE-ARUPS spectra of PEN/HOPG taken at (a) HT (165 K) and (b) LT (14 K) phases integrated at $k = 0.00 \text{ \AA}^{-1}$ with $\Delta k = 0.04 \text{ \AA}^{-1}$. The spectra are shown after subtracting the background (see Fig. S4). A small intensity peak observed around 0.95 eV at $h\nu = 8.5$ eV at 14 K corresponds to an unoccupied σ^* band of pristine graphite [14]. (c) Photon-energy dependence of the peak intensity of HOMO (00) in panels (a) and (b), with intensity normalized at a photon energy of 8.5 eV and (d) the intensity obtained by dividing the spectra of LT by that of HT in panel (c).

In the LT phase, the relative intensity of HOMO diminishes at around 7.7 eV, while in the HT phase, it decreases at around 7.6 eV with a noticeable broadening. Subsequently, the intensity ratio between the LT and HT spectra shown in Fig. 2(d) was used to normalize the data by removing the HT-phase contribution as a background. This normalization reveals a distinctive asymmetric lineshape resembling a Fano profile, which arises from the interference between direct photoemission and Auger-like processes as the photon energy varies [20,22]. In this study, the Fano profile reflects the interplay between a discrete molecular state and a continuum state, as discussed further below. Fano analysis further reveals the dispersive bands associated with each resonance channel, depending on the excitation energy. For Fano profile analysis, the spectrum was fitted by the following Fano formula:

$$I = d_1 \frac{(\varepsilon + q)^2}{1 + \varepsilon^2} + d_2, \quad (1)$$

$$\varepsilon = \frac{2(E - E_0)}{\gamma}. \quad (2)$$

Here, q denotes the asymmetric parameter, E_0 is the resonance energy, γ represents the linewidth, d_1 signifies the amplitude of resonance, and d_2 is a background factor. Using Fano-line profile fitting [Fig. 2(d)], we obtain $E_0 = 7.6 \pm 0.0$, $q = -1.4 \pm 0.8$, and $\gamma = 0.1 \pm 0.1$. The factor γ is associated with the lifetime of the excited resonance state. The derived value of 5.1 fs closely matches the photogenerated hole lifetime estimated from the high-resolution ML spectrum using a Lorentzian spectral tail [37]. The error margin of γ appears large due to the limited number of data points for fitting. However, for the boundary value of q (-2.2 and 0.6), γ is estimated to be 0.1 ± 0.0 and 0.2 ± 0.1 , respectively (see Fig. S3 for details). In both cases, γ remains not zero, indicating a finite lifetime of the resonant state. An alternative depiction of the intensity profile as a function of photon energy is provided in Fig. S5.

Figure 3 displays intensity maps of the energy-momentum (E - k) relation for the LT phase [Figs. 3(a)–3(d)], where prominent dispersive electronic structures are visible, along with the corresponding region for the HT phase [Figs. 3(e)–3(h)]. The data acquired at additional excitation energies are shown in Fig. S6. In the LT phase, a convex (hole-like) band exhibiting a constant kinetic-energy feature across different photon energies is observed, while the flat, discrete HOMO band remains at a constant binding energy as the photon energy increases. Focusing on the dispersive band, a convex band with enhanced positive contrast (POS) emerges at an excitation energy of 7.4 eV, reaching its maximum energy point approximately 100 meV above the HOMO (00) band at the Γ point [Fig. 3(a)]. At 7.6 eV, the POS band diminishes, and a new band with negative contrast (NEG) appears [Fig. 3(b)]. The NEG band intensifies at $h\nu = 7.9$ eV [Fig. 3(c)] and at 8.0 eV, the another POS band becomes apparent in the higher kinetic-energy region [Fig. 3(d)]. Considering the periodic structures observed in crystalline MLs via LEED, the dispersive band is modeled using a one-dimensional tight-binding approximation,

$$E(k) = E_c + 2t \cos(ck), \quad (3)$$

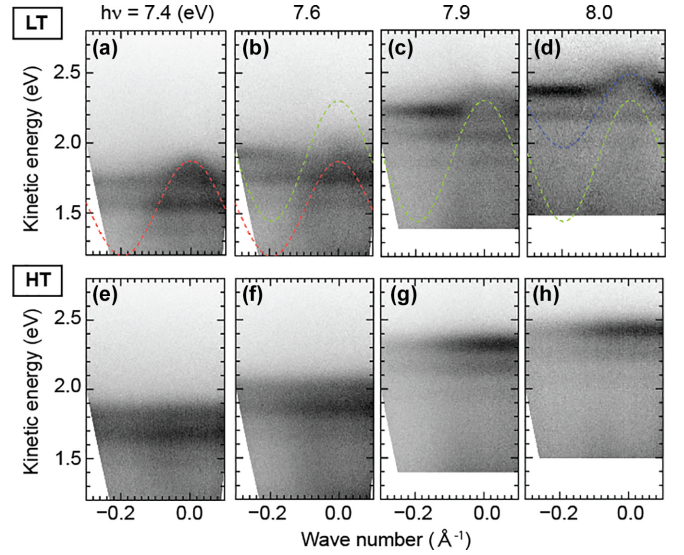


FIG. 3. Photon energy dependence of the E - k map of PEN/HOPG recorded at LT (50 K for 8.0 eV and 14 K for others in the top panel) and HT (165 K in bottom panel) phases taken at photon energies of 7.4, 7.6, 7.9, and 8.0 eV from left to right, respectively, along with the fitting curves (POS: blue and red, NEG: green). Details of the fitting are shown in Fig. S6.

where E_c represents the position of the band center, t represents the transfer integral, and c denotes the lattice constant. These parameters E_c and t were obtained through least squares fitting of the corresponding plot in the E - k map shown in Fig. S7. Using a lattice constant of 16.1 Å, we determined $E_c = 2.23 \pm 0.02$ eV and $t = 0.13 \pm 0.02$ eV for the upper POS band, and $E_c = 1.53 \pm 0.03$ eV, $t = 0.17 \pm 0.02$ eV for the lower POS band. For the NEG band, the fit yielded $E_c = 1.88 \pm 0.03$ eV and $t = 0.21 \pm 0.02$ eV. These band structures are clearly distinct from those found in other polymorphs of PEN single crystals [38–40], and from the K - and M -point features of graphite within the corresponding energy range (Fig. S8). This suggests that the observed dispersive bands are not due to Umklapp scattering from periodic surface arrays. Our results indicate that PEN adsorption induces a novel interfacial state in the CB at the PEN/graphite interface, characterized by highly ordered physisorbed structures. Importantly, no corresponding wide dispersive feature is observed in the VB as confirmed by theoretical calculations for Structures A and D (Fig. S2). Furthermore, the energy position of the convex band falls within the gap region of the CB of bulk graphite, as supported by both experiment and theoretical studies [16,41,42]. A quantitative discussion of periodicity is challenging due to weak band features in the experimental data, the azimuthal rotational disorder of the HOPG, and the presence of multiple rotational molecular domains of PEN on SCG (Fig. S8).

Figure 4 illustrates a proposed scheme depicting the transition channels at the PEN/graphite interface, highlighting the origin of the POS bands that overlap with the HOMO band in the LT phase. It is assumed that the interfacial state consists both of molecular- and graphite-weighted bands. According to the standard FC principle, transition T_1 occurs from the ground state to the molecular-weighted state in CB, similar

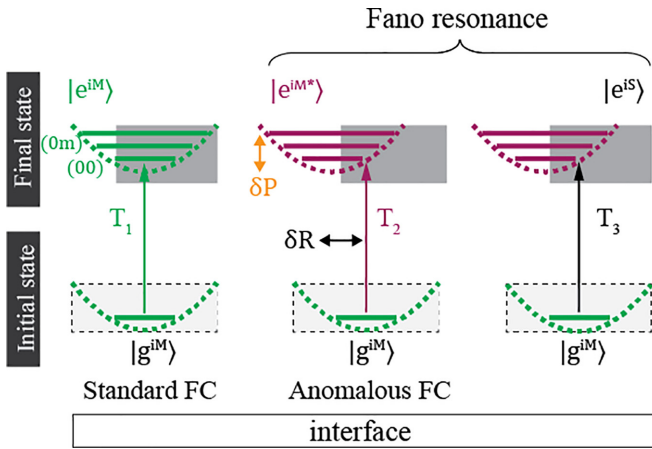


FIG. 4. Scheme of possible transition channels at the interface between pentacene and graphite describing the photon-energy dependence of ARUPS features. Potential curves indicate molecular-weighted CB state, e^{IM} and e^{IM*} and gray boxes indicate graphite-weighted CB state, e^{IS} .

to the case of gaseous molecule, as illustrated in left panel of Fig. 4. This transition is considered to be observed in spectra recorded at higher excitation energy, such as those using HeI or HeII sources, due to weak overlap between the wave functions of the molecule and the graphite in the high-momentum region. On the other hand, the dispersive band exhibiting Fano resonance primarily observed near the Γ point is associated with the coupling of transitions T_2 and T_3 as illustrated in middle and right panels of Fig. 4, respectively. The transition T_2 involves a potential shift from g^{IM} to e^{IM*} , in which the excited molecular potential is substantially altered due to the hybridization with the graphite wave function. Modification in polarization energy δP and/or atomic bonding distances δR lead to a vertical transition to a vibronic excited state (01) of the molecule. As an example of anomalous FC behavior, this transition is considered to generate intensity maximum approximately 100 meV above the HOMO(00) band at the Γ point. The transition T_3 occurs resonantly with the T_2 from g^{IM} to the graphite-weighted CB state e^{IS} generating the dispersive feature. The NEG band is believed to arise through an inelastic-scattering pathway, involving a transition from a bulk excited state to an interfacial state via the Auger process [19]. Characterizing the second POS band is challenging with the currently available data (for tentative interpretation of the overall transition scheme involving molecule and bulk contributions, see Figs. S6 and S10). Their precise origins remains unclear based on the present findings, which are constrained by limitations in both theoretical simulations and experimental resolutions.

In the HT phase, distinct CB features are not visible in momentum space. However, notable energy-dependent variations in the FC factor for the HOMO(00) intensity are observed [Fig. 2(a)]. Assuming that the adsorption distance is similar in both phases under the vdW approximation, this guarantees that there exists a strong coupling between the molecular wave function and the graphite in the CB, including in the 2D gas phase and in other ML films. The absence of clear dispersion is likely attributable to the lack of periodicity characteristic

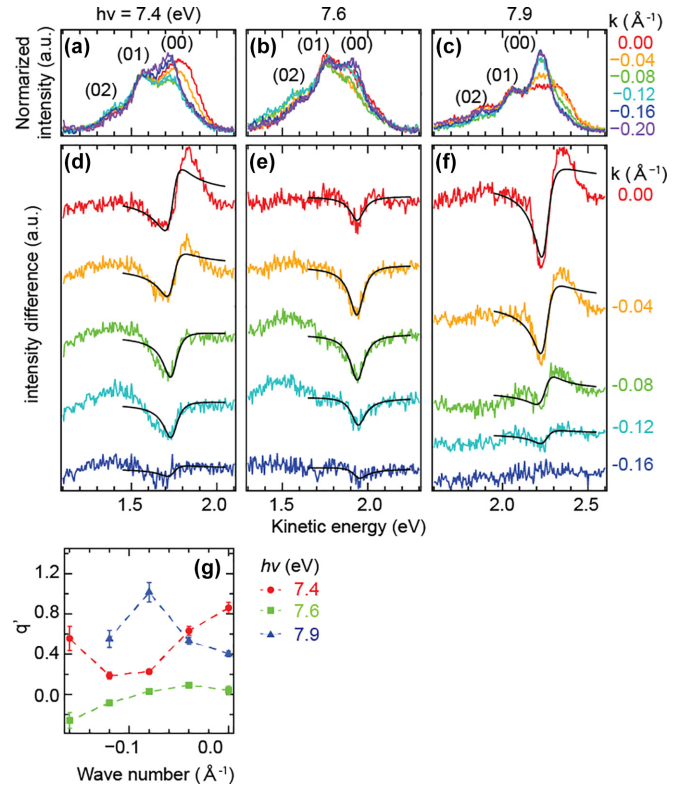


FIG. 5. Momentum-resolved, background-subtracted spectra of PEN/HOPG taken at photon energies of (a) 7.4, (b) 7.6, and (c) 7.9 eV with intensity integrated for each wave number and normalized to the intensity at the (01) peak. (d)–(f) Intensity difference of the momentum-resolved spectra, obtained by subtracting the spectra recorded at the edge momenta $-0.02 \text{ \AA}^{-1}$ with the fitting of the Fano-line profile for the HOMO (00) feature shown as black lines. (g) Obtained asymmetric parameter q' as a function of wave number for various excitation energies.

of the HT phase. A high-level computations suggest that some CB features related to experimental convex features for PEN/graphene involve the molecular wave function (Fig. S9; see also Ref. [43] therein).

As a preliminary study, we examined the momentum dependence of the Fano profile in the crystalline LT phase across various excitation energies. First, EDC spectra were extracted from the E - k map of PEN/HOPG taken at various photon energies in Fig. 3 [Figs. 5(a)–5(c)]. Notably, the peak shape near the HOMO (00) band is significantly modified at $k = 0.00 \text{ \AA}^{-1}$, while changes at higher wave numbers are less pronounced. Second, the asymmetric parameter q' was determined for each EDC spectrum by subtracting the spectrum at the momentum edge ($-0.2 \text{ \AA}^{-1}$ from Γ point) and fitting with the Fano profile [Figs. 5(d)–5(f)]. The parameter q' is defined as a function of wave number as shown in Fig. 5(g). At $h\nu = 7.4 \text{ eV}$ and 7.9 eV , where the POS band is prominently observed in ARUPS, q' exhibits drastic changes as the dispersive interfacial band intersects with the discrete HOMO(00) band in the E - k map (Fig. 3). Conversely, at $h\nu = 7.6 \text{ eV}$, where the NEG band appears near the resonance energy, the q' profile remains nearly zero and symmetric, showing less variation compared with other excitation energies. A comprehensive

analysis of q' is beyond the scope of the present study; however, the observed drastic changes as the dispersive POS and NEG interfacial bands intersected the discrete HOMO band provide valuable insights. This momentum-resolved Fano profile analysis offers an alternative perspective on the phase connection of wave functions and establishes a benchmark for quantum simulation approaches.

IV. CONCLUSION

In this study, we evaluated the influence of weak interactions on the electronic structure by examining oriented MLs of PEN on graphite, an ideal physisorption system transitioning from a 2D gas (HT phase) to a crystalline ML (LT phase). Using high-energy and momentum resolutions in LE-ARUPS achieved through synchrotron radiation experiments, we uncovered the effects of these weak interactions on electronic states. Both ML phases exhibited a characteristic asymmetric Fano profile that varied with excitation energy, attributed to the resonant coupling between the discrete molecule-based HOMO state and the continuum dispersive band at the interface. Additionally, in the crystalline ML phase, Fano profile analysis of the momentum-resolved LE-ARUPS data identified a constant kinetic-energy feature originating from a

newly formed CB at the physisorbed interface. This discovery underscores the significant role of weak electronic coupling in shaping wave-function connectivity, highlighted by the broader spread of unoccupied states. This spread serve as a spectral fingerprint for proving weak interactions at the vdW interface. The asymmetric parameter q and the lifetime associated with a given interference will provide quantifiable metrics for characterizing weak interactions, with further theoretical developments anticipated.

ACKNOWLEDGMENTS

This work was supported in part by the Japan Society for the Promotion of Science (JSPS) KAKENHI (Grants No. 26248062, No. 18H03904, No. 20K15176, No. 23K04667, and No. 23H05461). This work was performed on the BL7U beamline of UVSOR Synchrotron Facility, Institute for Molecular Science (IMS program 15-534, 16-547, 17-547, 18-572, 19-570). We thank UVSOR Synchrotron Facility staff members for their support during these measurements. Numerical calculations were performed using the supercomputer facilities at the Cyberscience Center, Tohoku University, and the Institute for Solid State Physics, the University of Tokyo.

-
- [1] A. Stroppa, P. Jain, P. Barone, M. Marsman, J. M. Perez-Mato, A. K. Cheetham, H. W. Kroto, and S. Picozzi, Electric control of magnetization and interplay between orbital ordering and ferroelectricity in a multiferroic metal–organic framework, *Angew. Chem. Int. Ed.* **50**, 5847 (2011).
 - [2] P. Judeinstein and C. Sanchez, Hybrid organic–inorganic materials: A land of multidisciplinary, *J. Mater. Chem.* **6**, 511 (1996).
 - [3] Y. Kang and Q. Wu, A review of the relationship between the structure and nonlinear optical properties of organic-inorganic hybrid materials, *Coord. Chem. Rev.* **498**, 215458 (2024).
 - [4] N. Ueno and S. Kera, Electron spectroscopy of functional organic thin films: Deep insights into valence electronic structure in relation to charge transport property, *Prog. Surf. Sci.* **83**, 490 (2008).
 - [5] S. Kera, H. Yamane, and N. Ueno, First-principles measurements of charge mobility in organic semiconductors: Valence Hole–vibration coupling in organic ultrathin films, *Prog. Surf. Sci.* **84**, 135 (2009).
 - [6] S. Kera and N. Ueno, Photoelectron spectroscopy on the charge reorganization energy and small polaron binding energy of molecular film, *J. Electron Spectrosc. Relat. Phenom.* **204**, 2 (2015).
 - [7] H. Yamane, S. Nagamatsu, H. Fukagawa, S. Kera, R. Friedlein, K. K. Okudaira, and N. Ueno, Hole-vibration coupling of the highest occupied state in pentacene thin films, *Phys. Rev. B* **72**, 153412 (2005).
 - [8] P. B. Paramonov, V. Coropceanu, and J.-L. Brédas, Electronic and vibronic interactions at weakly bound organic interfaces: The case of pentacene on graphite, *Phys. Rev. B* **78**, 041403(R) (2008).
 - [9] P. Puschnig, S. Berkebile, A. J. Fleming, G. Koller, K. Emtsev, T. Seyller, J. D. Riley, C. Ambrosch-Draxl, F. P. Netzer, and M. G. Ramsey, Reconstruction of molecular orbital densities from photoemission data, *Science* **326**, 702 (2009).
 - [10] M. Grimm, C. Metzger, M. Graus, M. Jugovac, G. Zamborlini, V. Feyer, A. Schöll, and F. Reinert, Molecular orbital imaging beyond the first monolayer: Insights into the pentacene/Ag(110) interface, *Phys. Rev. B* **98**, 195412 (2018).
 - [11] S. A. Wella, H. Sawada, N. Kawaguchi, F. Muttapien, K. Inagaki, I. Hamada, Y. Morikawa, and Y. Hamamoto, Hybrid image potential states in molecular overlayers on graphene, *Phys. Rev. Mater.* **1**, 061001(R) (2017).
 - [12] M. Shibuta and A. Nakajima, Imaging of ultrafast photoexcited electron dynamics in pentacene nanocrystals on a graphite substrate, *Nanoscale* **16**, 12397 (2024).
 - [13] T. Yamada, N. Kawakita, C. Okui, and T. Munakata, Hybridization of an unoccupied molecular orbital with an image potential state at a lead phthalocyanine/graphite interface, *J. Phys.: Condens. Matter* **31**, 044004 (2019).
 - [14] T. Takahashi, H. Tokailin, and T. Sagawa, Angle-resolved ultraviolet photoelectron spectroscopy of the unoccupied band structure of graphite, *Phys. Rev. B* **32**, 8317 (1985).
 - [15] S. K. Mahatha, K. S. R. Menon, and T. Balasubramanian, Unoccupied electronic structure of graphite probed by angle-resolved photoemission spectroscopy, *Phys. Rev. B* **84**, 113106 (2011).
 - [16] V. N. Strocov, P. Blaha, H. I. Starnberg, M. Rohlfing, R. Claessen, J.-M. Debever, and J.-M. Themlin, Three-dimensional unoccupied band structure of graphite: Very-low-energy electron diffraction and band calculations, *Phys. Rev. B* **61**, 4994 (2000).
 - [17] U. Fano, Effects of configuration interaction on intensities and phase shifts, *Phys. Rev.* **124**, 1866 (1961).
 - [18] M. F. Limonov, Fano resonance for applications, *Adv. Opt. Photon.* **13**, 703 (2021).

- [19] F. Matsui, S. Makita, H. Matsuda, E. Nakamura, Y. Okano, T. Yano, S. Kera, and S. Suga, Valence band dispersion embedded in resonant Auger electrons, *J. Phys. Soc. Jpn.* **90**, 124710 (2021).
- [20] D. L. Ederer, Cross-section profiles of resonances in the photoionization continuum of krypton and xenon (600–400 Å), *Phys. Rev. A* **4**, 2263 (1971).
- [21] S. Svensson, N. Mrtensson, and U. Gelius, Observation of autoionizing resonances in core electron shakeup spectra, *Phys. Rev. Lett.* **58**, 2639 (1987).
- [22] E. Schmidt, H. Schroder, B. Sonntag, H. Voss, and H. E. Wetzel, Resonant vacuum ultraviolet photoemission of atomic Fe, Co and Ni, *J. Phys. B: At. Mol. Phys.* **16**, 2961 (1983).
- [23] F. Patthey, M.-H. Schaffner, W.-D. Schneider, and B. Delley, Observation of a Fano resonance in photoemission, *Phys. Rev. Lett.* **82**, 2971 (1999).
- [24] H. Ota, E. Salehi, M. Fujimoto, K. Hayashi, T. Horigome, H. Iwayama, M. Katoh, N. Kondo, S. Makita, F. Matsui, H. Matsuda, T. Mizukawa, A. Minakuchi, E. Nakamura, M. Nagasaka, Y. Okano, T. Ohigashi, M. Sakai, K. Sugita, K. Tanaka, Y. Taira, F. Teshima, J.-I. Yamazaki, T. Yano, H. Yuzawa, and S. Kera, Uvsor synchrotron facility update, *J. Phys.: Conf. Ser.* **2380**, 012003 (2022).
- [25] G. Kresse and J. Hafner, *Ab initio* molecular dynamics for liquid metals, *Phys. Rev. B* **47**, 558 (1993).
- [26] G. Kresse and J. Hafner, *Ab initio* molecular-dynamics simulation of the liquid-metal–amorphous-semiconductor transition in germanium, *Phys. Rev. B* **49**, 14251 (1994).
- [27] G. Kresse and J. Furthmüller, Efficiency of *ab-initio* total energy calculations for metals and semiconductors using a plane-wave basis set, *Comput. Mater. Sci.* **6**, 15 (1996).
- [28] G. Kresse and J. Furthmüller, Efficient iterative schemes for *ab initio* total-energy calculations using a plane-wave basis set, *Phys. Rev. B* **54**, 11169 (1996).
- [29] P. E. Blöchl, Projector augmented-wave method, *Phys. Rev. B* **50**, 17953 (1994).
- [30] I. Hamada, van der Waals density functional made accurate, *Phys. Rev. B* **89**, 121103(R) (2014).
- [31] Y. Morikawa, H. Ishii, and K. Seki, Theoretical study of *n*-alkane adsorption on metal surfaces, *Phys. Rev. B* **69**, 041403 (2004).
- [32] J. P. Perdew, K. Burke, and M. Ernzerhof, Generalized gradient approximation made simple, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [33] F. Otto, T. Huempfer, M. Schaal, C. Udhardt, L. Vorbrink, B. Schroeter, R. Forker, and T. Fritz, Ordered growth and electronic properties of 1,2:8,9-Dibenzopentacene (trans-DBPen) on Ag(111), *J. Phys. Chem. C* **122**, 8348 (2018).
- [34] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/2k7h-h8jm> for additional figures and details on the fitting procedure, which include Ref. [44].
- [35] J. Götzen, D. Käfer, C. Wöll, and G. Witte, Growth and structure of pentacene films on graphite: Weak adhesion as a key for epitaxial film growth, *Phys. Rev. B* **81**, 085440 (2010).
- [36] S. A. Abd-Rahman, T. Yamaguchi, S. Kera, and H. Yoshida, Sample-shape dependent energy levels in organic semiconductors, *Phys. Rev. B* **106**, 075303 (2022).
- [37] S. Kera, H. Yamane, I. Sakuragi, K. K. Okudaira, and N. Ueno, Very narrow photoemission bandwidth of the highest occupied state in a copper-phthalocyanine monolayer, *Chem. Phys. Lett.* **364**, 93 (2002).
- [38] Y. Nakayama, Y. Mizuno, M. Hikasa, M. Yamamoto, M. Matsunami, S. Ideta, K. Tanaka, H. Ishii, and N. Ueno, Single-crystal pentacene valence-band dispersion and its temperature dependence, *J. Phys. Chem. Lett.* **8**, 1259 (2017).
- [39] M. Ohtomo, T. Suzuki, T. Shimada, and T. Hasegawa, Band dispersion of quasi-single crystal thin film phase pentacene monolayer studied by angle-resolved photoelectron spectroscopy, *Appl. Phys. Lett.* **95**, 123308 (2009).
- [40] H. Kakuta, T. Hirahara, I. Matsuda, T. Nagao, S. Hasegawa, N. Ueno, and K. Sakamoto, Electronic structures of the highest occupied molecular orbital bands of a pentacene ultrathin film, *Phys. Rev. Lett.* **98**, 247601 (2007).
- [41] I. Schäfer, M. Schlüter, and M. Skibowski, Conduction-band structure of graphite studied by combined angle-resolved inverse photoemission and target current spectroscopy, *Phys. Rev. B* **35**, 7663 (1987).
- [42] F. Maeda, T. Takahashi, H. Ohsawa, S. Suzuki, and H. Suematsu, Unoccupied-electronic-band structure of graphite studied by angle-resolved secondary-electron emission and inverse photoemission, *Phys. Rev. B* **37**, 4482 (1988).
- [43] A. M. Ganose, A. J. Jackson, and D. O. Scanlon, sumo: Command-line tools for plotting and analysis of periodic *ab initio* calculations, *J. Open Source Softw.* **3**, 717 (2018).
- [44] D. Brandstetter, X. Yang, D. Lftner, F. S. Tautz, and P. Puschnig, kMap.Py: A python program for simulation and data analysis in photoemission tomography, *Comput. Phys. Commun.* **263**, 107905 (2021).