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<th>Impact of the molecular quadrupole moment on ionization energy and electron affinity of organic thin films: Experimental determination of electrostatic potential and electronic polarization energies</th>
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<td>Author(s)</td>
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I. INTRODUCTION

Understanding the factors that determine the energy levels of organic solids is of great importance to the research and development of organic semiconductor devices, e.g., organic light emitting diodes, organic photovoltaic cells, and organic transistors [1,2]. The organic solid is an aggregate of molecules bound by weak intermolecular interactions such as dispersion and electrostatic forces, while the constituent molecules consist of atoms bound by covalent bonds. As the intermolecular interactions are usually one order of magnitude smaller than the intramolecular ones, the energy levels of an organic solid can be regarded as the electronic levels of an isolated molecule perturbed by weak intermolecular interactions due to the classical and quantum effects [3]. The classical effect is the interaction between the localized charge carrier and neutral surrounding molecules [4]. The magnitude is in the range between 1 eV (1 eV $\approx$ 1.602 $\times$ 10$^{-19}$ J) and 2 eV [5]. On the other hand, the quantum effect can be observed as the band dispersion. The bandwidth is usually less than 0.1 eV in common organic semiconductors, while that of organic solids with high carrier mobility exceeds 0.4 eV [6–11].

The energy levels of organic solids are represented by the ionization energy $I$ and electron affinity $A$, corresponding to the edges of hole and electron conduction levels with reference to the vacuum level, respectively. In the previous work [12], we proposed the $I$ and $A$ expressed in connection with the ionization energy $I_g$ and electron affinity $A_g$ in the gas phase, respectively, as

$$I = I_g - P^+ - \Delta^+,$$
$$A = A_g + P^- + \Delta^-,$$  \hspace{1cm} (1)

where the contribution from the polarization energies for positive $P^+$ and negative $P^-$ charges and the effect of bandwidths of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) derived bands, $\Delta^+$ and $\Delta^-$, respectively, are taken into account. This is a modification of the well-known relation by Lyons [4]. Although the polarization energy includes contributions from molecular and lattice relaxations, they are smaller than 0.1 eV [13]. Only the electronic effects are discussed here.

The polarization energy $P^+$ and $P^-$ can further be divided into two terms, the electrostatic energy $W$ and electronic polarization energy $E_p$ [14–18]. The latter is also referred to the induction contribution [17] or dynamic interaction [18]. The $E_p$ is an induced effect that minimizes the total energy and approximated by the charge-induced dipole interaction. In contrast, the electrostatic energy $W$ is the interaction between the excess charge and the molecular charge (charge distributed
over the neutral molecules) and is approximated by the charge-
permanent multipole interaction.

The electronic polarization interaction is short range and
isotropic. Further, its magnitude does not strongly depend
on the materials [5]. As far as the electronic polarization
is concerned, the energy levels of an organic solid can be
estimated from those of its constituent single molecule. Based
on this assumption, the ionization energy \( I \), and electron
affinity \( A \), are routinely estimated using the cyclic voltammetry
or the density functional theory (DFT) calculation for an
isolated molecule.

On the other hand, the electrostatic interaction is long range
and highly anisotropic. It has been highlighted recently as the
origin of the orientation dependence of the energy levels in
molecular films [19,20] and continuous tuning of the energy
levels by mixing two molecules having permanent quadrupole
moments with opposite direction [21,22]. Further, theoretical
studies have pointed out that the energy level may also depend
on the macroscopic shape of the sample [16,17,23]. Such
electrostatic interaction can play an important role in the charge
separation in organic photovoltaic cells [24–26].

Among the above examples, the orientation dependence of
the energy levels has been most intensively discussed so far.
The orientation dependences of ionization energies have been
observed for many organic solids using ultraviolet photoelec-
tron spectroscopy (UPS) [19,27–36]. The origin is proposed to be
the electrostatic potential generated by the permanent
quadrupole moment of molecules. This argument has been
supported by good agreement between the experimental data
and theoretical predictions [12,16,20]. The opposite orien-
tation dependence of energy level was observed for similar
molecules with opposite quadrupole moment (e.g., copper ph-
thalocyanine and copper hexadecafluorophthalocyanine [27],
pentacene and perfluoropentacene [28]) providing a further
support. This phenomenon has been applied to modification of
the work function [37] and optoelectronic devices [38]. In any
case, however, the mechanism of the orientation-dependent
energy levels are mainly discussed based on the theoretical
consideration and the experimental data have provided only
indirect evidence. More specifically, the quantitative values
of the electrostatic potential have never been evaluated from
experimental data alone.

Recently, we developed low-energy inverse photoelectron
spectroscopy (LEIPS) [39–41] demonstrating that electron
affinities of various organic materials can be determined with
precision similar to that of the ionization energy by
UPS [42–50]. Based on the precisely determined electron
affinity together with the ionization energy, we precisely
determined the increase of electronic polarization energy upon
the crystallization of the 6,6-phenyl C61-butyric acid methyl
ester (PCBM) films [51]. Extending this idea, we anticipate
determining the \( W \) and \( E_p \) solely from the experimental data.

In this work, we first propose a procedure to determine
the electronic polarization and electrostatic energies from the
experimental data, bearing the situation described above in
mind. Then this method is effectually applied to the study of
the molecular-orientation dependence of energy levels
of 6,13-pentacenequinone [also called 6,13-pentacenedione
(PNQ), C22H12O2] films. In the earlier studies, the molecular-
orientation dependence of ionization energies was examined
only roughly for standing and lying orientations [12,19,27–36].
Further, the molecular orientations are controlled by preparing
the films on different substrates, e.g., the naturally oxidized
surface of Si wafer (SiO2) and highly oriented pyrolytic
graphite (HOPG). The effect of different substrates cannot
be neglected. We pay special attention to (1) quantitatively
controlling the molecular orientation and the direction of
molecular quadrupole and (2) preparing the film on the same
kind of substrates to minimize the effects of the substrate.
The obtained data will be able to be compared quantitatively
with calculated results with different levels of theory. Here,
we perform the first-principles calculations using DFT and the
\( G_0W_0 \) approximation to calculate the electrostatic and
electronic polarization energies, respectively. We also calculate
the electrostatic energy of charge-multipole interaction to draw
the potential maps and to examine the relation between the
energy levels and the macroscopic shape of the sample.

II. THEORY

As mentioned above, the polarization energies, \( P^+ \) and \( P^- \),
can be expressed as the sum of the electronic polarization
energy, \( E_p^\pm \), and the electrostatic energy, \( W^+ \) and \( W^- \),
respectively, for positive and negative ions,

\[
P^+ = E_p^+ + W^+. \\
P^- = E_p^- + W^-.
\]

As Topham and Soos pointed out, the polarization energy
may contain a cross term between the electronic polarization
energy and the electrostatic energy [16]. Since the cross term is
a few tenths of an eV, we neglect it. The electronic polarization
energy \( E_p \) is proportional to the square of the excess charge and
the value does not depend on the sign of the charge. Thus the
electrostatic polarization energies for positive \( E_p^+ \) and negative
\( E_p^- \) charges are approximated to be the same, \( E_p \equiv E_p^+ = E_p^- \).
In contrast, the electrostatic energy \( W \) is a linear function of
the excess charge and the sign of \( W \) depends on the polarity of
the excess charge. The electrostatic energies for positive \( W^+ \)
and negative \( W^- \) charges are approximately the same in the
magnitude but of opposite sign, \( W \equiv W^+ = -W^- \). Inserting
these relations into Eq. (2) yields

\[
E_p = (P^+ + P^-)/2, \\
W = (P^+ - P^-)/2.
\]

Note the above relation holds rigorously when the multipole
expansion is applied [15]. In practice, \( E_p^+ \) and \( E_p^- \), and also \( W^+ \)
and \( W^- \), may not be exactly the same because the charge
distributions are not always the same between the cation and
anion of the same molecule.

III. EXPERIMENT

We purchased PNQ and pentacene from Aldrich and pu-
fified by cycles of vacuum sublimation before use. Silicon
substrates with native oxide surface (SiO2) were sonicated in
acetone and ultrapure water, followed by heating to 700 K in
vacuum for 2 h. PNQ or pentacene was vacuum deposited at the
rate of 0.1–0.5 nm min\(^{-1}\) under the vacuum of 5 × 10\(^{-7}\) Pa.
A SiO2 substrate covered with a single layer of graphene
(Graphene Platform Corporation) was heated at 700 K for 24 h
in order to remove polymer residues [52].
The polymorphs and molecular orientations were examined by grazing-incidence x-ray diffraction (GIXD), near-edge x-ray absorption fine structure (NEXAFS), and Fourier transform infrared spectroscopy (FTIR). The GIXD measurements were carried out at the beam line BL46XU of SPring-8. An x-ray with a wavelength of 0.1 nm was incident to the sample surface with an angle of 0.06°−0.16° and diffraction was observed using a two-dimensional (2D) detector (PILATUS 300K). NEXAFS in the O K-edge region was recorded in a total electron yield mode at the BL-13B of the Photon Factory (KEK-PF). FTIR was measured on a Thermo Scientific Nicolet iS10.

UPS and LEIPS were performed in separate apparatuses without air exposure of the samples. UPS spectra were measured with a He discharge lamp (hν = 21.22 eV) and a SPECS Phoibos 150 electron energy analyzer. The vacuum level was determined from the cutoff energy for the secondary electron region in an obtained spectrum. Details of the LEIPS apparatus are described elsewhere [53]. The measurements were carried out at photon energies of 3.71, 4.13, and 4.89 eV. The vacuum level was determined as the inflection point of the rising edge of the sample current. No discernible change due to the sample damage was observed during the LEIPS measurements.

IV. RESULTS

We employ PNQ because it has a large quadrupole moment along the molecular long axis. The charge distribution in PNQ, as shown by the electrostatic potential map in Fig. 1(a), calculated at the B3LYP/6-31G(d) level [54] can be approximated by a quadrupole moment along the molecular long axis [55]. Thus it is essential to discuss the angle of the molecular long axis with respect to the substrate surface. For the substrate, we adopt SiO2 because it has a chemically inert surface as well as sufficient conductivity for the electron spectroscopies, flat surface for grazing-incidence x-ray diffraction (GIXD), and transparency in the infrared region for Fourier transform infrared spectroscopy (FTIR) (see the Supplemental Material [56]).

Fabricating organic films with controlled molecular orientations is challenging. The PNQ film shows two polymorphs with standing molecular orientation on SiO2 [57–60]: a monoclinic structure (P21/b) and a triclinic structure (P1) in which the molecular long axes tilt by 55° and 33° from the normal to the substrate surface, respectively [60]. Thus thin films with at least two different molecular orientations can be prepared when the polymorphs are codeposited. While the monoclinic form grows on the SiO2 surface normally, it is reported that the triclinic form of PNQ is exclusively observed when pentacene and PNQ are codeposited [59]. Inspired by this, we inserted a monolayer of pentacene between SiO2 and PNQ for preferential growth of the triclinic form. On the other hand, PNQ is expected to show a lying orientation on HOPG and graphene as is usually observed for polyacene molecules, e.g., pentacene [8,52,61,62] and perfluoropentacene [63,64].

Figure 1(b) shows GIXD patterns of the differently prepared PNQ films in the thickness of 5 nm. The PNQ film on graphene/SiO2 shows the (0 2 0), (0 4 0), and (0 6 0) diffractions of the monoclinic form (M) tilted by 40° from the surface normal, signifying that the molecules take a lying-flat orientation with the [1 4 0] axis normal to the substrate surface. A similar diffraction pattern was observed for PNQ on HOPG (Fig. S3, Supplemental Material [56]) showing that the films on the graphene and HOPG are the same in the crystallographic structure and molecular orientation [56]. On the pristine SiO2, the (0 2 0) diffraction of the monoclinic form (M) was observed normal to the substrate surface. The triclinic structure (T) was observed on pentacene/SiO2 with the (0 0 1) diffraction along...
the normal to the substrate. The determined polymorphs and orientations are summarized in Table I.

The orientations are further examined by oxygen K-edge spectra from NEXAFS (Fig. S1 [56]). The observed angle dependence of the peak intensities shows the angles of the molecular planes with reference to the normal of the surface are $\theta_z = 19^\circ$ on graphene/SiO$_2$, $57^\circ$ on SiO$_2$, and $69^\circ$ on pentacene/SiO$_2$. These results are in essentially good agreement with the x-ray diffraction results as shown in Table I. The slight differences between GIXD and NEXAFS data are due to the fact that the x-ray diffraction examines only the crystalline area while the NEXAFS examines both the crystalline and amorphous areas in the film. Actually, $\theta_z = 9^\circ$ for PNQ on HOPG (Fig. S3: panels (c,d) [56]) is in excellent agreement with $9.6^\circ$ of the XRD result [56], suggesting that the PNQ film on graphene is less perfect than that on HOPG. We also assessed the purity of the polymorph by observing the C-C in-plane vibrational mode using FTIR [60]. The spectra in Fig. S2 clearly confirm the high purity of each polymorph in the prepared PNQ films [56]. Thus we will employ the angles determined by x-ray diffraction to represent the molecular orientations for further discussion.

Now that the PNQ films with the controlled molecular orientations were obtained, we carried out UPS and LEIPS measurements to determine their ionization energies and electron affinities. We confirmed that the spectra are independent of the film thickness between 5 and 15 nm (Fig. S6, Supplemental Material [56]). The electron affinities are determined from the data taken systematically at the different photon energies (Figs. S4 and S5 [56]). Figure 2 shows the combined UPS and LEIPS spectra of 15-nm-thick PNQ films. The ionization energies and electron affinities are determined from the onset of spectra which are considered to be the values corresponding to the Fermi level of the vacuum level $E_{\text{vac}}$ of PNQ films with respect to the Fermi level $E_F$ are about 4.5 eV and little depends on the molecular orientation.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Crystal system</th>
<th>Orientation</th>
<th>GIXD $\theta_z$ (deg)</th>
<th>NEXAFS $\theta_z$ (deg)</th>
</tr>
</thead>
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<tr>
<td>Graphene/SiO$_2$</td>
<td>Monoclinic</td>
<td>1 4 0</td>
<td>80.4</td>
<td>9.6</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>Monoclinic</td>
<td>0 2 0</td>
<td>64.7</td>
<td>45.6</td>
</tr>
<tr>
<td>Pentacene/SiO$_2$</td>
<td>Triclinic</td>
<td>0 0 1</td>
<td>67.4</td>
<td>67.3</td>
</tr>
</tbody>
</table>

V. DISCUSSION

From the determined energy parameters, $I_s$ and $A_s$, of the film, we evaluate the polarization energies for positive and negative charges, $P^+$ and $P^-$, respectively, according to Eq. (1) [12]. For the energy parameters in the gas phase, we use the values of $I_g = 7.89$ eV and $A_g = 1.54$ eV calculated by HSE06/6-311 + +G** [69] since the calculation was found to be sufficiently reliable [12]. Actually the calculated $A_g$ is in close agreement with experimental data determined by negative ion photoelectron spectroscopy (the adiabatic electron affinity of $1.43 \pm 0.13$ eV and vertical detachment energy of $1.55 \pm 0.02$ eV) [70]. The electron affinity in Ref. [69] is calculated for the neutral molecular structure and does not take the structural relaxation into account. The values are the vertical electron affinity and should be similar to the vertical detachment energy if the reorganization energies are the same between the anion and neutral molecules. On the other hand, the experimental value of electron affinity for the film is determined from the spectral onset of LEIPS; we can assume...
The polarization energy.

The polarization energy in the following discussion. The above procedure and the evaluated polarization energies are shown in Fig. 3.

From the polarization energies, the electrostatic $W$ and electronic polarization $E_p$ energies are derived according to Eq. (3) as summarized in Table II. The electronic polarization energy $E_p$ is in the range between 0.9 and 1.1 eV and almost independent of the molecular orientation. The electrostatic energy $W$, on the other hand, varies from $-0.4$ to $+0.5$ eV predominantly contributing to the orientation dependence of the polarization energy.

Since we have experimentally obtained the quantitative values for the electrostatic $W$ and electronic polarization $E_p$ energies, we compare them with calculated values at various theoretical levels. First, we performed the first-principles calculations. The electrostatic energy can be calculated based on DFT calculation. Details of the method are described in the Supplemental Material [56]. Here, the electrostatic contribution in the polarization energy, $W^+$ (or $W^-$), depending on the molecular orientation is approximated by the difference in the HOMO (or the LUMO energy) between a 1-monolayer slab and an isolated molecule. The approximation may be validated by the “nearsightedness” of the quantum mechanical effects: Perturbation of the external potential at a region separated from a given location by larger than a typical de Broglie wavelength has a small effect upon any static property of a many-particle system at that location [71,72]. In other words, there is similarity in a local chemical environment, i.e., intramolecular chemical interaction, between a single molecule and a freestanding monolayer. On the other hand, the different electrostatic properties in a monolayer and in the gas phase were discussed [72]. The electronic polarization energy $E_p$ is obtained by the many-body perturbation theory within the $G_0W_0$ approximation for the bulk system [73–76]. Further, the result is calculated as the narrowing of the band gap; we evaluated the average value $E_p$ for positive and negative charges assuming $E_p^+ = E_p^-$. The results are compared with the experimental data in Table II.

The electrostatic energies $W^+$ and $W^-$ are calculated for the 1-monolayer slab and may not be directly compared with the experimental value for the thick film. Nevertheless, the values agree well with each other. As we assumed in Eq. (2), the magnitude of the electrostatic energy for the positive $W^+$ and negative $W^-$ charges are almost the same. The difference of about 0.1 eV is due to the differences in the charge distribution between the cation and anion as well as the different molecular polarizability to negative and positive charges. As mentioned before, the experimentally obtained electronic polarization energies $E_p$ correspond to the bulk value rather than the surface value; this can be compared with $E_p$ calculated by the $G_0W_0$ approximation for the bulk. Again the agreements are reasonable. These results suggest that the procedure represented by Eq. (2) gives us the $W$ and $E_p$ values from the experiment within the uncertainties of 0.1 eV.

When the multipole expansion is applied, the leading term of the electronic polarization energy is the charge-induced dipole interaction in the case of nonpolar molecules. In order to further explore the effect of the electrostatic energy, we calculate the electrostatic potential formed by permanent quadrupoles located at the molecular positions within a disk cluster of thickness $t$ and diameter $d$. The potential energy is calculated by $U = e/(4\pi \varepsilon_0 r^3) \sum |\mathbf{r}Q|$, where $e$ and $\varepsilon_0$ are the elementary charge and the permittivity of vacuum, respectively, and the sum runs over the center-of-mass positions of the neutral molecules $r$ with respect to the charge.

FIG. 3. The energy parameters (in eV) obtained by the UPS and LEIPS measurements for the different molecular orientations with indicated molecular tilt angles. The polarization energies for positive $P^+$ and negative $P^-$ charges calculated according to Eq. (1). The height of a gray block indicates the bandwidth $2\Delta^+$ or $2\Delta^-$.
FIG. 4. The electrostatic potential generated by the quadrupole moments distributed at the molecular position in a disk cluster with the thickness of 4 nm and diameter of 20 nm. The calculation was made for the 140 and 020 surfaces of the monoclinic form (indicated by \textit{m}140 and \textit{m}020, respectively), and the 001 surface of the triclinic form (t001). (a) Potential maps. The arrows indicate the position of molecules and direction of quadrupole moments. (b) The potential as a function of distance from the center of the disk along the normal to the surface. (c) The potential energy at the center of disk clusters as a function of aspect ratio \(t/d\) and that of a spherical cluster with a radius \(d\) ranging from 20 to 200 nm.

(in a cluster with the 140 surface of the monoclinic form), 55° (the 020 surface of the monoclinic form), and 33° (the 001 surface of the triclinic form), respectively. These values are in qualitative agreement with the experimental results. Note that the positive \(U\) value for positive (negative) charge means the destabilization (stabilization) of the system and corresponds to the negative (positive) \(W\).

Figure 4(b) shows the potential energy along the normal to the substrate surface. The energy in the cluster (\(-2.5\ \text{nm} < r_{\perp} < 2.5\ \text{nm}\)) is mostly uniform and different from that at the infinite distance as mentioned above. The potential energy near the surface outside the cluster (\(2.5\ \text{nm} < r_{\perp} < 10\ \text{nm}\)) also varies by \(-0.18\ \text{eV} (\theta_y = 90^\circ)\), 0 eV (55°), and 0.25 eV (33°) meaning that the orientation dependence of the surface potential leads to variation of the vacuum level and hence of the ionization energy and electron affinity. The results indicate that the molecular quadrupole affects the ionization energy and electron affinity through the following two ways: (1) the electrostatic potential in the cluster (bulk effect) and (2) the shift of vacuum level (surface effect). In the PNQ films, the bulk effect (1) is larger than the surface effect (2).

Since the charge-permanent quadrupole interaction is a long-range interaction, the potential inside the cluster is affected by the macroscopic shape of the cluster \[16,17\]. Figure 4(c) shows the potential energy of the center of the disk cluster with various thicknesses \(t\) and diameters \(d\) (between 20 and 200 nm). It is found that the potential energy depends on only the aspect ratio \(t/d\) and converges to that of the spherical cluster which does not depend on the radius of the sphere. These results indicate that the sample shape is crucial to the electrostatic energy.

VI. CONCLUSION

We demonstrated that the electrostatic \(W\) and electronic polarization \(E_p\) energies of organic thin films can be determined based solely on experimental results of ultraviolet and low-energy inverse photoelectron spectroscopies. First, the polarization energies for positive \(P^+\) and negative \(P^-\) charges are evaluated precisely from Eq. (1). Then, the polarization energies are decomposed into the induction \(E_p\) and electrostatic \(W\) terms based on the different response to the polarity of the charge [Eq. (3)]. This procedure was applied to the orientation-dependent energy levels of 6,13-pentacenequinone (PNQ) films with controlled molecular orientations on the same silicon oxide surface. It turns out that the electrostatic energy \(W\) predominantly depends on the molecular orientation. Since \(W\) is approximated by charge-permanent quadrupole interaction, the present results confirm the previous prediction that the electrostatic energy or the permanent-quadrupole moment of molecule is the origin of orientation-dependent
energy levels [16,20]. The results are also fully consistent with the first-principles calculation and the electrostatic energy of charge-permanent quadrupole interactions. The present work will stimulate further experimental and theoretical studies on the role of the electrostatic and electron polarization energies in organic semiconductors.

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The quadrupole tensor $Q_{ij}$ is discussed in detail in Refs. [41–79]. The components of the tensor are modeled as a linear array of three point charges as shown in Fig. 1(a) where the components of the tensor are being almost the same as each other. Such a quadrupole is being almost the same as each other. Such a quadrupole is twice as large as another component $Q_{zz}$. The $Q_{zz}$ component is twice as large as another component $Q_{zz}$ and $Q_{yy}$, being almost the same as each other. Such a quadrupole is modeled as a linear array of three point charges as shown in Fig. 1(a) where the components of the tensor are $Q_{yy} = +4lq^2$ and $Q_{zz} = -2lq^2$. 

See Supplemental Material at [link](http://link.aps.org/supplemental/10.1103/PhysRevB.97.245206) for NEXAFS and FT-IR data; GIXD and NEXAFS results of PNQ on HOPG; photon energy dependence of LEIPS spectra and the determination of electron affinities; thickness dependence of LEIPS spectra; and the detailed description of the first-principles calculations (see also Refs. [78–90]).


