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Polarization Energies, Transport Gap and Charge Transfer States of Organic Molecular Crystals

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Summary: A self-consistent calculation of electronic polarization in organic molecular crystals and thin films is presented in terms of charge redistribution in nonoverlapping molecules in a lattice. The polarization energies P_+ and P_- of a molecular cation and anion are found for anthracene and perelynetetracarboxylic dianhydride (PTCDA), together with binding energies of ion pairs and transport gaps of PTCDA films on metallic substrates. The 500 meV variation of $P_+ + P_-$ with film thickness agrees with experiment, as do calculated dielectric tensors. Comparisons are made to submolecular calculations in crystals.

Keywords: charge-transfer states; electronic polarization; organic molecular crystals; thin film devices; transport states

Electronic polarization and transport gap

Organic molecular crystals feature weak intermolecular forces, van der Waals contacts, and electronic excitations that correlate with gas-phase transitions. They are typically insulators with dielectric constant $\kappa \sim 3$. Since a charge in a cavity of radius $a \sim 5$Å in a dielectric medium has energy $e^2(1 - 1/\kappa)/2a \sim 1$ eV, electronic polarization has a central role for ionic states. Gutmann and Lyons[1] considered long ago a molecular ion or two embedded in a crystal lattice. Subsequent treatments are discussed by Pope and Swenberg[2] and by Silinsh and Capek,[3] who showed that electronic polarization substantially exceeds lattice (polaronic) relaxation in acenes. As sketched in Fig. 1, the ionization potential of a molecular crystal is reduced from the gas-phase value by the polarization energy, P_+, of a molecular cation, while the electron affinity is increased by P_-, the polarization energy of a molecular anion. The energy needed to create a well-separated pair of ions in the crystal is the transport gap,

$$E_t = I - A - P \qquad (1)$$

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where $P = P_+ + P_-$ is primarily electronic polarization. The corresponding energy for creating an ion pair at finite separation **r** is associated with charge-transfer (CT) states,

$$E_{\mathrm{CT}}(\vec{r}) = E_{\mathrm{t}} - V(\vec{r}) \qquad (2)$$

Here **r** is a lattice vector and (2) defines V(**r**), which is sometimes approximated by an effective dielectric constant.[4] Both expressions assume zero overlap between molecules, while recent studies of mixed Frenkel and CT excitons invoke finite overlap between neighbors.[5] Our discussion below is restricted to zero overlap and to electronic polarization in a fixed lattice.

Recent advances in preparation and characterization of ordered thin films have made possible organic electronic devices, such as light-emitting diodes and thin-film transistors, whose operation relies on charge transport.[6,7] Thin films mitigate the low mobility of organic molecular crystals or conjugated polymers. Although E_t or E_{CT} traditionally refers to bulk (infinite) crystals,[1-3] the transport gap of thin films requires the ionization potential and electron affinity at surfaces and photoelectron spectra yield surface properties. We present below the first evaluation of P for crystalline thin films on metallic substrates.[8] Electronic polarization directly affects E_t and thus the matching of energy levels for efficient charge injection. Moreover, in sharp contrast with inorganic semiconductors, the transport gap in several prototypical molecules used in organic devices exceeds[9] the optical gap, E_{opt} in Fig. 1, by about an eV. This reflects small overlap or organic narrow bands in organic crystals and is closely related to electronic polarization.

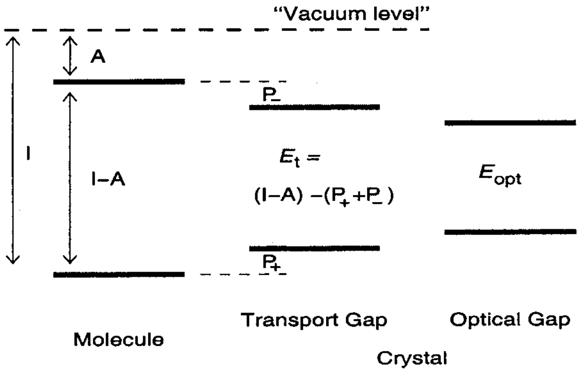

Fig. 1.Schematic energy diagram showing (a) the gas-phase adiabatic ionization potential and electron affinity of a molecule, (b) the transport levels of relaxed molecular ions with polarizations P_+ and P_- in the crystal and (c) the optical gap of the neutral molecule.

Molecular exciton theory describes the optical spectra and excitations of organic crystals. Intermolecular interactions are treated as perturbations to gas-phase (isolated) molecules that do not overlap. First-order corrections to excitation energies typically suffice. Even in this approximation, however, electronic polarization is more challenging because, by definition, first-order corrections to wave functions are required. Zero overlap nevertheless provides the major simplification of purely electrostatic interactions between molecules in the crystal lattice.[10] Such interactions redistribute the gas-phase charge density $\rho_G(\mathbf{r})$ and molecules can still be considered separately, albeit in a complicated crystalline potential.

Munn,[11] Silinsh[3] and coworkers have treated electronic polarization in infinite crystals, primarily the acenes, using the electrostatics of submolecules. The polarizability tensor α of an isolated molecule is taken from theory or experiment and partitioned equally among the rings or heavy atoms of a conjugated molecule. An ion in the crystal induces dipoles at submolecules and the resulting electrostatic problem is solved self consistently by a Fourier transform technique. As well recognized, the choice of submolecules is chemically motivated but arbitrary. Submolecules deal exclusively with induced dipoles and relate polarization to the molecular α. Instead, we incorporate α and induced atomic dipoles as corrections to charge redistribution.[10]

Self-consistent treatment of charge redistribution

Zero overlap reduces the problem to electrostatic interactions between molecules whose charge density $\rho(\mathbf{r})$ can be viewed as confined to volumes that, in one-component crystals, are given by the volume per molecule. The electrostatic energy is a functional of $\rho(\mathbf{r})$ and electronic polarization is the change, $\rho(\mathbf{r}) - \rho_G(\mathbf{r})$, from gas phase to crystal. The problem is formally similar to pairs of molecules[12] or changes in atomic charge densities in a molecule.[13] Direct quantum chemical treatments[12,13] do not require zero overlap but are restricted to small systems and contain other approximations. We are examining such studies and related work on atomic multipole expansions[14,15] as corrections to approximating $\rho_G(\mathbf{r})$ by discrete atomic charges. In addition to zero overlap, we take[10]

$$\rho_{\mathrm{G}}(\vec{r}) \approx \rho^{(0)}(\vec{r}) \equiv \sum_{a,j} \rho_i^{\mathrm{a}(0)} \delta(\vec{r} - \vec{r}_i^{\,\mathrm{a}}) \qquad (3)$$

Here $\mathbf{r}_i^{\mathrm{a}}$ is the position of atom i in molecule a in the crystal lattice and $\rho_i^{\mathrm{a}(0)}$ is its gas-phase atomic charge. To avoid the complicated sums-over-states encountered in perturbation theory, we consider solid-state or semiempirical models in which the electrostatic potential φ_i^{a} is a site energy $\varepsilon_i^{\mathrm{a}}$. Site energies in Hückel theory represent heteroatoms and yield inductive effects.[16] As a practical alternative, we include all valence electrons and find the ground state energy E_0 and $\rho^{(0)}(\mathbf{r})$ of an isolated molecule or molecular ion using INDO/S.[17] We then construct orthogonal molecular orbitals to obtain Löwdin charges $\rho_{\mathrm{i}}^{\mathrm{a}(0)}$ in (3). Finally, we evaluate the atom-atom polarizability tensor Π and the polarizability α^{C} due to charge redistribution,[10]

$$\begin{aligned} \Pi_{ij} &\equiv \left(\partial^2 E_0 / \partial\varphi_i \partial\varphi_j\right)_0 \\ \alpha^C &\equiv \sum_{ij} \Pi_{ij} \vec{r}_i \vec{r}_j \end{aligned} \tag{4}$$

Here i,j refer to atoms of one molecule or ion, the partial derivative is evaluated at $\varphi_i = \varphi_j = 0$ and dyadic notation is used for the tensor α^{C}.

We now have a discrete approximation for electronic polarization. The crystal structure and Löwdin charges $\rho_i^{\mathrm{a}(0)}$ define an electrostatic potential $\varphi_i^{\mathrm{a}(0)} = \varphi^{(0)}(\mathbf{r}_i^{\mathrm{a}})$ at each atom due to all other molecules. These charges are sources for molecules with inversion symmetry. Since α^{C} is in general different from α, we introduce atomic polarizabilities $\tilde{\alpha} = \alpha - \alpha^C = \sum_i \tilde{\alpha}_i$ that generate induced dipoles in the electric field $-\nabla\varphi_i^{\mathrm{a}}$; the partitioning into $\tilde{\alpha}_i$ is based on the number of valence electrons at atom i. Self-consistent atomic charges and induced dipoles lead to a system of four linear equations per atom,[10]

$$\begin{aligned} \rho_i^{\mathrm{a}} &= \rho_i^{\mathrm{a}(0)} - \sum_j \Pi_{ij} \varphi_j^{\mathrm{a}} \\ \vec{\mu}_i^{\mathrm{a}} &= -\tilde{\alpha}_i \cdot \vec{\nabla} \varphi_i^{\mathrm{a}} \end{aligned} \tag{5}$$

These equations can be solved iteratively for systems of 10^5 atoms or more. Charges redistribute within molecules in the potential generated by atomic charges and induced dipoles, while dipoles are induced by the crystal's electric fields.

The polarization energy of the crystal is extensive and depends on the specified location of ions in the lattice. The general expression in terms of self-consistent potentials and gas-phase charges is[10]

$$E_{\mathrm{tot}} = \frac{1}{2} \sum_a \sum_i \rho_i^{a(0)} \varphi_i^a \tag{6}$$

The translational symmetry of a lattice of neutral molecules yields E_{tot} by Madelung techniques. Alternant hydrocarbons such as acenes have small atomic charges and negligible polarization, < 5 meV per molecule. The stabilization is 330 meV per molecule for perylenetetracarboxylic dianhydride (PTCDA) due mainly to atomic charges of CO groups. Charge redistribution in the neutral lattice is significant for molecules containing heteroatoms and differs qualitatively from submolecules, where E_{tot} vanishes in the absence of charges.

In the presence of an ion, the linear equations (5) are solved[10] relative to the self-consistent charges of the neutral lattice in spheres of radius $R \sim 100$ Å centered on the ion and containing up to $M \sim 2000$ molecules. The crystal structure relates R and M. Thus P_+ or P_- in Fig. 1 for a single ion is the difference between two extensive quantities, a lattice with a molecular ion and a neutral lattice. Convergence goes as $1/R$, or $M^{-1/3}$, for a single charge and as $1/R^3$, or M^{-1}, for a CT state. As seen in Fig. 2, $P = P_+ + P_-$ converges properly for anthracene and PTCDA crystals; "charges only" refers to $\tilde{\alpha} = 0$ in (5) while the other lines have α computed using B3LYP density functional theory[18] with a large basis (6-311++G(d,p)). The slopes in Fig. 2 are related[10] to the crystal's dielectric constants,[19] which can be found independently using (5) for a crystal in a uniform electric field.[20] The slopes agree within 3% in all cases. We obtain P = 1.82 eV for PTCDA and 2.20 eV for anthracene.

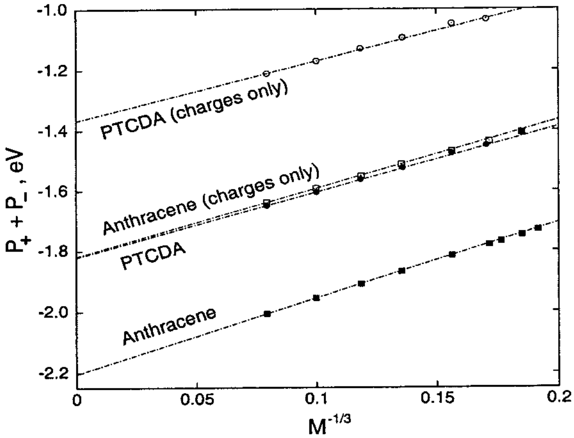

Fig. 2. Convergence of $P = P_+ + P_-$ for anthracene and PTCDA with $M^{-1/3}$, the number of molecules in a sphere of radius R. Straight lines are linear fits and „charges only" means $\tilde{\alpha} = 0$.

The binding energy $V(\mathbf{r})$ in (2) between a molecular cation and anion is anisotropic in general and contains both a direct Coulomb interaction and electronic polarization.[4] We center a molecular cation at the origin, place the anion at the crystallographic position $\mathbf{r}$ = (na,mb,lc), and solve Eq. (5) in spheres that contain both ions.[10] The CT energies of anthracene and PTCDA in Fig. 3 are for zero overlap and self-consistent charges and induced dipoles in (5). $V(\mathbf{r})$ converges rapidly as 1/M. We have a practical approach to electronic polarization energies of molecular ions or ion pairs in infinite crystals using discrete atomic charges (3) and induced atomic dipoles based on the best available molecular polarizability α. We avoid partitioning into submolecules. Our numerical results[10] agree best with the largest number of submolecules, 14 at carbon atoms in anthracene[21] and 11 at the centers of rings and CO bonds in PTCDA.[22] Self-consistent treatment of charge redistribution rests on the well-defined limit of zero overlap and the atom-atom polarizability tensor Π in (4). The approximation of $\rho_G(\mathbf{r})$ by $\rho^{(0)}(\mathbf{r})$ is improved below to first order. Nearest-neighbor mixing of Frenkel and CT excitons raise separate spectroscopic issues.[5] Finite overlap is essential for charge transport, for example as hopping of a charge and its polarization cloud, and can be included as a perturbation.

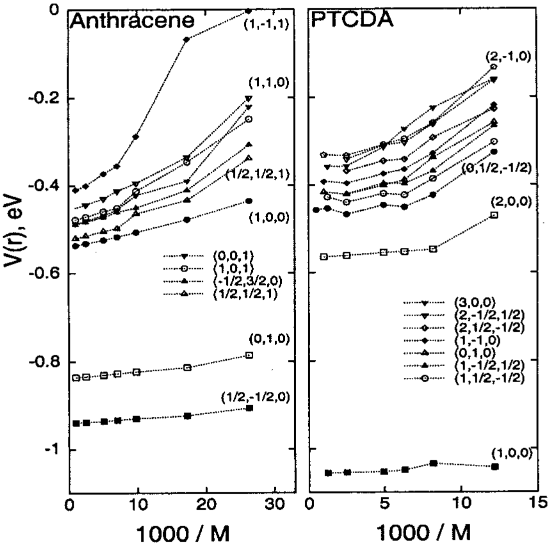

Fig. 3. Interaction energy V($\mathbf{r}$) in Eq. (2) for ion pairs at the origin and $\mathbf{r}$ = (na,mb,lc) in spheres of M molecules.

Electronic polarization in crystalline thin films

As noted above, organic electronic devices contain thin films on metallic substrates and photoelectron spectra (UPS) probe surfaces.[23] Inverse photoelectron spectra (IPES) is a recent tool for measuring electron affinities or P_{-}. Hence electronic polarization in thin films has direct implications for transport states. The structure of organic thin films is a separate topic, and multiple phases are possible. PTCDA films[6] are close to having a (102) plane at the organic-metal interface. Given the film's structure, a plane of the bulk crystal can be used to define an infinite slab of $N = 1, 2,\ldots$ layers. This is an excellent approximation in view of the weak distance dependence of electrostatic interactions.

The simplest approximation for an inert metal is a constant-potential surface, as sketched in Fig. 4, which introduces a parameter h for the separation of the first layer and generates N layers of images charges.[8] The translational symmetry of the slab yields atomic charges and induced dipoles by solving Eq. (5) for neutral molecules. Instead of spheres, we compute P_{+} and P_{-} of molecular ions using $2N$-layer thick pillboxes of radius R. We again solve Eq. (5) self-consistently relative to the neutral slab for M molecules and M images, now in a pillbox, and extrapolate as $1/R$ for the infinite slab.[8] UPS and IPES probe transport levels and P at the outermost layer in Fig. 4, while charge injection from the metal is related to P at the interface and P can be computed in any layer. We set $\phi = 0$ since P is independent of the magnitude of ϕ.

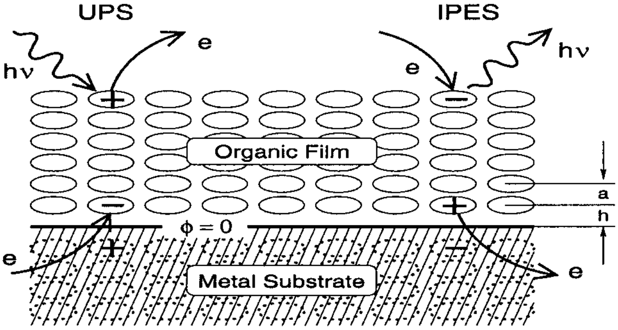

Fig. 4. Idealized model for electronic polarization in crystalline thin films on a metallic substrate at separation h. The N layers of the film appear as image charges. UPS and IPES generate a cation and anion at the surface, while charge injection generates ions in the interface layer.

The calculated $P = P_+ + P_-$ in Fig. 5 are for PTCDA at the surface of $N = 1, 2, 3, 5$ and 10 layer films at the indicated $h = \mathrm{x}a$, where $a = 3.214$ Å is the crystal spacing between (102) planes. Since the metal-organic interface is N layers away, P cannot depend on h as $N \to \infty$ and all curves converge to $P_{\mathrm{surf}} = 1.41$ eV. Electronic polarization at a (102) surface of an infinite PTCDA crystal is 410 meV less than in the bulk. For a free-standing film, we obtain 0.64 eV in Fig. 5 on extrapolating to infinite h.

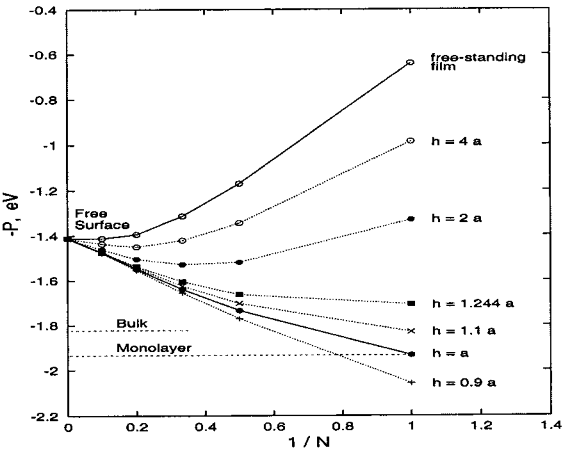

Figure 5. Calculated P at the outer surface of PTCDA films of $N = 1,2,3,5$ and 10 layers at several values of $h = \mathrm{x}a$, where $a = 3.214$ Å is the spacing between (102) planes. The polarization at the free surface, a free-standing (102) monolayer and the bulk are indicated.

While h is not known, van der Waals radii suggest $h \sim a$. The monolayer ($N = 1$) then has $P_{\mathrm{mon}} = 1.93$ eV, which exceeds the bulk value. Image charges represent the greater polarizability of metals compared to the crystal, while the vacuum at the outer surface in not polarizable. This is the physical basis for decreasing P at the surface with N at small h and increasing P with N for large h. We find $P_{\mathrm{mono}} - P_{\mathrm{surf}} \sim 500$ meV for PTCDA and striking agreement with experiment.[8] As an excellent film former as well as a good hole conductor, PTCDA is a prototypical molecule for organic devices and has been studied on Au, Ag and other substrates.[24] Photoelectron spectra on Ag show a 450 meV increase of E_t between a monolayer and a 64 Å ($N \sim 20$) film.[8] The corresponding increase of 500 meV on Au is based on scanning tunneling spectra[8] of the monolayer and photoelectron spectra of 50-100 Å films.[9] As expected from their Fermi energies, Au and Ag form opposite surface dipoles with PTCDA,[24] but surface dipoles cancel in P.

Figure 6 shows the variation of E_t across a 10-layer PTCDA film, with $h = a$ and $n = 1$ next to the metal.[8] Surface effects extend several layers into the sample, as is natural for electrostatic interactions, and greater polarizability at $n = 1$ is also expected. These are direct applications for calculations of electronic polarization in thin films. Transport-level shifts of ~200 meV at the interface are large compared to kT. They are neglected in current modeling of charge injection, as is the long-range nature of polarization.

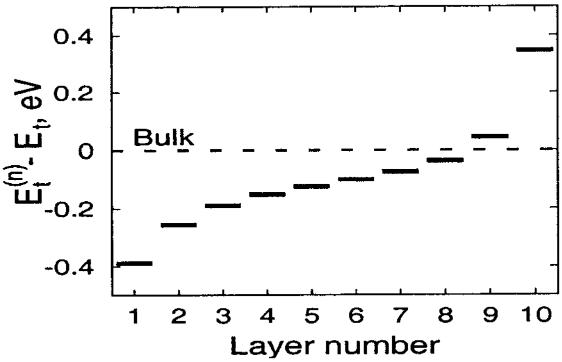

Fig. 6. Variation of the transport gap, $E_t^{(n)} - E_t$, across a 10-layer PTCDA film with $n = 1$ next to the metal and $n = 10$ at the outer surface. The dashed line is the bulk value, $P = 1.84$ eV.

UPS data for solid-state ionization potentials, $I - P_+$ in Fig. 1, are fairly common;[2,3] their detailed interpretation still has open questions. The frequent assumption of $P_+ = P_-$ is more convenient than correct. Molecular quadrupoles lead to divergent, shape-dependent contributions in crystals for P_+ or P_- that cancel in P. Measurements of P_+ in UPS and P_- in IPES are typically referenced to the subtrate's Fermi energy. In terms of submolecules, Munn has evaluated corrections $W_{q\text{-}Q}$ due to fixed molecular quadrupoles.[25,11] They increase P_+ for anthracene by 0.18 eV and decrease P_- by the same amount. At least qualitatively, observed[26] shifts of $I - P_+$ in films, monolayers or even lower coverage can be understood in terms of electronic polarization.[8]

Discussion and Conclusions

We have presented a new, self-consistent calculation of electronic polarization in organic molecular crystals. The principal approximations are no overlap between molecules, which makes it possible to limit quantum theory to individual molecules, and semiempirical theory for electrostatic potentials, which yields the atom-atom polarizability tensor Π in (4) that governs charge redistribution. The discrete problem of self-consistent atomic charges and induced dipoles leads to the linear equations (5) whose solutions are discussed above. Experimental comparisons to date have been in terms of E_t for PTCDA films and electronic parts of the dielectric tensor[20] of crystalline anthracene and PTCDA. Theoretical comparisons are to submolecular results for P_+, P_- and $V(\mathbf{r})$ of CT states.[10] We anticipate wider comparisons, especially to thin films. The procedure is general and INDO/S is readily applicable to conjugated molecules used in organic devices. Molecular polarizabilities α are more demanding, but if necessary, such corrections can be found in a smaller basis. The crystal structure and α are inputs, as in the submolecular approach, but we explicitly compute atomic charges and charge redistribution. Induced atomic dipoles due to $\tilde{\alpha} = \alpha - \alpha^C$ are 10-20% corrections that are particularly important for polarization normal to the molecular plane.

The approximation (3) of discrete atomic charges $\rho^{(0)}(\mathbf{r})$ reduces the polarization problem to four linear equations per atom. Although atomic charges are not observables, the widespread usage of Mulliken, Löwdin and other charges speak to their appeal. But the potential $\varphi(\mathbf{r}')$ generated by any localized charge distribution $\rho_G(\mathbf{r})$ *is* unique at any $\mathbf{r}'$ outside the charge distribution. There is interest[14,15] in expanding $\varphi(\mathbf{r}')$ for molecules in terms of atomic multipoles (charges, dipoles, and perhaps quadrupoles) chosen by least-squares fitting procedures. In the same spirit, we associate atomic multipoles with $\Delta\rho(\mathbf{r}) = \rho_G(\mathbf{r}) - \rho^{(0)}(\mathbf{r})$, the difference between the actual charge density of an isolated molecule or ion and the INDO/S atomic charges in (3). For zero overlap, the potential $\Delta\Phi_a(\mathbf{r}_i^a)$ at atom i of molecule a due to $\Delta\rho(\mathbf{r})$ of all other molecules can readily be computed;[27] convergence is rapid because there are no monopole (1/r) contributions by construction.

The potential $\Delta\Phi_a(\mathbf{r})$ represents fixed sources that are neglected in (3) and hence in the linear equations (5). The polarization energy E_{tot} in (6) can also be expresses as self-consistent atomic charges ρ_i^a and induced dipoles μ_i^a coupled to $\varphi_i^{a(0)}$ and $\nabla\varphi_i^{a(0)}$, respectively, the potential due to

$\rho^{(0)}(\mathbf{r})$. The extra potential due to higher atomic multipoles increases E_{tot} by

$$E_{\text{tot}}^{(1)} = \sum_{a} \sum_{i} [\rho_i^{\text{a}} \Delta\Phi(r_i^{\text{a}}) + \vec{\mu}_i^{\text{a}} \cdot \vec{\nabla} \Delta\Phi(r_i^{\text{a}})] \tag{7}$$

The correction is first order, since ρ_i^a and μ_i^a are not recalculated in the new potential. For acenes, PTCDA and other conjugated molecules with inversion symmetry, the π-system's quadrupole makes the largest contribution to $\Delta\Phi_a(\mathbf{r})$. The first term of (7) then gives the charge-quadrupole contribution to P_+ or P_-. This is $qW_{q\text{-}Q}$ term[3,11] for fixed quadrupoles and submolecules. With $\Delta\Phi_a(\mathbf{r})$ based on a B3LYP-6311++G(d,p) calculation[18] of $\rho_G(\mathbf{r})$, we find −0.23 eV for anthracene, compared to $W_{q\text{-}Q} = -0.18$ eV for three fractional charges at ring centers .[27] The PTCDA result is larger and implies contributions beyond the perylene π-system. First-order corrections in $\rho_G(\mathbf{r}) - \rho^{(0)}(\mathbf{r})$ can readily be added to self-consistent electronic polarizabilities.

In PTCDA films, the molecular plane is nearly parallel to the substrate. Other film formers such as α-sexithiophene or pentacene, by contrast, have molecular planes nearly perpendicular to the metal. Image charges in Fig. 4 then generate fields along the long axis, the direction of greatest polarizability. Care must be taken with iterative solution Eq. (5) for pentacene films on metals,[28] whose transport gaps as a function of thickness are quite different than PTCDA. Even in terms of ideal inert surfaces, electronic polarization of thin films remains to be explored and applied to issues such as matching transport states for charge injection. Electronic polarization is a major effect in organic molecular crystals that can now be evaluated in a well-defined approximation. We anticipate many applications to thin films in organic electronic devices.

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