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Journal of Luminescence 110 (2004) 332-341



www.elsevier.com/locate/jlumin

Polarization in organic molecular crystals and charge-transfer salts

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Available online 23 September 2004

Abstract

Polarization in insulators is a general phenomenon that extends over nanometer distances. Two special cases illustrate recent theoretical progress. Polarization energies of localized charges in organic molecular crystals exceed the bandwidth and redistribute the charge density. A systematic treatment of electronic polarization is summarized in the limit of zero intermolecular overlap for pentacene crystals or thin films on metallic substrates, with special attention to the transport gap for producing a separated electron–hole pair and the optical dielectric tensor of the crystal. When overlap cannot be neglected, the general formulation of polarization in extended insulators is in terms of the exact ground state's phase. This formulation is applied to organic charge-transfer (CT) salts whose correlated electronic structure is described by one-dimensional Peierls–Hubbard models. Near the Peierls instability, coupling to lattice modes generates large peaks in the dielectric response that is primarily due to lattice vibrations. Comparisons with experiment are mentioned for both organic molecular crystals and CT salts. (C) 2004 Elsevier B.V. All rights reserved.

Pacs: 77.22.-d; 71.70.ch; 71.20.Rv; 71.30.+h

Keywords: Polarization; Dielectric response; Organic molecular crystals; Thin films; Peierls transition

1. Introduction

Molecular or plastic electronics is an emerging area with widespread applications to organic light

emitting diodes, thin film transistors, photovoltaic cells and a variety of sensors. Conjugated molecules and polymers have different advantages and limitations. In either case, applications presuppose the formation and characterization of multiple thin films down to nanometer thicknesses. Thin films are crucial because molecular electronics implies currents and organic materials have limited

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^{0022-2313/\$ -} see front matter © 2004 Elsevier B.V. All rights reserved. doi:10.1016/j.jlumin.2004.08.029

mobility that normally involves hopping transport between localized states. Low mobility is related to narrow bands (4t < 1 eV) or small overlap in organic molecular solids with weak intermolecular interactions. Band theory is suitable for wide bands in metals or inorganic semiconductors with delocalized valence states, and its proper extension to narrow bands remains a longstanding challenge.

Transport states in organic molecular crystals are usually visualized as anions (electrons) or cations (holes) localized on individual molecules [1,2]. The transport gap $E_t = I(s) - A(s)$ sketched in Fig. 1 is the minimum energy for creating an e-h pair at infinite separation in the solid [3]. It depends on the ionization potential and electron affinity of the crystal, which differ from the gasphase values by the polarization energies $E(P_{+})$ and $E(P_{-})$ of the two charges. We consider electronic polarization and ignore lattice contributions that are thought [2] to be corrections of 10%or less. A charge in a cavity of radius $a \sim 5$ Å in a medium with dielectric constant $\kappa \sim 3$, a typical value for organics, leads to $E(P) = e^2(1-1/\kappa)/\kappa$ $2a \sim 1 \text{ eV.This}$ simple estimate demonstrates the major role of electronic polarization in narrowband systems. In contrast to inorganic semiconductors with essentially identical transport and optical gaps, the optical gap in organic molecular

crystals is ~1 eV less than E_t . In terms of Fig. 1, charge-transfer (CT) states with fixed separation R between the anion and cation are further stabilized by the interaction V_{e-h} as R decreases. Several molecules with electronics applications have nearly degenerate optical (Frenkel) and CT excitations, although for neighbors these states are expected to mix [4].

Fig. 1 introduces at a glance several topics discussed below as well as general problems associated with transport states. Frenkel excitons rather than CT excitations dominate the optical spectra of organic molecular *crystals*, as expected in view of small overlap, and CT contributions are extracted from electroabsorption. In contrast to optical spectra, transport states are probed by surface techniques that have vacuum- and metalorganic interfaces. The ionization potential I(S) at the surface and electron affinity A(S) are obtained from photoelectron and inverse photoelectron spectroscopy, respectively. Scanning tunneling spectroscopy is another route to I(S) - A(S) for mono or bilayers. Since $E_t = I(s) - A(s)$ in Fig. 1 refers implicitly to crystals in most discussions, corrections between bulk and surface polarization are needed. We summarize in Section 3 the first calculation [5] of $E(P_+) + E(P_-)$ for crystalline thin organic films, down to monolayers, on inert



Fig. 1. Schematic energy diagrams of (a) a molecule's gas-phase adiabatic ionization potential, electron affinity; (b) the transport levels of relaxed molecular ions with polarization energy $E(P_+) + E(P_-)$; (c) CT excitation forming adjacent ions;, (d) the crystal's optical gap.

metallic substrates. Charge injection from or into the metal is essential for organic electronics and its optimization is a major goal. Localized charges and organic films with low κ imply electronic polarization that extends over distances that include surfaces and interfaces.

The organic CT salts discussed in Section 4 have dielectric peaks of $\kappa > 100$ on cooling [6] or under pressure [7] that call for entirely different theoretical methods [8]. Intermolecular overlap is of central importance in stacks of π -electron donors (D) and acceptors (A), and the electronic system is strongly coupled to lattice and molecular vibrations. Moreover, the dielectric peaks signal a structural (Peierls) instability with increasing ionicity ρ of the ... $D^{\rho}A^{-\rho}D^{\rho}A^{-\rho}$... ground state. Polarization is then dominated by electronic fluxes induced by lattice phonons. We still neglect overlap between D and A in different stacks and resort to Hubbard models for the electronic structure of extended stacks, as done previously for ion-radical organic crystals [9]. Polarization P in extended insulators can be formulated [10] rigorously as a Berry phase, and electronic fluxes due to phonon modes [11] are derivatives of P. We adopt a Peierls-Hubbard model of CT salts that includes site energies and electron-phonon coupling to obtain the dielectric response, dP/dF, to a static electric field. Dielectric peaks of the proper magnitude are found [8] near the Peierls transitions and are mainly due to vibrations. Modelexact results using P for correlated electronic states are a powerful approach for understanding systems whose direct treatment is prohibitive at present.

We emphasize in Section 2 that polarization is a general phenomenon that dates back to the classic studies of Mossotti [12] and Clausius [13]. In this context, crystalline insulators are an extensive and diverse special case based on unit cells and translational invariance. Organic molecular crystals are a subset with small intermolecular overlap; organic CT salts are another subset in which intermolecular overlap is largely restricted to onedimensional stacks; inorganic insulators are yet another subset with significant overlap or covalent bonding in three dimensions. Polarization in the gas phase, in solution or in aggregates is beyond the scope of the present discussion, although clearly related to it.

2. Polarization in insulators

The polarization, P, of a material is the electric dipole moment per unit volume. Finite P in ferroelectric materials can be viewed as a deviation from a centrosymmetric structure, which has P = 0by symmetry. Hence polarization can also be associated with a response or a deformation. Linear polarizability is the linear response to a uniform electric field F, which alters the charge distribution. While internal fields due to molecules or to added charges are not uniform, they also change the charge distributions. Polarization is a materials property [14]: even in perfectly localized systems without overlap, it differs from the sum of molecular polarizabilities because the crystal or the environment changes the response. In molecular exciton theory, [1,2], weak intermolecular forces in organic molecular crystals are treated as perturbations that shift and split the excitations of isolated molecules in the gas (G) phase. The corresponding change in the wave function or charge density, $\Delta \rho(\mathbf{r}) = \rho(\mathbf{r}) - \rho_{\rm G}(\mathbf{r})$, can be associated with internal fields.

The proper formulation of polarization in extended insulators is a recent development. The fundamental problem for infinite crystals is that there is no obvious way to define the basic unit cell that, in turn, fixes *P*. A different perspective on the same problem is to recognize that periodic boundary conditions (PBC) are difficult to reconcile with finite *P* or with a uniform static *F*. Indeed, as discussed by Resta [10], only variations of *P* and not its absolute magnitude are relevant physically or accessible experimentally in extended insulators. Aside from an irrelevant additive term, *P* can be related [15] to the *phase* of the exact ground state (GS) wavefunction ψ ,

$$P = \frac{1}{2\pi} \operatorname{Im} \ln \left\langle \psi \middle| \exp \left(\frac{2\pi i M}{N} \right) \middle| \psi \right\rangle, \tag{1}$$

where M is the conventional dipole operator. Localized (Wannier) functions are used in inorganic salts to approximate ψ , while narrow bands in organic CT salts require a correlated ψ of quantum cell models.

A static field *F* is included [16] by treating $P(\psi_F)$ as a constraint and finding ψ_F that minimizes the energy of $H-N^3F P(\psi_F)$. In a linear system, this is equivalent to finding the GS of $H(F) = H-F\Delta M$, where the induced-dipole operator is [8]

$$\Delta M(F) = \frac{N}{2\pi} \operatorname{Im} \frac{\exp(2\pi i M/N)}{\langle \psi(F) | \exp(2\pi i M/N) | \psi(F) \rangle}.$$
 (2)

The exact GS of H(F) is accessible in correlated models whenever the F=0 solution is known. The polarizability, $(dP/dF)_0$ evaluated at F=0, is related to the motion of charges under the applied field. Due to differences in mass, nuclear displacements are far smaller than electronic displacements. Hence polarization is usually dominated by electronic contributions. There are important exceptions, however, for example near structural transitions where electronic and nuclear degrees of freedom are strongly coupled.

The general formulation of P as a phase bypasses the unit-cell problem in extended insulators. There is no unit-cell problem in the special case of *zero intermolecular overlap*, which is a first approximation to organic molecular crystals with weak dispersion forces between molecules with closed electronic shells. Charge redistribution is then purely *intramolecular* and conventional molecular approaches to polarization are sufficient.

The remainder of this Section summarizes the calculation [17] of polarization in the limit of zero intermolecular overlap or complete localization (t=0). The goal is to find charge-density changes, $\Delta\rho(r)$, due to arbitrary perturbations. In the spirit of molecular exciton theory, the crystal structure fixes the location of all atoms and the molecular polarizability α is an input. Still another approximation is introduced: continuous charge distributions are replaced by discrete atomic charges and induced atomic dipoles. These approximations make possible the general treatment of polarization energies of localized charges in Fig. 1 or the crystal's optical dielectric tensor κ .

Given a charge distribution $\rho(\mathbf{r}')$ localized to a molecule, the potential $\varphi(\mathbf{r})$ at any point \mathbf{r} outside the molecule can readily be found. The inverse

problem, the change in $\rho(\mathbf{r}')$ due to an arbitrary potential $\varphi(\mathbf{r})$, is quite difficult even for pairs of molecules. Polarization entails both problems, since the charge distributions that generate the potentials are functionals of the potential. A selfconsistent treatment of $\rho(\mathbf{r}')$ and $\phi(\mathbf{r})$ is required in the crystal. The simplification in solid-state models is to consider $\rho(\mathbf{r}')$ at discrete sites, either atomic or molecular. Then $\varphi(\mathbf{r}_m)$ at the position \mathbf{r}_m of atom m can be viewed as a site energy that modulates the electron count. Site energies in semiempirical quantum chemistry are parameters related to the ionization potentials of valence orbitals. The modification of atomic site energies by the potential $\varphi(\mathbf{r}_n)$ due to all other molecules provides a simple general approach to changes of $\rho(\mathbf{r})$ that, in discrete systems, corresponds to atomic charges ρ_n and induced atomic dipoles μ_n . Charges couple to $\varphi(\mathbf{r}_n)$, dipoles to the electric field $\mathbf{F}_n = -\nabla \varphi(\mathbf{r}_n)$. The key quantity is the atom-atom polarizability tensor and the associated polarizability [17]

$$\Pi_{nm} = -\frac{\partial \rho_m}{\partial \varphi_n} = -\frac{\partial^2 E}{\partial \varphi_n \partial \varphi_m},$$

$$\alpha^{\rm C} = \sum_{nm} \vec{r}_n \Pi_{nm} \vec{r}_m.$$
(3)

Here *E* is the ground-state energy of the isolated molecule, which is conveniently obtained using [18] INDO/S, $\varphi_n = \varphi(\mathbf{r}_n)$ is the potential at atom *n* and ρ_m is the Löwdin charge of atom *m*. The tensor $\alpha^{\rm C}$ is the molecular polarizability of point atomic charges. Charge redistribution within a molecule is given by [17]

$$\begin{aligned}
\rho_n &= \rho_n^{(0)} - \sum_m \Pi_{nm} \varphi_m, \\
\vec{\mu}_n &= -\tilde{\alpha}_n \cdot \vec{\nabla} \varphi_n,
\end{aligned} \tag{4}$$

where $\rho_n^{(0)}$ is the gas-phase atomic charge and the potential φ_m is due to the atomic charges and induced atomic dipoles of all other molecules. We partition $\tilde{\alpha} \equiv \alpha - \alpha^C$, where α is the molecular polarizability, either experimental or calculated, according to the number of valence electrons on atom *n*. Induced atomic dipoles μ_n are 10–20% corrections to charge redistribution. Their selfconsistent treatment parallels microelectrostatic theory [19], in which polarization is entirely due to α .

3. Pentacene crystals and thin films

Pentacene is a good candidate for thin film transistors [20]. Fig. 2 shows a pentacene bilayer in van der Waals contact with a gold substrate [21]. The atomic positions are taken from the crystal with an exposed *ab* plane and the metal is a constant-potential surface. Pentacene is known to stack with the long axis almost normal to the substrate and its anisotropic mobility is high in the ab plane parallel to the surface. Thiophene oligomers are good film formers with similar stacking and high mobility. The hole conductor perylenetetracarboxylic dianhydride (PTCDA) forms crystalline films in which the molecular plane is almost parallel to the surface. PTCDA has several surface structures that resemble the bulk [22]. The crystal structure cleaved along specific planes is a convenient and excellent approximation for current modeling of crystalline thin films.

While not prominent for molecular electronics, anthracene is probably still the prototypical and best characterized organic molecular crystal [1,2], and microelectrostatic theory has been primarily applied to acenes [19,2]. The optical dielectric tensor κ and indices of refraction, $n_i^2 = \kappa_{ii}$, are difficult to measure in anisotropic crystals. There are numerous measurements of κ or n_i on anthracene, but to date none on pentacene. The tensor κ is related to the electronic polarizability per unit cell. As noted above, the molecular polarizability α and crystal structure are inputs for computing κ . The failure of the "oriented gas" model for κ indicates that the response is not simply additive.

We mention polarization results for crystals before turning to thin films and surfaces. Zero overlap and discrete atomic potentials reduce the calculation of electronic polarization to solving a system of eight linear equations per atom, as indicated in Eq. (4), a procedure that is readily implemented for more than 10⁵ atoms. Translational symmetry reduces GS calculations [17] to unit-cell problems using standard Madelung methods for crystal sums. There are two molecules per unit cell in anthracene, PTCDA and pentacene; they are equivalent crystallographically in the first two, but not in pentacene. We always start with charge redistribution in the GS using Π_{nm} in Eq. (3) and the molecular α in Eq. (4). The field *F* does not break translational symmetry in the limit of zero overlap, since the potential can be defined separately for each molecule. We find the induced dipole per unit cell for three orthogonal orientations of *F* and resolve *F* into external (applied) and internal (induced) fields to obtain κ . The principal values and axes of κ are in good agreement with experiment for anthracene [23]. The calculated principal values for pentacene are [21] κ_{11} =5.336 (along the long axis in Fig. 2), κ_{22} =3.211 and κ_{11} =2.413. Increased κ_{11} is a delocalization effect whose magnitude remains to be confirmed.

Localized charges generate electric fields and break translational symmetry. The transport gap in Fig. 1 depends on the polarization energies of separated charges. After finding the self-consistent GS of the neutral lattice, we place [17] a charge at the origin and compute $E(P_{+})$ or $E(P_{-})$ by relaxing M molecules according to Eq. (4) whose centers fall within an imaginary sphere around the ion. Increasing M leads as expected to convergence as $M^{-1/3}$, proportional to the inverse radius of the sphere, and the slope vs. $M^{-1/3}$ is directly related to κ at large M and hence is the same for cations and anions. We find [21] $E(P_+) = 1.03 \,\text{eV}$ for either cation in pentacene, $E(P_{-}) = 0.98$, 0.99 eV for the anions, and $E(P_+) + E(P_-) = 2.014 \text{ eV}$ for the polarization part of E_t . The resulting $E_t = 2.74 \text{ eV}$ based on a molecular calculation of I-A with a large basis agrees with the 2.78 eV extracted from electroabsorption [24]. Accurate polarization calculations open the way to resolving scatter of ~0.5 eV in current estimates of $E_{\rm t}$.

The polarization energy of CT states at fixed R is found using imaginary spheres of M molecules that contain both ions. Convergence is faster, as M^{-1} , since the sphere encloses a dipole. Polarization energies of CT states in anthracene and PTCDA generally agree [17] with microelectrostatic results with the most extensive partitioning of α , for example over all heavy atoms rather than at centers of rings or of the molecule.

We use pillbox-shaped clusters for polarization calculations of charge in thin films on metallic substrates [5]. The thickness is twice the number of



Fig. 2. Schematic molecular packing of pentacene layers on a metal. Image charges below the metal surface are also sketched.

molecular layers in order to include image charges and induced dipoles. As before, translational symmetry in the plane yields charge redistribution in the neutral film. A charge is then placed at the surface or interface or in between. All molecules and images whose centers are inside the pillbox are relaxed. Increasing the pill box's radius yields $E(P_{+})$ or $E(P_{-})$ on extrapolating to infinite radius. Convergence is fast since image charges ensure overall neutrality and is most demanding for charges at the surface of thick films, when the distance to the image is greatest. We consider $E(P_{+}) + E(P_{-})$, the quantity that appears in E_{t} , and show [21] in Fig. 3 the difference between surface and bulk values for N-layer and pentacene films in Fig. 2. The monolayer (N=1) value is almost that of the bulk. The high polarizability of image charges on one side offsets the vacuum on the other side. As N increases, $E(P_+) + E(P_-)$ decreases on the surface as pentacene layers are interposed between the metal, while polarization at the interface increases as pentacene layers are interposed between the surface. Calculations up to N=5 layers in Fig. 3 are extrapolated to give a 0.23 eV decrease at the free surface and a 0.13 eV increase at a deep interface.



Fig. 3. Calculated variation of the electronic polarization energy of *N*-layer thick films of pentacene of a metal: $P = E(P_+) + E(P_-)$ is the bulk value for separated charges; $P^{S,M}(N)$ is the corresponding polarization energy for separated charges at the surface (S) or next to the metal (M).

Similar calculations for PTCDA films on a metallic substrate showed a 0.5 eV decrease of $E(P_+) + E(P_-)$ between a monolayer (N=1) and a

thick film, in excellent agreement with experiments on both Au and Ag substrates [5]. Comparable polarization is expected at interfaces whether or not it can be treated in the zero-overlap approximation. Polarization is always an issue for matching energy levels across organic interfaces in the quest for good ohmic contacts. Of course, many other chemical and roughness effects also come up in connection with charge injection and may well dominate in particular cases. The point is that significant polarization contributions are expected.

4. Dielectric response of CT salts

Fig. 4 shows schematically a mixed stack of planar donors (D) and acceptors (A). Although the molecules are usually tilted in crystals, they are at inversion centers when the spacing is equal along the stack. Weak donors and acceptors form 1:1 complexes with largely neutral GS (small ionicity ρ) and regular spacing. Strong D and A form have ionic GS with $\rho > \frac{1}{2}$ and dimerized spacing that breaks inversion symmetry. The spectacular vibrational consequences [25,26] of dimerization have been studied in detail in CT salts with variable ρ such as the prototypical [27] TTF-CA (tetrathiafulvalene-chloranil), in ion-radical salts with segregated stacks of donors or

mixed regular stack



Fig. 4. Schematic representation of mixed regular, dimerized stacks, with spacing *a*, transfer integrals *t* in regular stacks, $a \pm u$, $t(1 \pm \delta)$ in dimerized stacks.

acceptors, and in organic conductors with partially filled bands.

Organic ion-radical or CT salts feature π electron overlap in face-to-face stacks at less than van der Waals separation [9]. Electron correlation is important in these narrow bands (4t~1 eV). Half filled (ρ =1) bands are Mott insulators [9], even in segregated D⁺D⁺ or A⁻A⁻ stacks that become good conductors for ρ <1. The electronic structure of CT salts has been discussed using Peierls–Hubbard models for individual stacks [8], with D and A at odd and even sites, respectively,

$$H_{CT} = \sum_{p,\sigma} -t_p (a_{p\sigma}^+ a_{p+1\sigma} + hc) + \sum_p \Gamma(-1)^p n_p + N\delta^2 / 2\varepsilon_d + V \sum_p q_p q_{p+1}.$$
(5)

The first term is the Hückel model for electron transfer between neighbors in the stack; we take $t = \langle \mathbf{DA} | \mathbf{H} | \mathbf{D}^+ \mathbf{A}^- \rangle = 1$ as the unit of energy and $t_{\rm p} = [1 - \delta(-)^{\rm p}]$ for dimerized stacks. The second term has site energies $-\Gamma$ at D, $+\Gamma$ at A and number operators n_p that are restricted to 1 or 2 at odd p and to 0 or 1 at even p. The ionicity ρ is the average number of electrons per A site in the GS. The exclusion of doubly ionized sites leads for $\Gamma < <0$ to a Heisenberg antiferromagnetic chain with $\rho = 1$ and a spin $\frac{1}{2}$ at each site. The third term of Eq. (5) represents a harmonic lattice with inverse stiffness ε_d in units of t. Such an adiabatic approximation follows the Su-Schrieffer-Heeger model [28] for the Peierls instability of polyacetylene, $(CH)_x$. The final term is a nearest-neighbor Coulomb attraction V that, in mean-field (mf) theory, adds $-2V\rho$ to Γ ; the charge operator q_p is $-n_p$ at A sites and $2-n_p$ at D sites. Since the full electrostatic (Madelung) energy of the crystal leads to a similar modification of Γ in mf theory, at this level V represents any Coulomb or vibronic interaction that modifies site energies [8].

Previous studies, both analytical and numerical, of $H_{\rm CT}$ with V=0 focused on the neutral-ionic crossover [29] of the rigid regular stack ($\delta = \varepsilon_{\rm d} = 0$) at $\Gamma_{\rm c} = -0.666$ and $\rho_{\rm c} = 0.684$. The ionic stack is unconditionally unstable to dimerization. The Peierls transition to a dimerized GS is consequently on the neutral side at some $\Gamma_P > \Gamma_c$ that depends on ε_d . Stiff lattices with small ε_d dimerize close to Γ_c while soft lattices with large ε_d dimerize at small ρ . The Peierls instability is given by the GS energy per site of Eq. (5) at fixed δ ,

$$\varepsilon_T = \varepsilon(\Gamma, \delta) + \delta^2 / 2\varepsilon_d. \tag{6}$$

The regular stack is stable as long as $\chi(\Gamma) = -(\partial^2 \varepsilon / \partial \delta^2)_0$ is less than $1/\varepsilon_d$ [30]. The relation $\chi(\Gamma_P)\varepsilon_d = 1$ defines Γ_P , and the equilibrium dimerization δ for $\Gamma < \Gamma_P$ is given by $\partial \varepsilon_T / \partial \delta = 0$.

The restriction to neutral and singly ionized sites in $H_{\rm CT}$ leads to a large but finite basis for N-site stacks that can be solved exactly. The top panel of Fig. 5 shows [8] the equilibrium dimerization vs. Γ for N = 14 (circles) and 16 (crosses) of a stiff lattice with $\varepsilon_d = 0.28$ that is representative of TTF-CA and a softer one with $\varepsilon_d = 0.64$. Both exact and mf results are shown for V=2. The soft lattice dimerizes at larger Γ and reaches $\delta_m > 0.3$, about three times that of the stiff lattice. The close coincidence of N = 14 and 16 shows that finite-size effects are negligible, presumably because $\delta > 0$ opens a gap at the crossover and the GS is always insulating. The asymmetry about $\Gamma = 0$ is entirely due to correlations that exclude D^{2+} and A^{2-} sites in $H_{\rm CT}$. The middle panel of Fig. 5 is the ionicity ρ and has small kink, more pronounced in mf, at the Peierls transition.

To compute the dielectric response κ for F along the stack, we add to $H_{\rm CT}$ the interaction $-NF\Delta M(0)$, where $\Delta M(0)$ is the induced dipole operator in Eq. (2), and solve for $\psi(F)$, the GS for small F. We then find [8] P(F) using (1) and its derivative, $(dP/dF)_0 = \alpha$. The polarizability per site is converted to κ using TTF-CA's unit cell and is shown in the bottom panel of Fig. 5 for N = 14 and 16. The dotted lines are the small, purely electronic contributions for N = 16. The large κ peaks at the Peierls transition are vibronic in origin and are significantly amplified by the softening of the Peierls mode in the far IR. The calculated κ using P for periodic boundary in Peierls-Hubbard models and otherwise typical parameters are in the range reported by Horiuchi et al. [6,7] for a series of 1:1 salts based on D = DMTTF (dimethyltetrathiafulvalene). Systematic Br/Cl substitution leads to six acceptors ranging from chloranil to bromanil. Direct modeling clearly shows that soft lattices dimerize on the neutral side, as observed.

5. Summary

Although well understood in principle, electronic polarization in condensed phases continues to be challenging. In this paper we have touched on two recent advances. The general expression for Pin Eq. (1) for insulators has made possible applications to organic CT salts with neutral-ionic or Peierls transitions. In addition to the dielectric response κ in the bottom panel of Fig. 5, the IR intensity [11] of the Peierls mode polarized along the stack is obtained as proportional to $(\partial P/\partial \delta)^2$. Similarly, the strong IR activity [31] of totally molecular modes dimerized symmetric in $(\delta > 0)$ stacks goes as $(\partial P / \partial \Gamma)^2$ and is borrowed from the optical CT excitation polarized along the stack.

The special case of zero overlap, an approximation that is frequently invoked for organic molecular crystals, is the key to the self-consistent pentacene results discussed in Section 3. Realistic and efficient calculation of electronic polarization energies of localized charges, $E(P_{+})$ and $E(P_{-})$, can be performed in crystalline thin films on inert metallic substrates, as shown in Fig. 3. The longrange aspects of polarization can readily be treated in this limit. Because many molecules contribute, approximate structures of the proper density should suffice for films or aggregates. Since organic materials with high mobility are of interest, a major extension is to find corrections in intermolecular overlap. Quadrupoles are the leading terms for the electrostatic potential of anthracene, pentacene and PTCDA. Conjugated molecules with permanent dipoles are both polar and polarizable, a combination that leads to interesting nonlinearities in molecular clusters [14] or in polar solvents [32]. It is now evident that, principally due to polarization, collective or environmental considerations must be addressed for molecular electronics materials, in addition to parallel efforts at optimizing molecular responses.



Fig. 5. Equilibrium dimerization amplitude δ (top panel), GS ionicity ρ (middle panel), dielectric response κ (bottom panel) of H_{CT} , Eq. (5), for stacks with V=2, inverse stiffness $\varepsilon_d=0.28$, 0.64. Circles, crosses refer to N=14, 16, respectively, with continuous, dashed lines joining exact, mean-field results. Dotted lines in the bottom panel are the purely electronic mf part for N=16.

Acknowledgements

We thank S.A. Bewick, A. Kahn, F. Terenziani and A. Girlando for discussions. We gratefully acknowledge partial support of work at Princeton by the National Science Foundation through the MRSEC program under DMR-9400632, and support for work at Parma by the Italian Ministry of Instruction, University and Research (MUIR) and by the Inter-university Consortium of Science and Technology of Materials (INSTM, project PRISMA 2002).

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