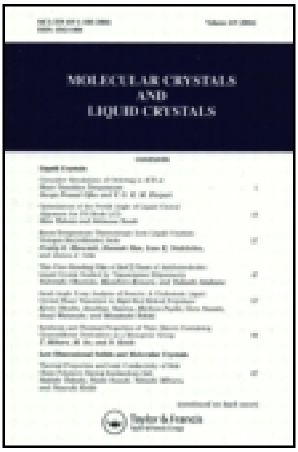

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Theory of Electrical Properties of Molecular Crystal Surfaces

R. W. Munn [a]

[a] Department of Chemistry and Centre for Electronic Materials, UMIST, Manchester, M60 1QD, U.K.

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THEORY OF ELECTRICAL PROPERTIES OF MOLECULAR CRYSTAL SURFACES

R.W. MUNN
Department of Chemistry and Centre for Electronic Materials, UMIST, Manchester M60 1QD, U.K.

Abstract Crystals inevitably have surfaces, near which crystal properties inevitably change. Quantitative changes in magnitude occur because of the loss of interactions near the surface, and qualitative changes in symmetry occur because of the loss of symmetry across the surface. This paper discusses the theory of some surface electrical properties of molecular crystals. All the properties depend on dipolar interactions between the molecules. The interactions are conveniently summed over planes of molecules parallel to the surface, when it is found that interactions between neighbouring planes are generally negligible. This result facilitates computation of surface properties. Applications discussed include surface electric fields, polarization and pyroelectricity, charge-carrier energetics, and nonlinear optics.

1. INTRODUCTION

By definition, a crystal is bounded by terminating surfaces, near which the crystal properties inevitably change. The surface properties may then be of interest or importance either in themselves or because access to the bulk crystal necessarily implies crossing a surface. Certainly in conventional solid-state materials, the properties of interfaces are known to exert a major influence on electrical behaviour. Hence it appears desirable to assess systematically the surface electrical and related properties of organic solids too. Among such solids, molecular crystals have ordered, well-defined surfaces and so offer a suitable class of materials for learning about surface effects.

The properties of any molecular material arise from the molecular properties, the molecular arrangement, and the molecular interactions.[1] At a surface, the major change from the bulk is in the molecular arrangement — molecules are missing. Other changes may ensue, such as relaxation of the lattice structure and modification of environmental effects on the molecular response, but these are likely to be of secondary importance. Hence the present paper considers molecular crystal surfaces obtained by removing all molecules on one side of a particular crystallographic plane in an infinite perfect crystal, with no subsequent structural or electronic readjustment. (However, much of the treatment could be modified to incorporate surface relaxation.)

The electrical and related properties considered here are those in which electric dipole interactions play an essential part. Such interactions can be treated rigorously to provide a coherent picture of many molecular crystal bulk properties.[2] There the key quantity is the lattice dipole sum that determines the electric field at one molecule due to permanent or induced dipole moments at the other molecules in the lattice. For molecular crystal surface properties, the corresponding quantity is the planewise dipole sum that determines the electric field at a molecule in one plane parallel to the surface of interest due to dipole moments at the molecules in that or another such plane. Planewise dipole sums were developed some time ago to treat surface excitons and polaritons in aromatic hydrocarbon crystals.[3-5] The following Section considers the calculation of such sums and how they depend on the choice of surface and the separation of the planes.

In fact, planewise sums fall off rapidly with separation, so that molecules experience the bulk environment except in a few planes close to the surface. This allows surface properties to be calculated by solving a manageable number of coupled equations. Subsequent Sections of this paper treat surface linear dielectric response, including the surface local field; surface polarization and pyroelectricity; surface polarization energy, for example of an excess charge carrier; and surface nonlinear optical response. The aim is to provide algebraic treatments and physical interpretation of the various phenomena.

2. PLANEWISE DIPOLE SUMS

Electrical properties imply the presence of electric fields, as indeed do optical properties. Electric fields in turn imply the presence of induced dipole moments. These dipole moments themselves produce electric fields, and it is a fundamental problem in dielectric response to treat the dipole moments and electric fields self-consistently, so that the total field induces precisely those dipole moments required to produce that field.

The electric field $\boldsymbol{E}$ produced at position $\boldsymbol{x}$ relative to a dipole moment $\boldsymbol{p}$ is given by

$$\boldsymbol{E} = \boldsymbol{T}\cdot\boldsymbol{p}/4\pi\varepsilon_0 , \tag{1}$$

where $\boldsymbol{T}$ is the dipole tensor $\nabla\nabla(1/x)$, which is defined to be zero for $x = 0$. In a crystal, each molecule contributes a term like (1) to the field at a given molecule. If all the dipole moments are equal, then the total field is given by an expression like (1) but with $\boldsymbol{T}$ replaced by a sum of dipole tensors over all vectors $\boldsymbol{x}$ between the given molecule and the others in the lattice. This quantity is a bulk lattice dipole sum.

As already argued, properties at a crystal surface cannot be the same as in the bulk. In particular, the dipole moments at the surface cannot equal those in the bulk. However, they can all be equal in any given layer parallel to the surface. This leads to the idea of obtaining the total electric field as a sum of contributions from each layer, with each contribution given by an expression like (1) but with $\boldsymbol{T}$ replaced by a sum of dipole tensors over all vectors $\boldsymbol{x}$ between the given molecule and the others in the layer. Such a treatment recognizes the loss of translational symmetry across the surface but the retention of symmetry within the layers.

Let a layer labelled g comprise unit cells labelled λ that are constructed to have one pair of faces parallel to the surface of interest. The molecules within each cell are labelled k. Then the planewise dipole sums are defined as

$$\boldsymbol{T}_{kk'}(gg') = (v/4\pi)\sum_{\lambda}\boldsymbol{T}(\lambda gk,0g'k') . \tag{2}$$

Here the summand is the dipole tensor evaluated for the separation $\boldsymbol{x}(\lambda gk) - \boldsymbol{x}(0g'k')$ between molecule k in unit cell λ of layer g and molecule k' in the origin unit cell of layer g'; the factor $v/4\pi$ is included for convenience and makes $\boldsymbol{T}_{kk'}(gg')$ dimensionless. Since structural relaxation at the surface is excluded here, the planewise sums depend only on the relative positions of the layers, i.e. on the difference $g - g'$ rather than on g and g' separately.

Planewise dipole sums are evaluated not by summing directly over the plane as implied by (2) but by transforming the summation so that part is summed over the direct lattice and part over the two-dimensional reciprocal lattice.[3,6] This process corresponds to the Ewald technique for evaluating bulk lattice sums, and similarly facilitates convergence. The resulting expressions use an obvious system of coordinates with X and Y parallel to the surface and Z perpendicular to it. It then proves convenient to transform the conventional crystallographic cell into one where the new a and b axes lie parallel to the crystal surface[7] (consistent with the definition of a layer, above).

Previous expressions have also been generalized to treat each molecule not as a single point but as a set of s point submolecules that represent the molecular size, shape and orientation, so that a molecule k comprises submolecules labelled j. Planewise dipole sums like (2) are then evaluated with kj replacing k and $k'j'$ replacing k', but excluding $\lambda = 0$ from the sum when $g = g'$ and $k = k'$ since a dipole moment on one submolecule cannot polarize another submolecule on the same molecule (their mutual influence is incorporated in the molecular polarizability). An improved molecular planewise dipole sum is finally obtained by averaging the submolecule sums over all s^2 pairs jj'.

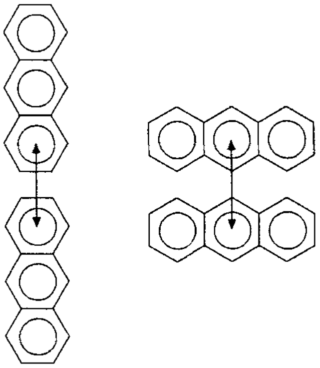

FIGURE 1. When elongated molecules are oriented perpendicular to the surface (horizontal) as on the left, the nearest pair of submolecules indicated by the arrow is much closer than the centres of the molecules; when the molecules are oriented parallel to the surface as on the right, the nearest pair of submolecules is the same distance apart as the centres. Hence the point-molecule treatment under-estimates the effective separation in the first case and over-estimates it in the second.

Extensive calculations of planewise dipole sums have been performed for various surfaces in anthracene, treated as a single point or as three submolecules.[7] The main qualitative findings concern how rapidly the sums fall off as the separation between layers g and g' increases. As usual, the point-molecule treatment exaggerates the anisotropy of the interactions. For molecules that extend roughly normal to the surface, as in the (001) planes, the point-molecule treatment omits interactions between submolecules in adjacent layers that are much closer than the molecular centres, and so predicts too rapid a fall-off. For molecules that extend roughly parallel to the surface, as in the (010) planes, the point-molecule treatment omits interactions between submolecules in adjacent layers that are somewhat farther apart than the molecular centres, and so predicts too slow a fall-off. These arguments are illustrated in Figure 1, above.

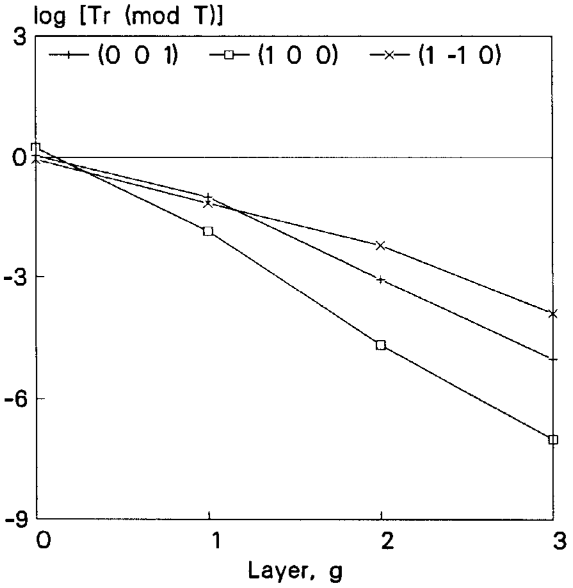

FIGURE 2. Logarithm of the sum of the moduli of the diagonal elements of the planewise dipole sum in the submolecule treatment as a function of layer for selected planes. Note the exponential decrease with layer.

In the submolecule treatment, interactions between adjacent layers are typically about 10% of those within a layer, but in subsequent layers each 10 Å separation decreases the sums by a factor of about 100, as shown in Figure 2, above. These results can be rationalized in terms of molecular packing. The closest approach of submolecules is much the same whether they belong to molecules in the same layer or in adjacent layers, so that there are some sizable contributions to the planewise sums between adjacent layers. However, other contributions between adjacent layers will tend to be much smaller than within the same layer because on average the submolecules must be more distant. Packing arguments no longer apply beyond adjacent planes and there is nothing to offset a rapid fall in the sums.

3. LINEAR DIELECTRIC RESPONSE

The results reported in the previous Section show that planewise dipole sums can be calculated efficiently and that they fall off rapidly beyond adjacent planes. With this established, it is appropriate to return to the discussion of dipole moments and electric fields.

Consider a crystal placed in a uniform applied electric field $\boldsymbol{E}^0$ produced by external electrodes and charges. Molecule k in layer g acquires a dipole moment $\boldsymbol{p}_k(g)$ and hence experiences the local polarizing field

$$\boldsymbol{F}_k(g) = \boldsymbol{E}^0 + \sum_{g'k'} \boldsymbol{T}_{kk'}(gg')\cdot\boldsymbol{p}_{k'}(g')/\varepsilon_0 v\ . \tag{3}$$

For self-consistency, the dipole moment must be that induced by the local field, i.e.

$$\boldsymbol{p}_k(g) = \boldsymbol{\alpha}_k\cdot\boldsymbol{F}_k(g)\ , \tag{4}$$

where α_k is the effective polarizability, assumed independent of layer g. Substitution of (4) in (3) then yields an equation for the local fields:

$$\boldsymbol{F}_k(g) = \boldsymbol{E}^0 + \sum_{g'k'} \boldsymbol{T}_{kk'}(gg')\cdot\boldsymbol{a}_{k'}\cdot\boldsymbol{F}_{k'}(g')\ , \tag{5}$$

where $\boldsymbol{a}_k = \alpha_k/\epsilon_0 v$ is a dimensionless reduced polarizability.

Equation (5) shows that the local field in each layer is determined by those in neighbouring layers. For the surface layer there is coupling to other layers only on one side, but successively deeper layers experience coupling which is increasingly comparable on either side, until eventually layers experience a constant bulk environment. Specifically, suppose the planewise dipole sum $T_{kk'}(gg')$ is negligible when r or more layers intervene between g and g'. Then r is the range of the interactions, and beyond layer $2r$ molecules experience the bulk environment because they interact only with layers out of range of the surface. Since some surface layers couple to bulk layers, the surface local fields are conveniently expressed in terms of the bulk ones.

For $g > 2r$, eq. (5) contains bulk local fields F_k^{b} independent of g, whence

$$F_k^{\mathrm{b}} = E^0 + \sum_{k'} T_{kk'}^{\mathrm{b}} \cdot a_{k'} \cdot F_{k'}^{\mathrm{b}} , \tag{6}$$

with the bulk dipole sum given by[3]

$$T_{kk'}^{\mathrm{b}} = \sum_{g'} T_{kk'}(gg') . \tag{7}$$

Equation (6) can be solved directly to yield

$$F_k^{\mathrm{b}} = \sum_{k'} (I - T^{\mathrm{b}} \cdot a)_{kk'}^{-1} \cdot E^0 \equiv h_k^{\mathrm{b}} \cdot E^0 . \tag{8}$$

Subtracting eqs (5) and (6) gives an expression for the surface deviation from the bulk local field in terms of the quantity

$$T_{kk'}^{\mathrm{s}}(g) = T_{kk'}^{\mathrm{b}} - \sum_{g'} T_{kk'}(gg') , \tag{9}$$

which is the surface-induced deviation from the bulk dipole sum and hence is nonzero for $g < r$. The resulting expression can be solved directly owing to the restricted range, with the result

$$\boldsymbol{F}_k(g) = \boldsymbol{F}_k^{\mathrm{b}} - \sum_{g'k'k''} \boldsymbol{H}_{kk'}(gg') \cdot \boldsymbol{T}^{\mathrm{s}}_{k'k''}(g') \cdot \boldsymbol{F}^{\mathrm{b}}_{k''} \equiv \sum_{k'} \boldsymbol{Q}_{kk'} \cdot \boldsymbol{F}^{\mathrm{b}}_{k'}. \tag{10}$$

Here $\boldsymbol{H}$ is obtained by inverting the matrix $\boldsymbol{J} - \boldsymbol{T} \cdot \boldsymbol{A}$; these matrices have dimension $2r + 1$ times those for the bulk, with submatrices $\boldsymbol{I}\,\delta_{gg'}$, $\boldsymbol{T}(gg')$ and $\boldsymbol{a}\,\delta_{gg'}$. Finally one obtains

$$\boldsymbol{F}_k(g) = \sum_{k'} \boldsymbol{Q}_{kk'}(g) \cdot \boldsymbol{h}^{\mathrm{b}}_{k'} \cdot \boldsymbol{E}^0 \equiv \boldsymbol{h}_k(g) \cdot \boldsymbol{E}^0 \ , \tag{11}$$

where $\boldsymbol{h}_k(g)$ is a surface local-field tensor computable from the given expressions.

Experimental quantities are usually expressed in terms of the macroscopic electric field. This gives the potential difference across the crystal, arising as it does from the applied field plus the field of the induced dipoles with microscopic variations averaged out.[8] For a crystal it suffices to average over a unit cell, but near the surface the average will depend on the layer. Hence the macroscopic field in layer g is

$$\boldsymbol{E}_g = \boldsymbol{E}^0 - \boldsymbol{n}(\boldsymbol{n} \cdot \boldsymbol{P}_g) / \varepsilon_0 \ , \tag{12}$$

where $\boldsymbol{P}_g$ is the polarization (dipole moment per unit volume) in layer g and $\boldsymbol{n}$ is the unit normal to the surface. It is now possible to recast the foregoing expressions in terms of $\boldsymbol{E}_g$ rather than $\boldsymbol{E}^0$, the effect being to replace the planewise dipole sums by the planewise Lorentz-factor tensors

$$\boldsymbol{L}_{kk'}(gg') = \boldsymbol{T}_{kk'}(gg') + \boldsymbol{n}\boldsymbol{n}\,\delta_{gg'} \ , \tag{13}$$

which via an equation like (7) provide a link to the previous bulk dielectric theory.[2]

However, these expressions relate the local field in layer g to the macroscopic fields in all other layers g', whereas eq. (12) shows that $\boldsymbol{F}_k(g)$ by determining $\boldsymbol{P}_g$ also determines $\boldsymbol{E}_g$ and hence conversely. This problem is resolved by expressing $\boldsymbol{P}_g$ in terms of $\boldsymbol{E}^0$, giving $\boldsymbol{E}_g$ in terms of $\boldsymbol{E}^0$. Inverting this result leads to

$$\boldsymbol{F}_k(g) = \boldsymbol{h}_k(g) \cdot [\boldsymbol{1} + \boldsymbol{n}(\boldsymbol{n} \cdot \boldsymbol{R}_g) / (1 - r_g)] \cdot \boldsymbol{E}_g \equiv \boldsymbol{d}_k(g) \cdot \boldsymbol{E}_g \ , \tag{14}$$

where $r_g = \boldsymbol{n} \cdot \boldsymbol{R}_g \cdot \boldsymbol{n}$; the quantity

$$\boldsymbol{R}_g = \sum_k \boldsymbol{a}_k \cdot \boldsymbol{h}_k(g) \tag{15}$$

is a linear susceptibility relating the polarization to the applied field.

Defining a layer susceptibility χ_g relating the polarization to the macroscopic field through

$$\boldsymbol{P}_g = \varepsilon_0 \boldsymbol{\chi}_g \cdot \boldsymbol{E}_g \tag{16}$$

leads at once to

$$\boldsymbol{\chi}_g = \sum_k \boldsymbol{a}_k \cdot \boldsymbol{d}_k(g) \ . \tag{17}$$

From eq. (14) this becomes

$$\boldsymbol{\chi}_g = \boldsymbol{R}_g \cdot [\boldsymbol{1} + \boldsymbol{n}(\boldsymbol{n} \cdot \boldsymbol{R}_g)/(1 - r_g)] \ , \tag{18}$$

showing χ_g to be a modification of $\boldsymbol{R}_g$. Because $\boldsymbol{h}_k(g)$ is computable, so are $\boldsymbol{R}_g$ and χ_g as well as $\boldsymbol{d}_k(g)$. This means that it is possible to calculate the local electric fields and susceptibilities layer by layer in a given crystal surface. In practice measurements are more likely to relate to average properties over surface regions (which were shown above to be very thin). These are given by eq. (18) with $\boldsymbol{R}_g$ replaced by a simple average. Among the quantities of interest are the surface dielectric constant $\boldsymbol{1} + \chi_g$ and the corresponding refractive indices.

4. SURFACE POLARIZATION

So far, only polarization induced by an external applied field has been considered. Crystals belonging to the polar classes can exhibit a net spontaneous polarization (usually annulled by surface charge) which depends on temperature to yield pyroelectricity. Other crystals should exhibit no spontaneous polarization. However, at a surface the symmetry is broken and a surface polarization may develop.

For crystals composed of polar molecules, it is clear how surface polarization can occur. In the bulk, the permanent dipole moment of each molecule is balanced by another equal and opposite to it; at the surface, cancellation need no longer occur. For crystals where the molecules occupy centres of symmetry and so cannot be polar, the same symmetry arguments predict surface polarization but the mechanism is more subtle. Since there are no permanent dipole moments, surface polarization arises from dipole moments induced by uncompensated surface electric fields caused by the permanent charge distributions of the molecules, i.e. normally the quadrupole moments. Such a mechanism could explain the surface pyroelectricity reported[9] in anthracene (to which special factors may also contribute).

In either case, molecules in the surface layers are polarized by fields $E_k^0(g)$ due to the permanent moments of the molecules. These fields give rise to local fields, which are found by procedures similar to those already used, with the result

$$F_k(g) = \sum_{g'k'} H_{kk'}(gg') \cdot E_{k'}^0(g') \, . \tag{19}$$

Detailed analysis shows that in either case the surface polarization can be written as the induced polarization

$$P = (1/v) \sum_{gk} [p_k(g) - p_k^{\mathrm{b}}] \, , \tag{20}$$

where the p_k^{b} are the bulk dipole moments (if any) including the bulk induced contributions. From this and eq. (19) comes the result

$$P = \varepsilon_0 \sum_{gg'} \sum_{kk'} K_{kk'}(gg') \cdot E_{k'}^0(g') \, , \tag{21}$$

where K is a surface susceptibility:

$$K = A \cdot H = (A^{-1} - T)^{-1} \, . \tag{22}$$

For polar molecules, the source field is given by

$$E_k^0(g) = - \sum_{g'k'} T_{kk'}^{\mathrm{s}}(gg') \cdot p_{k'}^{\mathrm{b}} / \varepsilon_0 v \, , \tag{23}$$

where T^{s} is the surface-induced deviation from the bulk dipole sum as before, and the bulk dipole moments are obtained from

$$\boldsymbol{p}_k^{\mathrm{b}} = \sum_{k'} (\boldsymbol{I} - \boldsymbol{a} \cdot \boldsymbol{T}^{\mathrm{b}})_{kk'}^{-1} \cdot \boldsymbol{\mu}_k \,, \tag{24}$$

μ_k being the free dipole moment. This result confirms that the surface polarization does not depend on how one chooses to assign molecules to unit cells, as sometimes suggested in sketches of surface polarization, provided there is a true bulk region. For quadrupolar molecules, the source field is

$$\boldsymbol{E}_k^0(g) = \sum_{g'k'} \boldsymbol{U}_{kk'}(gg') : \boldsymbol{\Theta}_{k'} \,. \tag{25}$$

Here $\boldsymbol{\Theta}_k$ is the quadrupole moment and $U_{kk'}(gg')$ is a planewise quadrupole sum defined by an equation like (2) but with T replaced by the quadrupole tensor $\nabla\nabla\nabla(1/x)$.

Calculations of planewise quadrupole sums have been performed for anthracene and pyrene and used to investigate surface electric fields, polarization and pyroelectricity in the surface layer.[10] Anthracene has two molecules per unit cell lying on centres of symmetry, so that bulk quadrupole sums are zero. Different surfaces induce nonzero components according to which symmetry elements are lost. The largest components are for $kk' = 12$ for the (010) and (100) surface, when molecules 1 and 2 lie in different planes less than one lattice spacing apart. Pyrene has the same symmetry, but with two molecules related by each centre of symmetry, so that only the bulk quadrupole sum for $kk' = 11$ is zero. Much the largest components of the planewise sums are for $kk' = 12$, i.e. for the closest pair of molecules, related by the centre of symmetry.

Surface electric fields are found to be of the order of 1 GV m^{-1}. They are smallest when the inequivalent molecules lie in the same plane, e.g. 0.4 GV m^{-1} for the (001) surface in anthracene, and largest when they lie in different planes, eg. 14 GV m^{-1} for the (001) surface in pyrene. The fields decay to the bulk values within about three layers. (Note that the bulk field is not zero at the molecular sites in pyrene.) These fields are rather smaller than the bulk fields in crystals of polar molecules.[11]

Surface polarizations naturally reflect the surface electric fields, unless a large field component happens to interact with a small polarizability component or vice versa. The values found are of the order of 1 C m^{-2}, varying between 0.004 C m^{-2} for the (001) surface in anthracene and 11 C m^{-2} for the (001) surface in pyrene. The largest values correspond to induced dipole moments as large as the permanent moments in very polar molecules. Though surprising at first sight, this result is consistent with the strong interactions between molecules in pyrene that leads to excimer formation.[12] Strong electric fields are also to be expected between even non-polar molecules at the separations found in crystals.

Surface pyroelectricity has been estimated for anthracene by calculating the surface polarization for crystal structures[13] at two different temperatures. Changes of polarization with temperature that would occur in the absence of thermal expansion (primary pyroelectricity) are ignored as small and difficult to estimate, so that only the secondary pyroelectricity is calculated. The surface pyroelectric coefficient reaches 3 mC m^{-2} K^{-1} for the (010) surface where the surface polarization is largest anyway, falling to 12 μC m^{-2} K^{-1} for the weakly polarized (001) surface. The latter value is comparable with values reported for polyvinylidene fluoride.[14] The larger value invites scepticism, but suggests that more experimental investigation of surface pyroelectricity may be fruitful, at least on selected surfaces.

5. SURFACE POLARIZATION ENERGY

When materials polarize, they do so in such a way as to lower their energy. This polarization is of general importance in the energetics of materials in electromagnetic fields. It is also of more specific importance in organic solids when the polarization is caused by an excess charge carrier. In the usual situation of weak carrier transfer interactions, this polarization energy is the leading correction to the energy of the molecular ion in the molecular crystal environment relative to the free ion. As such, the polarization energy determines the positions of the carrier bands, while variations of polarization energy lead to carrier scattering or trapping.[15]

Near a surface, the polarization energy must change. Molecules are missing compared with the bulk environment. Hence there is less polarization near the crystal surface and the polarization energy is less negative. As a result, surfaces are expected to offer energy barriers that tend to repel carriers into the bulk. (Note that the opposite situation holds if the crystal surface is bounded by a metal rather than a vacuum, since then the image charge in the metal lowers the carrier energy near the surface.[16]) Calculations of the polarization energy near selected surfaces in anthracene confirm that the polarization energy increases by 0.05 to 0.5 eV and that this change decreases to zero after three or four layers.[15]

These calculations used the self-consistent polarization field or SCPF method. This treats iteratively the polarization of discrete molecules within a given region (hemispherical for the surface calculations) and uses continuum electrostatics to obtain the polarization outside the region. According to the general arguments presented here, planewise techniques should offer a viable alternative to the SCPF method for surfaces, and the reported rapid fall-off in surface polarization energy supports this view. However, the electric field of the carrier is not uniform, and so the previous planewise technique needs modification. In essence, the spatial variation of the field is represented by a Fourier series, and the Fourier component for each wavevector polarizes the crystal according to a wavevector-modulated planewise dipole sum. Similar methods afford the bulk polarization energy.[17,18]

Label the sites in the crystal $n = \ell k$, and denote the field at site n due to a charge q_m at site m by $E^0(nm)$ and correspondingly the induced dipole moment by $p(nm)$. The total field and dipole moment are given by summing $E^0(nm)$ and $p(nm)$ over m. The polarization energy is then[18]

$$W = -\frac{1}{2} \sum_{nmm} \boldsymbol{E}^0(nm) \cdot \boldsymbol{p}(nm') \tag{26}$$

Using the analogues of eqs (4) and (5), not yet specialized to surface properties, eventually yields

$$W = -\frac{1}{2} \varepsilon_0 v \tilde{\boldsymbol{E}}^0 \cdot \boldsymbol{K} \cdot \boldsymbol{E}^0 \ . \tag{27}$$

Here $\boldsymbol{E}^0$ and $\boldsymbol{K}$ are matrices in site space, the tilde denoting the transpose, and $\boldsymbol{K}$ is the general analogue of the quantity in eq. (22).

Near the surface set $\ell = \lambda g$, where λ denotes the two-dimensional unit cell as previously, so that now $n = \lambda gk$. Sums over λ are then transformed into sums over the two-dimensional wavevector η by introducing the 2-D Fourier transforms of $\boldsymbol{E}^0$ and $\boldsymbol{K}$. That for $\boldsymbol{E}^0$ is defined by

$$\boldsymbol{E}^0(nn') = N^{-1}\sum_{\eta}\exp[-2\pi i\eta\cdot\boldsymbol{x}(nn')]\,\boldsymbol{E}^0_{kk'}(gg';\eta)\;, \tag{28}$$

while that for $\boldsymbol{K}$ depends on the transformed dipole lattice sum defined by

$$\boldsymbol{T}(nn') = N^{-1}\sum_{\eta}\exp[-2\pi i\eta\cdot\boldsymbol{x}(nn')]\,\boldsymbol{T}_{kk'}(gg';\eta)\;, \tag{29}$$

where N is the number of surface cells λ and hence of surface wavevectors η. The polarization energy can then be expressed as

$$W = -\tfrac{1}{2}\varepsilon_0 v N^{-1}\sum_{\eta}\sum_{gg'}\sum_{kk'}[\tilde{\boldsymbol{E}}^0(-\eta)\cdot\boldsymbol{K}(\eta)\cdot\boldsymbol{E}^0(\eta)]_{kk',gg'}\;, \tag{30}$$

with $\boldsymbol{K}(\eta) = [\boldsymbol{A}^{-1} - \boldsymbol{T}(\eta)]^{-1}$. This result is of the same form as for the bulk polarization energy[17] but with a sum over 3-D wavevectors replaced by a sum over 2-D wavevectors and a sum over layers. Hence the usefulness of the result will depend on how rapidly the modulated dipole sums fall off with the separation between planes.

The modulated sums obtained by inverting eq. (29) are an obvious modification of eq. (2):

$$\boldsymbol{T}_{kk'}(gg';\eta) = (v/4\pi)\sum_{\lambda}\exp[2\pi i\eta\cdot\boldsymbol{x}(\lambda gk,0g'k')]\,\boldsymbol{T}(\lambda gk,0g'k')\;, \tag{31}$$

where $\boldsymbol{x}(\lambda gk,0g'k') = \boldsymbol{x}(\lambda gk) - \boldsymbol{x}(0g'k')$. Modulated sums have been calculated for a mesh of wavevectors in the first 2-D Brillouin zone for the (001) surface of anthracene.[7] They show stronger interaction between adjacent planes than the unmodulated sums. They fall off more rapidly with separation as the wavevector η increases, as expected.[4] However, they do not decrease as rapidly as the unmodulated sums, and the rate of decrease depends markedly on η. Even so, the slowest decrease makes them negligible for $g - g' = 3$.

Hence the planewise Fourier-transform method appears to offer a workable approach to surface polarization energies. This could be extended as in the bulk case[2] to treat related problems. These include charge-transfer states, the effects of vacancies, and the Stark effect.

6. SURFACE NONLINEAR OPTICS

Surfaces may affect not only the magnitude of crystal properties but also their very existence, as in the case of surface-induced pyroelectricity already treated. Another such case arises in nonlinear optics. Even-order nonlinear optical coefficients, such as those governing second-harmonic generation and the Pockels effect, are zero in centrosymmetric media. Surfaces destroy centrosymmetry, and so can induce nonlinearities which do not exist in the bulk medium. These nonlinearities prove very useful for studying surfaces and adsorbates.[19]

A treatment of nonlinear optical response in molecular layers has already been presented,[20] but was restricted to one molecule per unit cell. Here a more general result is obtained in the context of the previous section on linear response. This conveniently starts from eq. (3) recast in terms of the macroscopic field via the planewise Lorentz-factor tensors (13):

$$\boldsymbol{F}_k(g) = \boldsymbol{E}_g + \sum_{g'k'} \boldsymbol{L}_{kk'}(gg') \cdot \boldsymbol{p}_{k'}(g') / \varepsilon_0 v \, . \tag{32}$$

For linear response, substitution of eq. (4) into eq. (32) leads to an equation that yields the local fields as

$$\boldsymbol{F}_k(g) = \sum_{g'k'} \boldsymbol{D}_{kk'}(gg') \cdot \boldsymbol{E}_{g'} \, , \tag{33}$$

where $\boldsymbol{D} = (\boldsymbol{J} - \boldsymbol{L} \cdot \boldsymbol{A})^{-1}$ is analogous to $\boldsymbol{H}$ introduced previously.

For nonlinear response, eq. (4) becomes

$$\begin{aligned} \boldsymbol{p}_k(g) / \varepsilon_0 v = \boldsymbol{a}_k \cdot \boldsymbol{F}_k(g) &+ \boldsymbol{b}_k : \boldsymbol{F}_k(g) \boldsymbol{F}_k(g) \\ &+ \boldsymbol{c}_k \,\vdots\, \boldsymbol{F}_k(g) \boldsymbol{F}_k(g) \boldsymbol{F}_k(g) + \dots \end{aligned} \tag{34}$$

where $\epsilon_0 v \boldsymbol{b}$ and $\epsilon_0 v \boldsymbol{c}$ are the first and second hyperpolarizabilities. This is now substituted in eq. (32). The linear terms are rearranged as previously, but the nonlinear local field has to be obtained by iterative solution to the desired order. After straightforward but tedious manipulations, this yields the surface polarization in layer g in terms of the macroscopic fields in all the surface layers, rather than just layer g, as indeed does eq. (33) via the sum over g'. As for linear response, this problem is resolved by relating all the $\mathbf{E}_g$ to the uniform field $\mathbf{E}^0$. Because all the $\mathbf{E}_g$ are related to $\mathbf{E}^0$, they are all related to one another. Thus eq. (14) can be generalized as

$$\mathbf{F}_k(g) = \mathbf{d}_k(g) \cdot \mathbf{U}_{gg'} \cdot \mathbf{E}_{g'} , \tag{35}$$

where it is found that

$$\mathbf{U}_{gg'} = \mathbf{1} - \mathbf{n}[\mathbf{n} \cdot (\mathbf{R}_g - \mathbf{R}_{g'})] - [(r_g - r_{g'})/(1 - r_{g'})]\,\mathbf{n}(\mathbf{n} \cdot \mathbf{R}_{g'}) . \tag{36}$$

Then the surface quadratic susceptibility is given by

$$\boldsymbol{\chi}_g^{(2)} = \varepsilon_0 \sum_{g'kk'} \mathbf{D}_{kk'}(gg') \cdot \mathbf{b}_{k'} : [\mathbf{d}_{k'}(g') \cdot \mathbf{U}_{g'g}]^2 . \tag{37}$$

This result is of the same general form as for a bulk molecular crystal,[21] but with extra contributions from the sum over layers. In practice, as for linear response an average response is likely to be the measurable quantity.

Previous treatments of surface nonlinear optics have invoked nonlocal polarizabilities and field-gradient polarizabilities.[22] These are not required in the present treatment, where assumption that the surface does not modify the molecular response in fact excludes any field-gradient polarizability for molecules in crystals such as anthracene. However, from another point of view both nonlocal and field-gradient effects are included in the present treatment. The response at one molecule depends on those at others via sums over g and k, and the variation of field through the surface has been considered explicitly. In effect, the *molecular* response is local and excludes field-gradient contributions, but the *crystal* response is not, because of the interactions. Using effective rather than free molecular polarizabilities also incorporates some nonlocal contributions.[23]

7. DISCUSSION

The present results provide a theoretical basis for several electrical and related properties of molecular crystal surfaces. Central to the theories is the idea of planewise summation of dipole (and sometimes other multipole) interactions. On the one hand, this is of conceptual significance. It reflects the symmetry of the physical situation, such that one sees directly how surface properties are modified from bulk properties through the loss of interactions with the layers removed to form the surface. On the other hand, planewise sums decrease exponentially with the separation between layers[3] (at least after adjacent planes, in the submolecule treatment). The restricted range of the interactions then leads to matrix inversions which, though large, are numerically tractable rather than just being of formal significance.

Surface relaxation has been ignored. If the relaxed surface structure were known, it could be used for the planewise summations, which would then depend on g and g' separately instead of only on their difference. If (less probably) the relaxed molecular response were known, it too could be incorporated into the algebra. For example, the polarizability in eq. (4) could depend on the layer g as well as on the molecule k and then the polarizability supermatrix A would remain block diagonal but with blocks depending on the layer.

Hence a basis exists for theories of molecular crystal surface properties comparable with those available for bulk properties.[2] Results available so far confirm that different surfaces may have markedly different properties that can be related to the molecular arrangement relative to the surface. This suggests various intriguing questions: Could a crystalline thin film of appropriate orientation afford a useful pyroelectric detector? Which surface is best suited for injection or emission of excess charge? It is hoped that this paper will stimulate and support investigation of such questions.

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