Chapter I-1

The Structure and Properties of the Organic Solid State

ROBERT SILBEY

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

I. INTRODUCTION

In most textbooks on the solid state, molecular solids are given at most a few paragraphs, and organic solids are never mentioned at all (the solid noble gases being the "best example of molecular solids" [1]). This is unfortunate since organic solids have an enormous range of interesting properties that are almost continuously "tunable." For the last 15 years there has been increasing awareness of these systems as their more interesting properties have been uncovered: for example, superconductivity [2], spinless conductivity in "doped" conjugated polymers [3], and large nonlinear optical responses [4].

In this review, I discuss the structure and properties of organic solids in a general and, hence, incomplete way with examples taken from the recent literature. It is clearly impossible to cover this field adequately in a few pages; I hope only to give the flavor of its vastness and variations, and, since my own field of research is the theory of optical properties, conductivity, and relaxation, the review is undoubtedly skewed in these directions. However, I hope the reader will come away with the feeling that understanding the properties of organic materials is an interesting and exciting challenge.

II. STRUCTURE

A. Crystal Structures

Most organic solids are molecular solids; that is, the molecules retain their geometric shape and properties to a large degree upon condensation from the vapor. Thus, benzene, for example, is (almost) hexagonal in the crystal with only small changes from the gas-phase molecule. In addition, the infrared and low-energy optical spectra of the solid are very similar to those of the gas. To be sure, there are changes; these are, however, small compared to those occurring in typical ionic crystals or metals. Finally, organic solids have small cohesive energies. Therefore, most organic solids are collections of molecules held together by weak intermolecular interactions, usually described by van der Waals forces. Because the molecules are non-simply shaped and the forces are weak and anisotropic, organic solids (1) often have more complicated structures than solids normally studied in elementary books on solid state physics, (2) exhibit polymorphism and many phase transitions, and (3) often have many structural defects.

Although a first-principles quantum-mechanical calculation of the equilibrium geometric structure of a typical organic crystal is impossible at present, phenomenological atom–atom two-body potentials to compute intermolecular interactions are available and useful. That is, assuming the molecules have a certain geometry (given perhaps by the gas-phase data), we can compute intermolecular forces by adding atom–atom (central force) interactions. This gives a highly anisotropic molecule–molecule interaction. The atom–atom interactions are usually assumed to be [5, 6] either Lennard–Jones or Buckingham potentials:

$$u_{\mathrm{LJ}}(r) = -\frac{A}{r^6} + \frac{B}{r^{12}} \tag{1a}$$

$$u_{\mathrm{B}}(r) = -\frac{A}{r^6} + B'e^{-Cr} \tag{1b}$$

where the parameters for carbon–carbon, carbon–hydrogen, and hyrdogen–hydrogen interactions are fixed by fitting a few model compounds (typically anthracene, naphthalene, etc.). Using these potentials, it is possible to compute crystal structures, thermodynamic functions, phonon frequencies, and others in reasonable agreement with experimental data. Although various authors have chosen different atom–atom parameters [5, 6], the final results of their calculations do not differ markedly. Since the mid 1970s, these methods have also been applied to the calculation of structural defects [7].

When Robertson [8] reviewed the organic crystals studied by X rays in the early 1950s, there were 10^2 structures known; when Dunitz [9] reviewed the field in the late 1970s, there were 10^4 structures known; in the late 1980s, the number is probably $>10^5$. The ability to study complex crystals of complex molecules using automated equipment and sophisticated computer software and hardware has led to an explosion in our knowledge of the static structure of these systems. This does not mean, of course, that our understanding of the other properties of these systems has increased in the same proportion.

Since 1960, the polyacenes have been the model organic molecular crystals for studies of static structure, optical spectra, dynamic studies, etc. Anthracene, naphthalene, and tetracene are relatively simple systems and exhibit many of the typical behaviors of organic crystals. Anthracene is a planar conjugated system with D_{2h} symmetry in the gas phase. The normal crystal structure was determined by Robertson [8] and Cruikshank [10], and the molecule in the solid is remarkably similar to the gas-phase structure (found by electron diffraction) [11]. The crystal structure is monoclinic (space group $P2_1/a$) with two molecules in the unit cell, related to each other by a screw axis (parallel to the *b* crystal axis). Naphthalene has an almost identical structure to anthracene, while tetracene and pentacene are very similar; however, the two molecules in the unit cell in the latter two cases are not related by screw axis symmetry as in naphthalene and anthracene. The crystal structures of pyrene and α-perylene are different from these by the fact that a dimer of pyrene takes the place of a single anthracene molecule [11]. This structure is quite interesting because the dimer then has considerable π-electron overlap, which is undoubtedly the reason for excimer formation [12] in these systems.

As already mentioned, these crystals often have phase transitions to other, more closely packed structures. (In addition, metastable forms of anthracene crystals [13] have been found under high pressure.)

Although the structure of the polyacenes is quite common in aromatic crystals, another structure is also often found. This is a linear stacked structure often found in halogenated aromatics, as in tetrachlorobenzene and 1,4-dibromonaphthalene. In this case, the closest molecules form a stack of aromatic planes tilted (i.e., nonperpendicular) in general to the stack axis. There may be one or more molecules in the unit cell, either crystallographically equivalent or not. In contrast, the benzene crystal is orthorhombic with four molecules in the unit cell related by screw axes parallel to the three crystal axes.

Kitaigorodsky [5] has discussed the reasons for the frequent occurrence of certain space groups and not others. His major thesis is that purely geometric packing leads only to certain possibilities. Since the unit-cell volume in these structures is often only $\frac{4}{3}$ the volume of the molecules, these molecules must pack very tightly, with the irregularities of shape fitting into one another like jigsaw-puzzle pieces. By attempting to fit irregularly shaped objects in optimal packing together with ~ 12 near neighbors, Kitaigorodsky finds that (1) in general only a *site* inversion symmetry can be retained in the crystal and (2) only a very few crystal space groups are allowed. Although this purely geometric approach cannot be completely general, it is a remarkably good guide to the structures of these systems. A rationale for its success can be found in the strength and steepness of the repulsive forces compared to the attractive forces between these molecules. At the densities of the crystal, the free energy is dominated by the repulsions, at least in the absence of specifically chemical forces.

A word of caution is in order here. Even though the site symmetry only contains the inversion (for example, for benzene) and so, in principle, the molecule is not D_{6h} in the crystal, the distortions from D_{6h} are at the limit of X-ray detectability, so for most purposes we can treat benzene as a regular hexagon even in the crystal.

Given these structures, we find that these crystals can exhibit large anisotropies in their properties. For example, the intermolecular interactions that give rise to exciton states in these crystals are largely due to π electrons. When these are analyzed for lower electronic states of benzene, naphthalene, and 1,4-dibromonaphthalene, we find that benzene can be considered three-dimensional, naphthalene two-dimensional and 1,4-dibromonaphthalene (or tetrachlorobenzene) one-dimensional. By this, we mean that the anisotropies in the exciton bands are such that, to a good approximation, these dimensionalities obtain. Obviously, the same is not true for the interactions responsible for the phonon band structures, so that these materials have some properties that are highly anisotropic, while other properties are not. Since the *optical properties*, at least in the visible and near ultraviolet (UV), probe the π-electron states, we expect to see large anisotropies in the optical response.

B. Vibrations and Phonon Bonds

Because of the complexity of the structure, few experiments on the phonon structure and dynamics in molecular crystals have been done [14]. It is clear, however, that the phonon density of states is not a simple function except at the lowest frequencies.

The number of vibrational modes (at any **k** value) in a molecular crystal is large. For example, the benzene molecule has 30 vibrational modes and three rotations; since there are four molecules in a unit cell, there are 144 vibrational modes (per **k** value) in the solid. Near $\mathbf{k}=\mathbf{0}$, three of these are acoustic modes, nine are translational optical modes, 12 are librational (or rotational) modes, and 120 are internal vibrations. Of course, these modes mix together so the designations are only approximate. The sheer number of modes forces us to consider the vibrational band structures in the simplest theoretical models only [15]. However, it is easy to see that the acoustic bands are ~ 50–$100\ \mathrm{cm}^{-1}$ wide and mix with librational modes at relatively low energies. (In naphthalene and anthracene, librations can be seen at $\sim 50\ \mathrm{cm}^{-1}$, while in 1,4-dibromonaphthalene there is a libration at $\sim 20\ \mathrm{cm}^{-1}$ and in benzene at $\sim 30\ \mathrm{cm}^{-1}$.)

Recently, inelastic neutron scattering studies of anthracene [16], naphthalene [17], and others have been reported, and the observed density of states has been compared to the predictions of the harmonic model. The agreement is good, suggesting that we can be confident in the details of the calculations.

C. Defects

Structural defects in molecular crystals are common [18]. Point defects such as misorientations, interstitials, vacancies, and impurities are well known. Extended defects such as dislocations and disclinations are often found, as well as stacking faults and others. Finally, polymorphic inclusions and impurity aggregations are known. At the present time, very little is known about these except for their existence. These defects will cause the electronic states of the ideal crystal to be perturbed and perhaps be localized [19]; they will cause inhomogeneous broadening in the optical spectrum; and they will cause the formation of local phonon modes that can interact strongly with electronic states.

III. ELECTRONIC STATES

In order to understand the frequency-dependent polarizability or dielectric function of the crystal in the optical region, we must know the energies of all the optical transitions, their oscillator strengths, and their widths. The energies and oscillator strengths can be computed based on a simple model of the molecular crystal, which treats the molecules as units and neglects overlap and exchange. This works quite well in those cases where it has been tested. The *widths* of the spectral lines depend on exciton–phonon coupling and inhomogeneities, which are less well understood.

A. Exciton States in Crystals

Because the molecules in the molecular crystal retain their identity to a great extent, the description of the electronic states of the crystal is quite different from that of metals or covalently bonded solids. The basic ideas were formulated by Frenkel [20], Peierls [21], and Davydov [22], and elaborated by others [23]. The ground electronic state wave function of the crystal must describe a collection of ground-state molecules and, to a good approximation, is then just a product of ground-state wave functions, one for each molecule:

$$\Psi^{(g)} = \prod_{i=1}^{N} \psi_i^{(g)} \tag{2}$$

Here $\psi_i^{(g)}$ is the ground-state wave function of the molecule at the ith site. Note that this wave function is not the same wave function that the molecule has in the gas phase but is changed by the interactions with the other molecules. The low-lying excited electronic states will be made by exciting a single molecule to an excited state; this is, however, N-fold degenerate in the crystal:

$$\Psi_i^{(e)} = \psi_i^{(e)} \prod_{j \neq 1} \psi_j^{(g)}, \qquad i = 1, 2, \ldots, N \tag{3}$$

The intermolecular interactions will split this degeneracy and form N nondegenerate states. For a perfect crystal with one molecule per unit cell, we find

$$\Psi^{(e)}(\mathbf{k}) = \sum_{i=1}^{N} \frac{e^{i\mathbf{k}\cdot\mathbf{R}_i^0}}{\sqrt{N}} \Psi_i^{(e)} \tag{4}$$

where $\mathbf{R}_i^0$ is the position of the lattice point at which the ith molecule sits. The intermolecular interactions will also cause mixing between the electronic states for each $\mathbf{k}$ value.

In the case that there is more than one molecule per unit cell, we form states as in Eq. (4) for each site and then diagonalize the Hamiltonian in the subspace of each $\mathbf{k}$. For two molecules in a unit cell, as in anthracene, there will then be two electronic states (for each $\mathbf{k}$) for every one in the molecule. In particular, at $\mathbf{k} = 0$ there will be two electronic states split by an energy now known as the Davydov splitting. Since the optical spectrum measures the $\mathbf{k} = 0$ region only, there will be two optical transitions for each one in the gas phase.

The energies of these electronic states can be found, to low order, by diagonalizing the electronic Hamiltonian in the basis of these states. To do this, we must compute the various Hamiltonian matrix elements. We take

$$H = \sum_n h_n + \sum_{n>m} V_{nm} \tag{5}$$

where h_n is the Hamiltonian of the electrons on site n and V_{nm} is the interaction between electrons and nuclei on site n and those on site m. (We are implicitly neglecting exchange here and will also neglect overlap; more careful procedures are possible but do not change the qualitative conclusions.) Since we have constructed the crystal states to be products of molecular states, we find

$$\langle \Psi^{(g)}|H|\Psi^{(g)}\rangle = N\varepsilon^{(g)} + \sum_{n>m} \langle \psi_n^{(g)}\psi_m^{(g)}|V_{nm}|\psi_n^{(g)}\psi_m^{(g)}\rangle \tag{6a}$$

$$\begin{aligned}\langle \Psi^{(e)}(\mathbf{k})|H|\Psi^{(e')}(\mathbf{k}')\rangle &- \langle \Psi^{(g)}|H|\Psi^{(g)}\rangle \\ &= \delta_{\mathbf{kk}'}\left[(\varepsilon^{(e)} - \varepsilon^{(g)})\,\delta_{e,e'} + \sum_{n\neq m} \exp i\mathbf{k}\cdot(R_n^0 - R_m^0)\langle \psi_n^{(e)}\psi_m^{(g)}|V_{nm}|\psi_n^{(g)}\psi_m^{(e')}\rangle\right]\end{aligned} \tag{6b}$$

where $\varepsilon^{(i)}$ is the energy of the ith state of the molecule (since they are assumed to be identical). Note that at this level, van der Waals attractions are missing; they can be easily included by considering excited states in which more than one molecule is excited [24]. The last terms in Eq. (6b) are energy-transfer matrix elements, which in the simplest approximation (nonoverlapping charge distributions) become dipole–dipole interactions in which the dipoles are the transition dipoles:

$$\begin{aligned}\langle \psi_n^{(e)}\psi_m^{(g)}|V_{nm}|\psi_n^{(g)}\psi_m^{(e')}\rangle &= -\mu_{ge}\cdot\left\{\frac{1}{R_{nm}^3} - \frac{3\mathbf{R}_{nm}\mathbf{R}_{nm}}{R_{nm}^5}\right\}\cdot\mu_{ge'} \\ &\equiv \hat{V}_{ne,me'}\end{aligned}$$

Therefore, we find that the electronic band structure [i.e., $E(\mathbf{k})$] is given by dipole sums, with all their interesting pathologies [25].

In principle, we should take into account excited states with more than one excited molecule. This has been done by Hopfield [26] and Agranovitch [27]. In the dipole approximation—that is, confining attention to states that have a transition dipole moment from the ground state—we can do this easily by second quantizing the Hamiltonian and taking $\varepsilon^{(g)} = 0$ for convenience.

$$H = \sum_{e,n} \varepsilon^{(e)} a_{ne}^{+} a_{ne} + \sum_{\substack{n>m\\ e,e'}} V_{ne,me'}(a_{ne}^{+} + a_{ne})(a_{me'}^{+} + a_{me'}) \tag{7}$$

Here, a_{ne}^{+} is an excitation operator that converts the ground state of molecule n to the eth excited state of molecule n. By transforming to excitation operators in $\mathbf{k}$ space and assuming periodic boundary conditions, we find

$$H = \sum_{\mathbf{k},e} \varepsilon^{(e)} a_{\mathbf{k}e}^{+} a_{\mathbf{k}e} + \frac{1}{2}\sum_{\mathbf{k},e,e'} \hat{V}_{\mathbf{k}e,\mathbf{k}e'}(a_{-\mathbf{k}e}^{+} + a_{\mathbf{k}e})(a_{\mathbf{k}e'}^{+} + a_{-\mathbf{k}e'}) \tag{8}$$

where $\hat{V}_{\mathbf{k}e,\mathbf{k}e'}$ is the dipole–dipole sum discussed earlier. At this point, the approximation is made that the exciton operators $a^+_{\mathbf{k}e}$ and $a_{\mathbf{k}e}$ obey Boson commutation relations; although this is not strictly correct, it is a good approximation for the low-lying states. The excited state energies can then be found, including the effect of multiply excited states.

When this is done, within the dipole approximation we find that this theory agrees precisely with the classical dipole theory. Thus, it should be clearly stated that the excited-state energies computed in this way can also be found from the classical equations for the frequency-dependent dielectric constant for this physical model of a molecular crystal [28]. If we were to evaluate the intermolecular matrix elements in a less approximate manner (than dipole–dipole interactions), we would change the value of the $V_{\mathbf{k}e,\mathbf{k}e'}$ and the excited-state energies, but the form of the equations would remain the same. To show this form, let us assume that only one excited state is important in Eq. (8), so that the sum over e can be suppressed. Then

$$H = \sum_{\mathbf{k}} \left[\varepsilon a^+_{\mathbf{k}} a_{\mathbf{k}} + \frac{1}{2} V_{\mathbf{kk}} (a_{\mathbf{k}} + a^+_{-\mathbf{k}})(a_{-\mathbf{k}} + a^+_{\mathbf{k}}) \right] \tag{9}$$

We find the eigenenergies by solving the Heisenberg equation of motion for a_k and $a^+_{\mathbf{k}}$ (the superdot represents time derivative),

$$\dot{a}_{\mathbf{k}} = i[H, a_{\mathbf{k}}] = -i\varepsilon a_{\mathbf{k}} - iV_{\mathbf{kk}}(a_{\mathbf{k}} + a^+_{-\mathbf{k}}) \tag{10a}$$

$$\dot{a}^+_{\mathbf{k}} = +i\varepsilon a^+_{\mathbf{k}} + iV_{\mathbf{kk}}(a_{-\mathbf{k}} + a^+_{\mathbf{k}}) \tag{10b}$$

where we have assumed that $a_{\mathbf{k}}$ and $a^+_{\mathbf{k}}$ obey Boson commutation relations. Therefore,

$$(\dot{a}_{\mathbf{k}} + \dot{a}^+_{-\mathbf{k}}) = -i\varepsilon(a_{\mathbf{k}} - a^+_{-\mathbf{k}}) \tag{11a}$$

$$(\dot{a}_{\mathbf{k}} - \dot{a}^+_{-\mathbf{k}}) = -i\varepsilon(a_{\mathbf{k}} + a^+_{-\mathbf{k}}) - i2V_{\mathbf{kk}}(a_{\mathbf{k}} + a^+_{-\mathbf{k}}) \tag{11b}$$

or

$$\ddot{a}_{\mathbf{k}} + \ddot{a}^+_{-\mathbf{k}} = -\{[i\varepsilon]^2 + 2V_{\mathbf{kk}}\}(a_{\mathbf{k}} + a^+_{-\mathbf{k}}) \tag{11c}$$

so that the eigenenergy $E(\mathbf{k})$ is given by

$$E(\mathbf{k}) = \{[\varepsilon]^2 + 2V_{\mathbf{kk}}\}^{1/2} \tag{12}$$

In the limit that $|V_{\mathbf{kk}}| \ll \varepsilon$, then

$$E(k) \approx \varepsilon + V_{\mathbf{kk}} \tag{13}$$

which is the usual (i.e., Frenkel or Davydov) result that only includes single excitations (i.e., one molecule excited). In the present formulation, the effect of multiple excitations is included and we can see that effect clearly on the excitation frequency.

Another amusing aspect of this formulation is the idea that (since the excitations are Bosons) the cohesive energy Δ of the molecular crystal can be computed as the change in zero-point energy of the collection of Boson (harmonic) oscillators.

$$\begin{aligned}\Delta = \frac{1}{2}\sum_{\mathbf{k},e}[E^e(\mathbf{k}) - \varepsilon^{(e)}] &\approx \sum_{\mathbf{k},e}\left[\frac{V_{\mathbf{k}e,\mathbf{k}e}}{2} - \frac{V^2_{\mathbf{k}e,\mathbf{k}e}}{4\varepsilon^{(e)}} + \cdots\right] \\ &\approx -\sum_e \frac{1}{4\varepsilon^{(e)}}\sum_{\mathbf{k}} V^2_{\mathbf{k}e,\mathbf{k}e} = -N\sum_e\sum_n \frac{|V_{ne,me}|^2}{4\varepsilon^{(e)}} \qquad (14)\end{aligned}$$

Since $V_{ne,me} \approx R_{nm}^{-3}$, this term corresponds to the sum of van der Waals interactions, which is the first term in the cohesive energy [24]. When interactions between different electronic states (e') are included, the computation is more difficult but the principles are the same.

We have written the electronic wave functions without showing the dependence on nuclear coordinates. In fact, these functions are indeed dependent, and using this dependence within the adiabatic approximation allows us to define vibronic functions [29]. In the case of weak electronic coupling (where the spread of electronic energies in **k** space is small compared to the vibrational frequency), each *molecular* wave function is a molecular vibronic function; in the strong electronic coupling case, the crystal electronic state is multiplied by a vibrational function. Thus for the low-lying, weakly allowed states, the weak coupling limit applies, and this modifies the Hamiltonian matrix elements by multiplying them by the overlaps of the vibrational wave functions (Franck–Condon factors). This approximation is equivalent to assigning a label e to each *vibronic* state in the molecule. This enlarges the number of equations to solve but is not a stumbling block to their solution.

An elegant and definitive discussion (and calculation) based on these ideas has been given by Philpott [30], who shows that very good agreement between theory and experiment in anthracene and tetracene can be found. It can thus be said that the theory of the energies of the low-lying dipole-allowed states of molecular crystals is in good shape. The calculation of the energies of nonallowed or weakly allowed transitions is not, on the other hand. Although we know in principle how to compute these energies, in practice we cannot.

B. Exciton–Phonon Coupling

Thus far, we have assumed that the lattice vibrations and librations do not play a role in the optical response of the crystal, so our theory is restricted to $T = 0$ K. Above this temperature, we must include these effects, the most obvious of which is the broadening of spectral lines.

The origin of the exciton–phonon coupling lies in the dependence of the electronic energies in the crystal on the positions of the molecules. It is easy to see that the dipole–dipole interaction depends on intermolecular separation; the excitation energy of a molecule at a given site will also depend on its position because of the van der Waals interactions with other molecules. Thus, if we make a Taylor series expansion of $\varepsilon_n^{(e)}$ and the matrix elements $V_{ne,me'}$ around the equilibrium position of the lattice, we find (in a schematic notation)

$$\varepsilon_n^{(e)} = \varepsilon^{(e)}(0) + \sum_m \left(\frac{\partial \varepsilon_n^{(e)}}{\partial R_m}\right)_0 (R_m - R_m^0) + \cdots \tag{15a}$$

$$V_{ne,me'} = V_{ne,me'}(0) + \sum_p \left(\frac{\partial V_{ne,me'}}{\partial R_p}\right)(R_p - R_p^0) + \cdots \tag{15b}$$

The first terms in these expansions are used in the theory we outlined earlier. The second and higher terms are the exciton–phonon coupling terms. Those couplings occurring in the expansion of ε_n are called (site) diagonal and those in the expansion of $V_{ne,me'}$ nondiagonal couplings. This description is of course based in the site representation; in the **k** representation, there will be terms diagonal in **k** and terms off-diagonal in **k**,

$$H_{\text{ex-phonon}} = \sum_{\mathbf{k}} W_{\mathbf{kk}} a_{\mathbf{k}}^{+} a_{\mathbf{k}} + \sum_{\substack{\mathbf{k},\mathbf{k}' \\ \mathbf{k} \neq \mathbf{k}'}} W_{\mathbf{kk}'} a_{\mathbf{k}}^{+} a_{\mathbf{k}'} \tag{16}$$

where $W_{\mathbf{kk}'}$ is a sum of terms linear in displacements, quadratic in displacements, etc. Consider a linear exciton–phonon interaction term

$$W_{\mathbf{kk}'}^{(\alpha)} a_{\mathbf{k}}^{+} a_{\mathbf{k}'} q_{\mathbf{k}-\mathbf{k}'}^{(\alpha)} \tag{17}$$

where $q_{\mathbf{K}}^{(\alpha)}$ is the coordinate of the phonon of branch α (i.e., labeling the type of phonon) and wave vector **K**. This perturbation allows scattering of the **k**′ exciton state with the creation or annihilation of a phonon of wave vector **k** − **k**′ (since wave vector is a conserved quantity). If energy is conserved in this process, this will be an allowed event in the lowest order of perturbation theory. Therefore, exciton state **k**′ can decay by emitting (or creating) a phonon of the correct energy and wave vector, and an exciton state **k** will broaden in a temperature-dependent manner (since the number of phonons of the correct energy and wave vector is temperature-dependent). Multiphonon and dephasing processes can also be important in broadening transitions; this is an area of current interest [31].

Another effect of exciton–phonon interactions is to scatter excitations as they move through crystals, so that the wavelike motion becomes diffusive. This phenomenon has been studied experimentally and theoretically for a number of years and was recently reviewed by Kenkre and Reineker [32].

Two important questions are often discussed when dealing with exciton–phonon coupling. The first has to do with the description of the motion of the excitation: is it bandlike or hopping? Band motion could be described as infrequent scattering of a state (**k**) by phonons such that the mean free path is much larger than a lattice spacing, while hopping is the motion of quasi-localized states with a mean free path on the order of the lattice spacing. The second question has to do with localization of the states. Toyozawa [33] has reviewed this for inorganic crystals. The idea is that strong local (i.e., diagonal) phonon interactions can cause the excitation to be quasi-localized on a site by lowering the energy sufficiently (the analogy to charge localization due to strong polarization is often made). Obviously, these two questions are intertwined; this is also an area of current interest. The possibility of localization is also complicated by the effect of defects and other kinds of disorder.

C. Disorder in Organic Solids

The work of Anderson [34] on the effect of static disorder on the electronic states of solids generated an enormous amount of theoretical and experimental work [35] that still continues. Anderson pointed out that if the site energies [$\varepsilon_n^{(e)}(0)$ in our notation] are not all equal, the states change in character. In particular, if the distribution of site energies is broad enough (greater than a multiple of the exciton bandwidth, in our case), *all* the states are localized. The effect of this on the dynamical properties of the system is dramatic; the effect on the spectral properties may be considerably less. Clearly, the effect of this site energy distribution will be to spread optical *intensity* throughout the band. This effect can be calculated, at least in certain cases, using the coherent potential approximation (CPA) [36]. This method has been applied to the exciton states in molecular crystals [37] where the site energy distribution can be caused by a number of effects. For example, the natural abundance of ^{13}C causes small shifts ($\sim 1-2$ cm^{-1}) in the excitation energies of organic molecules; also, since intermolecular interactions are anisotropic, the rotation of a molecule by a few degrees can also change its excitation energy, etc. Even though these effects may be small, the excition bandwidths are often small, too; therefore, these shifts can have observable and interesting consequences. For example, the optical absorption line shape of the first triplet state of 1,4-dibromonaphthalene at 1.2 K is quite anisotropic (non-Lorentzian); this can be explained by naturally occurring ^{13}C isotopic substitution in the molecule [38].

An important (and unsolved) problem is to understand the optical response of a molecular crystal allowing for exciton interactions, exciton–phonon interactions, and static disorder. Although we understand most of the effects of each (at least in principle) individually, we do not know how all of these interact with each other.

D. Recent Experimental Work on Organic Crystals

It is impossible to cover this topic adequately in less than a book-length manuscript (the journal *Molecular Crystals and Liquid Crystals* publishes an annual list of papers in the field of the spectroscopy of organic solids that normally has over 1000 entries) [39]. However, recent reviews and books [40] cover much of interest. A few topics of current interest are mentioned here, in particular those connected to nonlinear optical properties.

Coherent optical effects, such as photon echos [41] and four-wave mixing [42], have become possible in recent years and have been used to probe the dynamics of excited states in solids. Transient grating methods [43] have been used to attempt to measure exciton coherence and diffusion constants. Recently, Warren and Zewail [44] have proposed that, with the possibility of phase-shifting optical lasers, many of the coherent effects of nuclear magnetic resonance (NMR) can be transferred to the optical domain.

Optical hole burning in inhomogeneously broadened spectral lines has become an exciting field. The possibility of using this technique for information storage has been a motivating force in some of this work; however, the scientific questions as to the efficiency and mechanisms of this process remain unresolved and extremely interesting. An introduction to this is given in Small's paper [44a].

The spectroscopy of charge transfer crystals (usually linear stacks) have been reviewed by Haarer and Philpott [44b]. These are examples of crystals that radically change their electronic structure upon excitation (and charge transfer) but can still be studied within the framework of Frenkel exciton theory because of the localization of the charges.

The mobilities of electrons and holes in organic matter, whether solids, liquids, or crystals, have been measured since the mid 1970s, and interesting temperature and field dependencies have been seen. The detailed explanation of these remains a challenge to theorists, although many attempts have been made. In particular, Duke and Schein [45] suggest that the electrical and optical properties of organic molecular solids remain unexplained quantitatively by conventional theories.

IV. ELECTRONIC STRUCTURE OF CONJUGATED POLYMERS

Conjugated polymers, such as the polydiacetylenes, polyacetylene, and polypyrrole, have been intensely studied over the past few years; their optical and conducting properties are remarkable. It is not possible to give an adequate overview of this immense field, so we will restrict out discussion to a few topics only.

A. Highly Conducting Doped Conjugated Polymers

The conductivity of conjugated polymers such as polyacetylene and polypyrrole is extremely low; however, upon doping with electron acceptors or donors, the conductivity rises, in some cases, by up to 10–15 orders of magnitude [46]. At the same time, the optical properties change dramatically also. Because these systems have the possibility of combining the plastic properties of polymers with the conductivity properties of semiconductors or metals, there has been a tremendous amount of interest in them. In addition, fundamental scientific questions regarding the mechanisms of conductivity remain unanswered, although a qualitative picture may now be emerging.

Since these polymers are made up of covalently bound monomers, they are unlike the molecular crystals we discussed above in that there are large collective effects due to the π-electron conjugation. This changes the basic models we must use in order to describe the electronic states, vibrational states, etc. These systems are more like one-dimensional tight-binding models than molecular crystals.

At first, the large conductivities found in doped polyacetylene were quite puzzling. After all, the usual criteria for such conductivity were absent. The band gap is large (1.4 eV), the structure is rather soft, and the fluctuations and defects are numerous and large. All of these would rule out metallic conductivity and, when it was shown that the spin susceptibility was completely uncharacteristic of electrons moving in bands (i.e., spinless conductivity), physicists and chemists became very excited about understanding this phenomenon. Su *et al.* [47] (using a model based on earlier work by Pople and Walmsley [48] and reviewed by Salem [49]) rationalized much of the experimental data by invoking the idea of charged solitonlike defects being responsible for the high conductivity. This suggestion used the softness of the lattice and the large band gap (which was due in their model to a Peierls dimerization) to understand the physics of the process. Although this model needed some refinements [50], it is the Rosetta stone for understanding the conductivity of these systems.

In the ensuing years, chemists and physicists have collaborated to synthesize and study many other systems [46], all of which differ from polyacetylene in that free solitons (in the SSH [47] sense) do not exist, but bound pairs of such structures do [50]; these are called radical ions, dications (by the chemists), and polarons and bipolarons (by the physicists). Polypyrrole has been the best studied so far, and the experimental results for conductivity, optical spectra, and magnetic resonance are all understandable within this model [51].

In spite of the success of this model in describing the experiments to date, there is no *detailed* theory of conduction in these systems. Such a theory must include interchain transport, the presence of a broad distribution of inhomogeneities, and the existence of traps, in addition to understanding the role of the dopant. At the present time, the theoretical description of the optical properties of these systems is improving, but important questions remain; for example, what is the role of the low-lying *g* states (two photons allowed) in the conducting and are they related to the soliton states?

B. Polydiacetylenes

The solid-state reaction of a number of diacetylene monomers yields the polymer in a single crystal of macroscopic dimensions [52]. The polymer is fully conjugated and highly anisotropic in its optical properties. The π-electron conjugation in the backbone provides a quasi-one-dimensional electron band structure that should, according to Ducuing [53], yield high nonlinear optical susceptibilities; and, in fact, they do [54].

The initial step in the polymerization of the diacetylene crystals is the formation of a biradical dimer [55]; at a later stage, carbenes and dicarbenes can be formed. By a series of beautiful electron spin resonance (ESR) and optical experiments [55], these intermediates have been isolated and studied.

Polymerization is accompanied by a dramatic change in visible optical properties. The monomer is colorless, while the polymer absorbs strongly, beginning at ~6000 Å. The third-order optical susceptibility of the polymer crystal is comparable to the best inorganic systems [54]; however, recent work on soluble polydiacetylenes in solution [56] has indicated that large two-photon absorption plays a role in this.

These soluble polydiacetylenes, first discovered by Patel *et al.* [57], have been the focus of interesting light-scattering experiments and speculations on chain dynamics and gelation [58]. These solutions change color when nonsolvent (hexane) is added or as a function of temperature, indicating a conformational change in the polymer. This conformational change influences the π-electron conjugation length, which in turn governs the optical spectrum. These results indicate that good theoretical calculations of linear and nonlinear optical susceptibilities are important goals for the near future.

C. Electronic Structure

In order to understand theoretically the electrical and optical properties of these polymers, a variety of quantum chemical methods have been developed. These range from the most primitive Hückel theory [49], through semiempirical methods such as Pariser Parr Pople (PPP) [49] and CNDO/S [59], to pseudo-potential methods like VEH [60], and finally *ab initio* methods [61].

All of these have been applied to these polymers with varying degrees of success. However, it is clear that with the advent of supercomputers, the low-lying electronic states of polymers can be described, at least at the Hartree–Fock level and perhaps beyond. Calculations of this sort are already underway. Semiempirical methods still have their usefulness, since the amount of work (and computer time) for the *ab initio* calculations is still great. For example, in 1984 Ramesesha and Soos [62] developed a method for exactly solving the PPP equations that promises to be extremely useful when applied to polymers. At the present time, only short-chain polyenes have been studied; however, the method will soon be applied to polymers. Since this method gives both the low-lying one-photon and two-photon optically allowed excited states, it may provide a way to compute nonlinear susceptibilities in a reliable way. At the present time, such calculations use crude methods of quantum chemistry, although the results have been extremely encouraging [63].

V. CONCLUSION

In this chapter, I have tried to give the reader a taste of the physics and chemistry of the organic solid state. Organic solids have electronic and optical properties that can be tuned continuously, within certain broad ranges, making them extremely interesting from a practical view. On the other hand, because they are (largely) molecular solids, the standard models of solid-state physics (so successfully used in describing inorganic metals and semiconductors) must be applied with care. For example, because of the weak intermolecular interactions, the electronic band widths are narrow, and therefore inhomogeneities and molecular vibrations must play an important (and as yet unclarified) role in these properties [45]. Another example is the effect of large anisotropies in electronic band structures on optical and conduction properties. This will lead to extremely interesting possibilities, which are just beginning to be explored.

I hope I have convinced the reader that organic materials provide interesting challenges for experiment and theory and will continue to do so for the near future.

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