

# Organic solids: is energy-band theory enough?

The study of the electronic properties of organic solids is a major new frontier in solid state physics. On the practical side, organic solids provide electronic and optical materials whose properties can be tailored to suit specific applications. They also pose continuing challenges to fundamental concepts because they afford unique model systems for establishing the bounds of validity for the traditional energy-band models that have proven so successful in describing the electronic properties of inorganic metals and semiconductors.

In addition to their interesting optical, transport and photochemical properties, organic solids are versatile in their mechanical behavior and are easy to fabricate for a wide range of uses. Once relegated to a fairly narrow spectrum of applications in electronics (as dielectrics) and photochemistry (for lithography), organic solids are finding a host of new uses. Among these are:

- ▶ photo and electron-beam resists for microelectronics
  - ▶ radiation-cured (solventless) coatings
  - ▶ electromechanical and thermoelectric transducers
  - ▶ photodielectrics
  - ▶ insulators and encapsulants for microelectronics
  - ▶ photoconductors and developer materials for electrophotography
- Organic polymers also show promise for future uses as
- ▶ electrical conductors and perhaps even superconductors
  - ▶ optical light pipes, waveguides and nonlinear circuit elements

These applications have provided the impetus for research into the electronic, photoelectronic and photochemical properties of organic solids.

In a recent article in *PHYSICS TODAY* (December 1978, page 44), Philip Allen and William Butler argue that electronic conduction in metals at very low and high temperatures still poses a challenge to the transport theory based on Felix Bloch's work. In this article we develop a similar argument that organic solids constitute an important class of model systems that also

**Electron transport in naphthalene.** The diagram shows one possible mechanism of charge transport in molecular crystals: a localized electron (red arrow) hops from one molecule to the next when a rotation of the first molecule increases the hopping probability significantly.  
(Drawing by Stan Tracey)

Figure 1

Charles Duke and Larry Schein are at the Xerox Webster Research Center in Rochester, New York.

Their increasing usefulness, their chemical flexibility, and the inability of traditional models to explain their electronic properties makes the study of organic solids a fascinating frontier of solid-state physics.

Charles B. Duke and L. B. Schein

challenge the ("Bloch") one-electron energy-band description<sup>1</sup> of the electrical properties of solids. The basis for this challenge arises directly from the molecular nature of organic materials: In the solid state, organic molecules essentially retain their identity, interacting only weakly through van der Waals forces. When the interactions that bind mole-

cules into crystals are weak, the resulting bandwidths are small. For typical van der Waals crystals we expect the electron bands to be about 0.01 to 0.1 eV wide. Thus the bandwidths are on the order of thermal energies, phonon energies and estimated polaron binding energies. Consequently, transport models that were developed for inorganic metals and semiconductors, in which the charge carriers are weakly scattered within broad energy bands, may not be appropriate for the organic solids with their narrow bands. For example, in organic crystals the electron-vibration interactions may

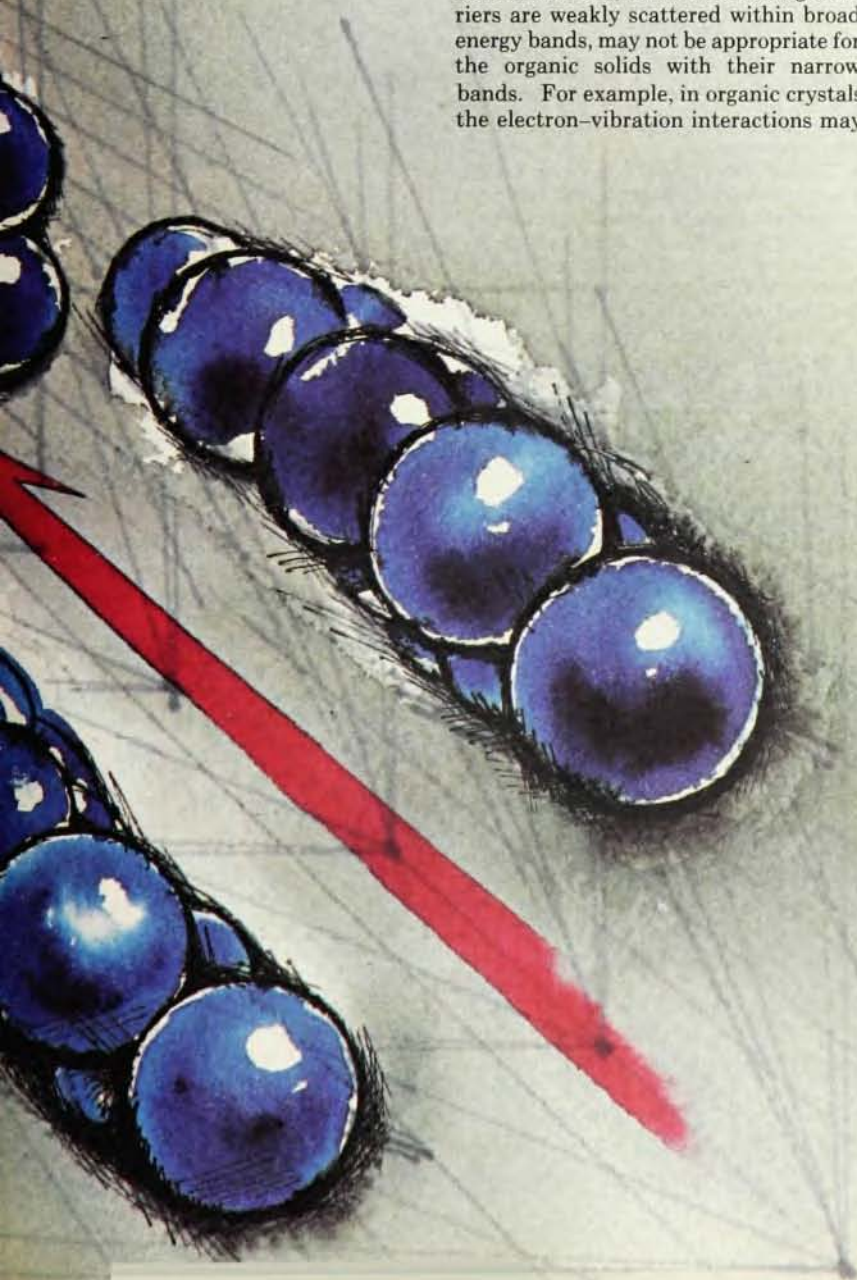
be sufficiently strong that large local lattice distortions accompany an electron as it moves through the crystal. An artist's conception of such a situation is shown in figure 1. The Hamiltonians for materials with narrow bands may have no solutions that correspond to the elementary excitations (electrons, holes, and so forth) of the standard theory.

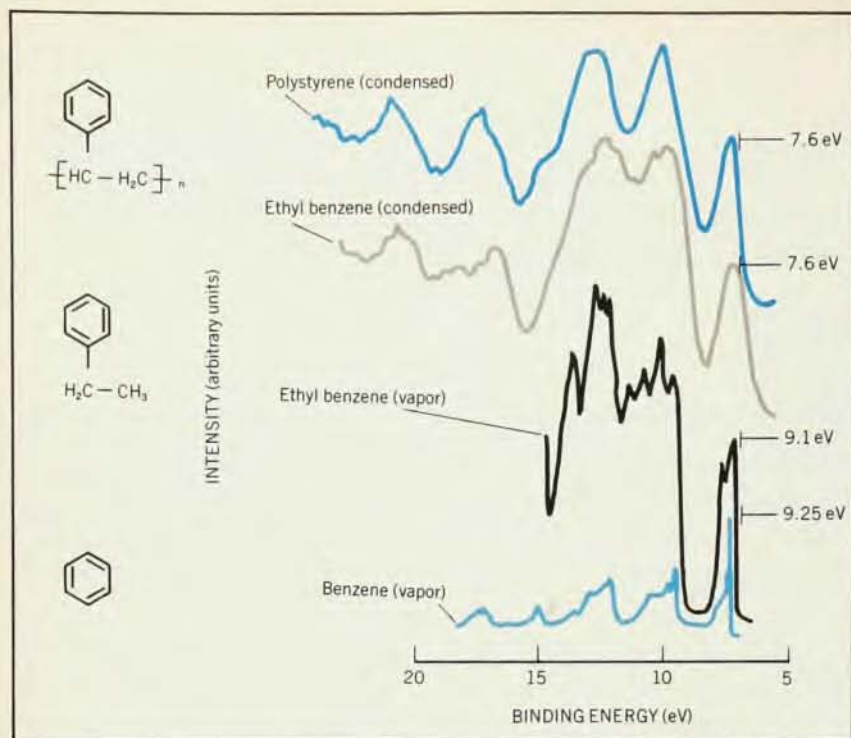
Polymers add an additional challenge: spatial variations in the local composition and structure. It is expected<sup>2</sup> that such variations cause the low-energy states of the electrons, holes and singlet excitons to be localized states. Therefore, models for the transport and optical properties of these materials, rather than being based on the extended Bloch states used in descriptions of crystals, are based on disorder-induced localized states originally described by Philip Anderson.<sup>3</sup>

We develop our theme, that organic solids are not bandgap semiconductors in the same sense as, for example, Si, Ge and GaAs, in four steps. First, we indicate the molecular nature of organic solids and introduce the model concepts needed to describe them. Second, we illustrate experimental realizations of these concepts by considering spectroscopic properties of molecular films and pendant-group polymers. Third, we consider transport phenomena in organic polymers: experiments that appear to require localized states based on static disorder for their interpretation. Finally, we consider the transport properties of molecular crystals: results that challenge severely both traditional band models and hopping models, thereby constituting one of the major outstanding mysteries in solid-state physics. We confine our attention to three-dimensional organic materials—homopolymers, molecular glasses and van der Waals crystals. Excellent discussions of one-dimensional organic solids (many of which appear to exhibit extended-state conduction bands) can be found elsewhere.<sup>4</sup>

#### The organic solid state

The pre-eminent feature of the organic solid state for our present purposes is the persistence of molecular identity (both geometrical and electrical) in the solid state. This result derives from the weakness of the interactions between





**Relaxation of binding energies.** We show (from bottom to top) the structures of benzene, ethyl benzene and polystyrene, together with their ultraviolet photoemission spectra. With increasing condensation and structure, the peaks in the spectra widen and shift ("relax") to smaller binding energies. To emphasize the similarity of the spectra, they have been shifted to align their high-energy peaks; the actual energy of the peaks is indicated. (From reference 2.) Figure 2

molecules, and leads to small electronic hopping integrals (and hence a narrow bandwidth), low-energy intermolecular ("lattice") vibrations, and weakly dispersive (intermolecular and intramolecular) vibrational modes. These facts have the consequence that electronic states in molecular solids are described by a different set of parameters in model Hamiltonians than would be the case for metals and covalent solids.<sup>1</sup> To make this concept more precise, we turn briefly to definitions of suitable models.

Consider first a simple schematic model for the transfer of an electron (an injected or "extra" electron) between two states (labelled by  $i = 1, 2$ ) that are centered on two different molecular sites. The electronic energy of state 1 at site 1 is  $\epsilon_1$ , that of state 2 at site 2 is  $\epsilon_2$ , when the atomic nuclei are all at rest. Vibration of the molecule affects the energies of the electronic states, so we must also consider the possible normal modes of the molecular vibration (labelled by  $n = 1, 2, \dots$ ), with frequencies  $\omega_n$ . The coupling between the electronic energies and vibrations arises from the fact that the potential  $V$  that determines the energies  $\epsilon_i$  depends on the positions of the atomic nuclei in the atoms. To lowest order, the energy  $\epsilon_i$  is shifted to  $\epsilon_i + Q_n \partial V / \partial Q_n$  where the amplitude of the  $n$ th normal mode (of the appropriate symmetry) is  $Q_n$ . Finally, the energies of the states are modified by their overlap, that is by the energy asso-

ciated with the electrons hopping between the two states.

We can describe these interactions most easily with the language of second quantization. Designate the operator that creates an electron in state  $i$  by  $a_i^\dagger$ ; the number of electrons (zero or one) in state  $i$  is then  $a_i^\dagger a_i$ . Similarly,  $b_n^\dagger$  is the operator that creates a quantum of vibrational excitation in mode  $n$ , so  $b_n^\dagger b_n$  is the number of vibrational quanta ("phonons") in mode  $n$ , and  $b_n^\dagger + b_n$  is proportional to the displacement  $Q_n$  of mode  $n$ . The Hamiltonian of a system, consisting of two electronic sites each of which is coupled to a common normal-mode spectrum of vibrations is:

$$H = H_e + H_v + H_c + H_T \quad (1)$$

This Hamiltonian comprises:

- the electron energies

$$H_e = \epsilon_1 a_1^\dagger a_1 + \epsilon_2 a_2^\dagger a_2$$

- the vibrational energies

$$H_v = \sum_n \hbar \omega_n (b_n^\dagger b_n + 1/2)$$

- the electron-"phonon" coupling

$$H_c = \sum_n g_{1n}^2 \hbar \omega_n a_1^\dagger a_1 (b_n^\dagger + b_n) + \sum_n g_{2n}^2 \hbar \omega_n a_2^\dagger a_2 (b_n^\dagger + b_n)$$

- the transfer Hamiltonian

$$H_T = t_0 (a_2^\dagger a_1 + a_1^\dagger a_2)$$

By considering electronic states for the different sites of a crystal lattice one can

account successfully for the transport properties of many inorganic crystals. In this case, for example,  $H_e$  becomes

$$H_e = \sum_i \epsilon_i a_i^\dagger a_i$$

and the vibrational quanta become true "lattice" phonons. If we neglect the electron-phonon interaction (that is, set  $g_{in} = 0$ ), the eigenstates and eigenvalues of the Hamiltonian are the well-known Bloch states and energy bands of solid-state theory.<sup>1</sup> The electron eigenstates display the full periodicity of the lattice, and the width of the resulting electron-energy bands is related to the overlap integrals  $t_0$  by an expression of the form

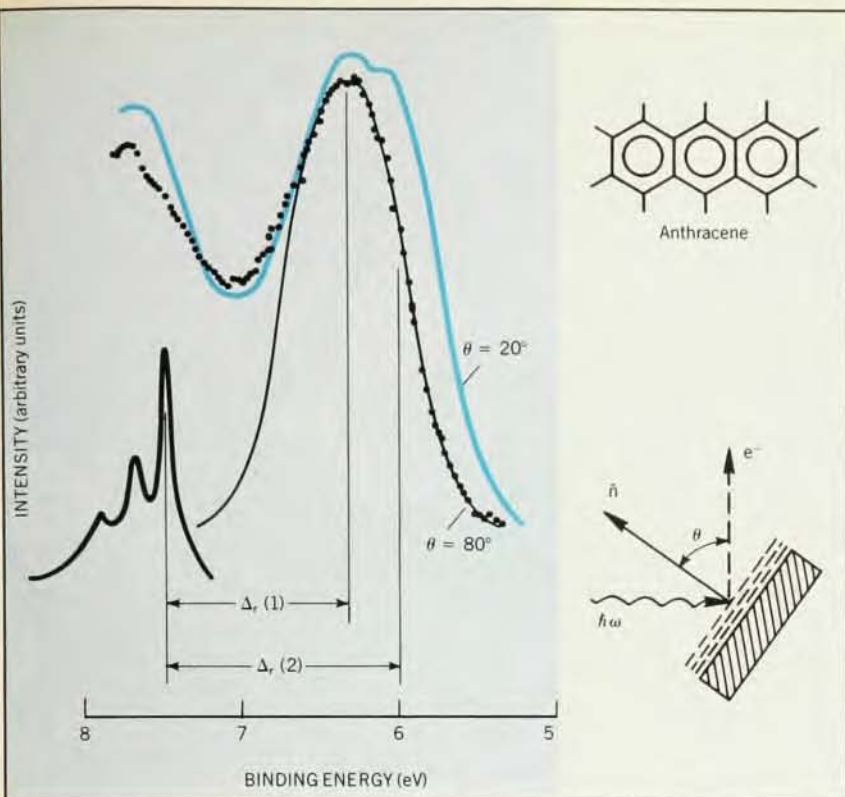
$$W = 2zt_0 \quad (2)$$

where  $z$  is the coordination number of the sites (presumed identical in this case) of the lattice.

In the presence of finite values of  $g_{in}$  the occupations of electron and phonon states are coupled. Nevertheless, at low temperatures electronic motion still occurs via extended states built from periodic superpositions of local electronic wave functions accompanied by a local lattice distortion.<sup>5</sup> The entity consisting of the localized electron with its accompanying distortion of the lattice is called a "small polaron." At high temperatures and for crystals with sufficiently small bandwidths (so the electron states become localized) the phonon population changes when the electron moves from one lattice site to another. The small polaron is thus effectively a localized state. Electron transport consists of a hopping motion between these localized states: This is the small-polaron hopping model.<sup>5</sup>

Neither the Bloch theory nor the models involving small-polaron motion appear to describe adequately the behavior of electrons in organic solids. There may be two reasons for this failure: we could either be using inappropriate solutions to the model Hamiltonian or neglecting important physical phenomena in constructing the model.

First, as indicated above and demonstrated experimentally as we shall see below, the overlap integral  $t_0$  is expected to be quite small in organic solids. Metals and covalent solids have overlap integrals on the order of 1 eV, which are large relative to all other energies in the problem ( $\hbar \omega_n \sim 0.01$  eV,  $g_{in} \hbar \omega \sim 0.05$  eV and  $kT \sim 0.025$  eV). Consequently, "band" motion via extended electronic states predominates in these materials. For van der Waals molecular crystals, however,  $t_0$  is in the range 0.01 to 0.1 eV and is comparable to or less than  $\hbar \omega_n$ ,  $g_{in} \hbar \omega$  and  $kT$  for some electronic and vibrational states. This led (in the mid 1960's) to speculation that the polaron limit of equation 1 may be applicable to organic crystals. Consequently, polaron models were investigated both for linear electron-phonon coupling (included in equation 1) and quadratic electron-phonon coupling.<sup>6</sup>



**Direct observation of the shift of ionization energies of surface states relative to bulk molecular-cation states in anthracene.** The graphs show the ultraviolet photoemission spectra for anthracene vapor (solid curve, lower left) and for condensed anthracene for two different exit angles. Anthracene molecules are flat and condense in planar films. The  $80^\circ$  data represent electrons from the top layer only, while the  $20^\circ$  data show electrons from both of the top two layers. The difference in relaxation energies is clearly visible. (From reference 11)

Figure 3

The failure of these models to account for the temperature and electric field dependence of the mobility in molecular crystals<sup>7</sup> led to the suggestion that additional important effects may have to be included in the Hamiltonian.

Several workers<sup>8,9</sup> suggested that one such additional effect is an alteration of the overlap integrals due to lattice vibrations. Including this phenomenon adds a term

$$H_T' = t_1(a_1^\dagger a_2 + a_2^\dagger a_1) \\ \times \sum_n f_{1,2,n}^2 \hbar \omega_n (b_n^\dagger + b_n) \quad (3)$$

to the electron-transfer Hamiltonian,  $H_T$ . An important motivation for adding this term arises from the fact that  $t_0$  is particularly small in certain directions of some molecular crystals. This small value can be attributed to cancellation of two large terms, so that vibrationally induced rotations from the symmetry positions could substantially modify the overlap integrals.

Second, in polymers both the electron energies,  $\epsilon$ , and the hopping integrals,  $t_0$ , vary from site to site in the lattice because of local variations in composition and structure. While a proper analysis of the resulting model is complicated,<sup>3,10</sup> the qualitative features of interest to us can be defined in terms of

- a mean site energy,  $\bar{\epsilon}$
- the rms deviation from this mean

$$\Delta = ((\epsilon_i - \bar{\epsilon})^2)_{AV}^{1/2}$$

- a mean hopping integral,  $\bar{t}$
- Variations from the mean in the site energies (described by  $\Delta$ ) are referred to as "diagonal disorder;" analogous variations of the hopping integrals are called "off-diagonal disorder." If these variations are caused by local time-independent fluctuations in composition or structure we speak of "static disorder," while if they are generated by the time-dependent thermal vibrations we call them "dynamic disorder." (Whereas static diagonal and off-diagonal disorder can occur in polymers, only dynamic disorder should be present in molecular crystals. Equation 3, for example, describes dynamic, off-diagonal disorder.) The task of analyzing the transport properties of organic solids begins with an examination of the site energies and hopping integrals: What are the mechanisms for—and the magnitudes of—the deviations from their mean values.<sup>2</sup>

These non-uniformities of organic solids can give rise to the localized states that determine the transport properties of electrons, holes or excitons. For example, consider an injected charge in an organic solid. For our purposes the solid is de-

fined by a collection of molecular excitation energies and overlap integrals associated with a spatial distribution of molecular sites in the solid. Lattice-gas models suggest that injected charges are localized—that is, form molecular anions or cations—if the spread of the electronic energies greatly exceeds the hopping integrals (or intrinsic bandwidth). Specifically, the charges are localized if the spread  $\Delta$  satisfies

$$\Delta > c z \bar{t} = c W / 2 \quad (4)$$

where  $c$  is a dimensionless number, on the order of unity, that depends on the connectivity (dimensionality) of the crystal and on the extent of the off-diagonal disorder.<sup>3</sup> Model predictions give values for  $c$  around 2.5 for (isotropic) three-dimensional systems and 1.5 for two dimensions. Evidence indicates that the inequality 4 is satisfied in polymers, so that electrons and holes injected into a polymer form molecular radicals (local anions and cations, respectively) rather than extended mobile states like those characteristic of crystalline covalent semiconductors. Consequently, under these circumstances the electrons and holes are more accurately visualized as ions in solution that move, however, by carrier hopping rather than ionic diffusion. On the other hand, there should be no static diagonal disorder (therefore  $\Delta$  should be zero) in a bulk organic crystal; inequality 4 is then not satisfied, and these considerations do not rule out the existence of extended band-like states.

### The molecular property

As we mentioned earlier, a pre-eminent feature of the organic solid state is the persistence of molecular identity. Spectroscopic evidence, such as that given by the emission of photoelectrons (which, of course, leaves an intrinsic hole in the substrate), demonstrates this persistence clearly.

The most important aspect of the photoemission spectra of single-component molecular solids is<sup>11</sup> their virtual identity to the spectra of the corresponding vapor phase molecules except for a shift to higher exit-electron energy (lower binding energy) by a "relaxation energy" of about an electron volt and for an increase in the width of prominent maxima in the spectra from less than a tenth of an electron volt to nearly 1 eV. In the vapor phase each prominent peak in the photoemission spectra corresponds to one (or more) eigenstates of the molecular cation generated by the injection of a hole into the molecule by virtue of the loss of the photoelectron.

To illustrate these observations, consider molecular films and pendant-group polymers built up from relatively large aromatic molecules suspended from aliphatic backbones. A common example of such a polymer is polystyrene, which consists of benzene molecules attached to

a polyethylene backbone. Figure 2 shows the structure of polystyrene as well as of the units from which it is built, together with their ultraviolet photoemission spectra. The spectra clearly show the shifts and broadening of the spectral lines that take place when ethyl benzene is condensed as a molecular glass on a cold substrate. The obvious implication of these spectra is that molecular-ion eigenvalues shift to higher energy and spread out to form an (inhomogeneous) distribution in the condensed (glass) phase, but that hole states in the condensed molecular solid are otherwise identical to those of the isolated molecules.

The shift ("relaxation") to smaller ionization energies of the hole states—that is, of the states of the molecular radical cations—is thought to arise from the polarization of the surrounding molecules by the charge localized on the molecular cation.<sup>2</sup> William Salaneck confirmed<sup>12</sup> this hypothesis by observing a difference in the relaxation energies for hole states in the bulk and on the surface: The surface relaxation is smaller, which is precisely what one would expect because the surface molecules are surrounded by only half as many polarizable neighbors than the bulk molecules. To observe the difference, Salaneck examined the ultraviolet photoemission spectrum of anthracene films condensed onto a gold substrate. The mean free path of photoelectrons in anthracene is quite small (a few angstroms), so photoelectrons emitted normal to the surface come from the uppermost two layers while photoelectrons emitted tangentially come predominantly from the surface layer. Salaneck's data, shown in figure 3, reveal that photoelectrons from the second layer (the extra bump on the 20° curve) produce holes with a higher relaxation energy than those from the surface. The induced relaxation energies for the intermolecular polarization in glassy anthracene, from these data, are deduced to occur in the range 1.2–1.5 eV. Figure 4 shows the apparatus used in these ultraviolet-photoemission experiments.

#### Polymers and molecular glasses

The large widths (around 1 eV) of the condensed-state radical cation ionizations observed in photoemission spectroscopy (figure 2) are due primarily to spatial inhomogeneities in the environments of surface cations.<sup>2</sup> Such variations in local environment give rise to analogous variations in the intermolecular relaxation energies. The resulting relaxation-energy fluctuations provide the major source of diagonal disorder in polymers and molecular glasses. Consequently, they constitute the ultimate reason for the localization of radical ions in these materials, as discussed in association with inequality 4. A quantitative model of the photoemission lineshapes embodying



**Ultraviolet photoemission spectroscopy.** Charles Duke, William Salaneck and H. R. Thomas (left to right) are shown with the apparatus used to obtain the data for figures 2 and 3. Figure 4

these concepts has been applied to describe measured ultraviolet photoelectron spectra from the polystyrene and poly(2-vinyl pyridine).<sup>2</sup>

Given the large values of the inhomogeneous electron-energy spread  $\Delta$  (around 1 eV), relative to the hopping integrals  $t$  (less than 0.01 eV), we expect charge carriers in organic pendant-group polymers to be highly localized. Depending upon the activation energy for hopping between sites, the charge carriers will either have small mobilities ( $10^{-7}$  cm<sup>2</sup>/Vsec is not unusual) or will exhibit range-limited electronic transport: That is, injected carriers traverse a finite range before becoming trapped essentially forever in the sample. While these effects are consistent with the localization of injected charges in polymers, they do not distinguish between extrinsic "trap" states and intrinsic localized states.<sup>13,14</sup> Nevertheless, such a model of localized injected charges is consistent with transport<sup>14</sup> and contact-charge-exchange<sup>15</sup> measurements in most polymers, and has been verified in more detail for a few model systems.<sup>15–17</sup> It is worth emphasizing, however, that conclusive experimental verification of inequality 4 is notoriously difficult because disorder localizes electronic states near the edges of extended-state bands even if the states in the center of the band remain delocalized.<sup>3,10</sup> Consequently, transport and contact charge exchange from localized states near the band edges can occur even if the radical anion and cation states near

the center of the band are extended in character.

As in the case of traditional covalent semiconductors, one can modify greatly the transport properties of polymeric materials by doping. An example of considerable historical interest<sup>16</sup> is trinitrofluorenone (TNF) dispersed in polyvinylcarbazole (PVK). Figure 5 shows the temperature dependences of the electron mobilities in various forms of TNF. Electron transport in glassy TNF and in TNF dispersed in PVK probably takes place via electron hopping from one molecular TNF anion to another. This mechanism is suggested by a comparison of the mobilities of the two substances, as shown in figure 5, and is verified by other experiments.<sup>16</sup> Specifically, the model utilized to describe this sort of hopping transport involves vibration-assisted electron transfer between molecular-ion states that are localized by static disorder.<sup>16–18</sup> This model is analogous to those used to describe similar transport in lightly doped (usually compensated) covalent semiconductors.<sup>19</sup> We conclude, therefore, that electronic states localized by relaxation-energy fluctuations induced by static disorder play a dominant role in determining both the extrinsic and intrinsic electronic states in polymers and molecular glasses. Consequently, the electronic states that are active in carrier transport in common polymeric organic materials are local, and usually molecular, in nature rather than being extended

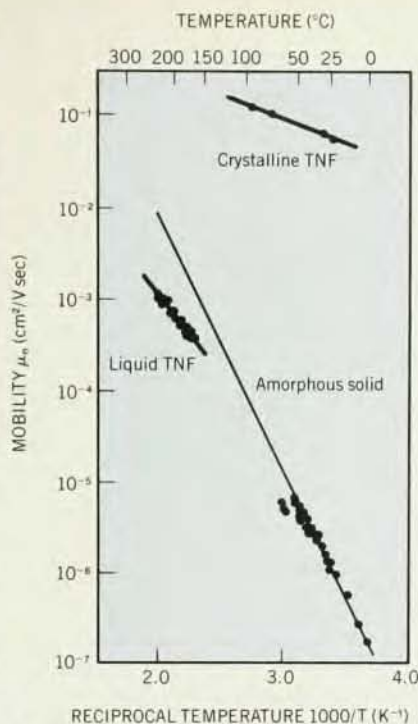
Bloch states encompassing many molecular units of the polymeric host.<sup>14-17</sup>

## Molecular crystals

The crystalline form of organic materials is of considerable interest in the present context because charge-carrier transport in single-component van der Waals crystals provides a particularly clear challenge to modern solid-state transport theory. The photoemission and optical-absorption spectra of van der Waals crystals differ little, if at all, from those of the corresponding glasses,<sup>2,11</sup> indicating that the intrinsic electronic states in both types of molecular solid are derived directly from those of their constituent molecules, as for molecular glasses. The transport properties of the crystalline and glassy forms of organic materials often differ dramatically, however, as illustrated in figure 5 for TNF. Molecular glasses and dispersions in polymers typically exhibit activated hopping transport and small mobilities (ranging from  $10^{-3}$  cm<sup>2</sup>/V sec down to  $10^{-9}$  cm<sup>2</sup>/V sec). Many van der Waals crystals, on the other hand, exhibit<sup>20</sup> intrinsic mobilities on the order of 0.1 cm<sup>2</sup>/V sec to 1 cm<sup>2</sup>/V sec that are at most weakly temperature dependent. Several examples of temperature independent molecular crystal carrier mobilities are shown in figure 6, and others are known.<sup>20,21</sup>

These temperature-independent mobilities, which also are nearly independent both of the material<sup>20</sup> and of the magnitude of the electric field<sup>7</sup> for fields below  $2 \times 10^5$  V/cm, have thus far defied detailed interpretation on the basis of either energy-band models or localized-state hopping models. We can readily demonstrate the difficulties involved by considering simple models in which the hopping integrals,  $t$ , are independent of temperature.

► Band models predict mobilities whose



**Temperature dependence** of the electron mobilities of 2,4,7-trinitro-9-fluorenone (TNF) as a liquid, a crystal, and three forms of amorphous solid: melt-quenched pure TNF (glass), TNF dispersed in polyvinyl carbazole and dispersed in a polyester. In the solid forms the mobility is field dependent; here the field was  $10^5$  V/cm. (After reference 16)

Figure 5

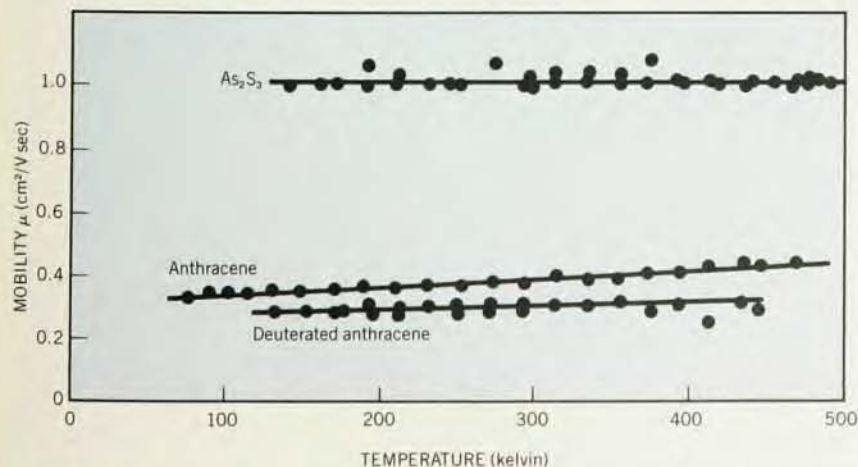
temperature dependence is the product of  $T^{-1}$  (from the Boltzmann equation for narrow-band materials<sup>20</sup>) and the temperature dependence of the scattering mechanism. For all known scattering mechanisms the resulting mobility is proportional to some power of the reciprocal temperature,  $T^{-n}$  with  $n > 1$ : A result that is inconsistent with the data shown in figure 6.

► Hopping models also predict strongly

temperature-dependent mobilities. Polaron models that have been worked out so far (that is, for adiabatic, non-adiabatic, high and low temperature, and weak and strong phonon-coupling approximations), including models with linear and quadratic couplings, predict mobilities proportional to  $T^{-m}e^{-E/kT}$ , with  $m$  near unity. Again, this prediction is inconsistent with the data, no matter what value the activation energy  $E$  may have.

In early 1978 experiments showed<sup>9</sup> that the mobility of electrons in naphthalene rises abruptly as the temperature decreases below 100 K, a result shown in figure 7. Subsequently, the same behavior was found<sup>21</sup> in deuterated naphthalene. The rising mobility with decreasing temperature was attributed to scattering by optical phonons of electrons in Bloch-type extended states. Such a mechanism leads to an exponential mobility with an exponent equal to a phonon energy divided by  $kT$ . This was the observed behavior. Hence, Bloch-type states *do* appear to occur in some molecular crystals in certain temperature ranges. Above 100 K in naphthalene, however, another mechanism appears to limit the mobility. The usual alternative to transport via Bloch-type states is the hopping of localized carriers. It would therefore appear that the correct starting point for understanding the mobilities shown in figure 6 is a hopping model, even though existing analyses based on equation 1 appear to be inadequate to explain the observed failure of the mobility to depend on the temperature and the electric field.

Because of the failure of models derived from the Hamiltonian of equation 1, several workers suggested<sup>8,9</sup> that these temperature-independent mobilities originated in electron transfer between localized states caused by the thermal-vibration-induced modulation of the electron hopping-integrals, that is, by the term in the transfer Hamiltonian given by equation 3. At higher temperatures the temperature-independent mobilities are associated with states localized by the dynamic disorder induced by thermal vibrations in the crystal. Recently, several groups have attempted detailed analyses of the transport data shown in figures 6 and 7. Two of these attempts<sup>8,9</sup> are based on equation 3 and another<sup>22</sup> is based on dynamical diagonal disorder and embodies quadratic electron-vibration interactions instead of the linear coupling given in equation 1. The results of these calculations are, however, not completely in accord with the observations. Specifically, they fail to describe the measured insensitivity of the mobilities to the magnitude of the electric field<sup>7</sup> and the fact that hopping motion occurs in two directions (along the  $c'$  and  $b$  axes) in naphthalene rather than along only one or all three.<sup>8,22</sup> Consequently, the mi-

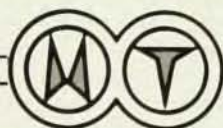


**Electron drift mobilities** in arsenic trisulfide, anthracene and deuterated anthracene. To measure the mobilities, the crystals were held between two biased electrodes and the time for a pulse of electrons to travel from one electrode to the other was measured. (From reference 7.) Figure 6

## PREAMP- AMP- DISC



**Model 509**  
**\$325.00**



- Charge Gain - 12 Volts per Picocoulomb
- Integral Linearity -0.1% to +10 Volts
- Variable Discriminator Threshold - - 100 Millivolts to 10 Volts

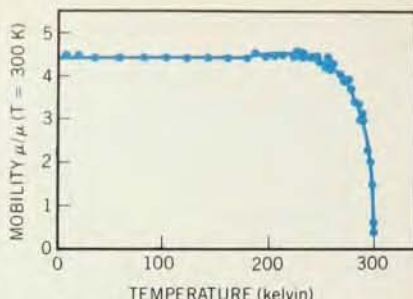
# Mech-Tronics

## NUCLEAR

430A Kay Ave., Addison, IL 60101

**For more information  
WRITE OR CALL COLLECT  
(312) 543-9304**

Circle No. 18 on Reader Service Card



**Mobilities of electrons in naphthalene.** We plot the mobility—relative to the mobility measured at 300 K—as a function of temperature. The change from an almost temperature-independent mobility above 100 K to one that increases with decreasing temperature below 100 K may indicate a band-hopping transition. (From references 9 and 21) **Figure 7**

croscopic description of the motion of charges injected into molecular crystals remains beyond all current models of solid-state transport, in spite of the fact that these materials are widely regarded as periodic systems in the same sense as crystalline metals and covalent semiconductors.

Because of their increasing usefulness in applications and because of some successes in developing models of their electrical and optical properties, organic solids will become more and more interesting for solid-state physicists. But perhaps their most interesting aspect, however, is the persistent challenge that organic crystals afford to conventional theories of transport in solids. After over two decades of intensive investigation, the temperature and field dependence of the mobilities of charge carriers in van der Waals crystals remain unexplained by extant models of either band or hopping transport. Thus, organic materials continue to afford both opportunities for technologists and stimulating challenges for solid-state physicists and chemists, alike.

### References

Reviews of properties and applications of organic polymers can be found in

Dielectrics: A. R. Blythe, *Electrical Properties of Polymers*, Cambridge U.P., Cambridge (1979).

Photochemistry: W. Moreau and N. Viswanathan, in *Ultraviolet Light Induced Reactions in Polymers*, S. S. Labana, ed., American Chemical Society Symposium Series, Washington (1976), 25, page 107.

Resists: L. F. Thompson and R. E. Kerwin, *Annu. Rev. Mater. Sci.* **6**, 267 (1976).

Transducers: A. L. Robinson, *Science* **200**, 1371 (1978).

Photodielectrics: S. Riech, *Angew. Chem (Int. Ed. Engl.)* **16**, 441 (1977).

Insulators and encapsulants: W. F. Gorham, *Adv. Chem.* **91**, 643 (1969).

Electrophotography: J. W. Weigl, *Angew. Chem (Int. Ed. Engl.)* **16**, 374 (1977).

Conductors and superconductors: E. P.

Goodings, *Chem. Soc. Rev.* **5**, 95 (1976).

Optical devices: H. Dislich, *Angew. Chem (Int. Ed. Engl.)* **18**, 49 (1979).

1. See, for example, C. Kittel, *Quantum Theory of Solids*, Wiley, New York, (1963); J. C. Phillips, *Bonds and Bands in Semiconductors*, Academic, New York (1973).

2. C. B. Duke, *Mol. Cryst. Liq. Cryst.* **50**, 63 (1979); *Surf. Sci.* **70**, 674 (1978); C. B. Duke, W. R. Salaneck, T. J. Fabish, J. J. Ritsko, H. R. Thomas, A. Paton, *Phys. Rev. B* **18**, 5717 (1978).

3. P. W. Anderson, *Rev. Mod. Phys.*, **50**, 191 (1978); D. Weaire, V. Srivastava in *Amorphous and Liquid Semiconductors*, W. E. Spear, ed., G. G. Stevenson, Dundee (1977), page 286.

4. J. S. Miller, A. J. Epstein, eds., *Synthesis and Properties of Low-Dimensional Solids*, New York Academy of Sciences, New York (1978).

5. T. Holstein, *Ann. Phys. (N.Y.)* **8**, 343 (1959); J. Yamashita, T. Kurosawa, *Phys. Chem. Solids* **5**, 34 (1958); *J. Phys. Soc. Jap.* **15**, 802 (1960).

6. R. W. Munn, W. Siebrand, *J. Chem. Phys.* **52**, 6391 (1970); *Chem. Phys. Lett.* **9**, 655 (1969).

7. L. B. Schein, *Chem. Phys. Lett.* **48**, 571 (1977); L. B. Schein, A. R. McGhie, *Chem. Phys. Lett.* **62**, 356 (1979).

8. A. Madhukar, W. Post, *Phys. Rev. Lett.* **39**, 1424 (1977). H. Sumi, *Solid State Commun.* **28**, 309 (1978); **29**, 495 (1979); *J. Chem. Phys.* **70**, 3775 (1979).

9. L. B. Schein, C. B. Duke, A. R. McGhie, *Phys. Rev. Lett.* **40**, 197 (1978).

10. N. F. Mott, *Rev. Mod. Phys.* **50**, 203 (1978) and references therein.

11. C. B. Duke, W. R. Salaneck, A. Paton, K. S. Liang, N. O. Lipari, R. Zallen, in *Structure and Excitations of Amorphous Solids*, G. Lucovsky, F. L. Galeener, eds., American Institute of Physics, New York (1976), page 23; W. D. Grobman, E. E. Koch, in *Photoemission of Solids*, L. Ley, M. Cardona, eds., Springer, Berlin (1979), page 261.

12. W. R. Salaneck, *Phys. Rev. Lett.* **40**, 60 (1978).

13. B. Reimer, H. Bassler, *Phys. Status Solidi (A)* **51**, 445 (1979).

14. H. Meier, *Organic Semiconductors* Verlag Chemie, Weinheim (1974).

15. C. B. Duke, T. J. Fabish, *J. Appl. Phys.* **49**, 315 (1978).

16. W. D. Gill, in *Photoconductivity and Related Phenomena*, J. Mort, D. M. Pai, eds., Elsevier, Amsterdam (1976), page 303.

17. J. M. Pearson, *Pure and Appl. Chem.* **49**, 463 (1977); G. Pfister, *Phys. Rev. B* **16**, 3676 (1977).

18. C. B. Duke, in *Tunneling in Biological Systems*, B. Chance, et al., eds., Academic, New York (1979), page 31.

19. See, for example, N. F. Mott, E. A. Davis, *Electronic Processes in Non-Crystalline Media*, Oxford U.P. (1971), page 152.

20. L. B. Schein, *Phys. Rev. B* **15**, 1024 (1977).

21. L. B. Schein, A. R. McGhie, *Phys. Rev. B* **70**, 1631 (1979).

22. S. Efrima, H. Metiu, *J. Chem. Phys.* **69**, 5113 (1978); *Chem. Phys. Lett.* **60**, 226 (1979). □