Carrier dynamics in organic molecular semiconductors

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Collaborations

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Introduction: band-like vs incoherent transport in organic molecular crystals

I) Transport: crossover from band transport to a resistivity saturation regime

II) Optics and particle self-diffusivity: dynamical localization in highly anisotropic structures
Organic molecular crystals
Transport theory, why interesting?
Duality band-like vs localized not solved yet
Chemist's view... real space
Electrons hop from molecule to molecule

Physicist's view... momentum space
Electrons form weakly scattered Bloch states

[Duke & Schein, Physics Today 1980]
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The molecular property
As we mentioned earlier, a pre-eminent feature of the organic solid state is the persistence of molecular identity.

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 con-
Chemist's view... real space
Electrons hop from molecule to molecule

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→ the problem is still open

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transport mechanism. Further, the relation between the contribution of the coherent bandlike transport and that of the incoherent hopping-related transport to the entire charge transport mechanism is still an outstanding issue in organic crystals. These mean that a proper understanding
Band structure

- VdW bonding, $a=4-8\text{Å}$, "persistence of molecular identity"
- High anisotropy
- Low overlap integrals $\rightarrow$ narrow bands $W\sim0.1-0.4\text{eV}$

Tendency to localization, polarons, breakdown of band picture?
nall energy scales $\sim0.1\text{eV}$

[Da Silva Filho et. al. Adv Mat05]
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Narrow bands of molecular origin seen in pentacene and rubrene
Large anisotropy
Good agreement with band structure calculation (rubrene $t=0.11$ eV)

Yamane et al PRB07

[Machida et al. PRL010]
Narrow bands of molecular origin seen in pentacene and rubrene
Large anisotropy
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Temperature dependent broadening e-ph interaction
Mobility from TOF/FET

«band-like» \( T^{-n} \) with \( n=0.5-3 \)

very low values \( \mu=0.1-400 \, \text{cm}^2/\text{Vs} \)

Rubrene \( \mu= \text{20-40 cm}^2/\text{Vs} \) at RT

(graphene \( >10^5 \), 2DEG \( >10^7 \))

naphthalene

[Karl et al. SynthMet 03]
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- mobility saturation?

naphthalene

[Karl et al. SynthMet 03]
Long-standing problem: mean-free-path

Several experiments prompts for a band space description of carriers but...

Extractred from hole mobility in naphthalene via band-structure calculations [Cheng JCP03]
Long-standing problem: mean-free-path

Several experiments prompts for a band space description of carriers but...

How can \( \mu \) be « band-like » and \( l_{\text{mfp}} < a \) ?

Extracted from hole mobility in naphthalene via band-structure calculations [Cheng JCP03]
Choosing a model

- Static vs dynamic disorder e-ph interaction dominates
- Intramolecular vibrations are “fast” no polaron formation instead coherent band shrinking!
- Intermolecular vibrations are “slow” efficient scattering mechanism
Intramolecular vs intermolecular coupling

Intramolecular

[Devos Lannoo PRB98]
Intramolecular vs intermolecular coupling

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[Coropceanu PRL02]

Polarons

Rubrene: $E_p=79\text{meV}$, $\omega_0=173\text{meV}$
Intramolecular vs intermolecular coupling

Intramolecular

[Devos Lannoo PRB98]
[Coropceanu PRL02]

Polarons

\[ V = \frac{1800}{N_\pi} \]

Electron-phonon coupling (meV)

[Coropceanu PRL02]

Rubrene

\[ E_p = 79 \text{meV} \quad \omega_0 = 173 \text{meV} \]

[Troisi AdvMat07]

Intermolecular: modulation of the hopping

\[ E_p = 24 \text{meV} \quad \omega_0 = 6 \text{meV} \]

Weak Coupl.
A paradigmatic model

\[ H = -t \sum_i \left[ 1 - g(X_i - X_{i+1}) \right] (c_i^+ c_{i+1} + c_{i+1}^+ c_i) + \sum_i \frac{M \omega_0^2}{2} X_i^2 \]

[Friedman PR 1964]
[Gosar & Choi PR 1966]
[Duke & Schein, Physics Today 1980]
[Munn & Silbey JCP 1985]
[Hannewald & Bobbert PRB 2004]
[Picon PRB 2007]

- molecular nature, narrow bands \( \rightarrow \) tight binding \( t=142 \text{ meV} \)
- mechanical softness, large thermal fluctuations of the lattice
- Optical mode \( \omega_0=6 \text{ meV} \), modulates transfer integral via
Inter-molecular coupling \( \lambda = \frac{g^2 t}{2M \omega_0^2} = 0.17 \)
- Neglect intra-molecular coupling
- restrict to 1D
Mobility in the semiclassical regime

- Phonons as “static disorder”
- Non pertubative calculation of spectral function and mobility from Kubo formula
Transport from spectral properties

- Classical phonons, $T > \omega_0$ thermal lattice disorder (variance $\sim kT$) $\rightarrow$ Exact Green function
- Almost all states are localized in 1D with off-diagonal disorder
- Finite $\omega_0$ $\rightarrow$ finite static conductivity
- Compute via the Kubo formula the \textit{diffusive part of conductivity} neglecting vertex corrections that lead to localization
Spectral function $A(k, \omega)$

$k$-states are well defined at moderate thermal disorder (rubrene, $\sim$RT)

- low-k states are partially protected by off-diagonal coupling
- broadening $s = t \sqrt{8\lambda(T/t)}$
- breakdown of qp picture when

$$l_{mf} < a \rightarrow v\tau = at/\Gamma = at/s < a \rightarrow s > t$$
Mobility from Kubo formula

Localized band-like

\[ \omega/t \]
Mobility from Kubo formula

\[ \mu = \mu_0 \frac{\pi}{k_B T Z} \int d\omega e^{-\beta \omega} \text{tr}[\langle \rho(\omega) \rangle \langle J^\dagger \rangle \langle \rho(\omega) \rangle J] \]

Two separate contributions for mobility: band states + incoherent tail states

As thermal disorder increases:
- the relative weight of tail states increases
- all states become more localized

Mobility saturation
Low temperature limit: band conduction $\mu \approx T^{-3/2}$

High temperature limit: mobility saturate regime $\mu \approx T^{-1/2}$

At temperatures of interest in OSC, transport occurs via a combination of band conduction and incoherent conduction.

T dependence is intermediate (but no $1/T^2$ behavior as predicted by Q/C simulations).
Mobility and optical conductivity beyond semiclassical regime...

- Optical conductivity
- Phonon dynamics via quantum classical approach: Ehrenfest dynamics
- Relation between self-diffusivity and mobility
- Optical conductivity: dynamical localization
Rubrene: charge modulation spectroscopy

«Drude-like» absorption + peak at 500cm^-1

[Fischer et al. APL06]
Rubrene: optical conductivity

- peak at 500 cm\(^{-1}\)
- light quasiparticles (m\(^*\)~1-2) from sum rule
- strong anisotropy ~ band struct.

FIG. 3 (color online). The optical conductivity of the two-dimensional system of field-induced charges at the rubrene-parylene interface $\Delta \sigma_{\text{rub}}(\omega)$ at different gate voltages $V_{\text{GS}}$ at 300 K. (a) $E \parallel a$-axis data. (b) $E \parallel b$-axis data. Black squares on the left axes: dc conductivity at $-280$ V. Insets: the evolution of the spectral weight $n_{2D}/m^*$ with $V_{\text{GS}}$. [Fischer et al. APL06]
Carrier diffusion (Q/C dynamics)

Ehrenfest Quantum/Classical dynamics
[Troisi&Orlandi PRL 2006]

\[ H = H_{cl}(X) + \sum_{i} \frac{P_{i}^{2}}{2M} + \frac{M\omega_{0}^{2}}{2} X_{i}^{2} \]

\[ M\ddot{X}_{i} = - \langle \psi | \frac{\partial H}{\partial X_{i}} | \psi \rangle \]

\[ i\partial_{t} | \psi \rangle = H_{el}(X) | \psi \rangle \]
Dynamical localization at $t_{\text{loc}}$

Diffusive behaviour for times $> t_{\text{diff}} \approx 1/\omega_0$

Ehrenfest dynamics predicts $1/T^2$ in mobility [Troisi et al. PRL 06]
but it is inadequate to describe equilibrium properties such as $D$!
[Parandekar et al. JCP 05]
Carrier diffusion & optical conductivity

\[ \frac{\sigma(\omega)}{n} = -\omega \tanh(\beta \omega/2) \text{Re} \int_0^\infty dt e^{i(\omega + i\delta) t} < |x(t) - x(0)|^2 > \]

- Low frequency maximum absorption at \( \omega_{\text{loc}} \rightarrow \) Dynamical localization peak
- Diffusive behaviour seen below \( \omega_{\text{diff}} \approx \omega_0 \)
Dynamical localization peak may explain the peak seen around 500 cm\(^{-1}\) at room temperature (peak saturation due to finite disorder, different model params?)

Need for experiments at different temperatures
A phenomenological model

\[ C(t) = \langle \{ J_x^+(t), J_x(0) \} \rangle \]

\[ \frac{\sigma(\omega)}{n} = \frac{\tanh(\beta \omega/2)}{\omega} \text{Re} C(\omega) \]

Single inelastic scattering time approximation

\[ C(t) = e^{-t/\tau_{in}} C_s(t) \]

Forward/backward elastic scattering time approximation

\[ C_s(t) = A [e^{-t/\tau_s} - \frac{\tau_s}{\tau_b} e^{-t/\tau_b}] \]

\[ \tau_{in}^{-1} = 120 \text{cm}^{-1} \]

\[ \omega_0 = 0.4 \tau_{in}^{-1} \]
Dynamical localization

Non diffusive (localization) properties can be accessed by Optical probes

Single inelastic scattering time approximation

\[ C(t) = e^{-t/\tau_{in}} C_s(t) \]

Localization length

\[ \ell^2 = \frac{1}{\pi} \int_0^\infty d\omega \frac{\sigma_s(\omega)}{\omega \tanh(\beta \omega/2)} \]

Dynamical localization length

\[ \ell^2 = \frac{1}{\pi} \int_{\tau_{in}}^{\infty} d\omega \frac{\sigma(\omega)}{\omega \tanh(\beta \omega/2)} \]
Conclusions

The puzzle on the microscopic nature of carriers in crystalline organic semiconductors can be understood by observing that both band-like and localized but non polaronic excitations (extending to a tenth of lattice spacings) are simultaneously present in these systems due to the large thermal fluctuations of the lattice structure.

Transport mechanism: both band-like and localized states contribute. The mobility gradually crosses over with $T$ from Boltzmann-like to a saturated behavior as $l_{mf} \sim a$.

Optical conductivity peak at 500 cm$^{-1}$ can be explained by "dynamical" localization of the diffusive carriers in strongly anisotropic samples.

Dynamically non diffusive (localization) properties can be accessed by optical probes in systems with large anisotropies.