Week 6

Electronic Properties 2

Ohmic and Space Charge Conduction

Measuring Mobility

Doping

Recombination

Heterojunctions

Chapter 4.4-4.7

Current and Conductivity

1. **Ohm's Law** (gives DC mobility).

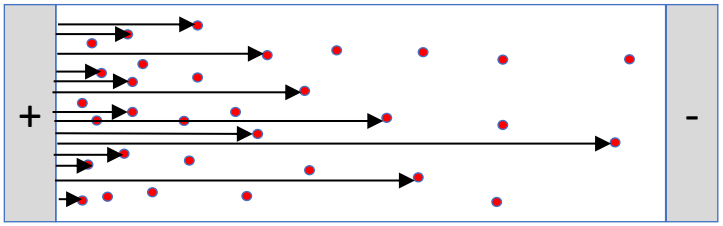
- For a single carrier (holes in this case) in a uniform electric field:

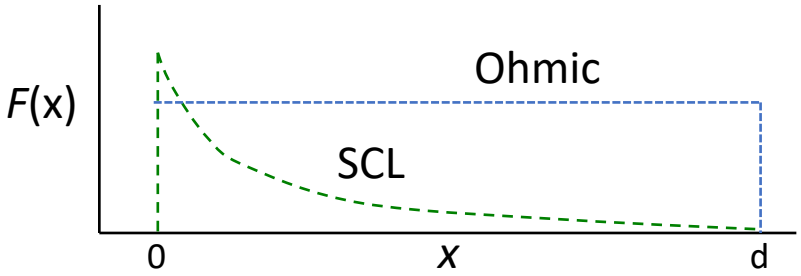
$$j = qp\mu F = qp\mu \frac{V}{d}$$

- Gives the product $p\mu \Rightarrow$ requires independent determination of charge density.
- *Ohmic regime* identified by *linear* relationship between *j* and *V.*

2. **Space charge limited current** (gives DC mobility).

- When the injected carrier density $p_{inj} > p_0$ (the background charge density), charge accumulates at electrodes:



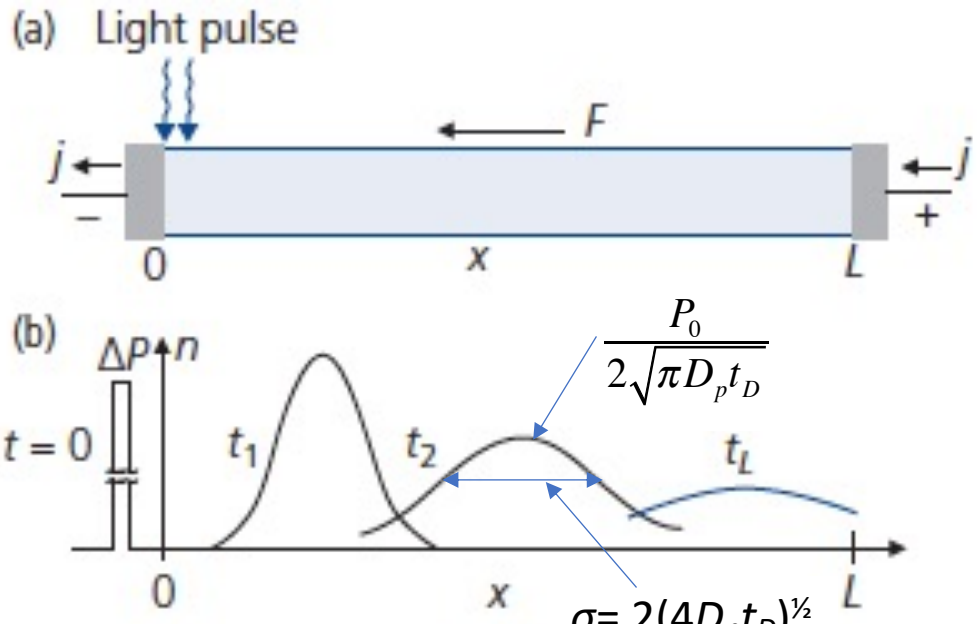


Extracting the Diffusion Constant

Shockley-Haynes method (time of flight)

- Bias sample at quasi-equilibrium to avoid injection (Ohmic at $V_a \rightarrow 0$).
- Light pulse generates excitons that separate into charges at $t = 0$
- Measure arrival time (t_D) of the photogenerated current pulse.

$$t_D = \frac{L^2}{\mu V_a}$$



Start with diffusion equation: $\frac{\partial p}{\partial t} = D_p \frac{\partial^2 p}{\partial x^2}$

With solutions: $p(x,t) = \left[\frac{P_0}{2\sqrt{\pi D_p t}}\right] \exp\left(-x^2 / 4D_p t\right)$ (A single μ ⇒ Gaussian spreading)

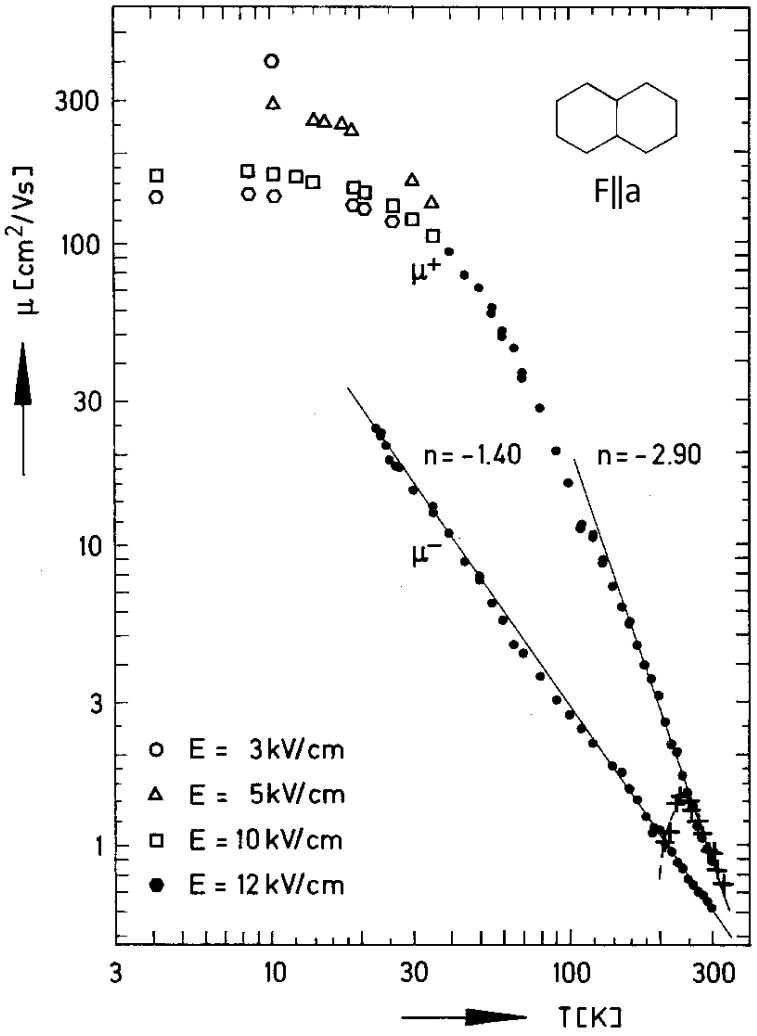
The peak decreases with t_D, and it spreads with half width at 1/*e* from max.: $\sigma = 2(4D_p t_D)^{½}$

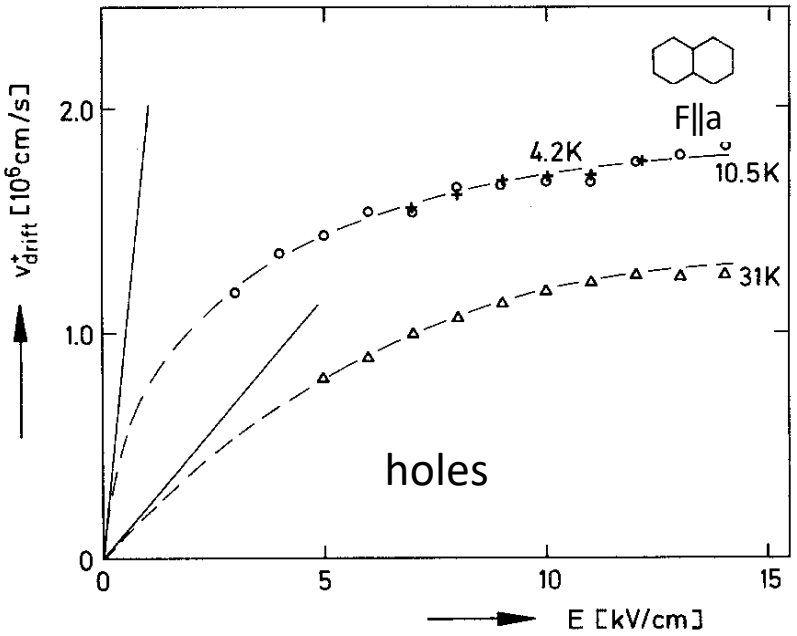
The <u>width</u> of the current pulse gives the diffusion constant of the charge, *D*.

D_p should be consistent with the Einstein relation ⇒ μ

Band Transport

- Ultra-purified naphthalene





- Mobility *vs*. majority carrier type
  e.g. If the mobility of holes > electrons,
  does NOT imply the material is *p*-type
- The "type" of a material depends on the polarity of the **majority** carrier

Space Charge Limited Current

- In the space charge regime, we make the following assumptions to solve *j* vs. *V* :
  - $p_{inj} > p_0$
  - Only one carrier type is present
  - $\mu \neq \mu(F)$ (Field-independent mobility)
  - Free carrier distribution follows Boltzmann statistics
  - Trapped charge occupation defined by Fermi statistics
  - *F* is large enough for drift (and not diffusion) to dominate
  - Field not so large that field emission is important

- In 1D, Gauss says: $\frac{dF}{dx} = \frac{q\left(p_{inj}(x) + p_t(x) + p_0\right)}{\varepsilon} \approx \frac{qp_{inj}(x)}{\varepsilon}$ (trap free case)
  - $\varepsilon = \varepsilon_0 \varepsilon_r$
  - Current in the absence of trapped charge, p_t(x): $j(x) = q\mu_p p_{inj}(x) F(x)$
  - Now: $\frac{dF^2(x)}{dx} = 2F(x)\frac{dF(x)}{dx} = \frac{2qp_{inj}(x)F(x)}{\varepsilon} = \frac{2j(x)}{\varepsilon\mu_p}$
  - Since *j* is constant across layer $\Rightarrow F^2(x) = \frac{2jx}{\varepsilon\mu_p}$ (This is current continuity)

j-V in the SCL regime

$$F^2(x) = \frac{2jx}{\varepsilon\mu_p} \Rightarrow F(x) = \sqrt{\frac{2jx}{\varepsilon\mu_p}}$$

Note: $F(x) \sim x^{1/2}$ vs. $F(x)$= constant for Ohmic

Now potential is: $-\frac{dV}{dx} = F(x)$

Integrating between $0 < V < V_a$ and $0 < x < d$

We obtain: $V_a = \frac{2}{3}\sqrt{\frac{2jd^3}{\varepsilon\mu_p}}$

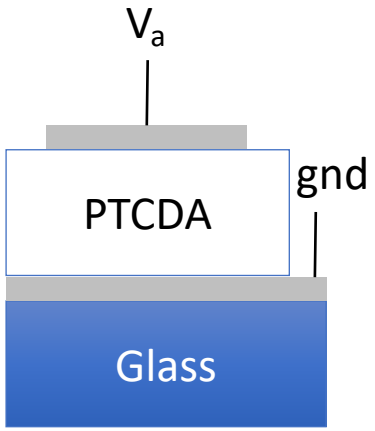
Giving the **Mott-Gurney relationship**:

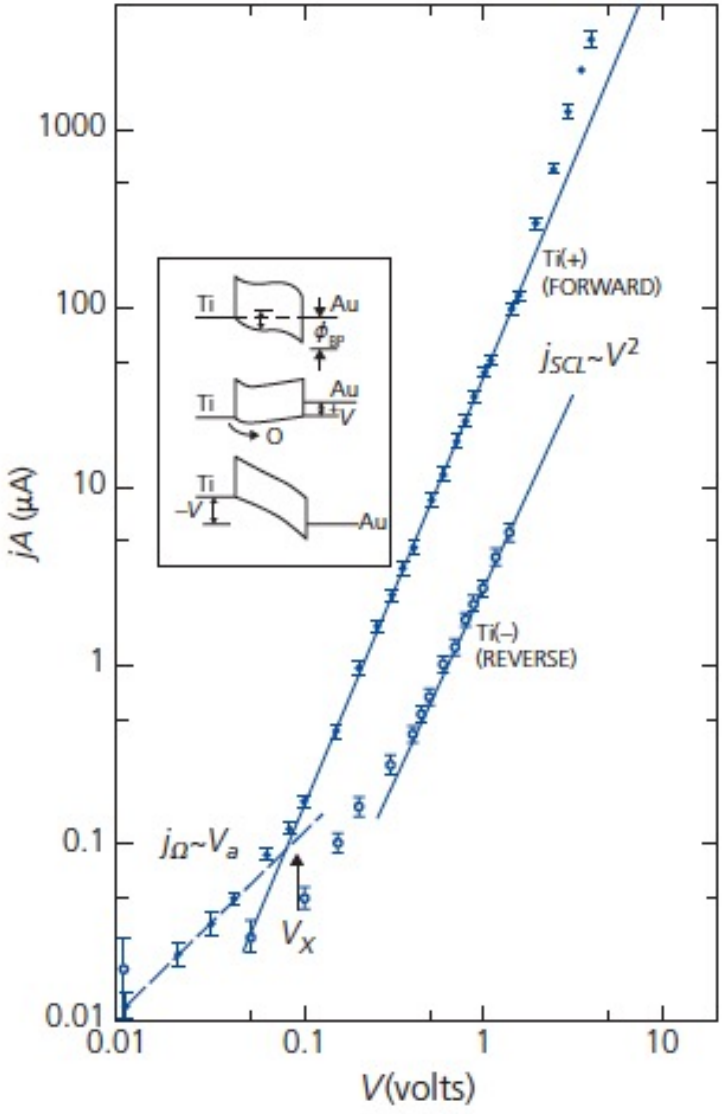
$$j = \frac{9}{8}\mu_p\varepsilon\frac{V_a^2}{d^3}$$

Note the absence of *p*!
⇒ Only need the dielectric constant and the film thickness.

Use the ohmic region of the *j-V* curve to determine p_0.

SCL Current in PTCDA





To find background carrier density:

At V_x: j(ohmic)=j(SCL)

$$\Rightarrow qn\mu\frac{V_x}{d}=\frac{9}{8}\mu\varepsilon\frac{V_x^2}{d^3}$$

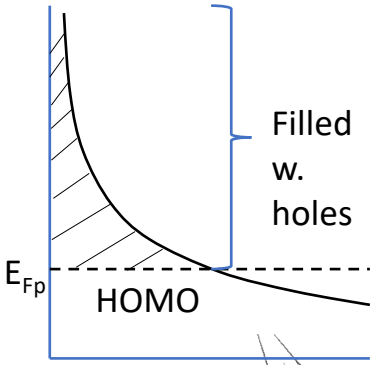
$$\Rightarrow n=\frac{9}{8}\frac{\varepsilon}{q}\frac{V_x}{d^2}$$

Forrest, S. R., Kaplan, M. L. & Schmidt, P. H. 1984 *J. Appl. Phys.*, 55**,** 1492.

But what happens if things aren't so simple?

- We have assumed no traps. In organics, this is not often the case due to ***static disorder***.
- Simplest case: A single discrete, shallow trap where $\frac{p_0}{p_t} = \Theta << 1$
- Then <u>you</u> can show: $j = \frac{9}{8}(\Theta\mu_p)\varepsilon\frac{V_a^2}{d^3}$
  - ➢ That is, the mobility is now reduced by Θ
- More often there is an exponential distribution of traps, in which case we have trap-filled limited conduction:

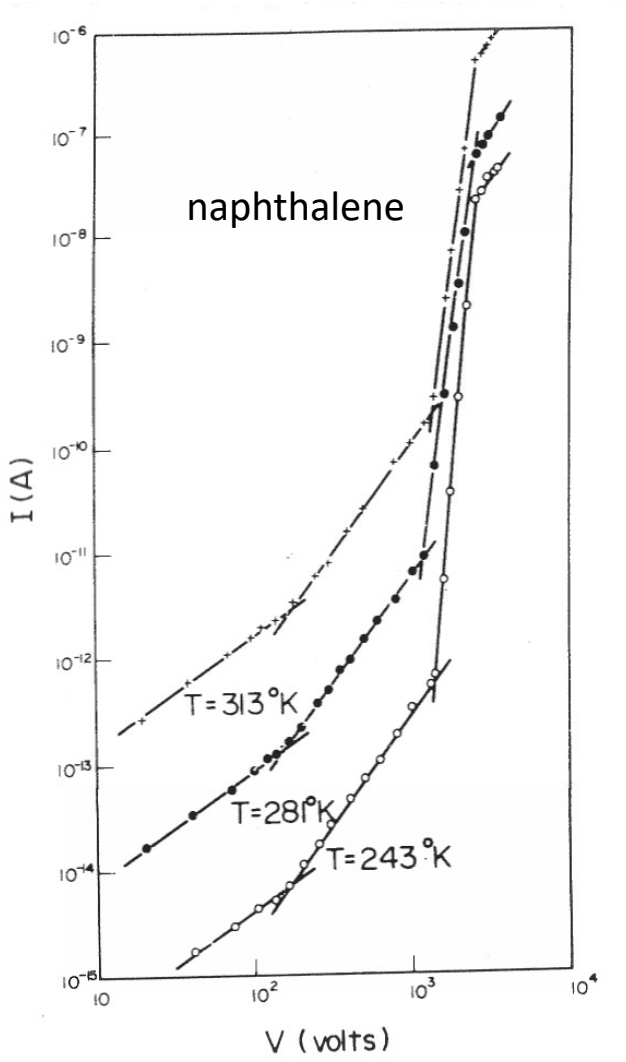
$$j_{TFL} = q\mu N_{HOMO}\left[\frac{\varepsilon m}{q(m+1)N_t}\right]^m\left[\frac{2m+1}{m+1}\right]^{m+1}\frac{V_a^{m+1}}{d^{2m+1}}$$

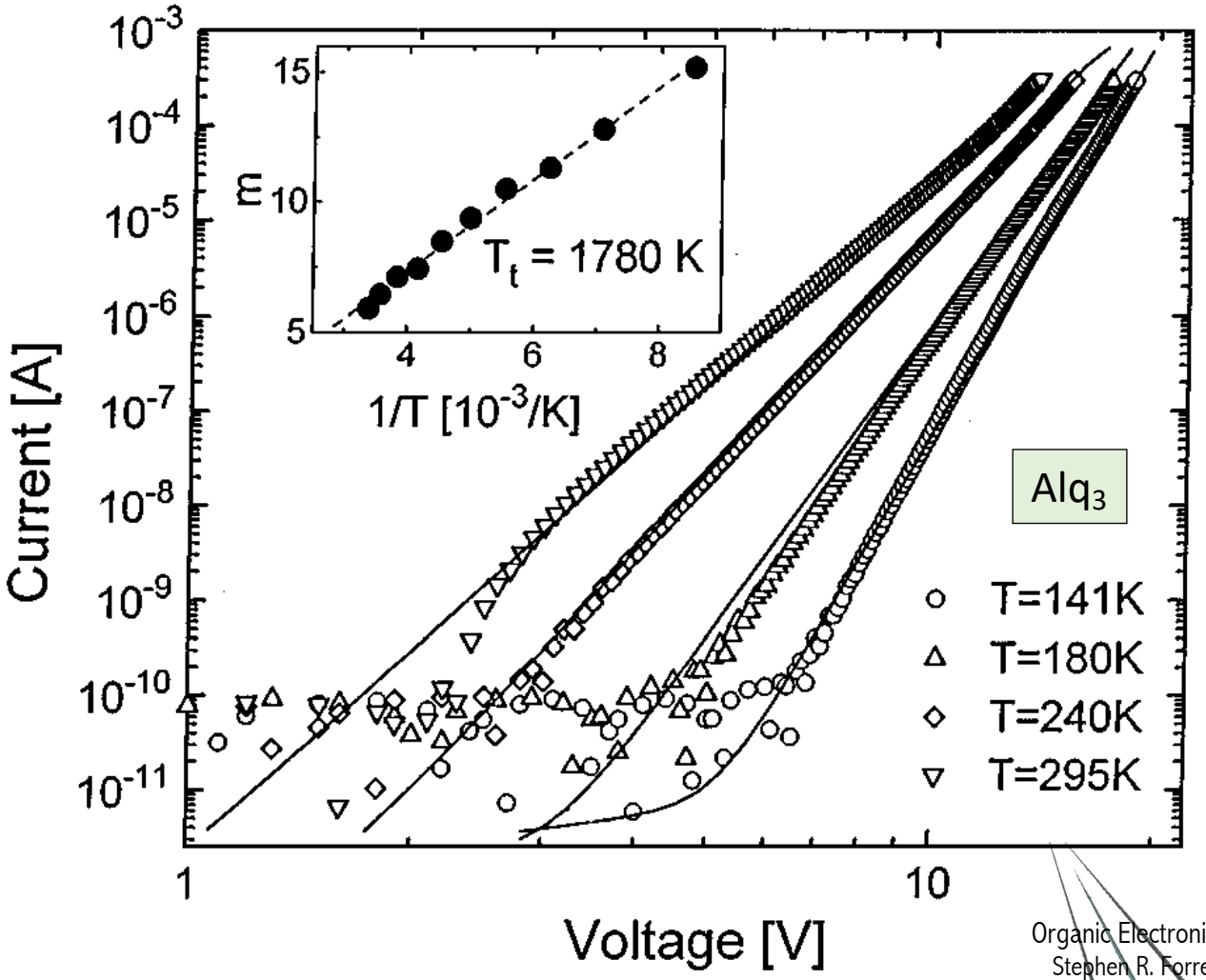


- $m=T_t/T$ where T_t is the characteristic trap temperature
  - Define $p_t = N_t\exp\left(-\left(E_{Fp}-E_{HOMO}\right)/k_BT_t\right)$
  - Leading to: $p = N_{HOMO}\exp\left(-\left(E_{Fp}-E_{HOMO}\right)/k_BT\right) = N_{HOMO}\exp\left(-\left(E_{Fp}-E_{HOMO}\right)/k_BT_t\left[T_t/T\right]\right)$

$$p = N_{HOMO}\left(\frac{p_t}{N_t}\right)^{T_t/T} \Rightarrow p_t = N_t\left(\frac{p}{N_{HOMO}}\right)^{1/m}$$

Examples of TFL-SCL





Multiple ohmic, SCL and TFL regions

M. Campos, Mol. Cryst. Liq. Cryst. **18**, 105 (1972)

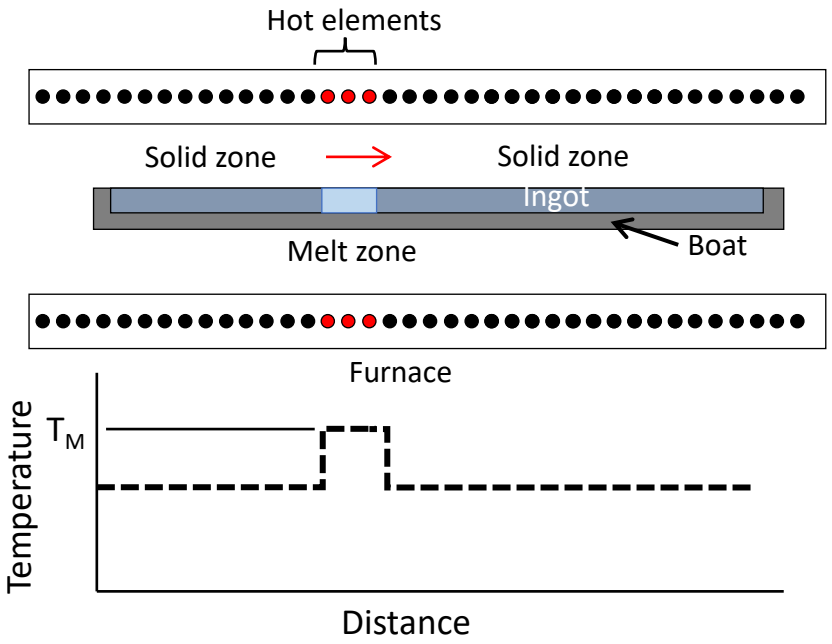
P. E. Burrows, et al., *J. Appl. Phys.*, **79**, 7991 (1996).

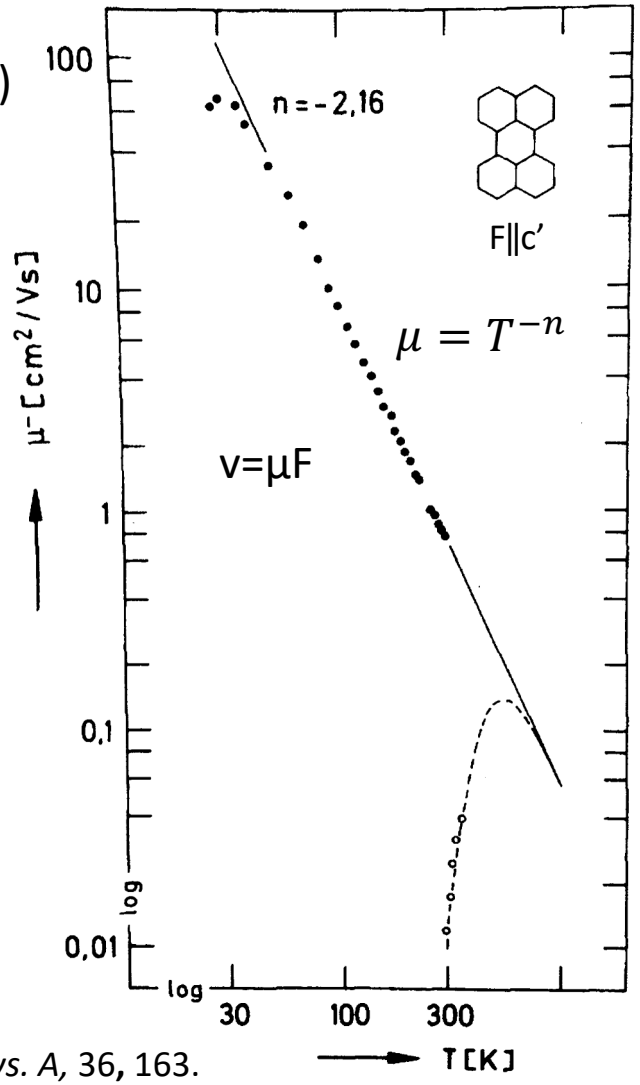
Non-Dispersive Mobility in Ultrapure Organics

n = 1.5 band transport

n = 2 acoustic phonon scattering

High purity achieved via zone refining (see Ch. 5)





W. Warta, R. Stehle & N.Karl, 1985. *Appl. Phys. A,* 36, 163.

Time of Flight Experiment
Ultrapurified Naphthalene Crystals

- Current pulse

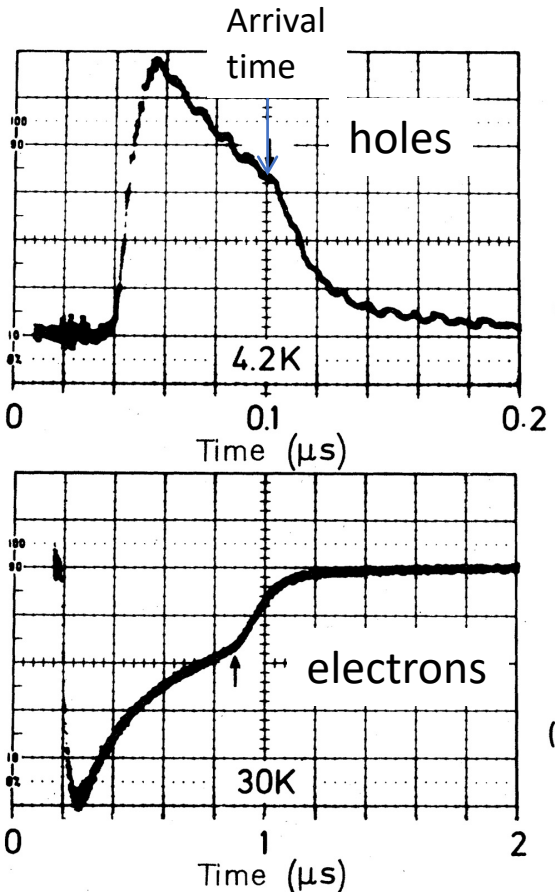
$v>10^6$ cm/s!

$\lambda=v\tau$

$\tau=\mu m^*/q$

$v=(3k_BT/m^*)^{½}$

➔$\lambda=(\mu/q)(3m^*k_BT)^{½}$



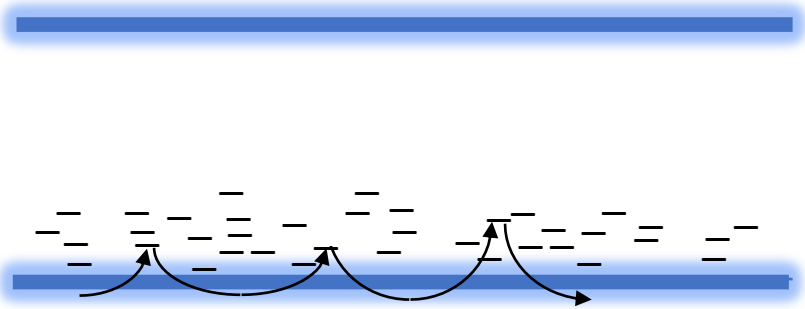
From the data on naphthalene:

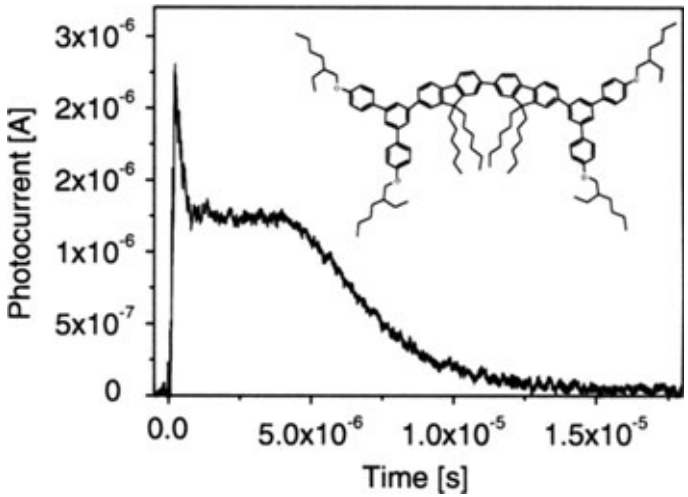
m^*~3-15m_0

$\lambda \sim 8a$: definitely in the band transport regime

TOF Mobility with Traps

- In the presence of defect states, charges continually trap and de-trap during transit
  - The mobility is not a good number—there are several mobilities, one for each carrier
  - Results in **dispersive transport**





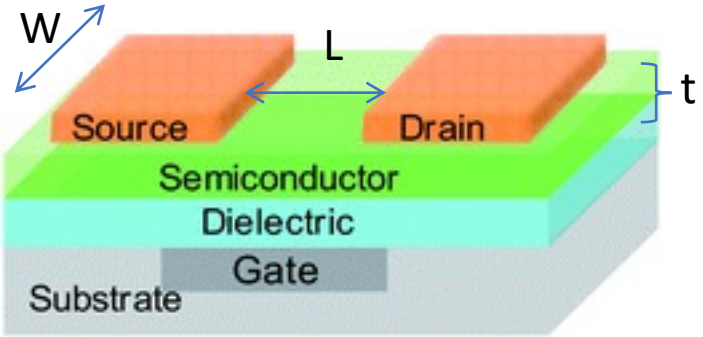
Gambino S, et al. (2008) Org Electron 9, 220

- Initial spike: Charge motion prior to energetic relaxation in the DOS if the RC time constant is short (i.e. reactance small)
- Plateau and broad tail indicate dispersive transport: many different arrival times from trapping/de-trapping during transit.

Measuring Charge Mobility

Transfer characteristics of thin film transistors (OTFTs)

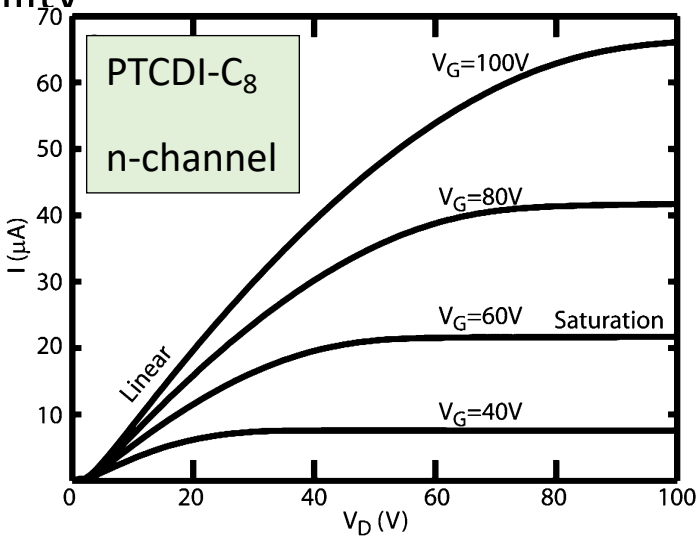
- This measures an interface property, **not** bulk mobility
- Can be strongly influenced by interface trapping
- Can be AC or DC Measurement
  - Almost always used in the less reliable DC mode

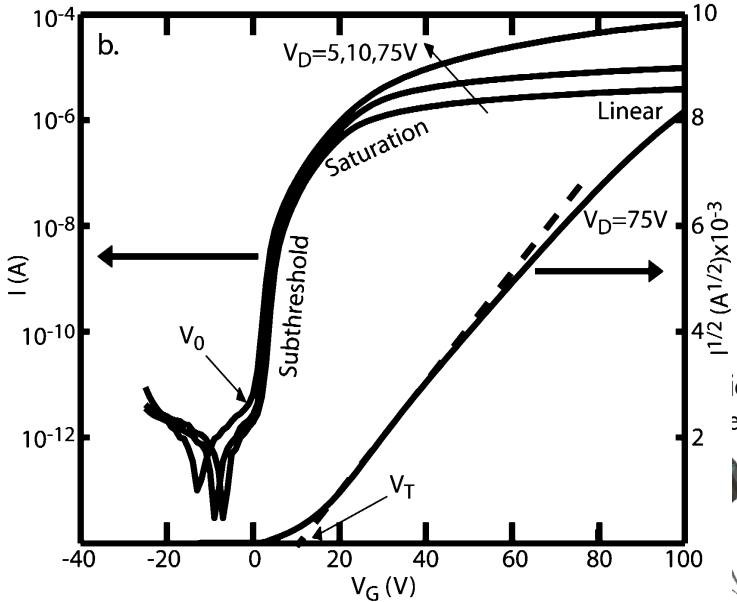


Bottom gate, top contact
(BG/TC) source-drain OTFT

$$I_D = = \frac{W}{2L} C_G \mu_{sat} \left(V_G - V_T \right)^2 \quad \text{(saturation)}$$

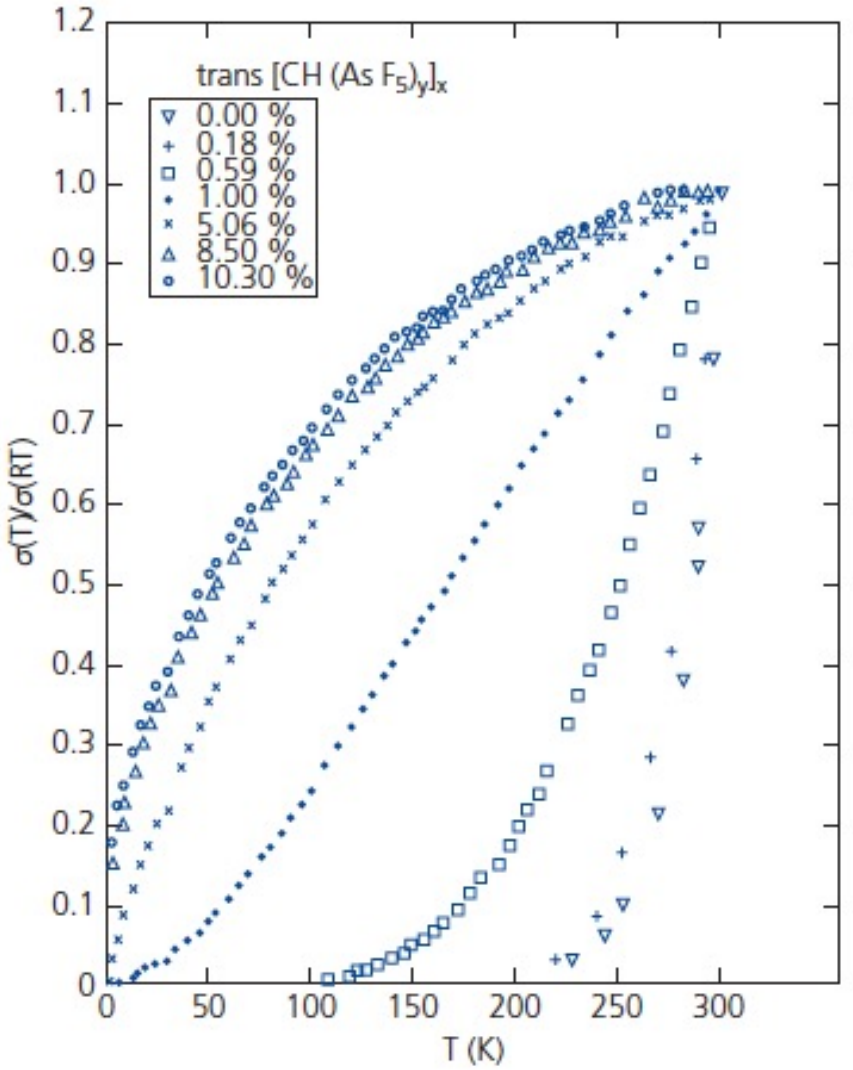
Plot of $I_D^{1/2}$ vs. V_G gives both μ_{sat} and V_T

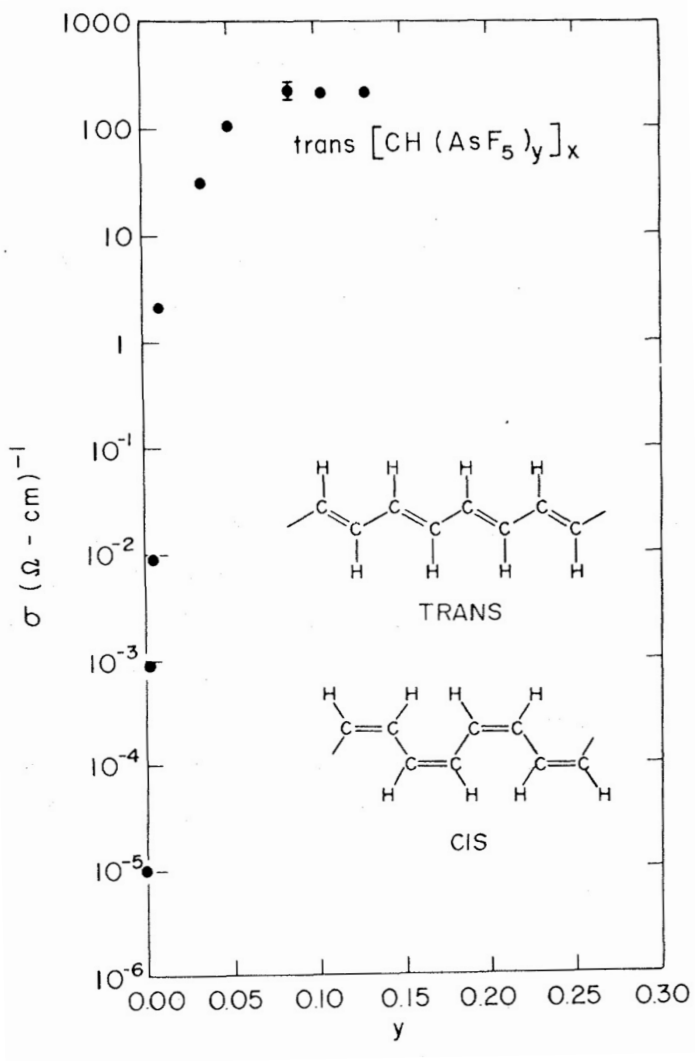




Doping of Organics to Increase Conductivity

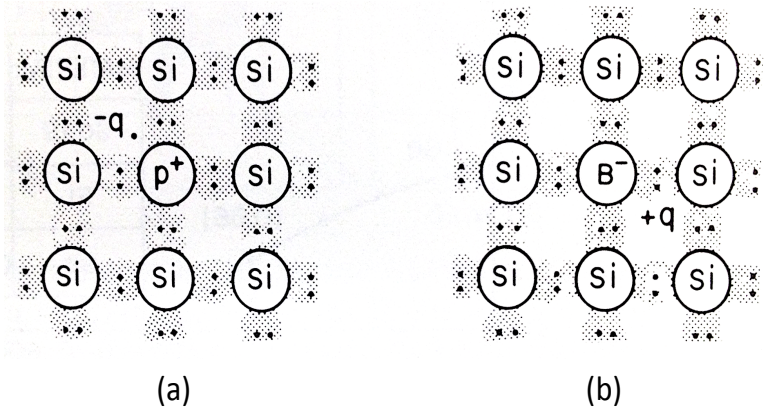
Heeger, Shirakawa, MacDiarmid, et al. Phys. Rev. Lett., **39** 1098 (1977)



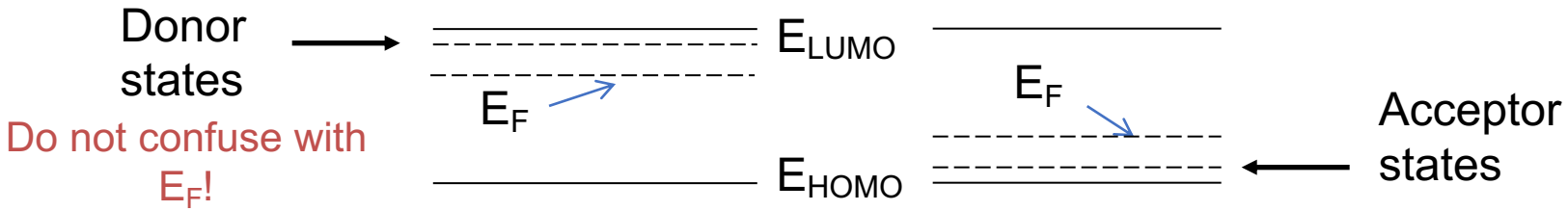


Doping in Organics: Not entirely similar to inorganics

Substitutional doping in inorganics



But no shared bonds in organics!

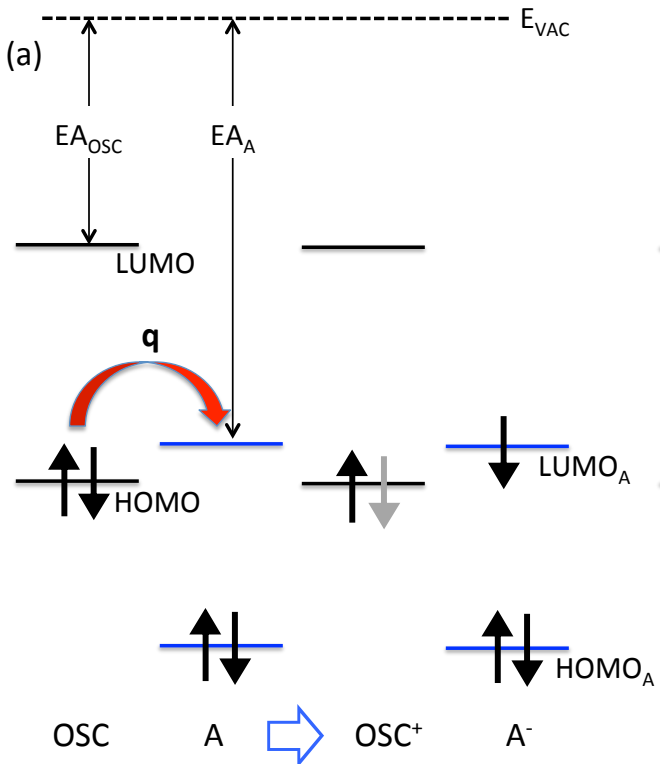


$$n = N_{LUMO} \exp\left(\frac{E_F - E_{LUMO}}{k_B T}\right) \qquad p = N_{HOMO} \exp\left(\frac{E_{HOMO} - E_F}{k_B T}\right)$$

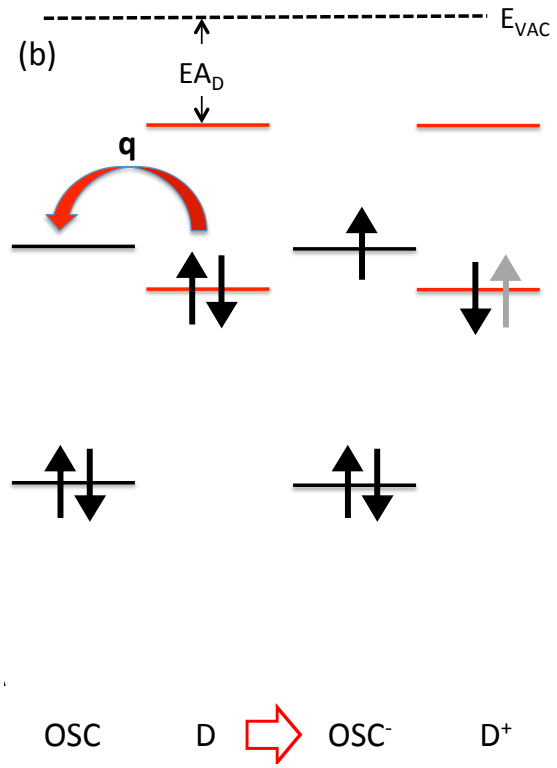
$\Rightarrow$ Law of mass action: $n_i^2 = N_{HOMO} N_{LUMO} \exp\left[-\frac{E_G}{k_B T}\right]$

Doping at the molecular level

Involves charge transfer between dopant and host

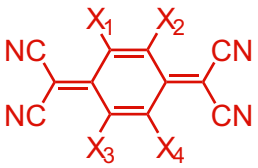


p-type doping

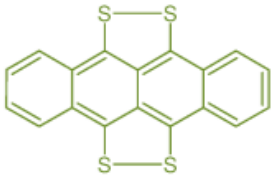


n-type doping

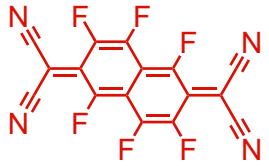
Example *molecular* dopants



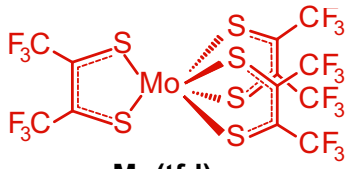
TCNQ: $X_{1...4}$= H
FTCNQ: $X_{1...3}$= H, X_4 = F
F_2TCNQ: $X_{1,4}$= H, $X_{2,3}$= F
F_4TCNQ: $X_{1...4}$= F



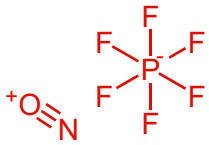
TTN



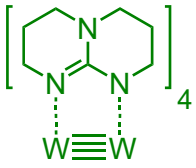
F_6TCNNQ



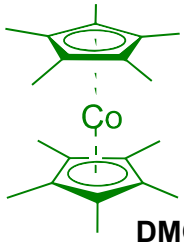
Mo(tfd)$_3$



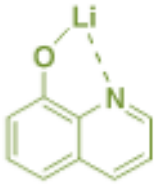
$NOPF_6$



W_2(hpp)$_4$



DMC



Liq

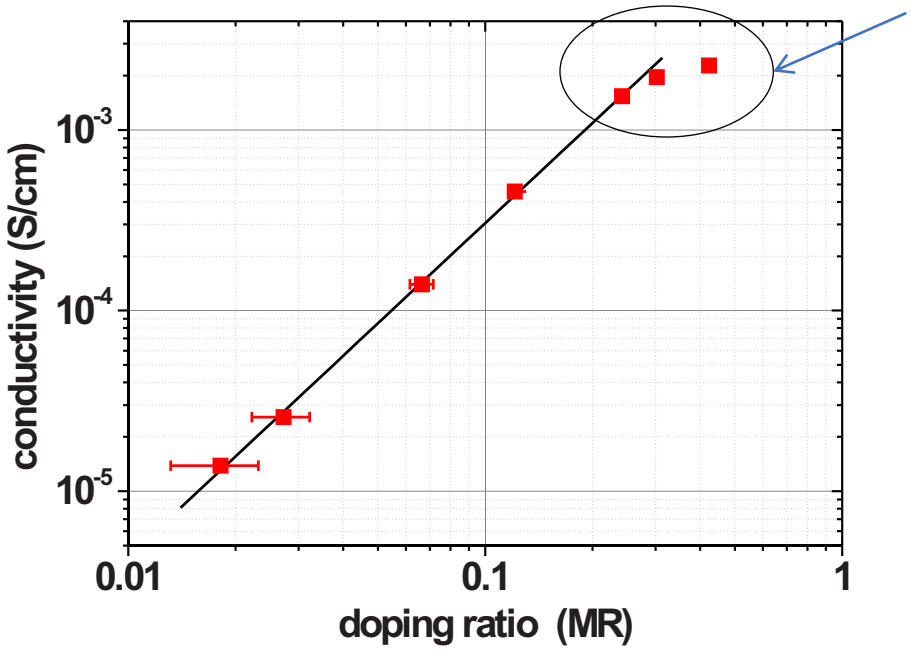
red=acceptors; green=donors

But there are metallic dopants too: Cs, Li, etc.

LiF + Al cathodes common in OLEDs:

$$LiF + Al \rightarrow Li^{+} + e^{-} + AlF$$

Difficult to get a high conductivity
(it takes *a lot* of dopant)



N,N,N',N'-tetrakis(4-methoxyphenyl)-benzidine with **F_4-TCNQ**.

Olthof et al., J. Appl. Phys., 106, 103711 (2009)

Recombination

Charge diffusion equations

$$\frac{\partial n}{\partial t} = \frac{1}{q}\nabla \bullet \mathbf{j}_e - R_e + G_e \qquad \frac{\partial p}{\partial t} = -\frac{1}{q}\nabla \bullet \mathbf{j}_h - R_h + G_h$$

Using Fick's Law

$$\mathbf{j}_e = qD_e\nabla n$$

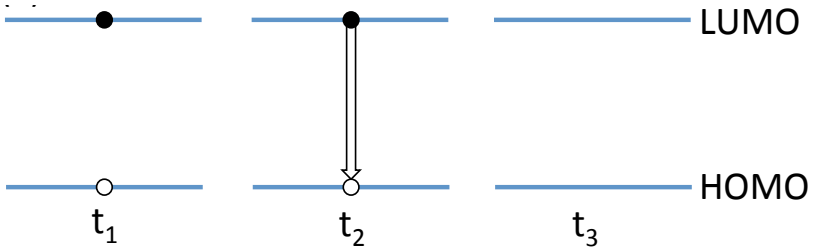
$$\mathbf{j}_h = -qD_h\nabla p$$

Gives:

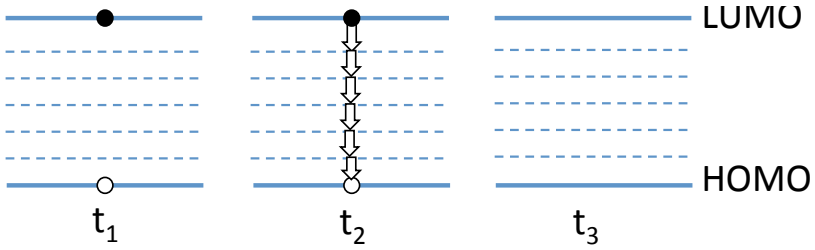
$$\frac{\partial n}{\partial t} = D_e\nabla^2 n - R_e + G_e \qquad \frac{\partial p}{\partial t} = D_h\nabla^2 p - R_h + G_h$$

Direct HOMO-LUMO Recombination and via Midgap States

Direct (Band-to Band) Recombination

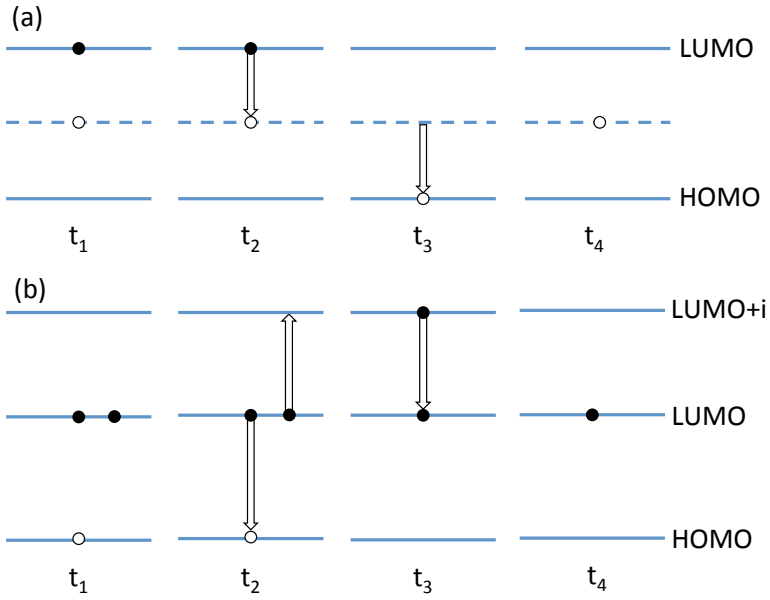


Multiple Step Recombination



$$R_e^{dir} = \frac{n - n_0}{\tau_e} = \frac{\Delta n}{\tau_e}$$

Shockley-Read-Hall Recombination



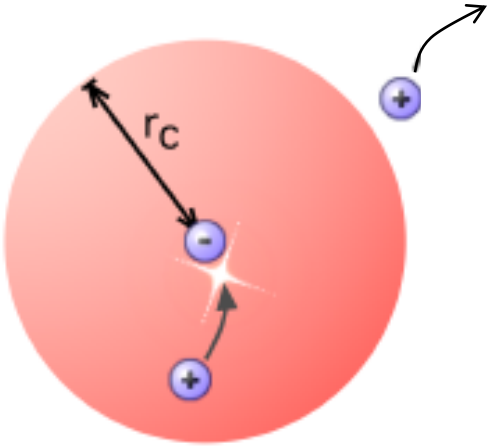
Auger Recombination

$$R^{SRH} = \frac{np - n_i^2}{\tau_e\left(p + p_1\right) + \tau_h\left(n + n_1\right)}.$$

equilibrium restoring force

Langevin (Bimolecular) Recombination

- When two carriers meet….



Capture radius: When Coulomb = thermal energy

$$r_c = \frac{q^2}{4\pi\varepsilon_r\varepsilon_0 k_B T}.$$

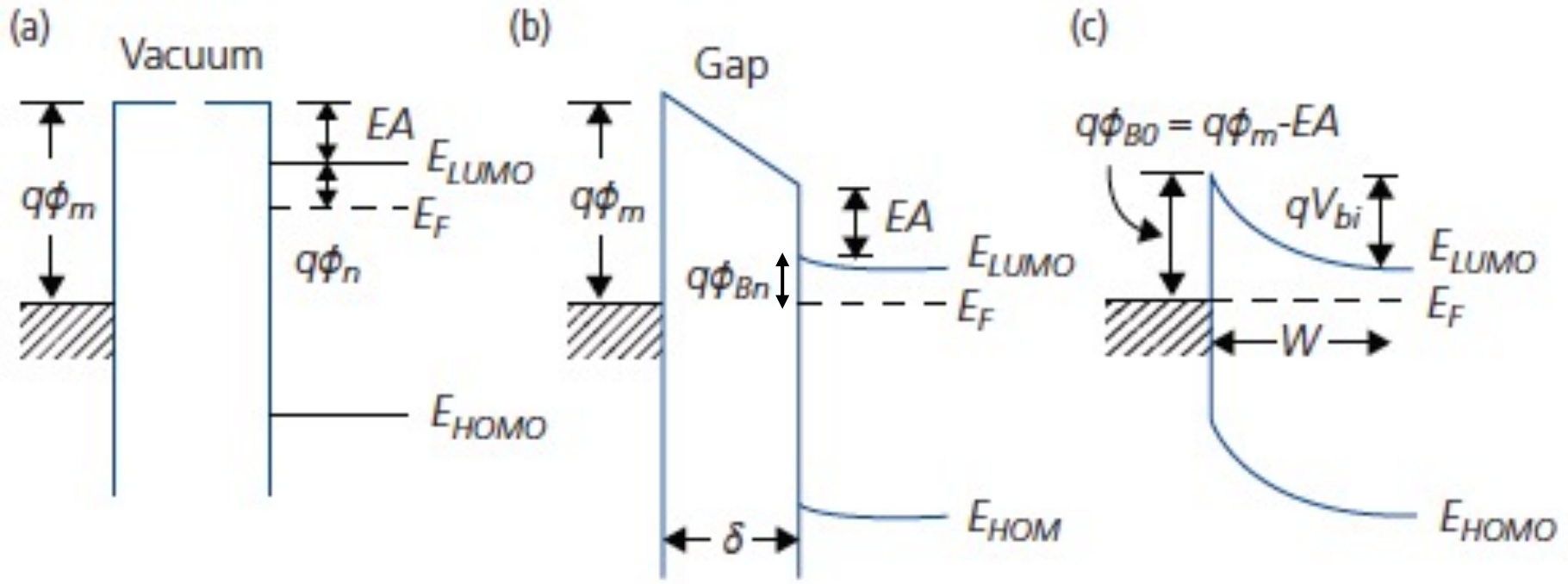
Langevin recombination rate constant:

$$\gamma_L = \frac{q}{\varepsilon_r\varepsilon_0}(\mu_e + \mu_h) = \frac{q}{\varepsilon_r\varepsilon_0}\mu_T.$$

Yielding the recombination rate (and hence current)

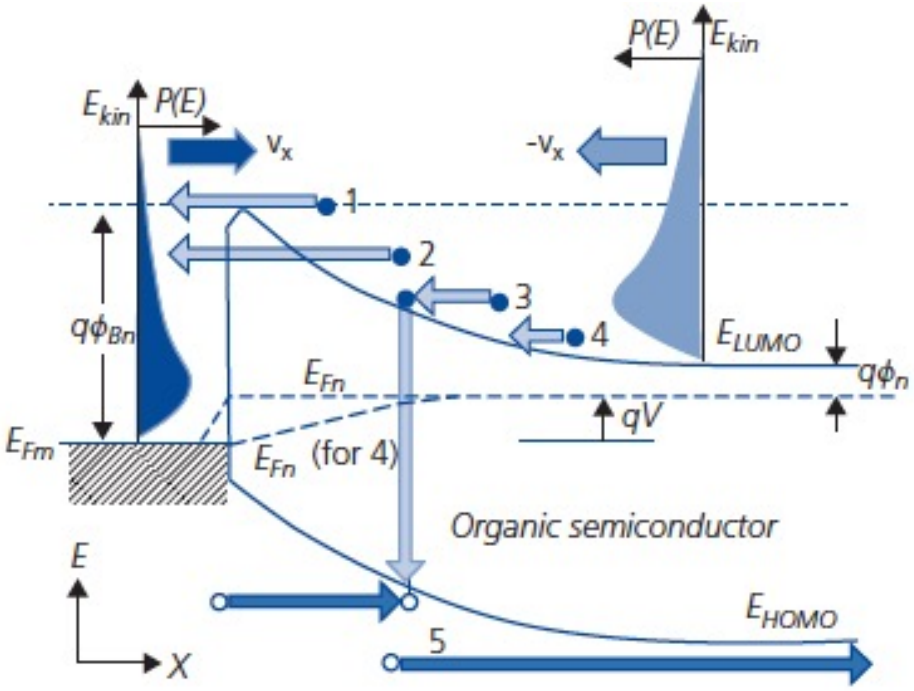
$$R^L = \gamma_L\left(pn - n_i^2\right)$$

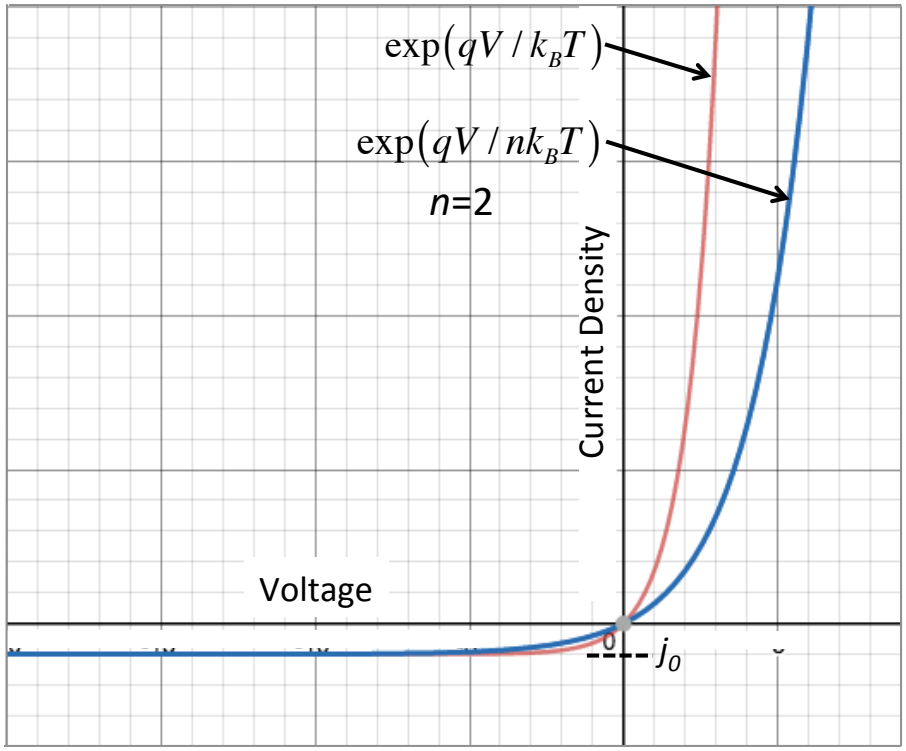
Schottky barriers



Traps Play a Big Role in Determining Barrier Heights at Metal-Semiconductor Junctions

Current sources across M-O Junctions



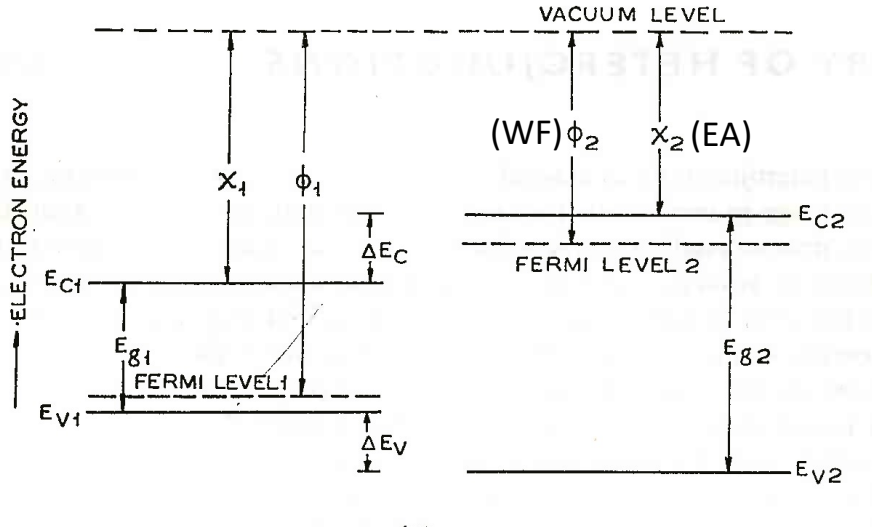


$$j = j_0\left(\exp\left(qV/k_BT\right)-1\right)$$

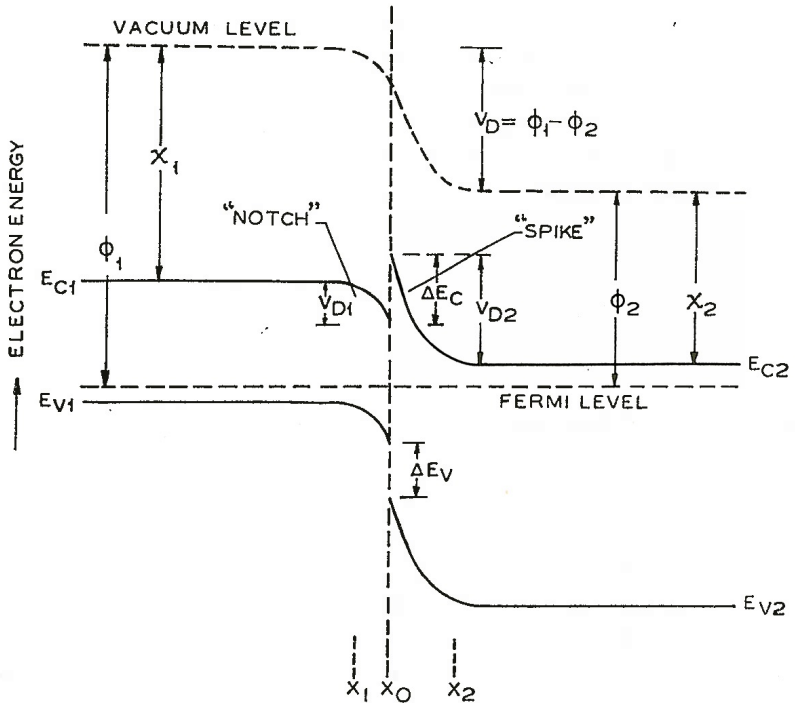
$$j_0 = j_{0TE} = A^*T^2\exp\left(-q\phi_{B0}/k_BT\right) \qquad A^* = \frac{4\pi q m^* k_B^2}{h^3}$$ (Richardson Constant)

Heterojunctions: Organic-organic contacts

- A heterojunction is a contact between two dissimilar materials (typically semiconductors)
- HJs play a vital role in all photonic devices, and many electronic devices too.
- Some definitions:

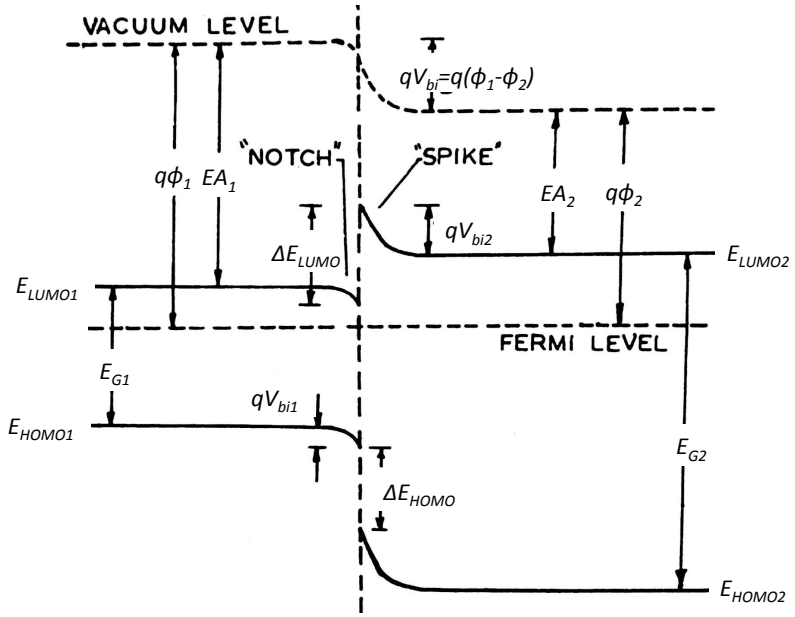


Anisotype HJ



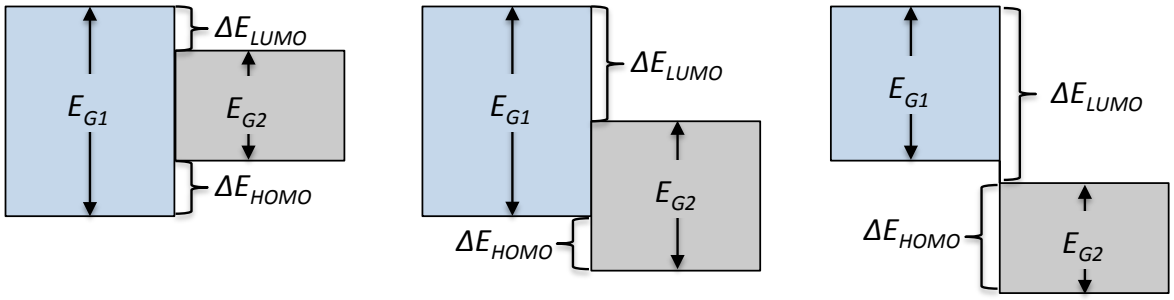
- Anderson's rule: $\Delta E_c = |\chi_1 - \chi_2|$ (doesn't work so well for inorganics due to charge transfer; better for organics)
- $\Delta E_v = \Delta E_g - \Delta E_c$
- Band bending due to free charge: organics tend toward flat bands

Isotype vs. Anisotype HJ



n-N isotype HJ

Classification of HJ types



Type I
Nested

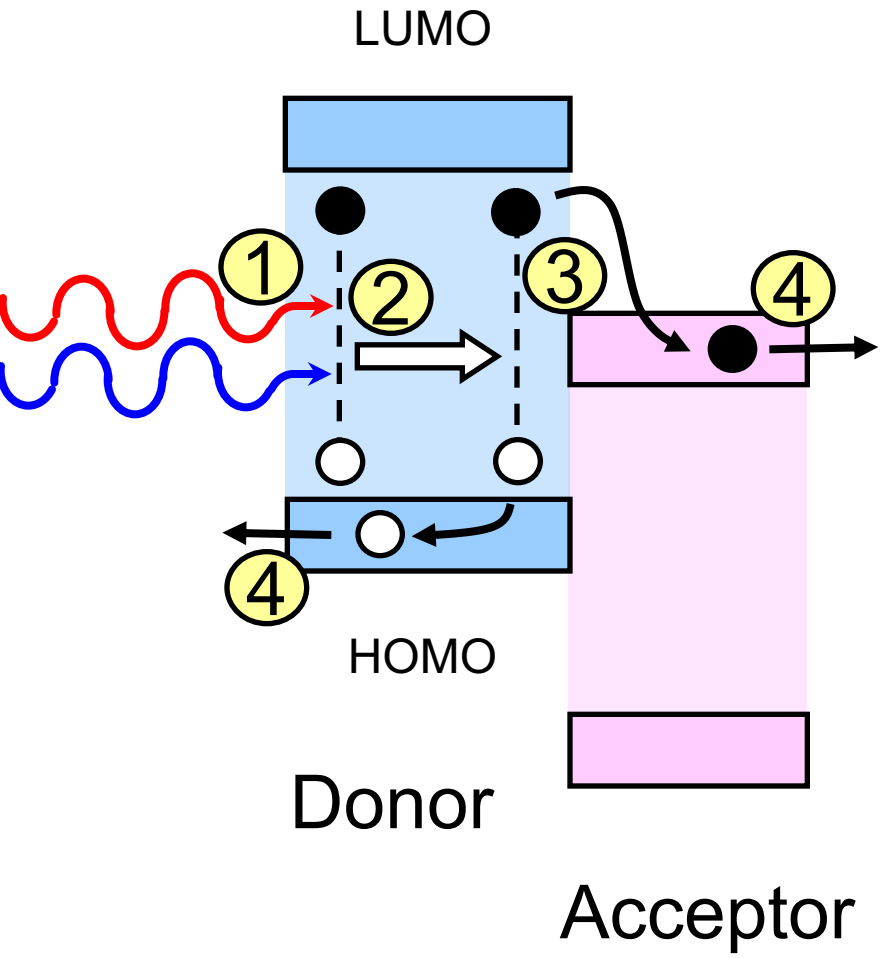
Type II
Staggered

Type III
Broken Gap

Photoinduced Charge-Transfer at a Type II HJ

The Basis of OPV Operation

Processes occuring at a Donor-Acceptor heterojunction



1. Exciton generation by absorption of light ($1/\alpha$)
2. Exciton diffusion over ~L_D
3. Exciton dissociation by rapid and efficient charge transfer
4. Charge extraction by the internal electric field

Typically: $L_D << 1/\alpha$

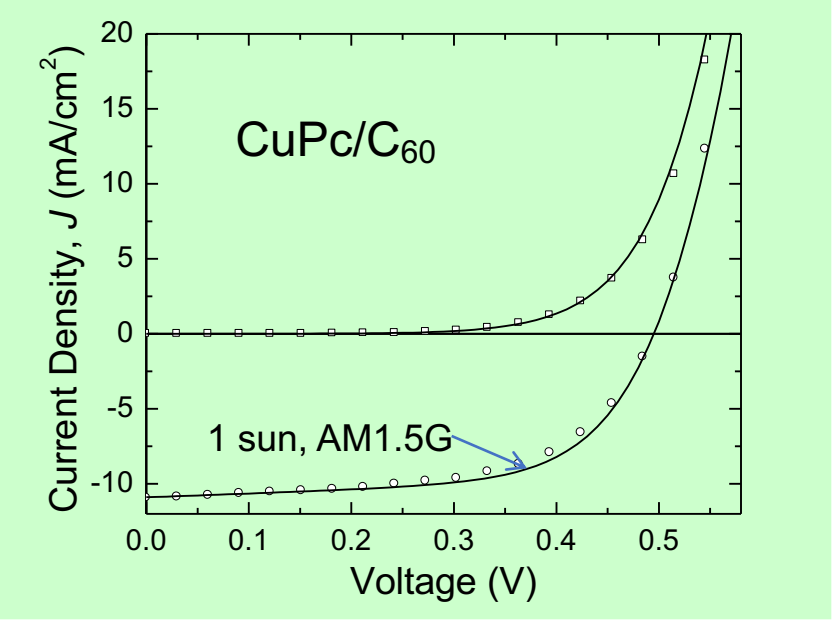
Ideal Diode Equation: Problem Statement

- The Shockley Equation (1949):

$$J = J_o(\exp(qV_a / k_bT) - 1) - J_{ph}$$

has been successfully applied (e.g. Xue and Forrest, 2004) to organic heterojunction cells. But the physics is wrong!

- Why does it "work"?
- Is there a more appropriate relationship for organic (i.e. *excitonic*) HJs?



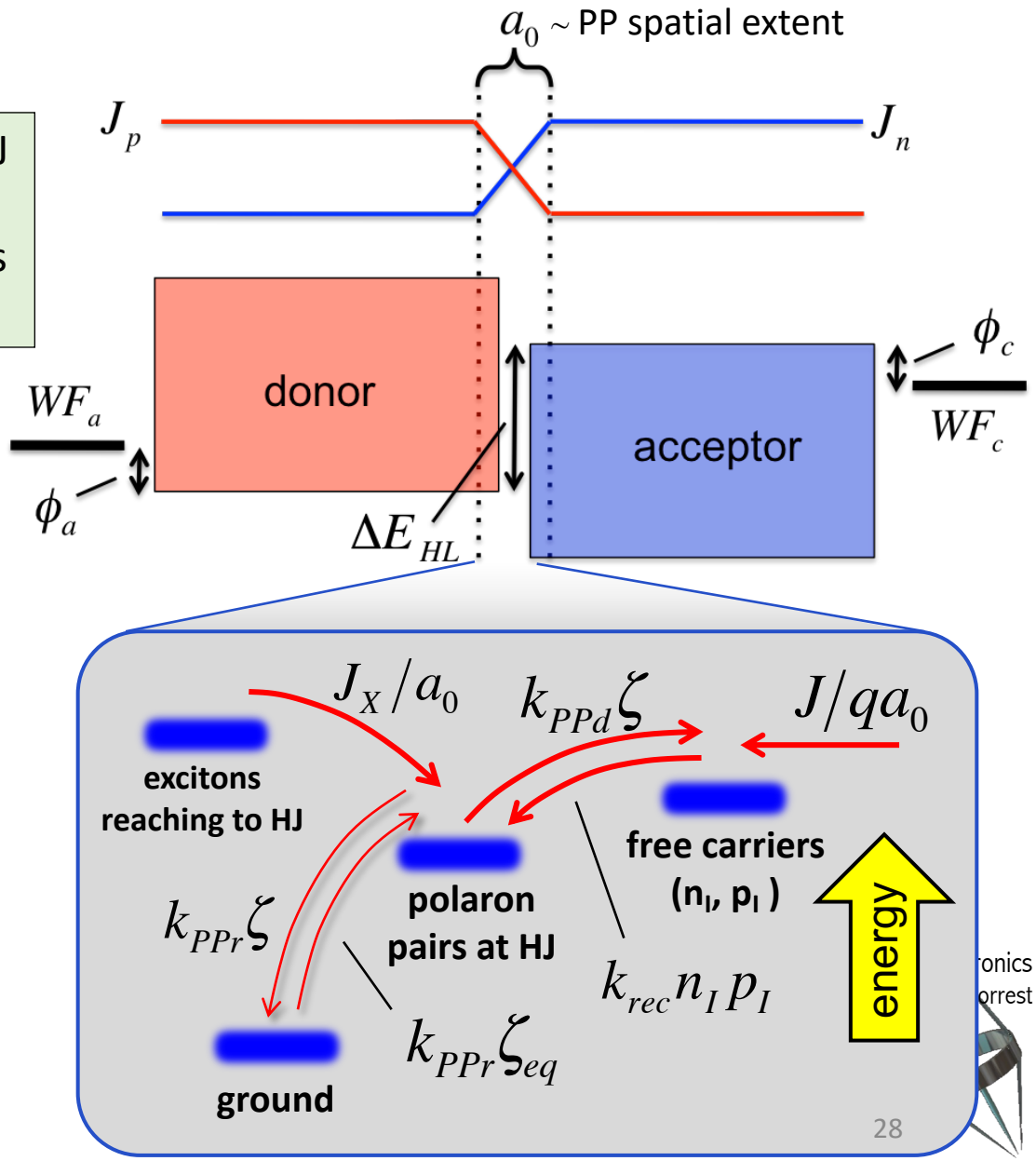
Excitonic Heterojunctions:

Controlled by **energy transport**, *not* charge transport

1. Excitons diffuse with current J_X to HJ
2. Separate into polaron pair across HJ
3. PP can either dissociate into carriers
4. Or recombine to ground state

ζ=PP density
k_{PPr}=PP recombination rate
k_{PPd}=PP dissociation rate
k_{rec}=charge recombination rate
J=electron current
WF=work function
n_I, p_I=charge at interface

A polaron pair at the interface is equivalent to a charge transfer (CT) state



N. C. Giebink, et al. Phys. Rev. B, **82**, 155305 & 155306 (2010).

Derivation of the Ideal Diode Eq.

"Just because you have an ideal diode equation does not mean you have an ideal diode"

- The rate equations in steady state:
  - Excitons: $\frac{J_X}{a_0} - k_{PPr}(\zeta - \zeta_{eq}) - k_{PPd}\zeta + k_{rec} n_I p_I = 0,$
  - Polarons: $k_{PPd}\zeta - k_{rec} n_I p_I + \frac{J}{q a_0} = 0,$

Rate Equations + Fermi Stats:

$$J_0 \left\{ \exp(qV_a / k_B T) - \frac{k_{PPd}}{k_{PPd,eq}} \right\} - J_{ph}$$

$$J = q a_0 k_{rec} N_{HOMO} N_{LUMO} (1 - \eta_{PPd}) \exp(-\Delta E_{HL} / k_b T) \left\{ \exp(qV_a / k_b T) - \frac{k_{PPd}}{k_{PPd,eq}} \right\} - q \eta_{PPd} J_X$$

electron & hole DOS

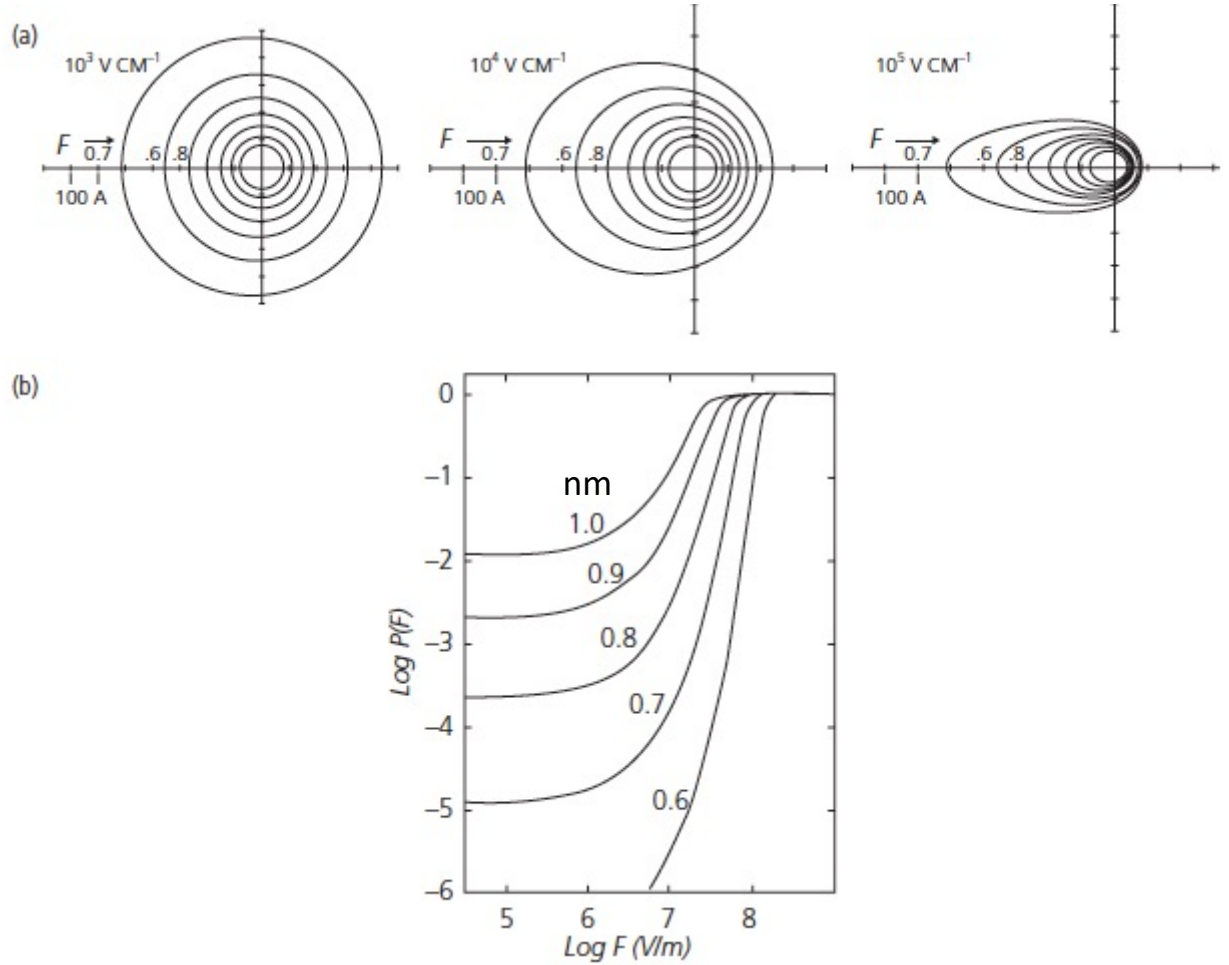
PP dissociation efficiency

$$\eta_{PPd} = \frac{k_{PPd}}{k_{PPr} + k_{PPd}}$$

equilibrium dissociation rate

Onsager-Braun Exciton Polarization

- Why there is a voltage dependence to k_{ppd} that gives *j-V* slope under reverse bias



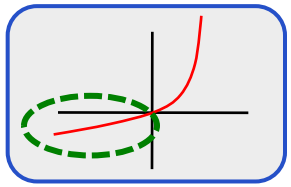
Probability for exciton ionization

Consequences of the diode equation

$$J_0\left\{\exp(qV_a / k_BT) - \frac{k_{PPd}}{k_{PPd,eq}}\right\} - J_{ph}$$

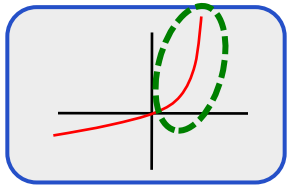
Reverse Bias:

- strong dissociation: $k_{PPd} > k_{PPd,eq}$ → saturation current increases →



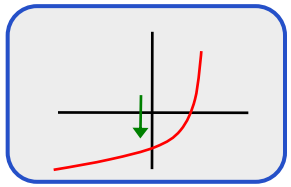
Forward Bias:

- weak dissociation: $k_{PPd} < k_{PPd,eq}$ → exponential diode current →



Illumination:

- photogenerated PPs: J_X , $\eta_{PPd} > 0$ → photocurrent addition →



N. C. Giebink, et al. Phys. Rev. B, **82**, 155305 & 155306 (2010).

Including traps

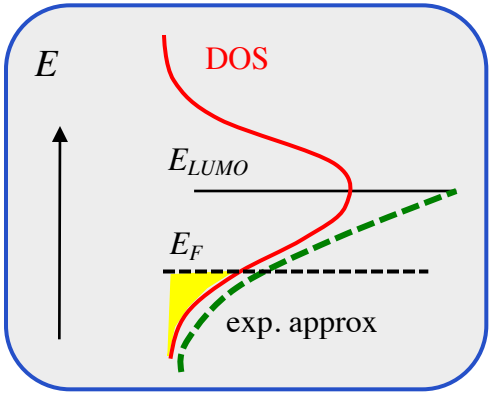
Disordered materials:

- broad density of states (DOS)⇒continuous trap distribution:

Trap Distribution Function

$$n_t \approx H_A \exp\left(\frac{E_{Fn} - E_{LUMO}}{k_b T_{t,A}}\right) \approx H_A \left(\frac{n}{N_{LUMO}}\right)^{1/l_A}$$

$$\text{where } l_A = T_{t,A}/T \Longrightarrow n_A = \frac{l_A}{\delta_D (l_A - 1) + 1}$$

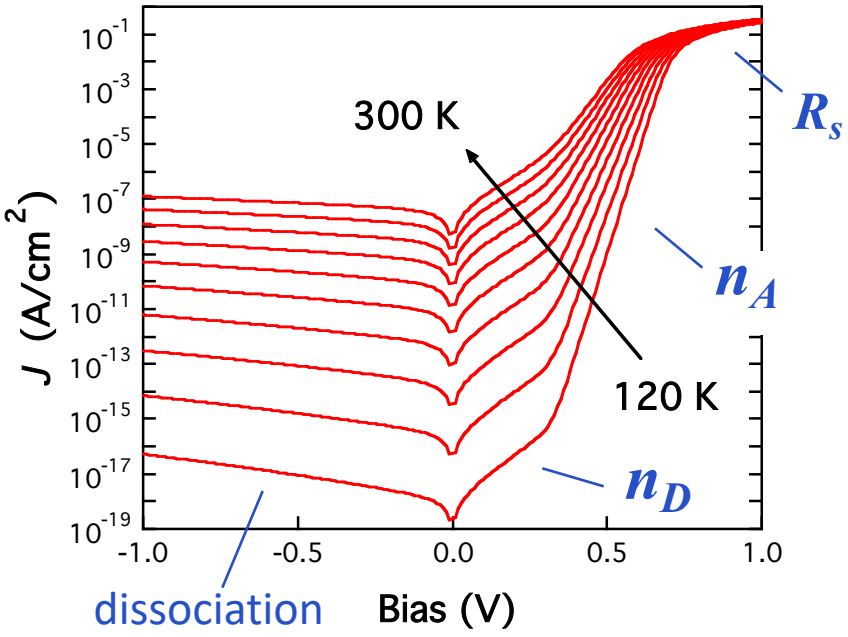


- Ideality factors: n_D, n_A depend on *shape* of trap DOS
  - e.g. n=2 for uniform distribution between HOMO and LUMO

Dark Current With Traps

- General form including series resistance:

$$J = J_{sD}\left[\exp\left(\frac{q\left(V_a - JR_s\right)}{n_D k_b T}\right) - \frac{k_{PPd}}{k_{PPd,eq}}\right] + J_{sA}\left[\exp\left(\frac{q\left(V_a - JR_s\right)}{n_A k_b T}\right) - \frac{k_{PPd}}{k_{PPd,eq}}\right] - q\eta_{PPd}J_X$$

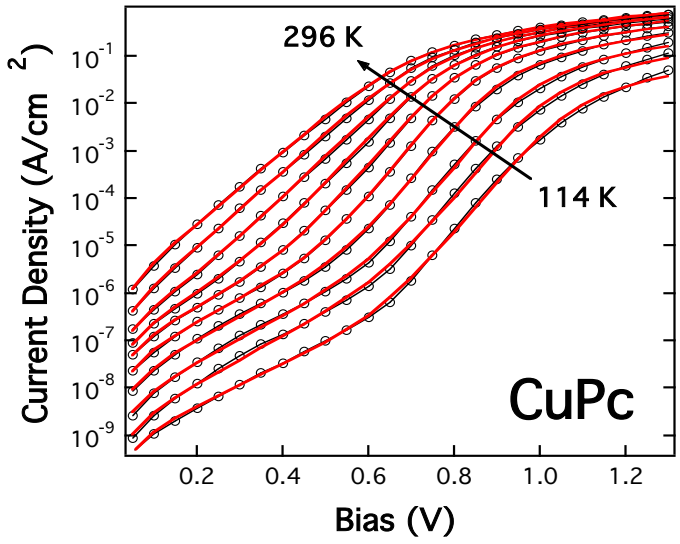


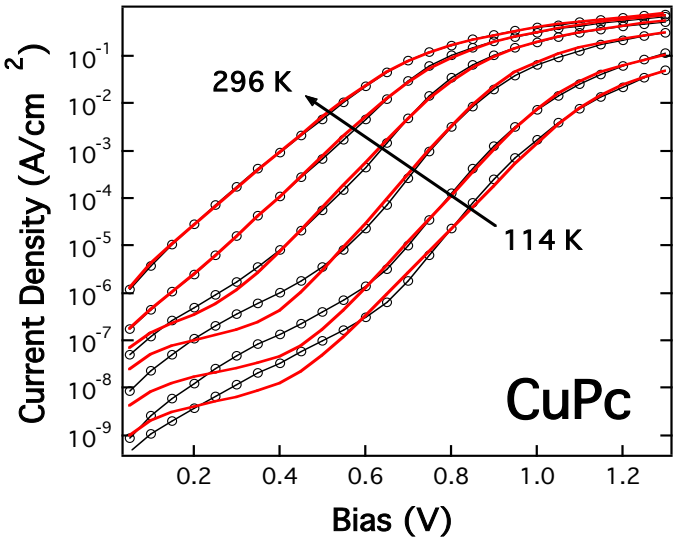
N. C. Giebink, et al. Phys. Rev. B, **82**, 155305 & 155306 (2010).

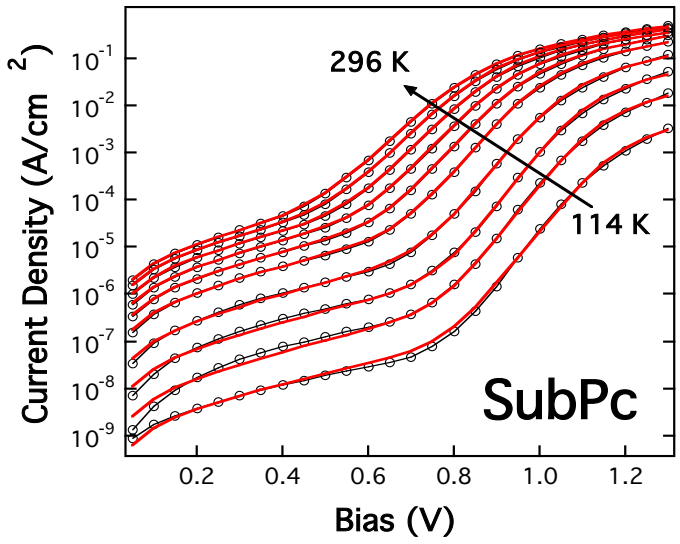
J-V Fits to Diode Eq. with Traps

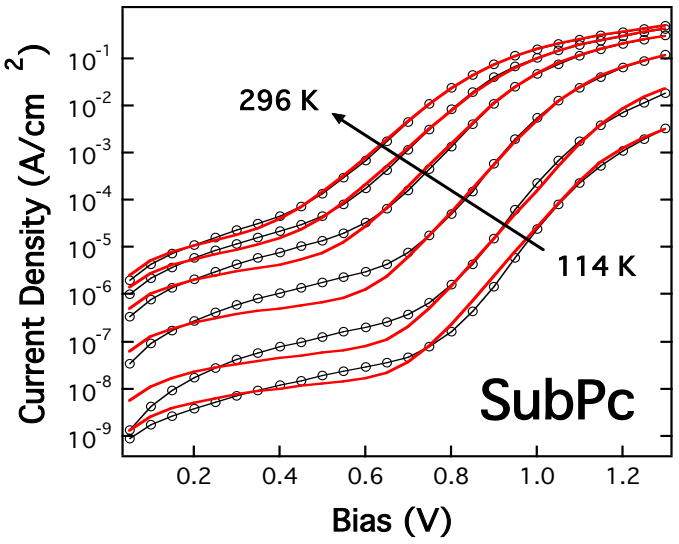
Org. HJ with Traps

Shockley Eq.







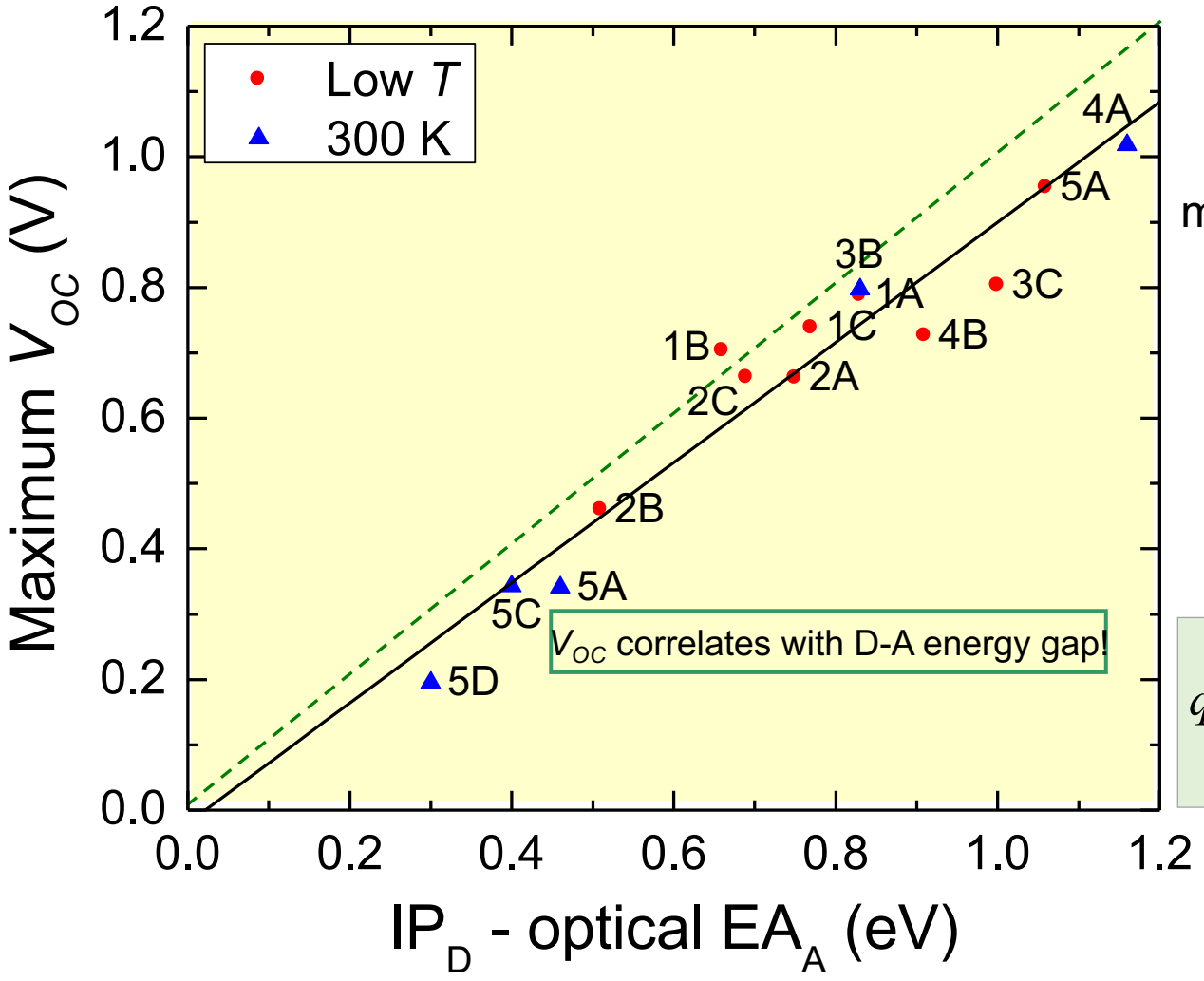


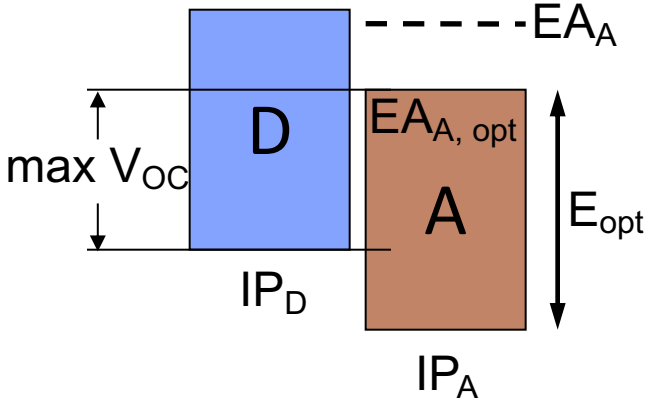
Acceptor

C_{60}

N. C. Giebink, et al. Phys. Rev. B, **82**, 155305 & 155306 (2010).

Dependence of V_{OC} on HJ Energies for Many Different D-A Combinations





A single rule fits all materials

E_{HL} $\quad$ $-E_B$

$$qV_{OC}^{\max} = IP_D - EA_A - \frac{q^2}{4\pi\varepsilon_0\varepsilon_r r_{DA}}$$

PP Binding Energy

B.P. Rand, et al., *Phys. Rev. B*, **75**, 115327 (2007).

What the theory tells us

Open Circuit Voltage

$$qV_{oc} = \left(\Delta E_{HL} - E_B\right) - k_b T \ln\left[\frac{k_{PPr} N_{HOMO} N_{LUMO}}{\zeta_{\max} J_X / a_0}\right]$$

- At maximum sustainable power $J_x \sim a_o N_{HOMO} k_{PPr}$
  - More excitons cannot be supported.

Also: $\zeta_{\max} \sim N_{HOMO} \sim N_{LUMO}$

Thus: $qV_{oc} = \Delta E_{HL} - E_B$ ➡ *as observed!* (*E_B=polaron energy*)

- Slope under reverse bias due to PP recombination – eliminates R_p

Electronic Transport in Organics -What we learned

- Origins of electronic band structure
- Concept of polarons (large and small)
- Charge transfer
- Conductivity, effective mass and mobility
- Doping
- Effects of trapped charge
- Schottky Barrier Diodes
- Organic Heterojunctions