

Week 1-10

Electronic Properties 4

Traps at Metal-Organic Contacts

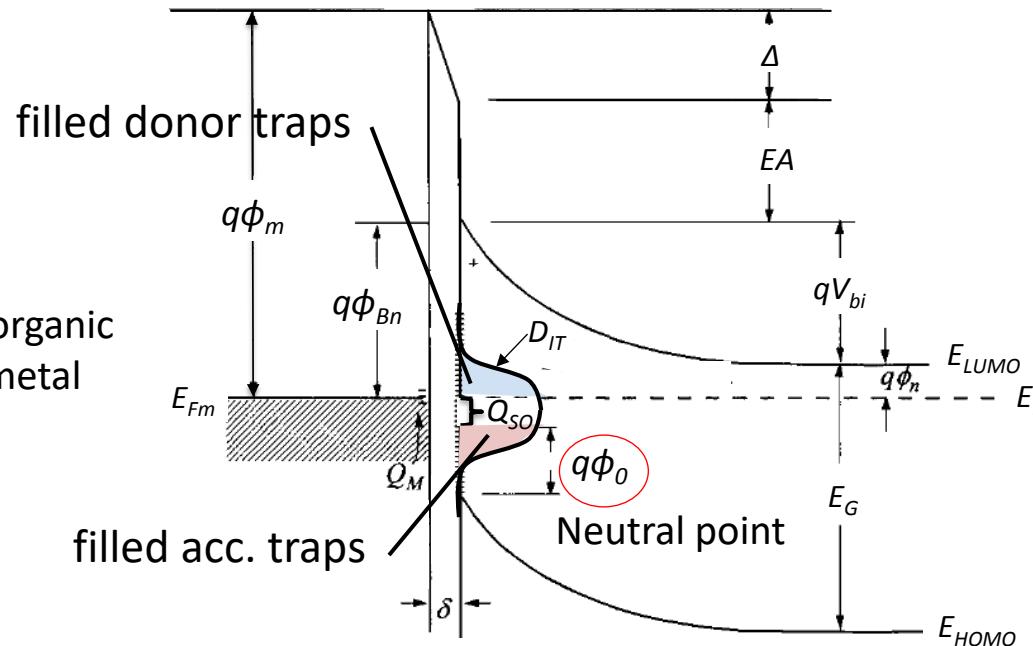
Organic Homojunctions and Heterojunctions

Chapter 4.6.3-4.7.2

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Traps Play a Big Role at Metal-Semiconductor Junctions

Q_{SO} =surface charge in organic
 Q_M =surface charge at metal

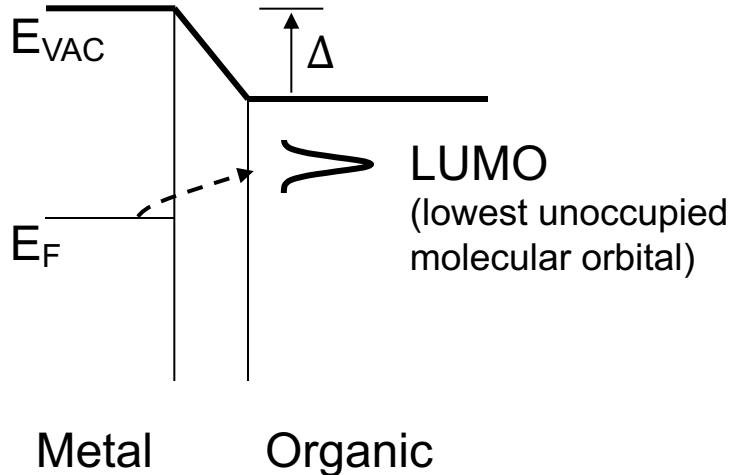


$$q\phi_{Bn} = -\sqrt{\frac{2q^2\varepsilon_r N_D \delta^2}{\varepsilon_\delta^2 \varepsilon_o}} (q\phi_{Bn} - q\phi_n) + \frac{q^2 \delta D_{IT}}{\varepsilon_\delta \varepsilon_o} (E_G - q\phi_{Bn} - q\phi_0) - EA + q\phi_m$$

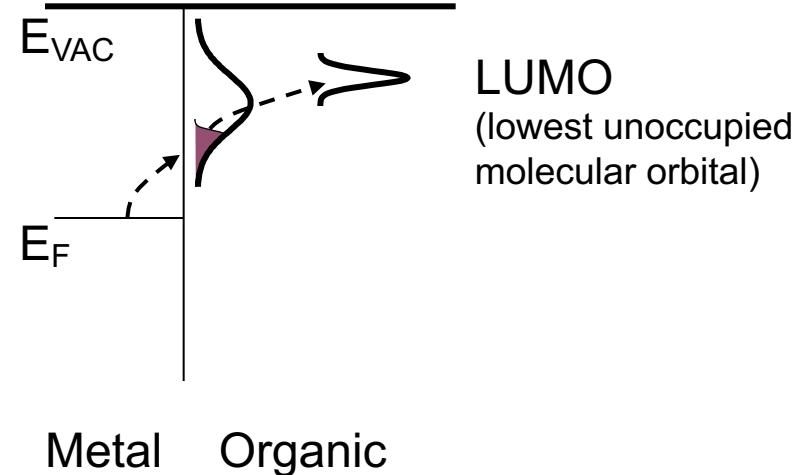
$D_{IT} \rightarrow \infty$, then $q\phi_{Bn} = E_G - q\phi_0$ (independent of $q\varphi_m$)

Charge Injection from Contacts: Mechanisms

The metal work function is not an accurate measure of cathode injection efficiency due to presence of interface dipole.



An interfacial dipole shifts the energy at the surface of the organic film

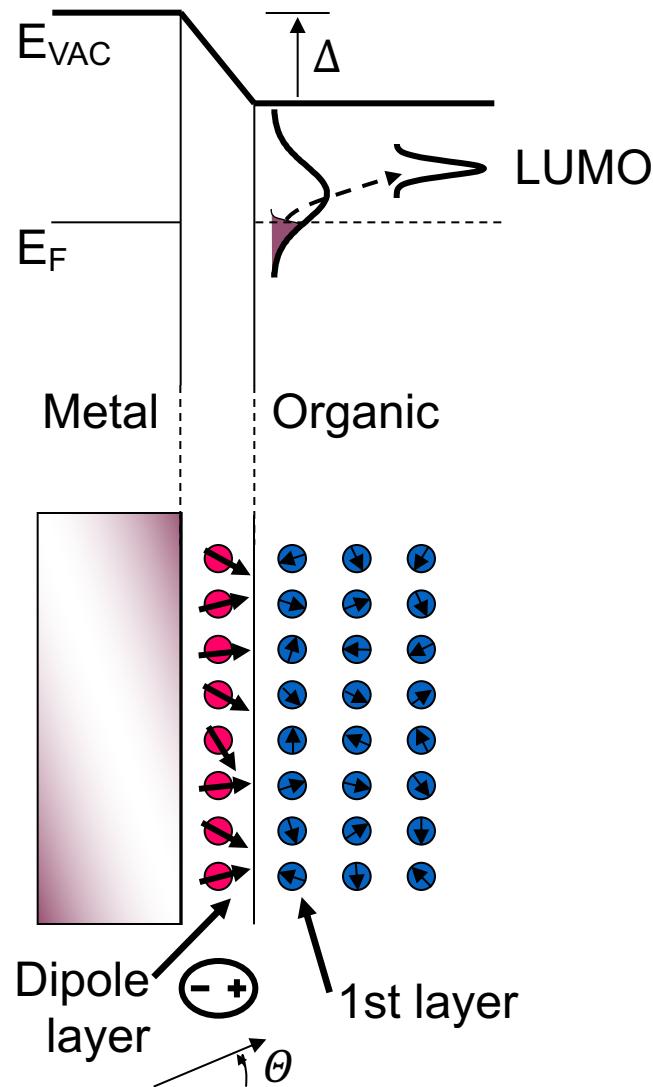


Intermediate states may reduce the overall hopping barrier

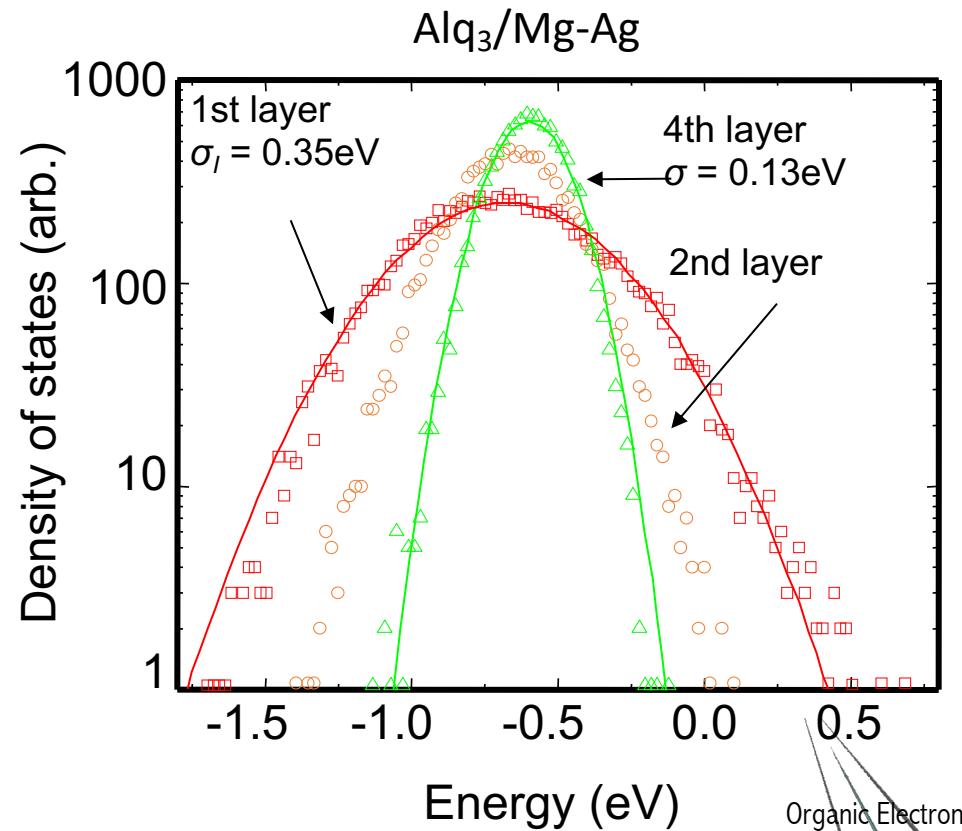
The presence of an interfacial dipole induces the intermediate states

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Origins and Disorder in the Interface Dipole



Assuming interfacial dipoles of strength $\sim 30D$, and Gaussian orientational disorder with variance $\sigma = \pi$ radians, we get:

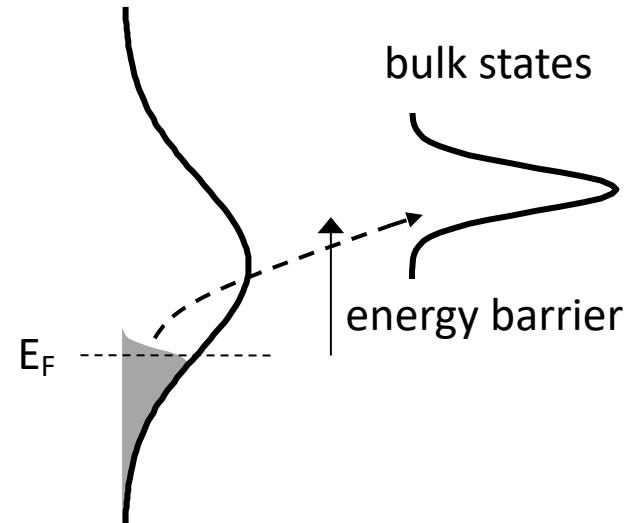


Alternatively, disorder may be due to local variation in the magnitude of the dipoles

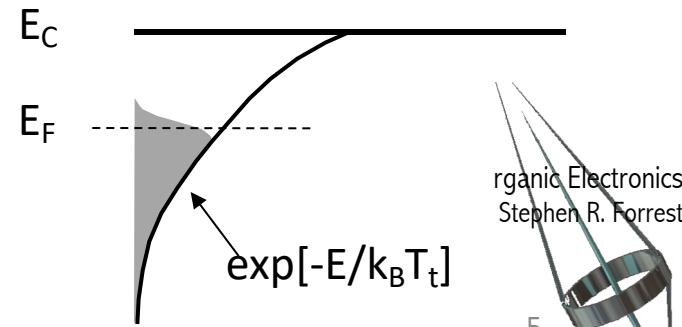
Features of the Interface State Model

- Limiting step is hop from organic interface to organic bulk
- Transport can be explained using only intrinsic properties: No need for extrinsic effects such as traps.
- Broad distribution of interface states generates power-law transport
-similar to trapped charge limited transport
(distribution of states below a conduction level)

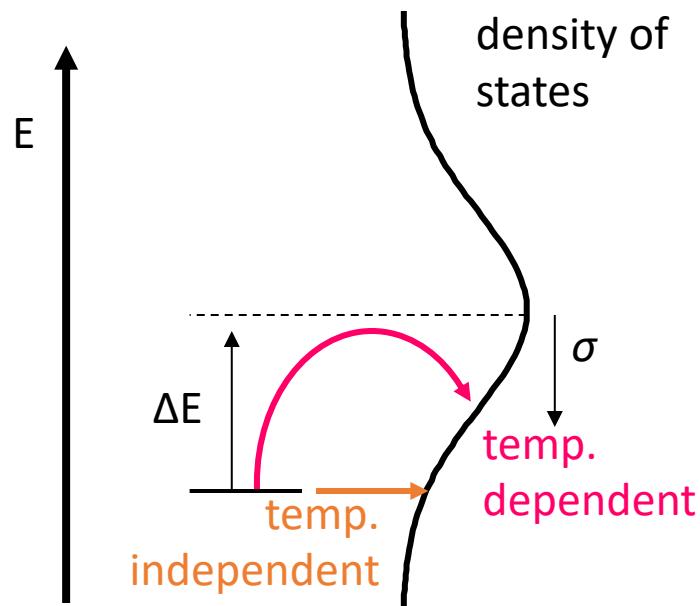
interface states



Classical trap charge limited conduction



Gaussian Disorder Revisited



TEMPERATURE DEPENDENCE & DISORDER

- Injection current is sum of upward and downward hops.

- But only upward hops are temperature dependent (Miller-Abrahams picture).

Transition between temperature dependent and independent regimes:

$$k_B T_0 \sim \frac{\sigma^2}{4E_b}$$

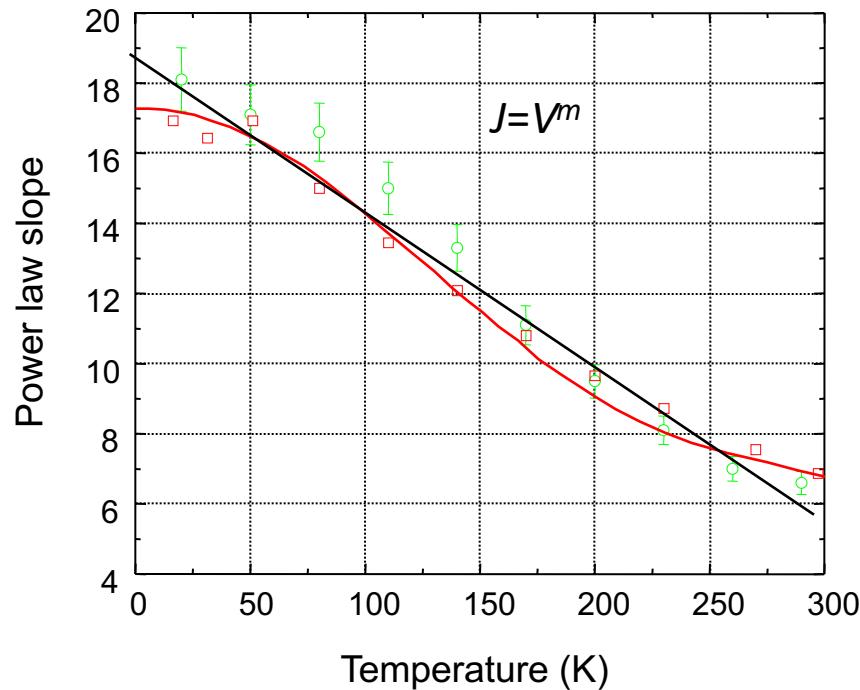
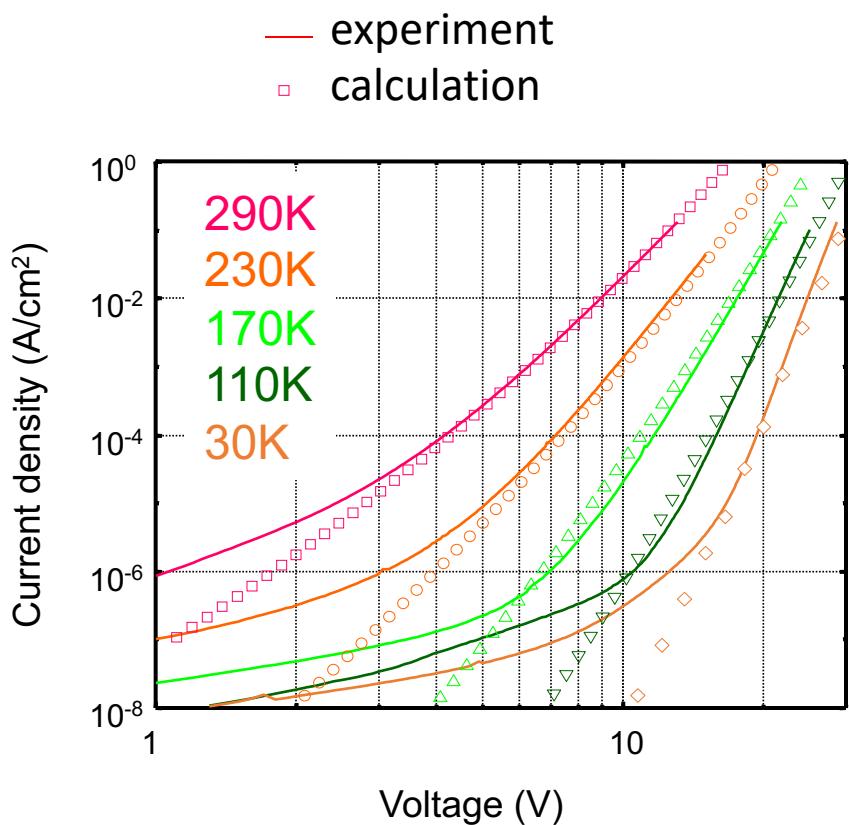
Polaron binding energy $\sim 0.2 \text{ eV}$

Disorder increases temperature-independent resonant current



T-Dependence of the Mg:Ag/Alq₃ Interface

Device: 300Å Ag / 1000Å 25:1 Mg:Ag / 1200Å Alq₃ / 1000Å Mg:Ag / SiN_x / Si



Fit using polaron model for interfacial hop:
includes temperature dependence of phonon distribution

Interface Charge Transport

Interfacial model accurately describes charge injection.

- Generates power law current-voltage characteristics.
- Approximately matches temperature and thickness dependencies.

Model also applicable to metal/polymer interfaces.

Best cathodes dope surface layers of organic material with low work function metal.

- Low work function metals (Li, Mg) induce defects (via reaction), improving injection

Metal/organic dipoles are crucial to charge injection.

Modification of the injection barrier possible with understanding of interfacial dipoles

- Chemistry at interface
- Mechanisms underlying dipole formation
- Damage due to metal deposition

Derivation of Shockley's Ideal Diode Equation

“Just because you have an ideal diode equation does not mean you have an ideal diode”

- To understand organic junctions, we first must understand inorganic homojunctions

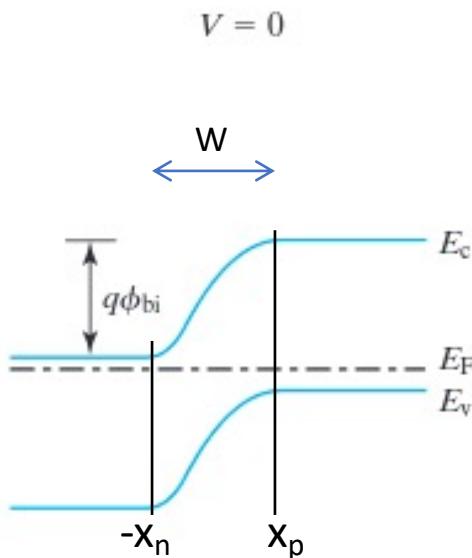
BUT

- Inorganic *p-n* junction diodes do not involve excitons, only free charges
- This derivation ignores the essential physics of organics.
- For *p-n* junctions, we solve the current equation (for electrons, low current limit):

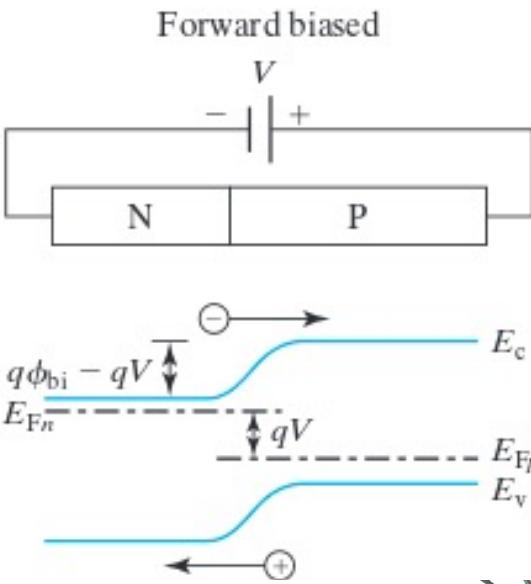
$$J_N = q\mu_n nF + qD_N \frac{dn}{dx} \approx 0$$

Drift

Diffusion



$V = 0$



Forward biased



Solution to the drift-diffusion equation

Assume near-equilibrium conditions

- Solve for F :

$$F = -\frac{D_N}{\mu_n} \frac{1}{n} \frac{dn}{dx} = -\frac{k_B T}{q} \frac{1}{n} \frac{dn}{dx}$$

$$V_J = \phi_{bi} - V_a = - \int_{-x_n}^{x_p} F dx = \frac{k_B T}{q} \ln n \Big|_{n(-x_n)}^{n(x_p)}$$

$$\Rightarrow n(-x_n) = n(x_p) e^{q(V_a - \phi_{bi})/k_B T}$$

- In thermal equilibrium: $n_{n0} p_{p0} = n_i^2 e^{q\phi_{bi}/k_B T}$ ϕ_{bi} = built in junction potential

$$\text{but } n_{p0} p_{p0} = n_i^2 \text{ (law of mass action) \& } \Delta n(x_p) = n(x_p) - n_{p0}$$

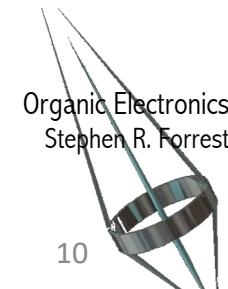
$$\text{BC: } n(x_p) = n_{p0} \text{ at } V_a = 0. \Rightarrow \Delta n(x_p) = n_{p0} (e^{qV_a/k_B T} - 1); \Delta p(-x_n) = p_{n0} (e^{qV_a/k_B T} - 1)$$

- Going back to the diffusion equation:

$$D_N \frac{d^2 \Delta p_n}{dx^2} - \frac{\Delta p_n}{\tau_p} = 0 \Rightarrow \frac{d^2 \Delta p_n}{dx^2} = \frac{\Delta p_n}{L_p^2}$$

with solutions

$$\Delta p_n(x) = p_{n0} (e^{qV_a/k_B T} - 1) e^{-x/L_p}$$



Ideal p-n junction diode equation

- The current density:

$$J_P(x) = -qD_P \frac{d\Delta p_n}{dx} = \frac{qD_P p_{n0}}{L_P} (e^{qV_a/k_B T} - 1) e^{-x/L_p}$$

but continuity says that $J(0) = J(x) = J$.

$$\Rightarrow J_P = \frac{qD_P p_{n0}}{L_P} (e^{qV_a/k_B T} - 1)$$

But for a doping density of N_D donors, law of mass action again says:

$$N_D p_{n0} = n_i^2$$

leaving us with:

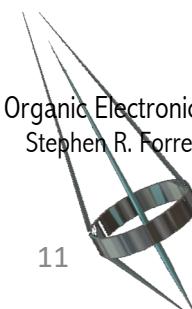
$$J_P = \frac{qD_P n_i^2}{N_D L_P} (e^{qV_a/k_B T} - 1) = q \frac{n_i^2}{N_D} \sqrt{\frac{D_P}{\tau_P}} (e^{qV_a/k_B T} - 1)$$

Finally adding in the contribution from electron minority carriers:

$$J = q \left[\frac{n_i^2}{N_D} \sqrt{\frac{D_P}{\tau_P}} + \frac{n_i^2}{N_A} \sqrt{\frac{D_N}{\tau_N}} \right] (e^{qV_a/k_B T} - 1)$$

Current determined by:

- Minority carrier diffusion and lifetime (not excitons)
- Doping concentrations
- Built-in junction potential



But is this relevant to organic homojunctions?

- The concept of recombination, and recombination statistics is relevant for all junction diodes
- But cannot ignore effects of
 - Broad density of states near frontier orbitals
 - Tunneling

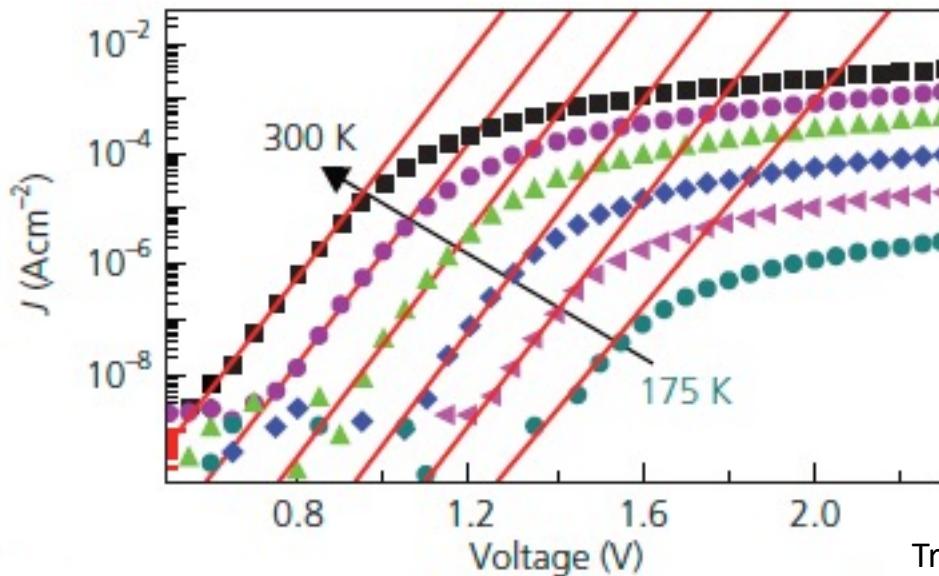
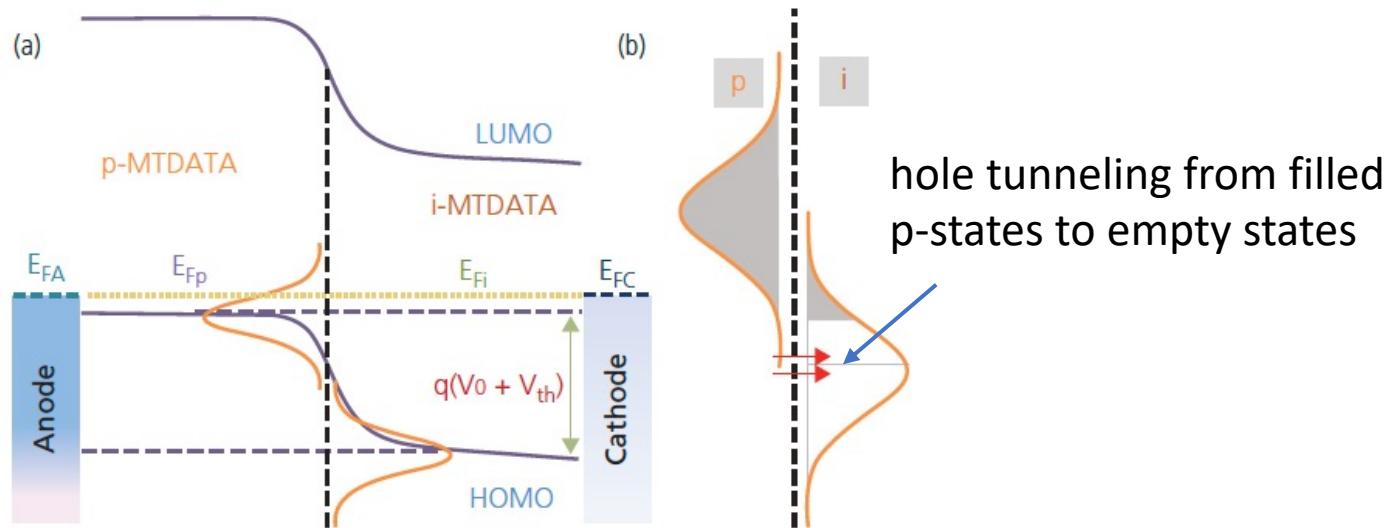
⇒ The exponential factor is unchanged, assuming there can be non-idealities such that:

$$I = I_0(e^{qV_a/nk_B T} - 1)$$

where the ideality factor, n , is > 1 , and I_0 is different from the minority carrier expressions in the Shockley equation.

Tunneling across the junction

Al-i-p MTDATA
homojunction

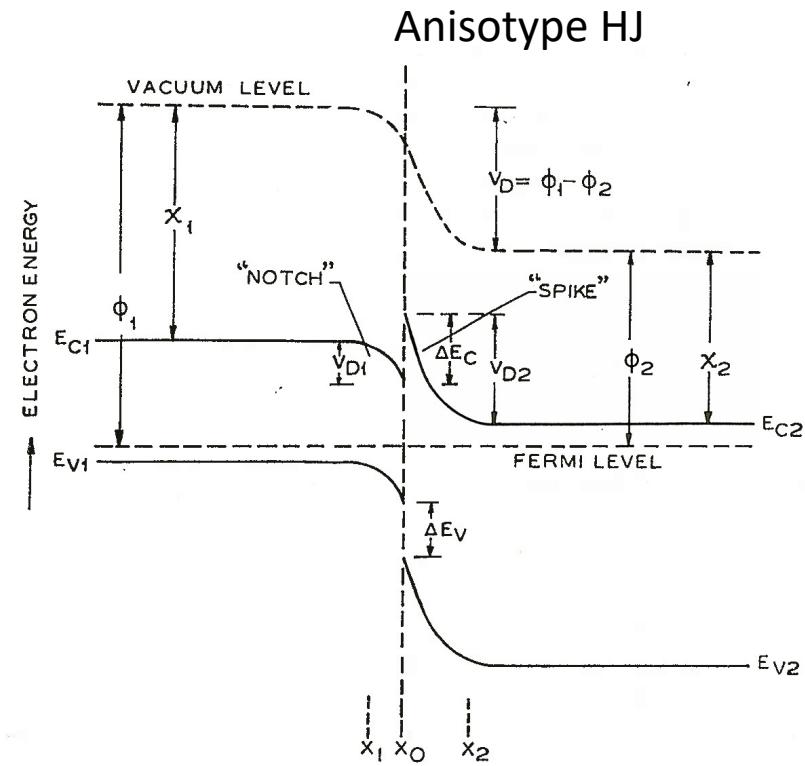
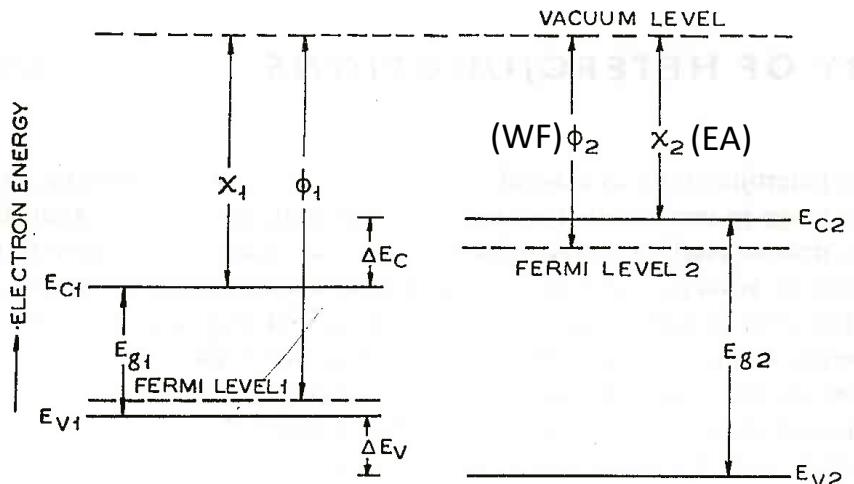


In forward direction this looks a lot like recombination, except the slope is not T-dependent

$$j = j_0 \exp(qV)$$

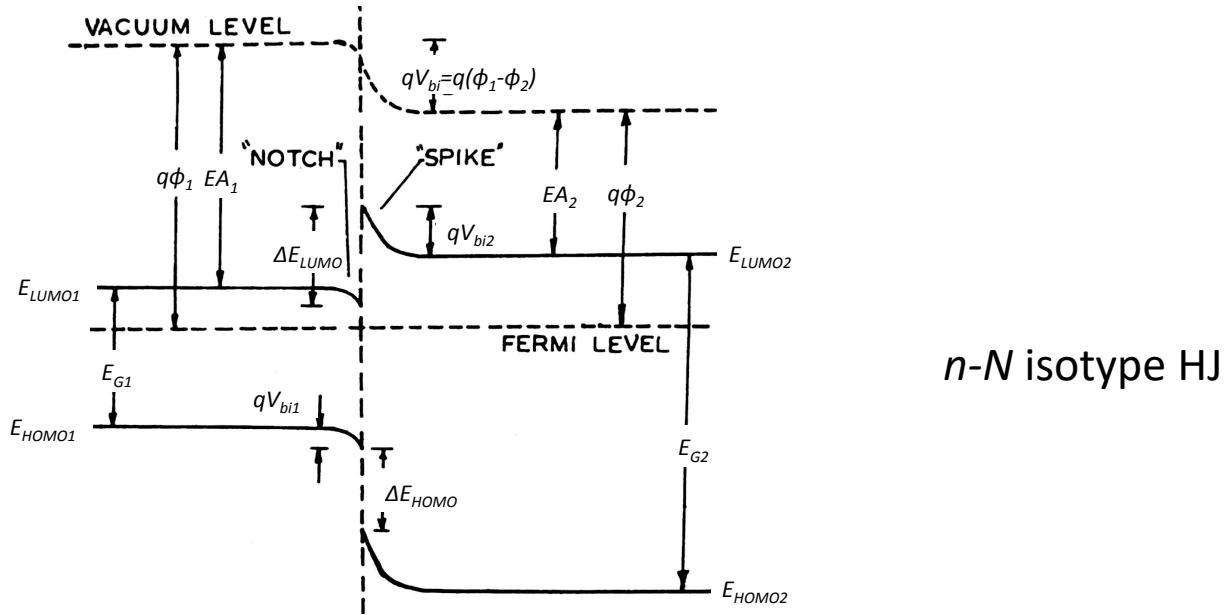
Heterojunctions: Organic-organic contacts

- 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:

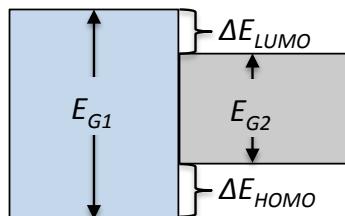


- Anderson's rule: $\Delta E_c = |\chi_1 - \chi_2|$ (doesn't work so well for inorganics due to charge transfer; better for organics)
- $\Delta E_v = \Delta E_g - \Delta E_c$
- Band bending due to free charge: organics tend toward flat bands

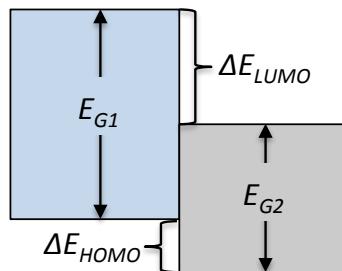
Isotype vs. Anisotype HJ



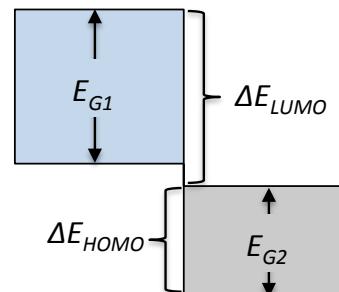
Classification of HJ types



Type I
Nested



Type II
Staggered

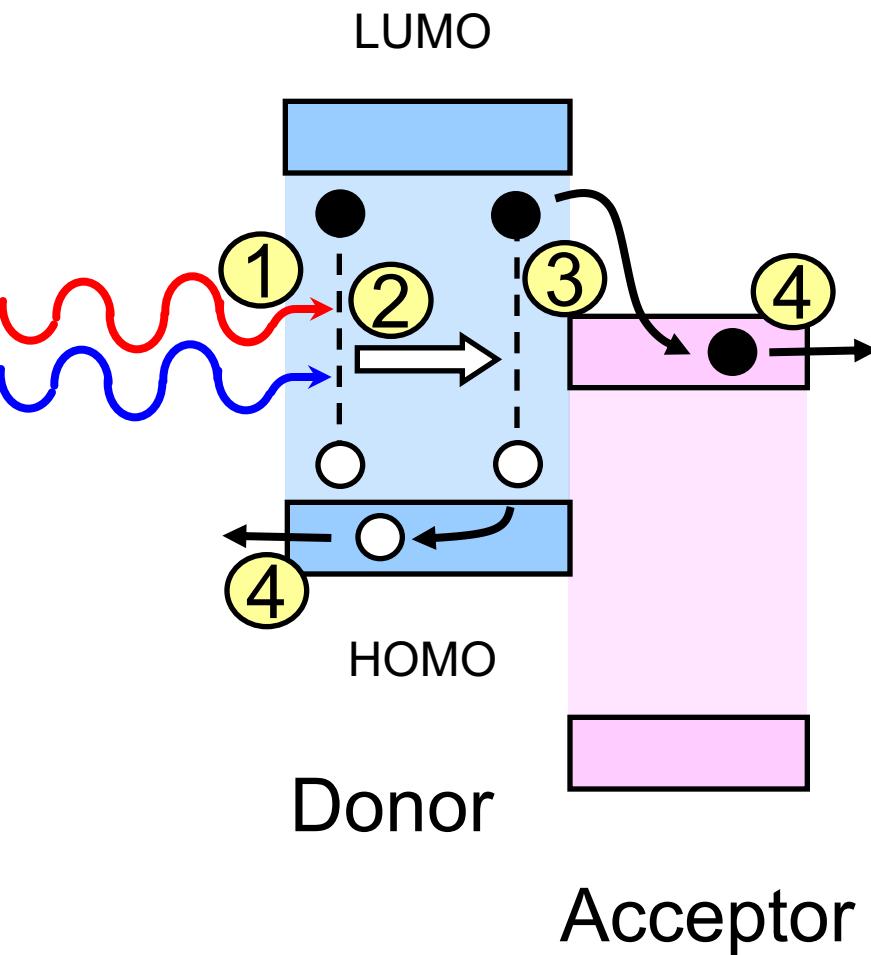


Type III
Broken Gap

Photoinduced Charge-Transfer at a Type II HJ

The Basis of OPV Operation

Processes occurring at a Donor-Acceptor heterojunction



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

Typically: $L_D \ll 1/\alpha$

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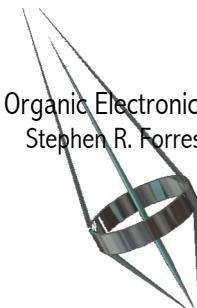
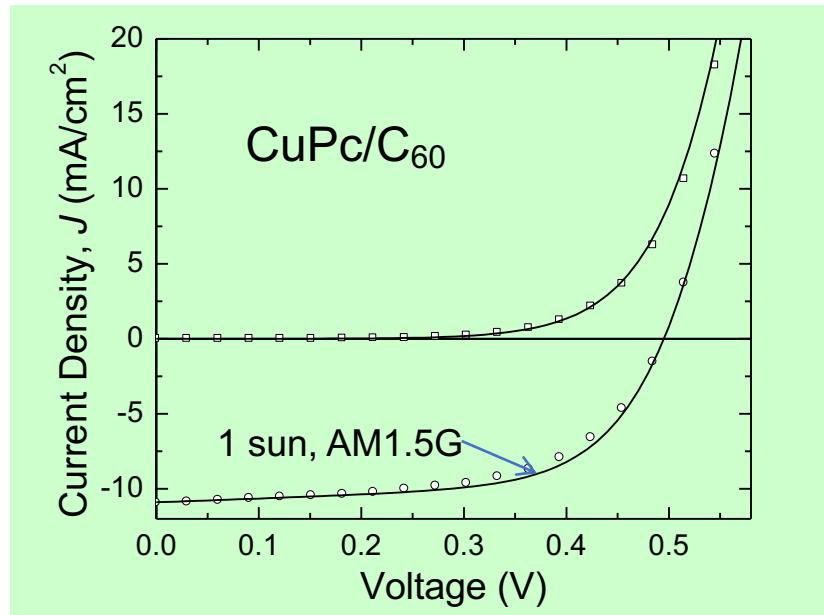
Ideal Diode Equation: Problem Statement

- The Shockley Equation (1949):

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

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

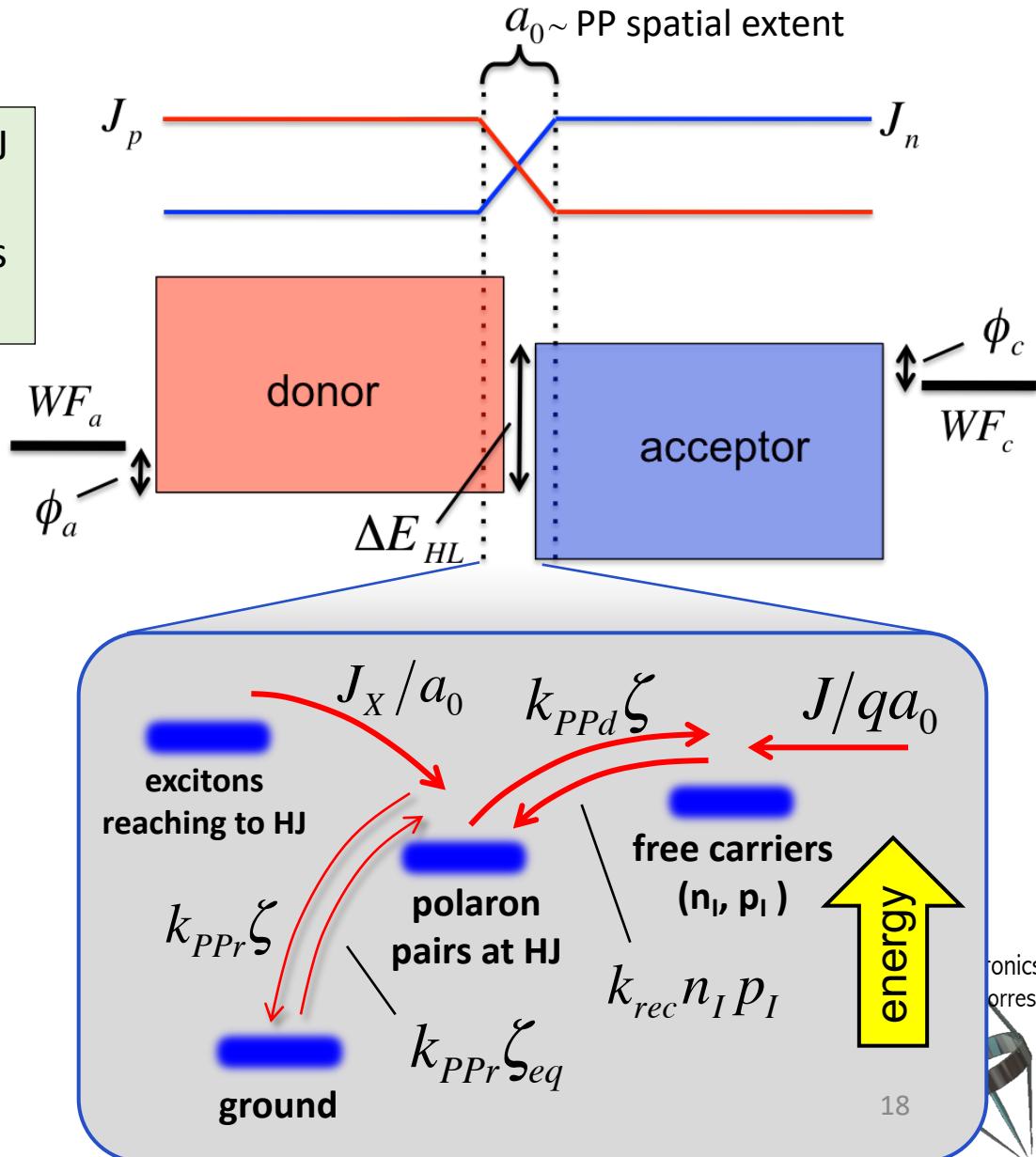
k_{rec} =charge recombination rate

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



Derivation of the Ideal Diode Eq.

- The rate equations in steady state:

- Excitons: $\frac{J_X}{a_0} - k_{\text{PP}_r}(\zeta - \zeta_{eq}) - k_{\text{PP}_d}\zeta + k_{rec}n_I p_I = 0,$

- Polarons: $k_{\text{PP}_d}\zeta - k_{rec}n_I p_I + \frac{J}{qa_0} = 0,$

- With solutions:

$$J = qa_0 k_{rec} \left(\frac{k_{\text{PP}_r}}{k_{\text{PP}_d} + k_{\text{PP}_r}} \right) \left(n_I p_I - \frac{k_{\text{PP}_d}}{k_{\text{PP}_d,eq}} n_{I,eq} p_{I,eq} \right) - qJ_X \left(\frac{k_{\text{PP}_d}}{k_{\text{PP}_d} + k_{\text{PP}_r}} \right)$$

- Now charge at interface is related to the charge at the contacts by the voltage division across the D and A layers:

$$p_I = p_C \exp \left[\frac{\delta_D q (V_a - V_{bi})}{k_b T} \right], \quad n_I = n_C \exp \left[\frac{\delta_A q (V_a - V_{bi})}{k_b T} \right]$$
$$\delta_A + \delta_D = 1$$

- Last step: Relating the contact densities, and voltage division factors, $\delta_{D,A}$ to the densities of states following Fermi statistics, we arrive at a solution:

The Ideal Diode Equation: Excitonic HJs

Rate Equations + Fermi Stats:

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

$$J = qa_0 k_{rec} N_{HOMO} N_{LUMO} (1 - \eta_{PPd}) \exp(-\Delta E_{HL} / k_b T) \left\{ \exp(qV_a / k_b T) - \frac{k_{PPd}}{k_{PPd,eq}} \right\} - q\eta_{PPd} J_X$$

electron & hole
DOS

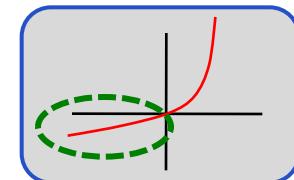
PP dissociation
efficiency

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

equilibrium dissociation
rate:
→ dark & zero bias

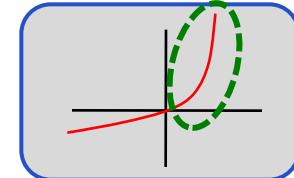
Reverse Bias:

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



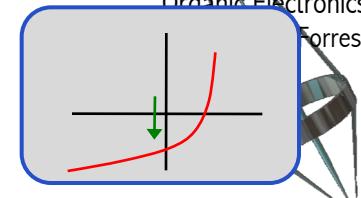
Forward Bias:

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



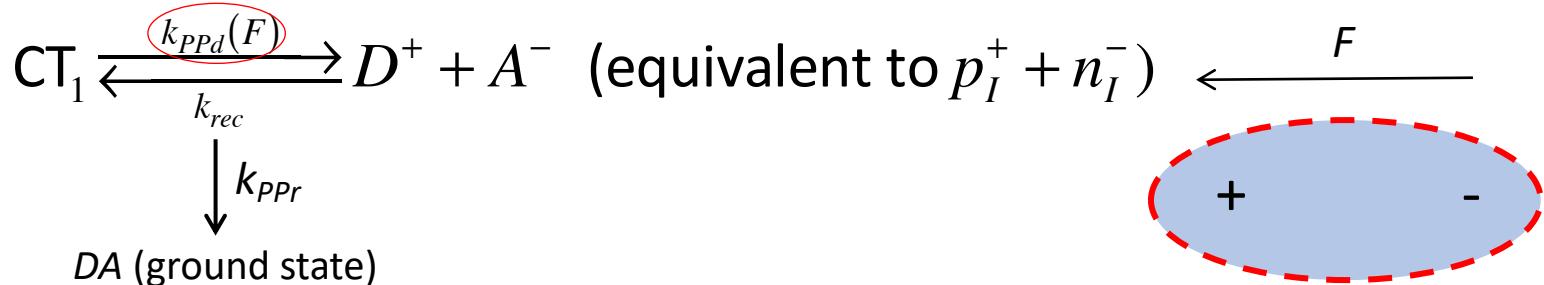
Illumination:

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



Exciton Dissociation in an Electric Field: Onsager-Braun Theory

- The lowest CT state (CT_1) is the precursor to charge generation:



- Onsager developed theory of dissociation of an ion pair in 1934, extended to CT states by Braun:

$$k_{PPd}(F) = v_0 \exp(-\Delta E / k_B T) J_1 \left[2\sqrt{2}(-b)^{1/2} \right] / \sqrt{2}(-b)^{1/2}$$

r(nm)=

where:

$$J_1 = \text{Bessel function of 1st order}; b = q^3 F / (8\pi\epsilon_r\epsilon_0 k_B T^2)$$

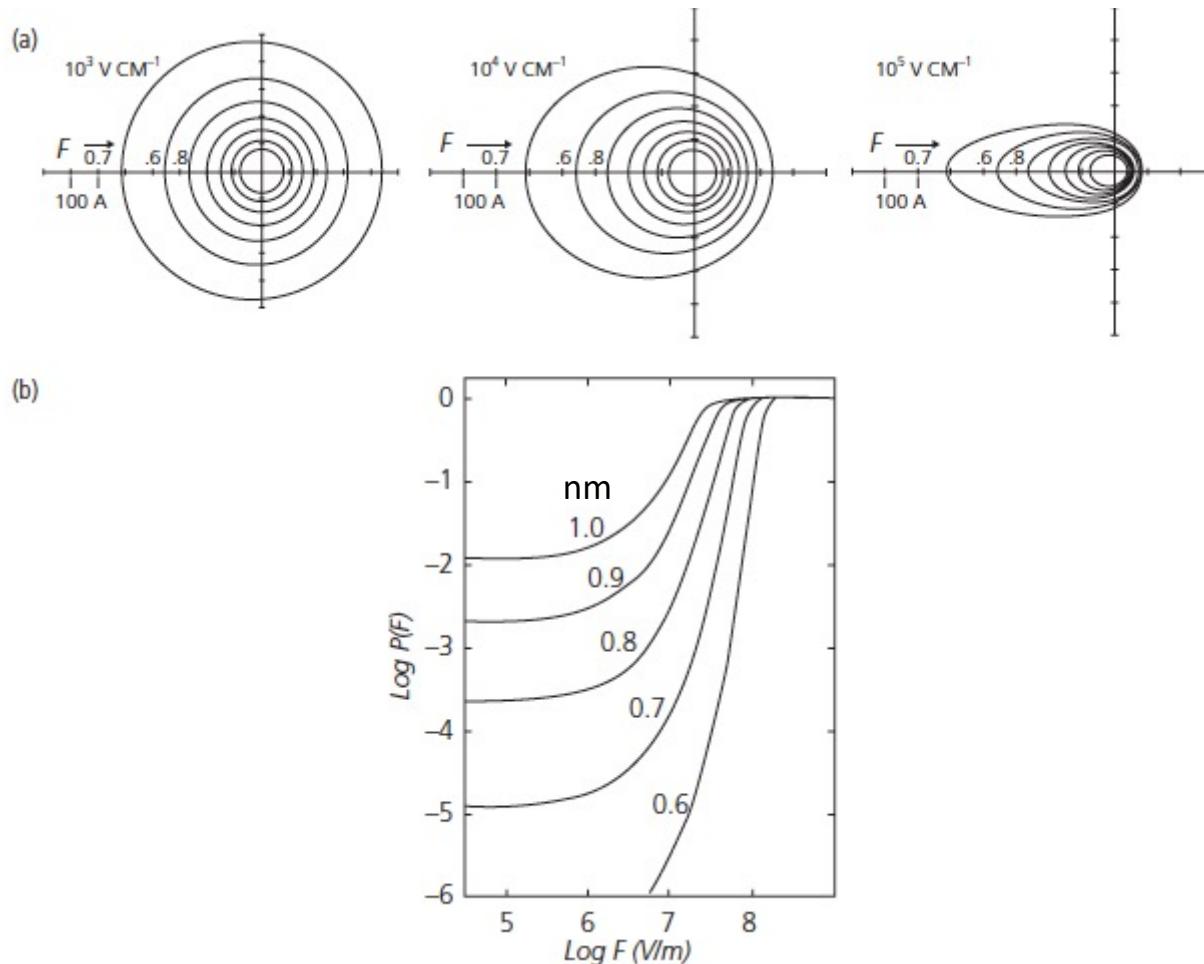
$$\Delta E = \text{CT state binding energy} = q^2 / 4\pi\epsilon_r\epsilon_0 r_{CT}$$

Probability for CT state
ionization

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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

Including traps

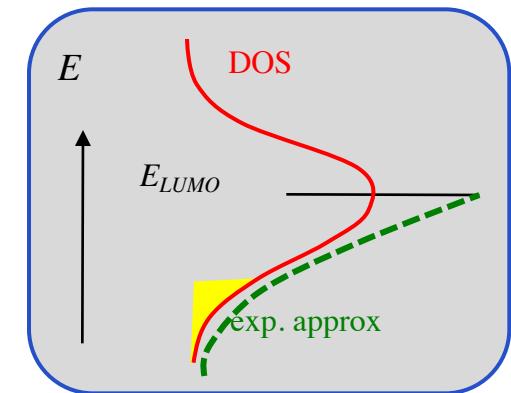
Disordered materials:

- Broad density of states (DOS) \Rightarrow continuous trap distribution:

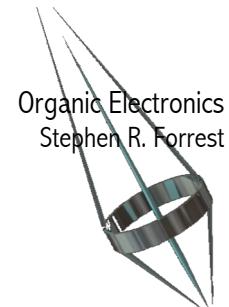
Trap Distribution Function

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

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



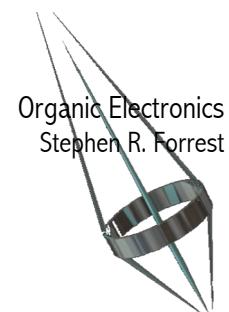
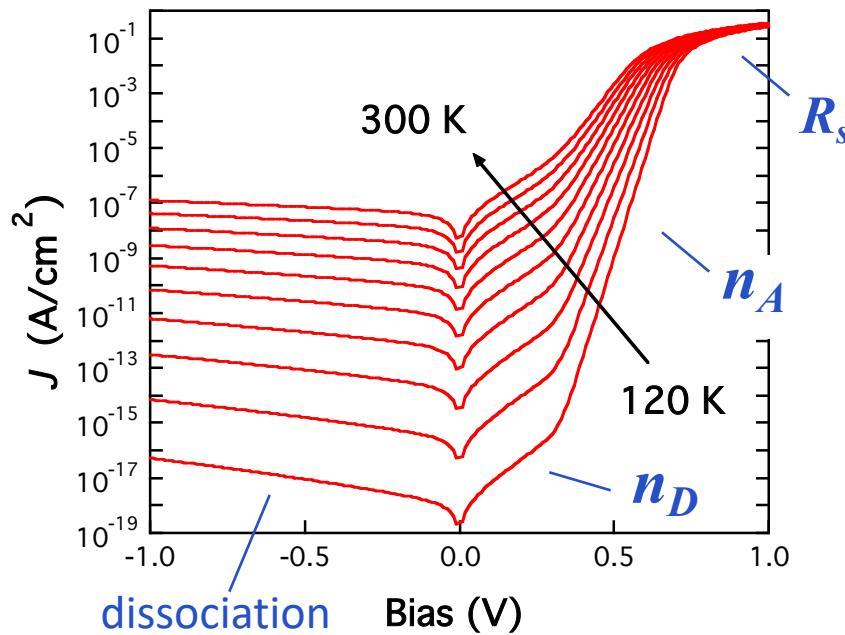
- Ideality factors: n_D , n_A depend on shape of trap DOS
 - e.g. $n=2$ for uniform distribution between HOMO and LUMO



Dark Current With Traps

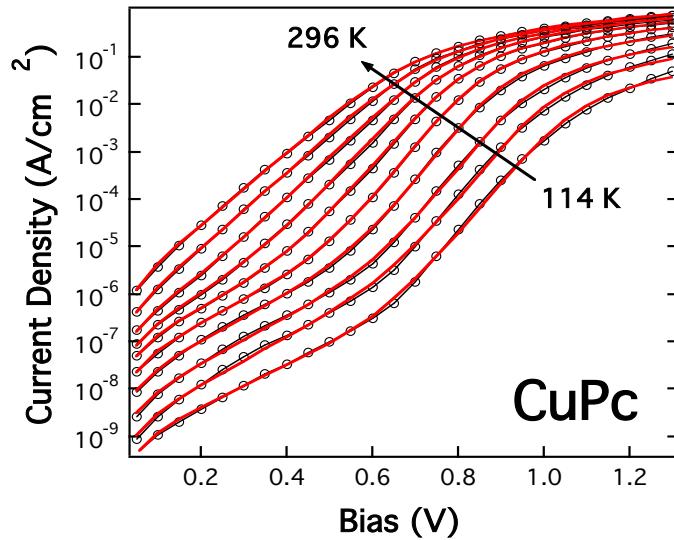
- General form including series resistance:

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

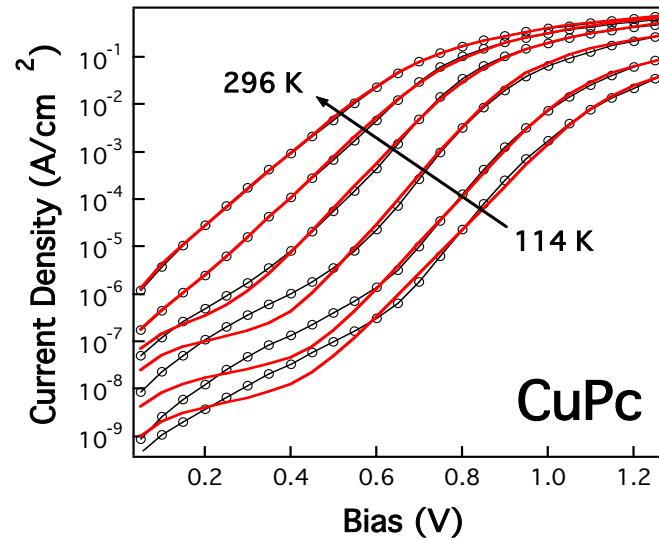


J - V Fits to Diode Eq. with Traps

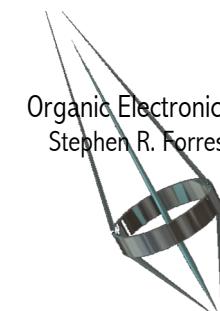
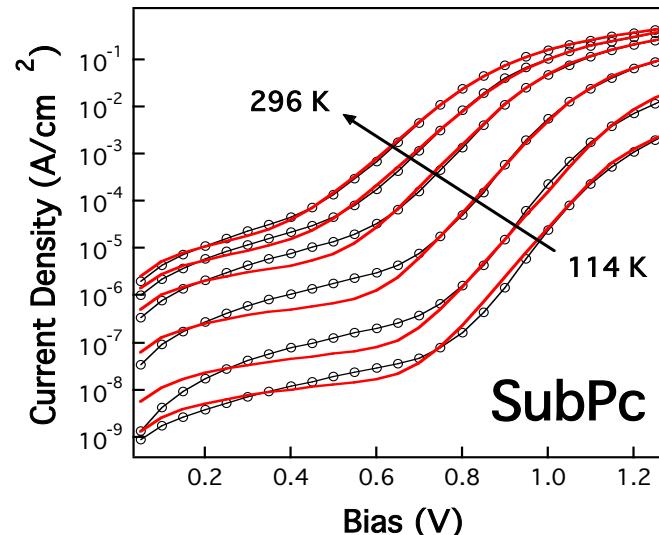
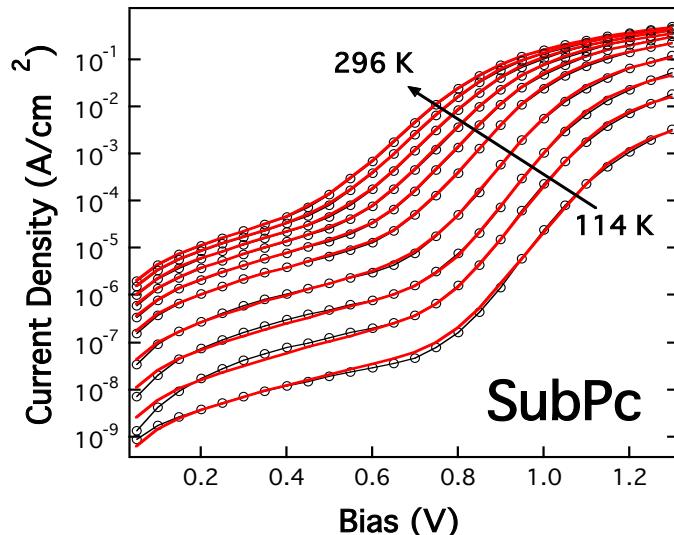
Org. HJ with Traps



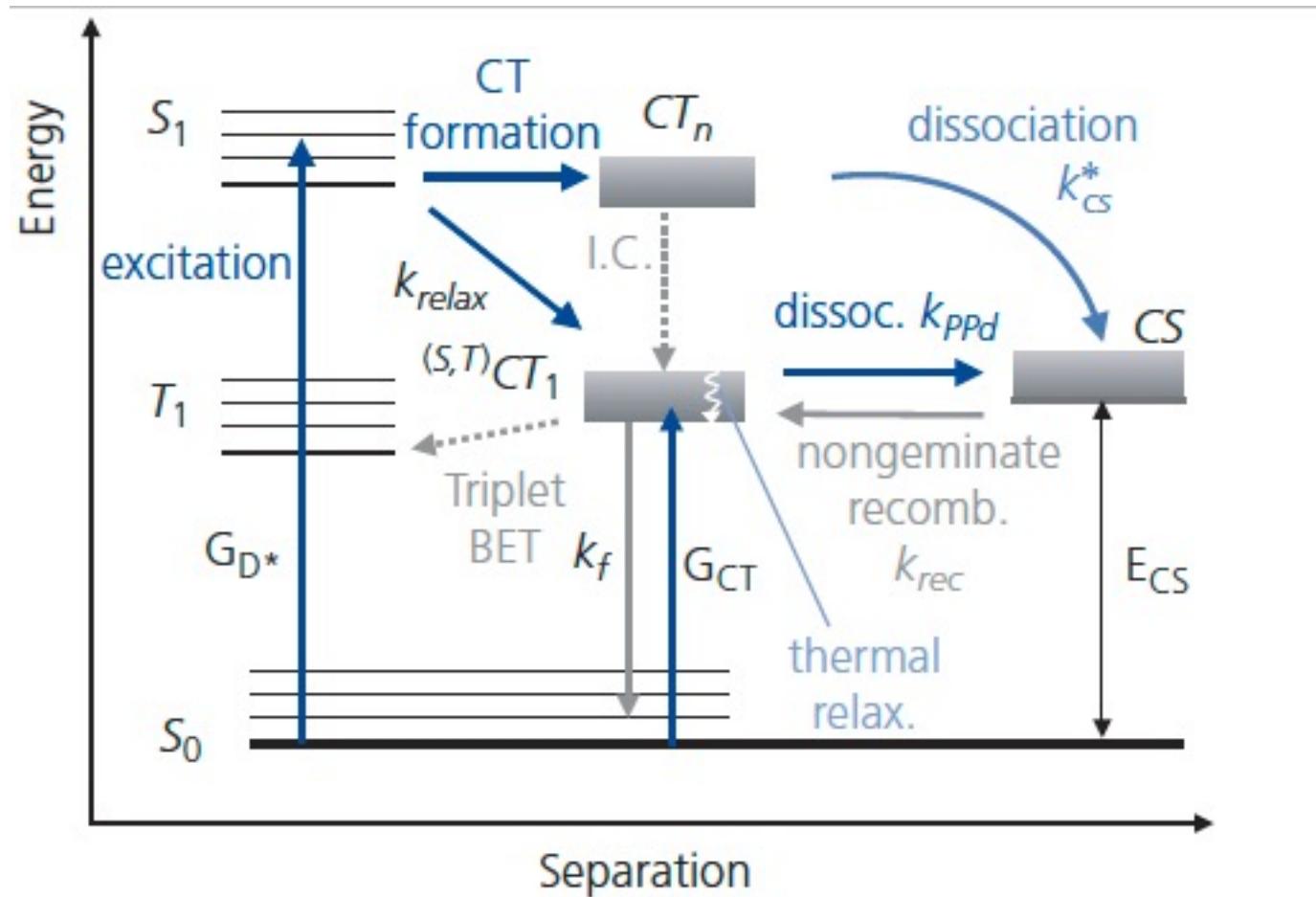
Shockley Eq.



Acceptor
 C_{60}

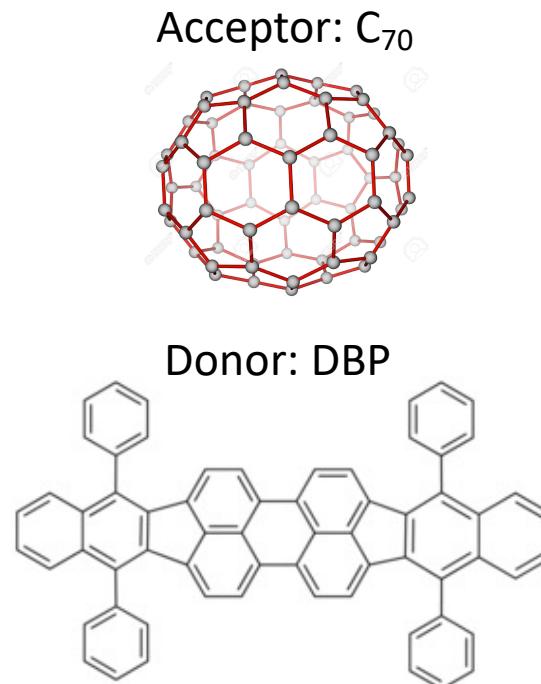
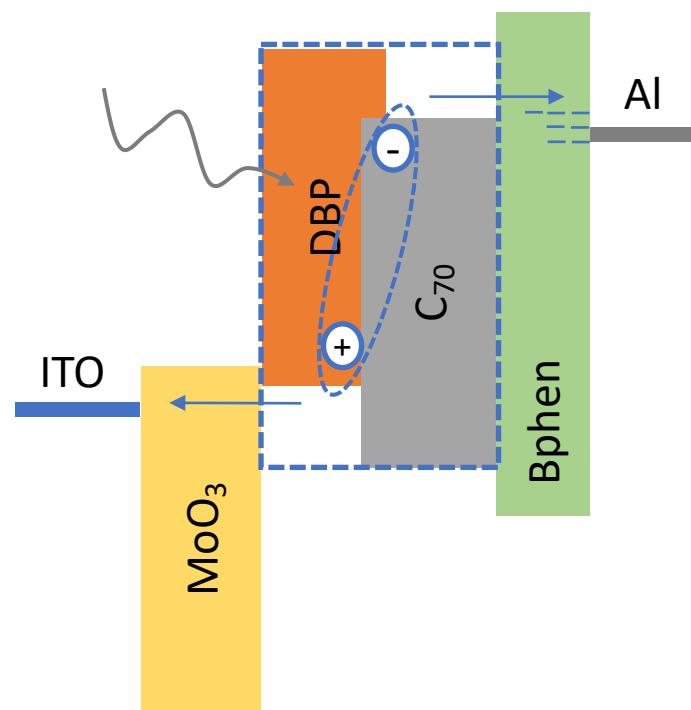


Do CT States Mediate The Current?



An archetype D-A junction -- DBP:C₇₀

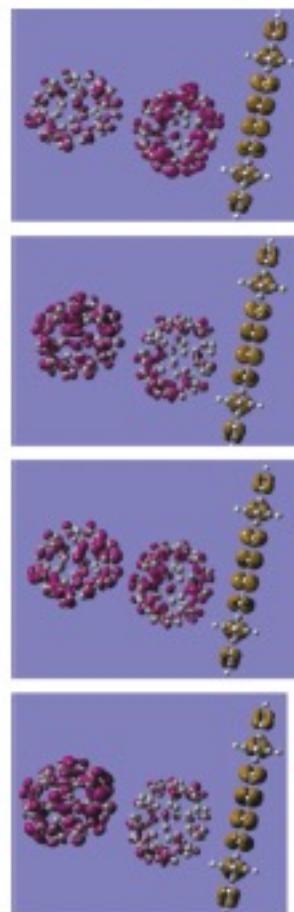
- CT states can be directly observed by electroluminescence following current injection (use the junction in the OLED mode)
- The spectra give the CT energy, the intensity gives the oscillator strength



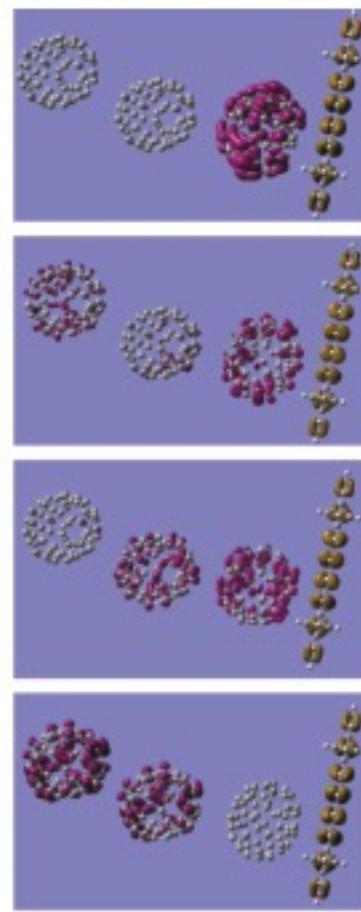
Many organic configurations lead to CT states

Here are a few between multimers of C_{70} and DBP

(a) DBP-2 C_{70}

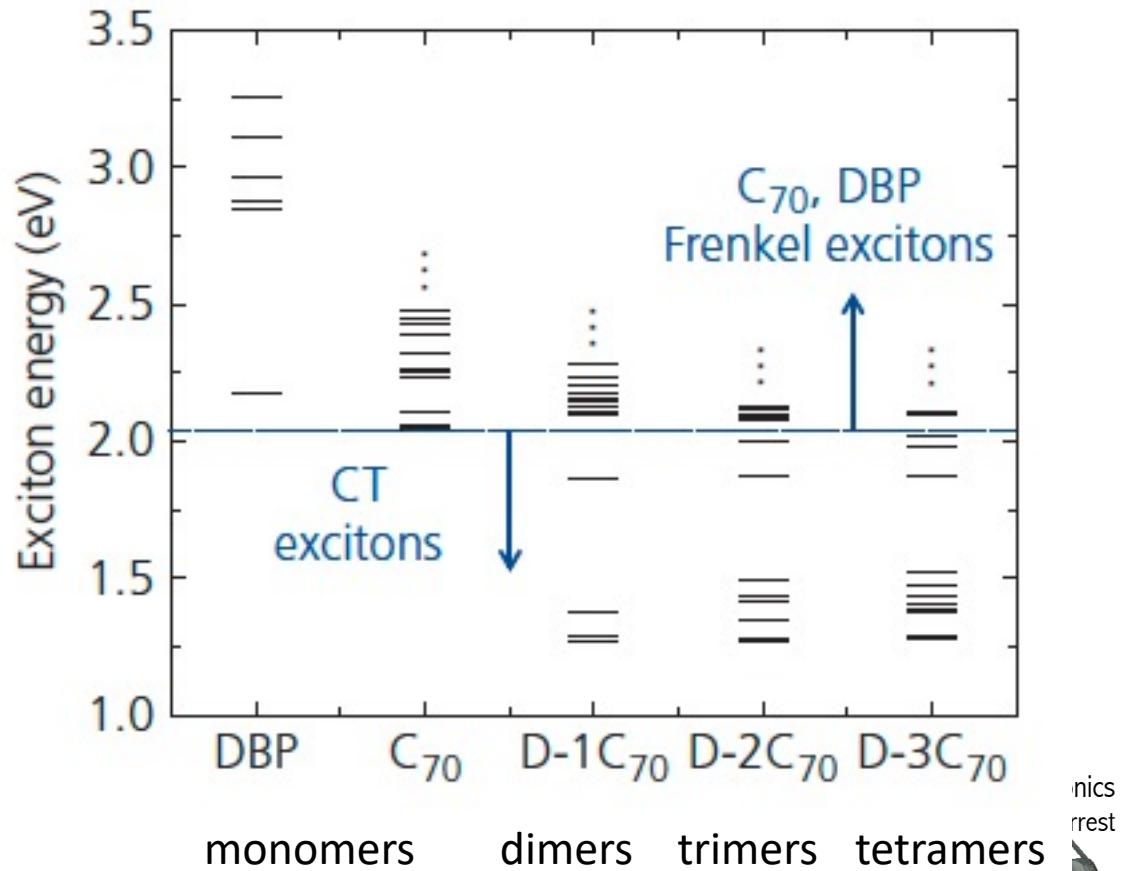


DBP-3 C_{70}

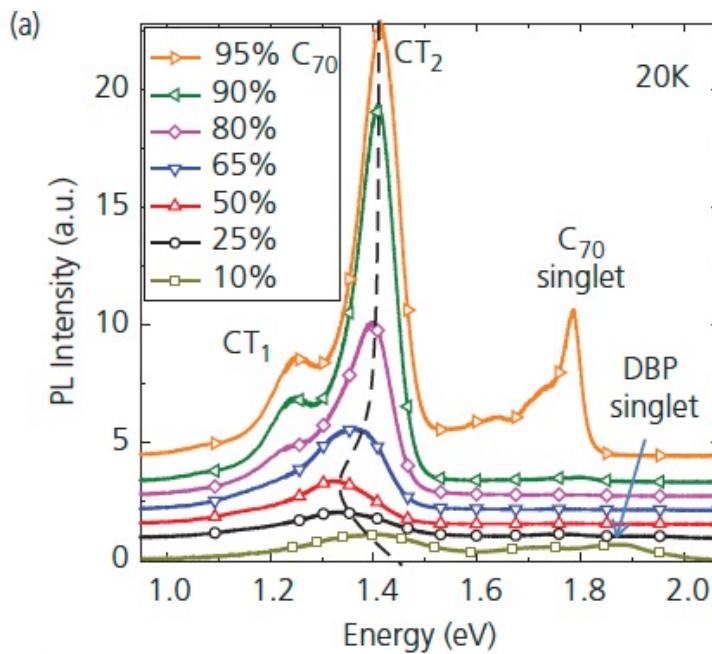


(b)

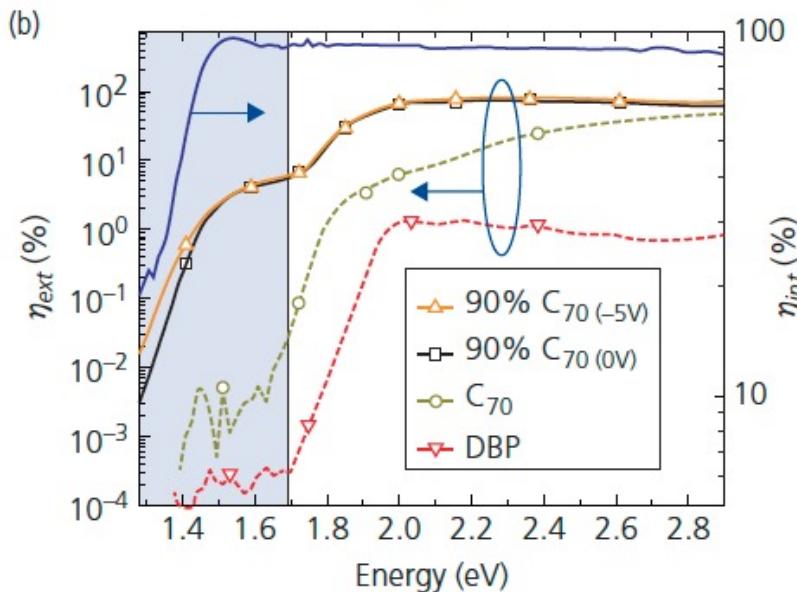
Energy level results from DFT calculations



Electroluminescence Shows 2 CT states

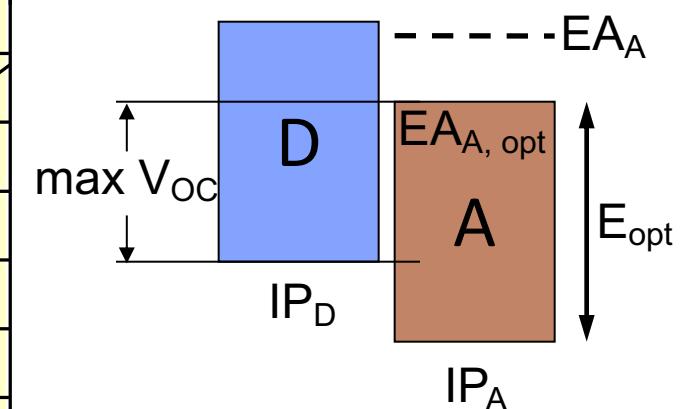
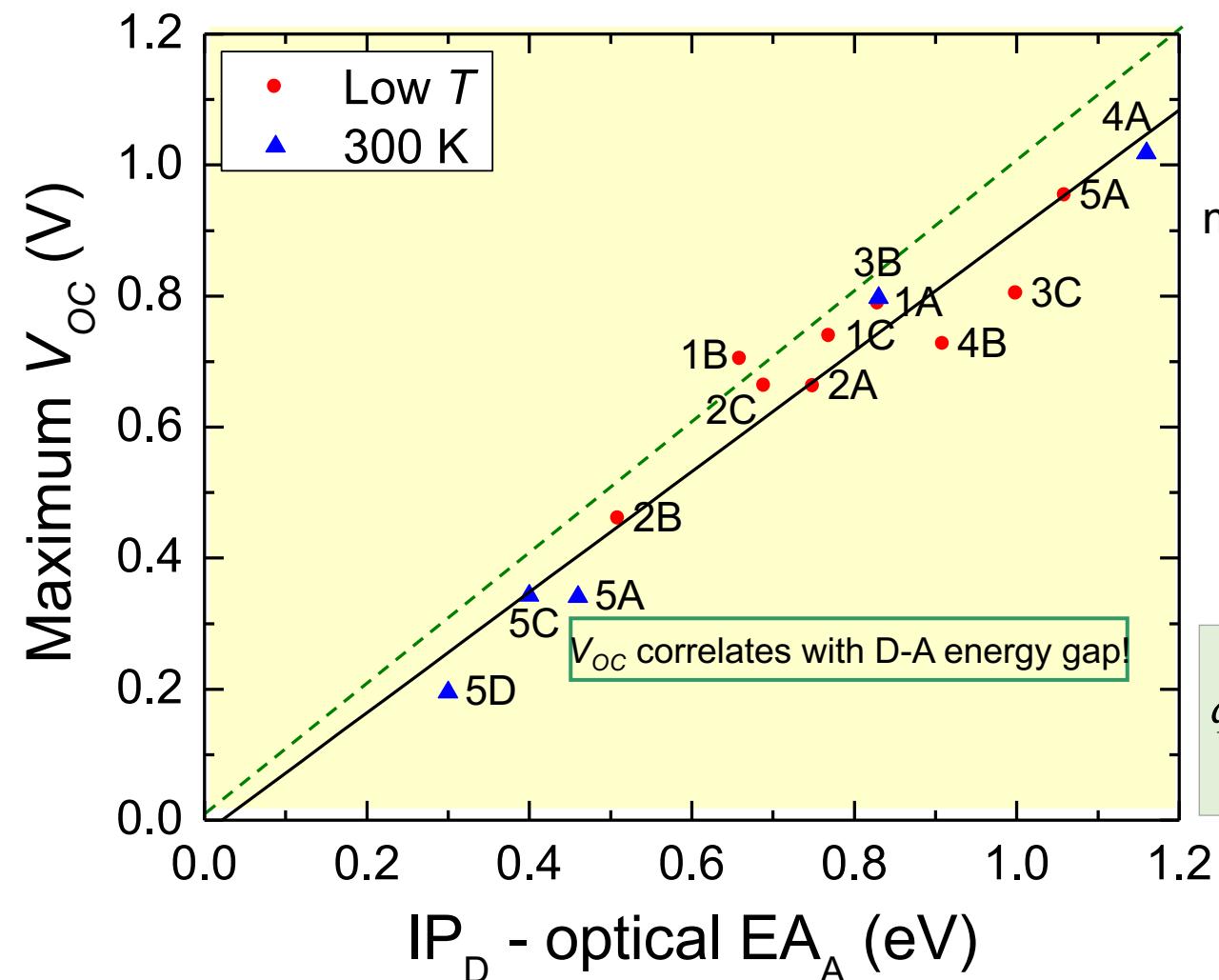


- Different blends under 3 V bias
- Energy of CT₂ depends on C₇₀ fraction in blend with DBP
⇒ Energy confinement in nanocrystallites



- External efficiency of a donor-acceptor OPV cell
- Shaded area: direct CT excitation
⇒ Photocurrent due to relaxed CT state

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



A single rule fits all materials

$$qV_{oc}^{\max} = IP_D - EA_A - \frac{q^2}{4\pi\epsilon_0\epsilon_r r_{DA}}$$

E_{HL}

$-E_B$

PP Binding Energy

Similar behavior found for polymer D-A junctions

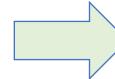
What the theory tells us-I

Open Circuit Voltage

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

- At maximum sustainable power $J_x \sim a_0 N_{HOMO} k_{cr}$
 - More excitons cannot be supported.

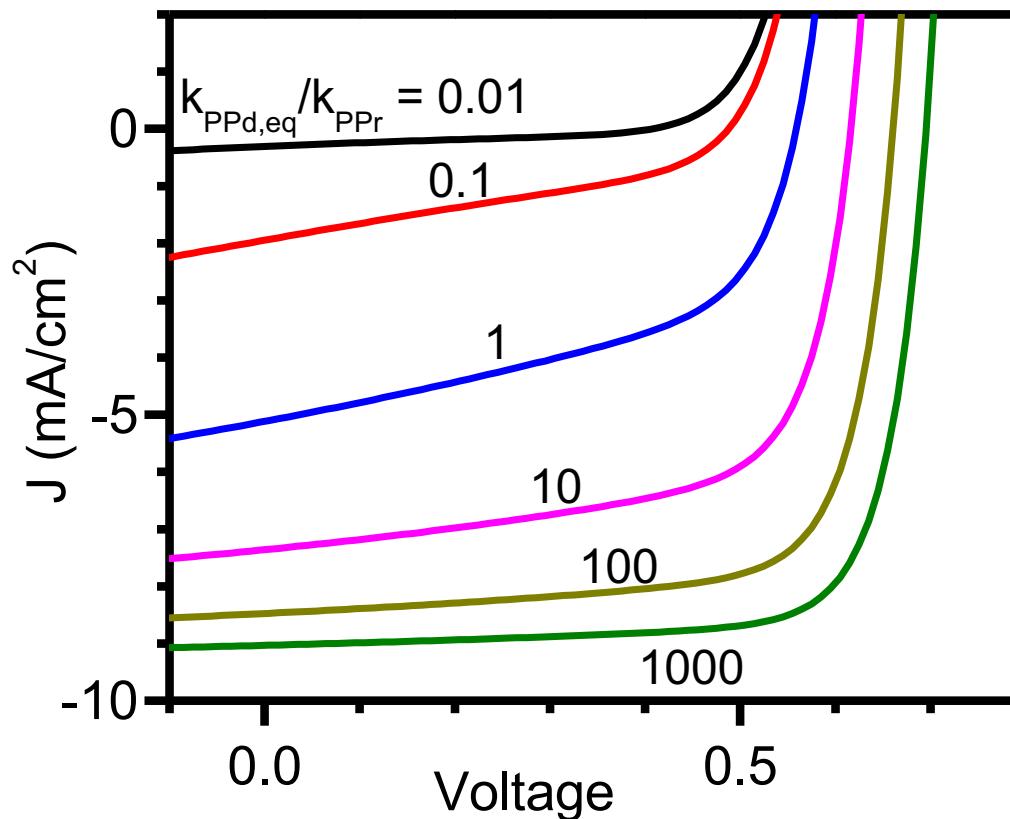
Also: $\zeta_{\max} \sim N_{HOMO} \sim N_{LUMO}$

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

What the theory tells us-II

Morphology



- PP recombination \Rightarrow Reverse Slope
- Best morphologies limit k_{PPPr} at interface:
 - Steric hindrance
 - Disorder at interfaces/order in the bulk

