Luminescence

Topics

Radiative transitions between electronic states
Absorption and Light emission (spontaneous, stimulated)
Excitons (singlets and triplets)
Franck-Condon shift(Stokes shift) and vibrational peaks
Energy transfer processes
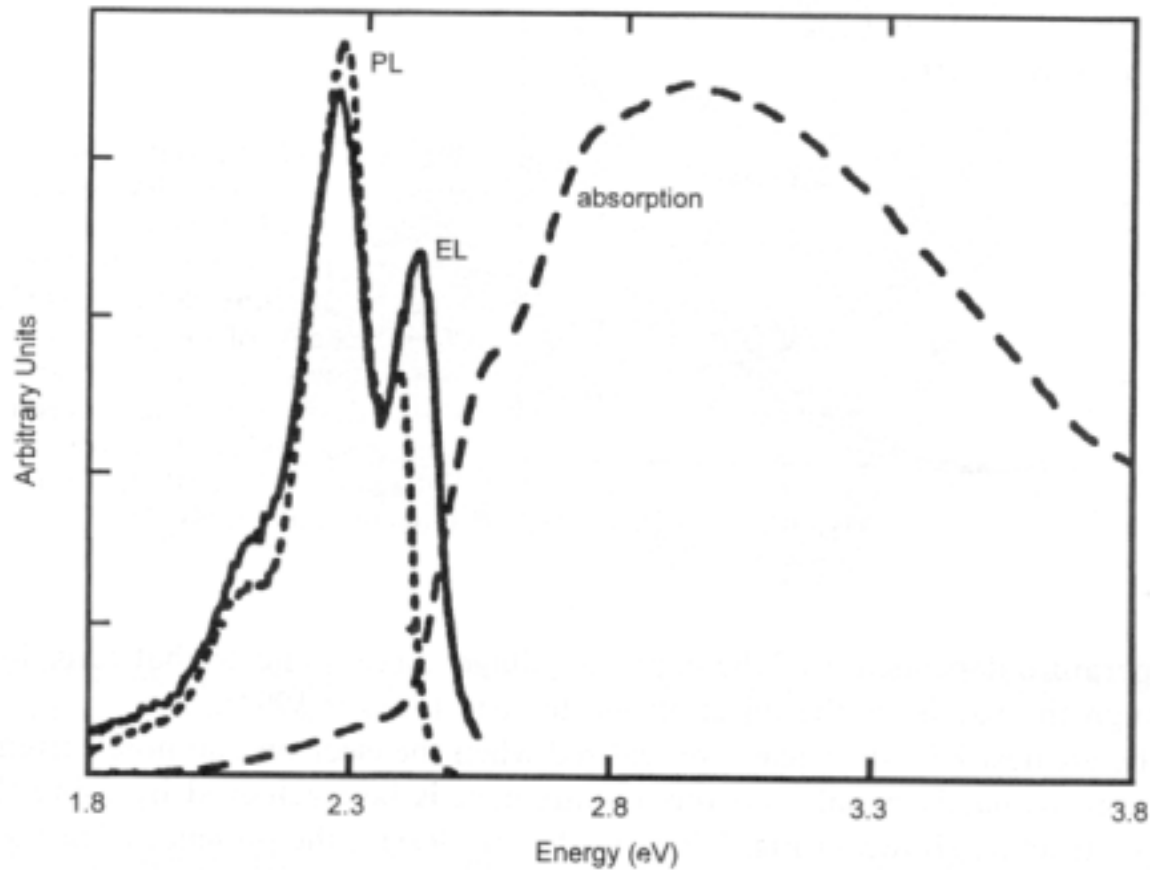
Luminescence

Luminescence is the emission of light.

Photoluminescence (PL) is luminescence that results from optically exciting a sample.

Electroluminescence (EL) is luminescence that results from electrically exciting a sample (e.g. in an LED).

Catholuminescence is luminescence that results from exciting a sample with an electron beam (e.g. in a cathode ray tube).
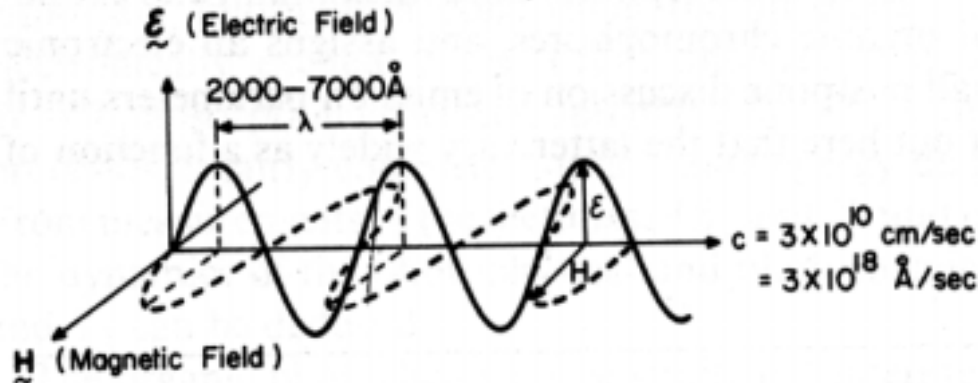
Chemiluminescence results from a chemical reaction.

Questions we will address

Why are the luminescence spectra shifted from the absorption spectrum?
Why do the luminescence spectra have several sharp peaks?
What the determines the quantum efficiency of luminescence?

Absorption

- Light is an electromagnetic wave.

- Electrons oscillate about their nuclei with a frequency $\omega = \dfrac{E}{\hbar}$.

- If the frequency of the photon is $\omega = \dfrac{E_1 - E_0}{\hbar}$
then the oscillating field of the photon
can excite the electron into a higher
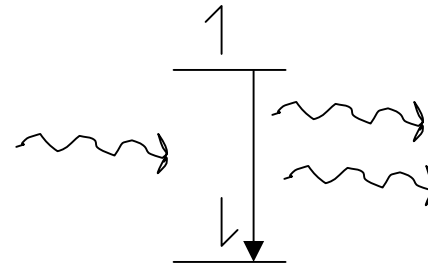energy level.

$$\psi = \psi_1 e^{-iE_1 t / \hbar}$$

$$\psi = \psi_0 e^{-iE_0 t / \hbar}$$

Spontaneous and stimulated emission

• An oscillating electron can also generate an oscillating electric field. In other words, an excited dipole can spontaneously emit a photon.

• Stimulated emission is the process by which a photon stimulates an electron to drop into a lower level by giving off another photon.
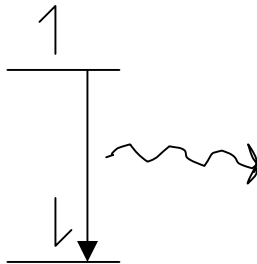
Spontaneous emission

Stimulated emission

The rate of spontaneous emission

k_r = rate of radiative decay = $2\pi\rho <H'>^2/h$ ⟵ Fermi's Golden Rule

Joint density of occupied
states and available
states to accept the electron

Matrix element

Assume that the density of excited states is n.
The rate of emission, -dn/dt, is proportional to n.

Thus if there is a collection of excited molecules that all emit at the same rate,
then the light emission decays exponentially.

The connection between absorption, spontaneous emission and stimulated emission

The absorption coefficient, rate of spontaneous emission and stimulated emission are all proportional to the matrix element

$$\left\langle \psi_i \left| H \right| \psi_f \right\rangle^2$$

where ψ_i and ψ_f are the wavefunctions before and after the transition and H, the Hamiltonian, is Ex.

E is the oscillating electric field of the photon
x is the distance from the center of the molecule.

Materials that absorb well emit well unless something quenches the luminescence.

Selection rules

• In some cases, due to the symmetry of the wavefunctions, the matrix element is zero.

• When this happens, we say that the transition is forbidden.

• Forbidden transitions still occur to a very minor extent due to second order processes.

Quantum efficiency and radiative rates

η_{PL} = quantum efficiency for PL = photons emitted/photons absorbed

η_{EL} = quantum efficiency for EL = photons emitted/majority charge carriers injected

$$\eta = \frac{k_r}{k_r + k_{nr}}$$

k_{nr} = rate of non-radiative decay

k_r = rate of radiative decay

To achieve high quantum efficiency, it is desirable, but not essential, to have a high radiative rate.
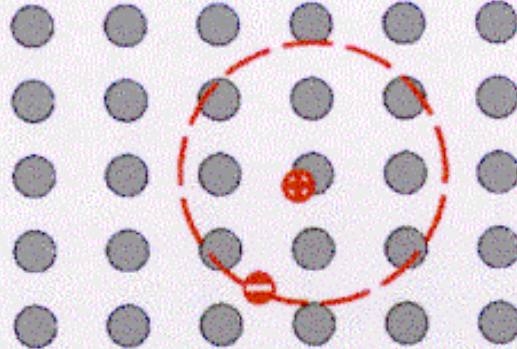
Excitons

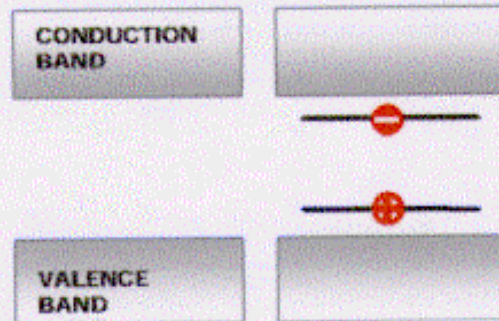treat excitons as chargeless particles capable of diffusion, also view them as *excited states of the molecule*

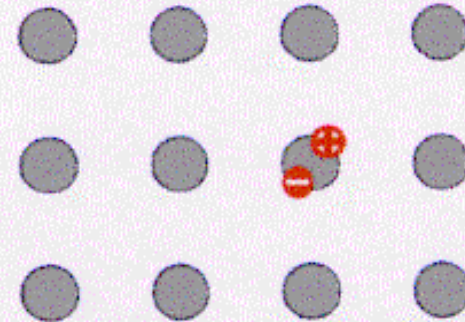**Wannier exciton**
(typical of inorganic semiconductors)

Frenkel exciton
(typical of organic materials)

SEMICONDUCTOR PICTURE

MOLECULAR PICTURE

CONDUCTION BAND

VALENCE BAND

S_1

S_0

GROUND STATE   WANNIER EXCITON
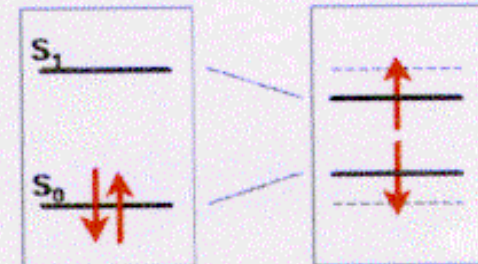
GROUND STATE   FRENKEL EXCITON

binding energy ~10meV
radius ~100Å

binding energy ~1eV
radius ~10Å

Source: Vladimir Bulovic (MIT)

Excitons in polymers

The size and binding energy of excitons in polymers is a very controversial subject.

Most people think that the electron and hole are on the same polymer chain and that the binding energy is approximately 0.2 eV.

Primary Photoexciations in Conjugated Polymers: Molecular Exciton versus Semiconductor Band Model (edited by Serdar Sariciftci, 1997).

Jean-Luc Bredas et al. *Adv. Mater.* **8** (1996) p. 447.

Excitons and exciton diffusion

At any one instance in time, an exciton is probably just on one chain.

Over a period of time, however, the exciton moves to new chains.

Example

An exciton can donate an electron to a C_{60} molecule if it is formed within 10 nm of that molecule. The exciton does not have to diffuse along one chain to get to the C_{60}. There is some evidence that diffusion perpendicular to the chains is much faster than diffusion along the chains.
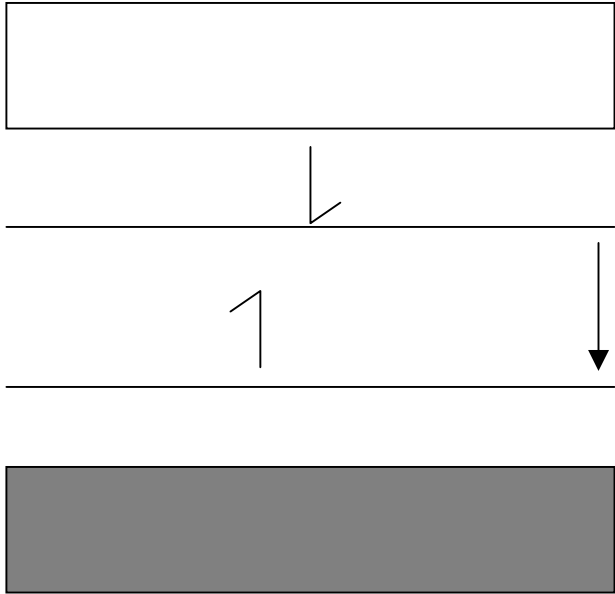
Excitons

Positive soliton

Negative antisoliton

Benzenoid   Quinoid   Benzenoid
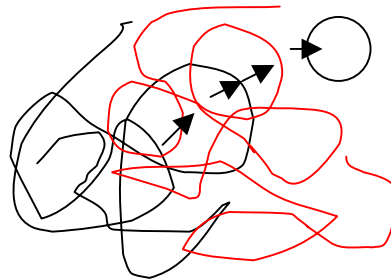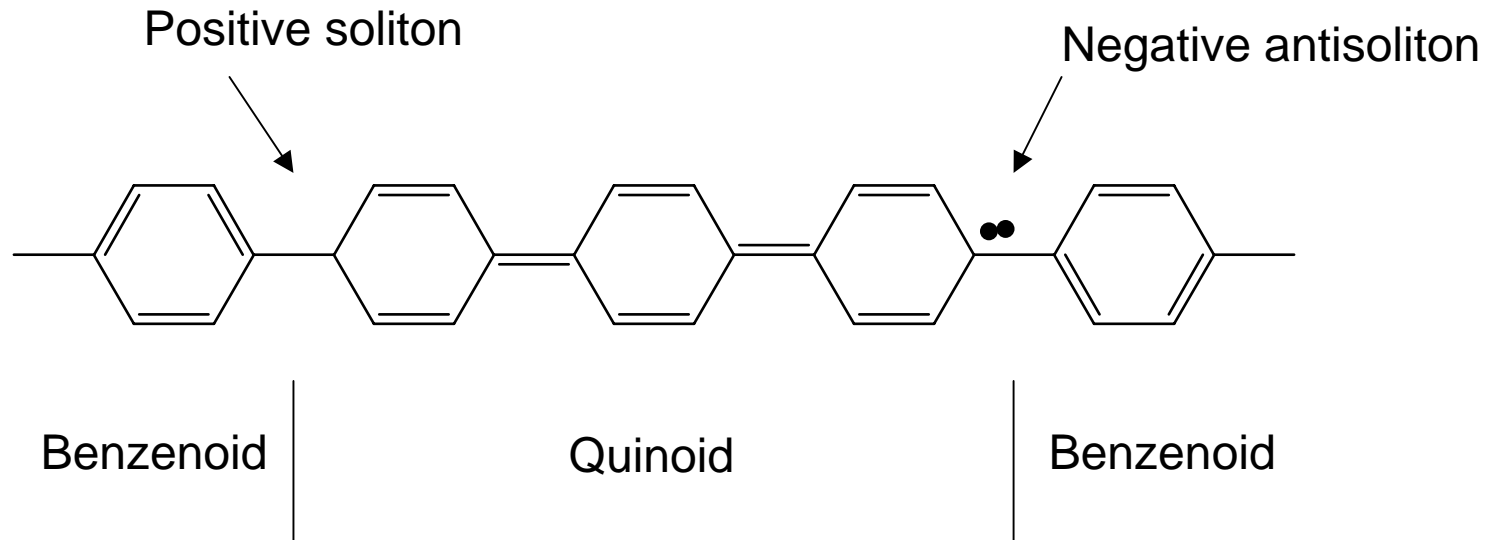
An exciton in a polymer can be thought of as a bound positive soliton-negative antisoliton pair.

Emission of light

The emitted photon has less energy than the absorbed photon that created the exciton. This is one of the reasons that the luminescence spectra are shifted from the absorption spectra.

Singlet and triplet excitons

There are 3 symmetric spin states, known as triplets, with an angular momentum of 1.

$$S = |\uparrow\uparrow\rangle$$

$$S = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)$$

$$S = |\downarrow\downarrow\rangle$$

There is one antisymmetric spin state, known as a singlet, with an angular momentum of 0.

$$S = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$$

The selection rule

Summary:

• The ground state is the singlet with no angular momentum.

• To first order, angular momentum must be conserved in electronic transitions.

• When light is absorbed, singlet excited states will be created.

• There is a process known as intersystem crossing that can convert singlets into triplets. For most organic semiconductors, the rate of intersystem crossing is usually slower than the rate of emission, so very few triplets are formed in most photoluminescence experiments.

• In an LED, there is no correlation in the spin of carriers injected at opposite electrodes. Triplets can form.   Since they can't emit, η_{EL} is $< \eta_{PL}$.

Fluorescence and phosphorescence

Allowed singlet emission is called fluorescence. For most organic lumophores, fluorescence occurs on a time scale of 0.2-10 ns.

Forbidden triplet emission is called phosphorescence. It typically has a time constant of 1-1000 μs.
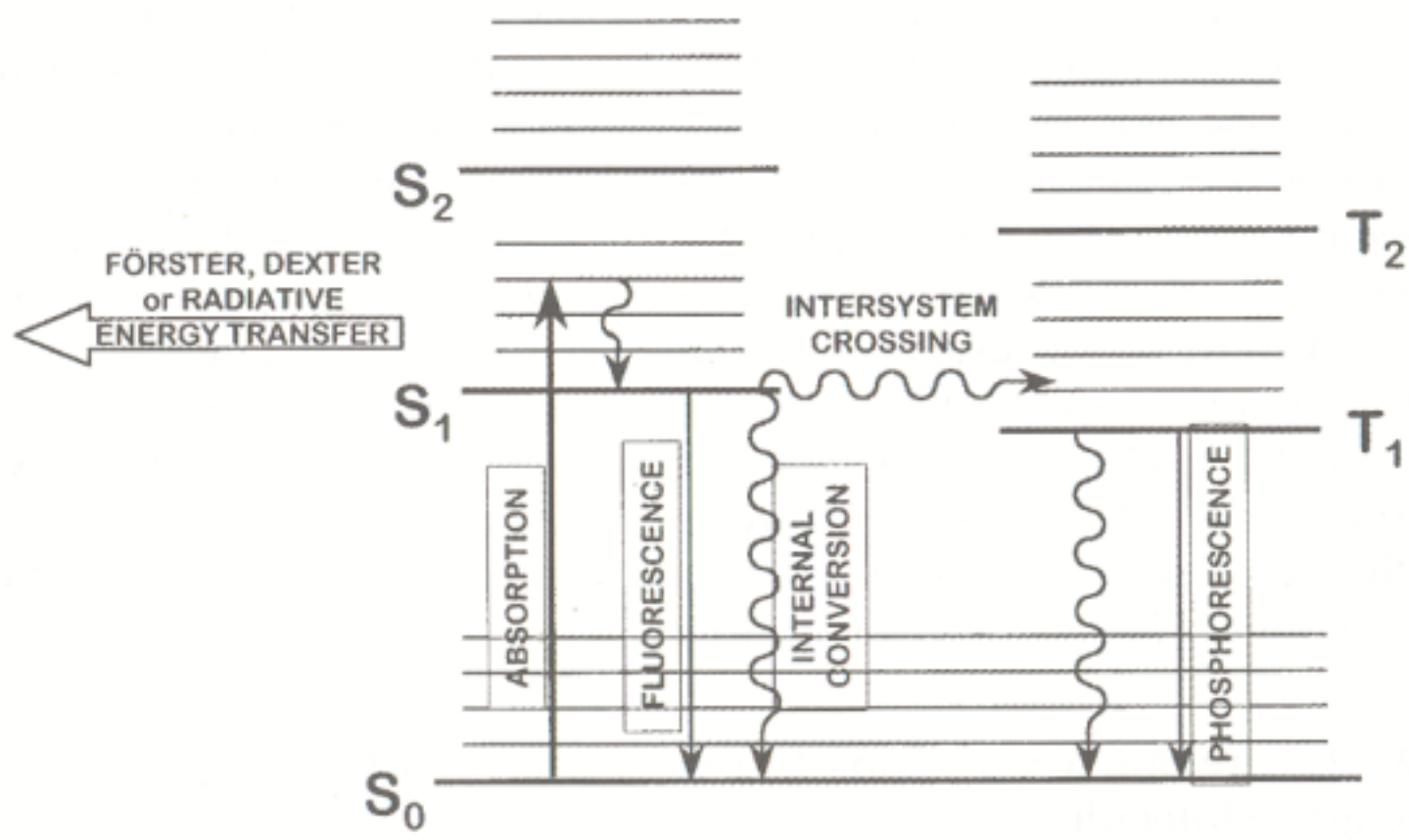
Fig. 11.1. Jablonski diagram of an organic molecule depicting typical energy levels and energy-transfer process. The *straight-line arrows* represent radiative processes, and *wavy-line arrows* non-radiative processes

Phosphorescence is almost never observed in organic materials

k_{nr} tends to be on the order of $(1\ ns)^{-1}$.

For fluorescence, k_r tends also to be on the order of $(1\ ns)^{-1}$.

Typical quantum efficiencies are

$$\eta = \frac{\dfrac{1}{1\,ns}}{\dfrac{1}{1\,ns} + \dfrac{1}{1\,ns}} = 0.5$$

For phosphorescence, a typical k_r is $(10^6\ ns)^{-1}$. Thus a typical phosphorescence efficiency is

$$\eta = \frac{\dfrac{1}{10^6\,ns}}{\dfrac{1}{10^6\,ns} + \dfrac{1}{1\,ns}} = 10^{-6}$$

Vibronic energy levels

Earlier in the course when we developed models for determining the energy levels of molecules, we didn't take into account the fact that the nuclei vibrate about their equilibrium potential.

The diagram to the left shows a curve of energy versus the distance between nuclei. χ is the eigenfunction for the nuclei separation and χ^2 is the probability that the nuclei are separated by r_{xy}.

The molecule can only have quantized amounts of vibrational energy.

Nicholas Turro,*Modern Molecular Photochemistry*

Conformational coordinate
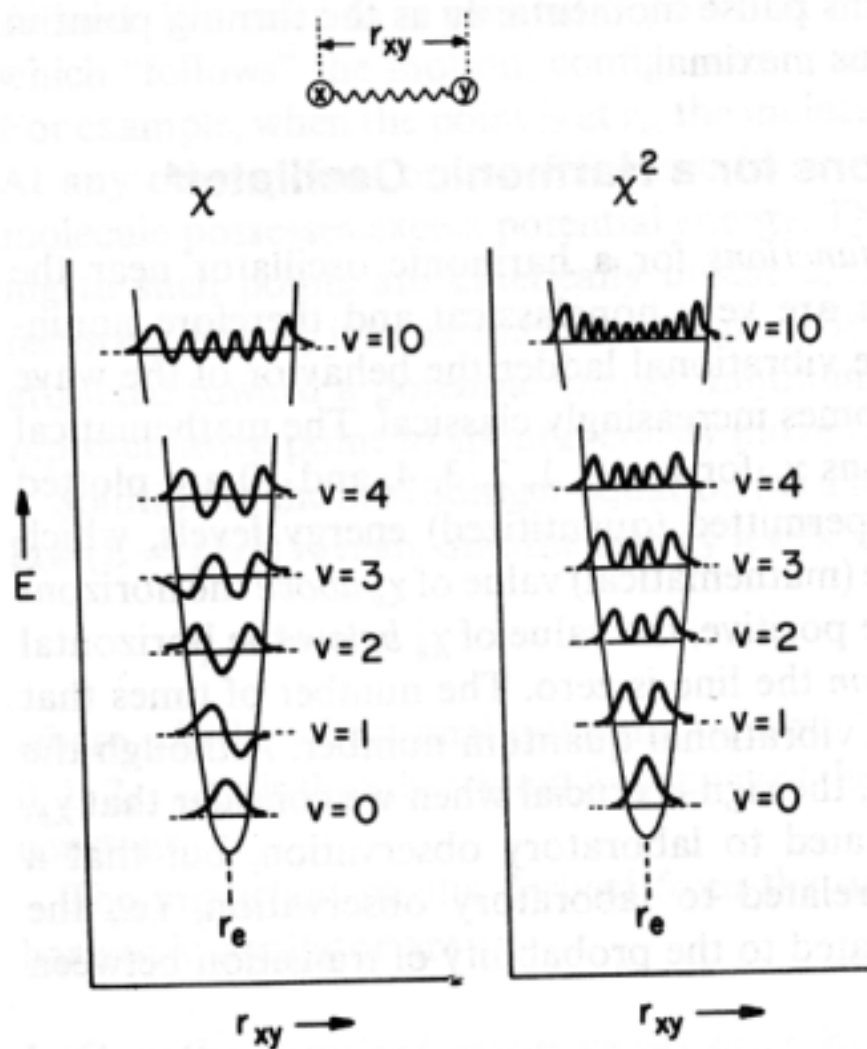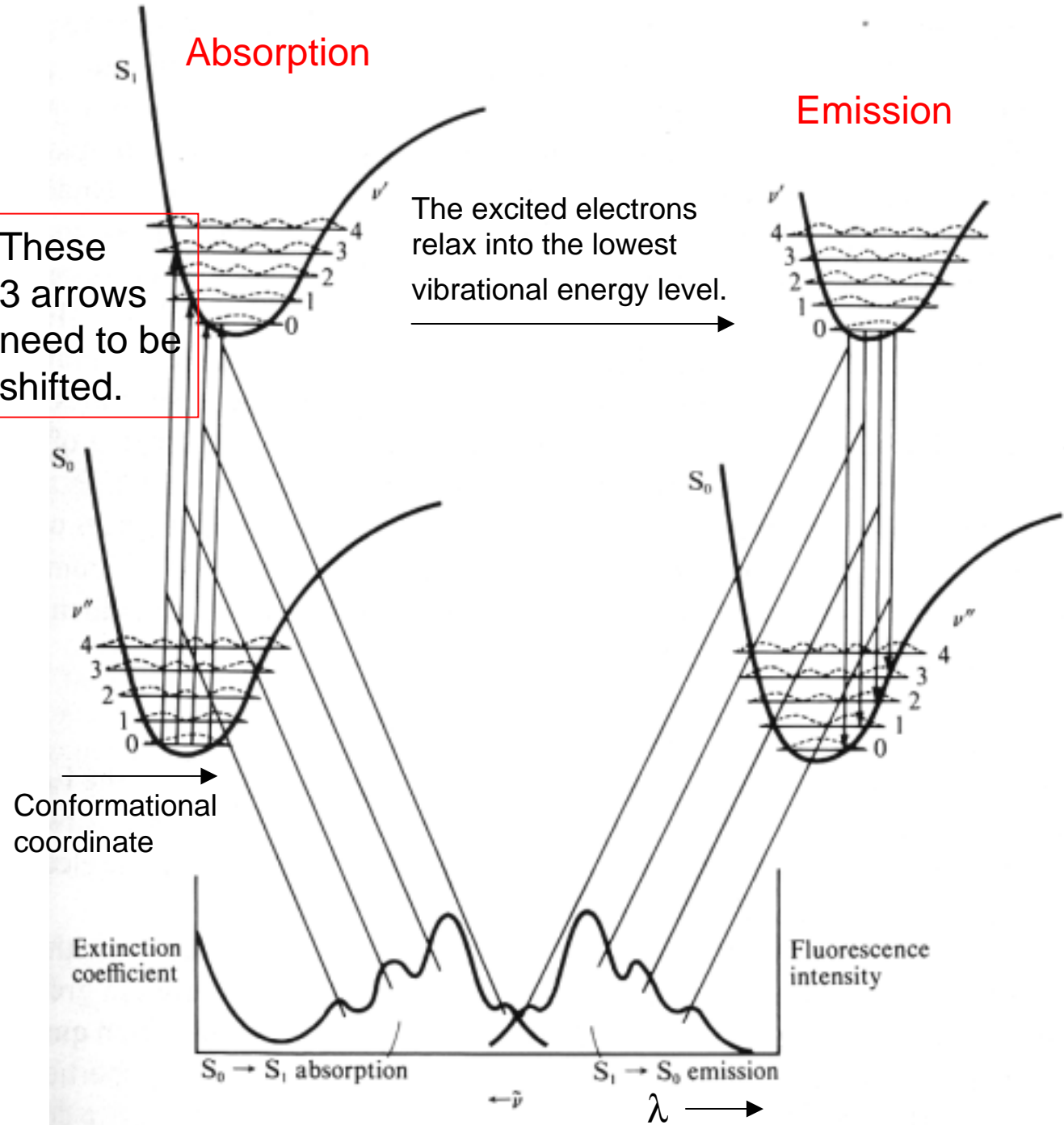

Conformational coordinate
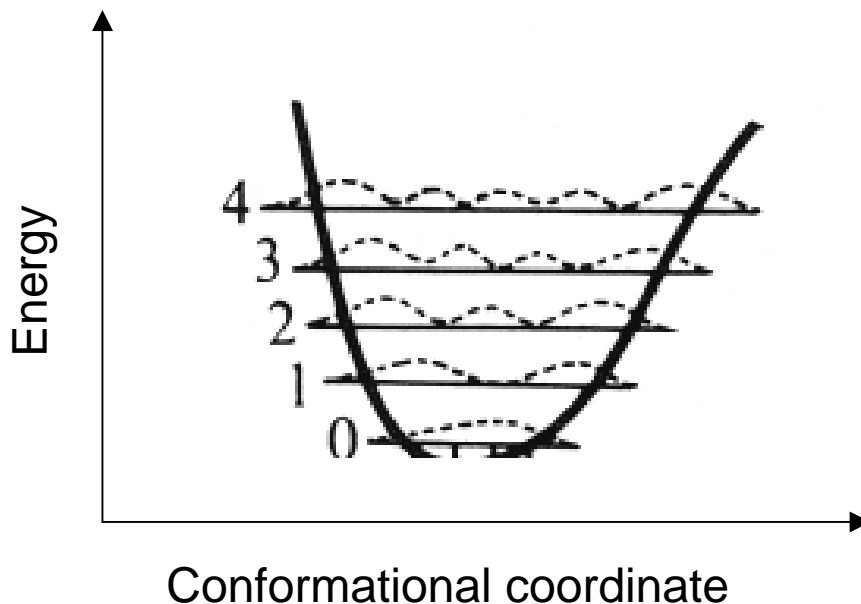
For conjugated molecules with far more than just two nuclei, we need to consider a plot of energy versus a mysterious conformational coordinate. To treat the problem rigorously we would need to consider a multidimensional plot where the energy depended on the position of every nucleus. It is helpful, however, to consider a two-dimensional curve where one coordinate described the conformation of the whole molecule.

Population of energy levels

Conformational coordinate
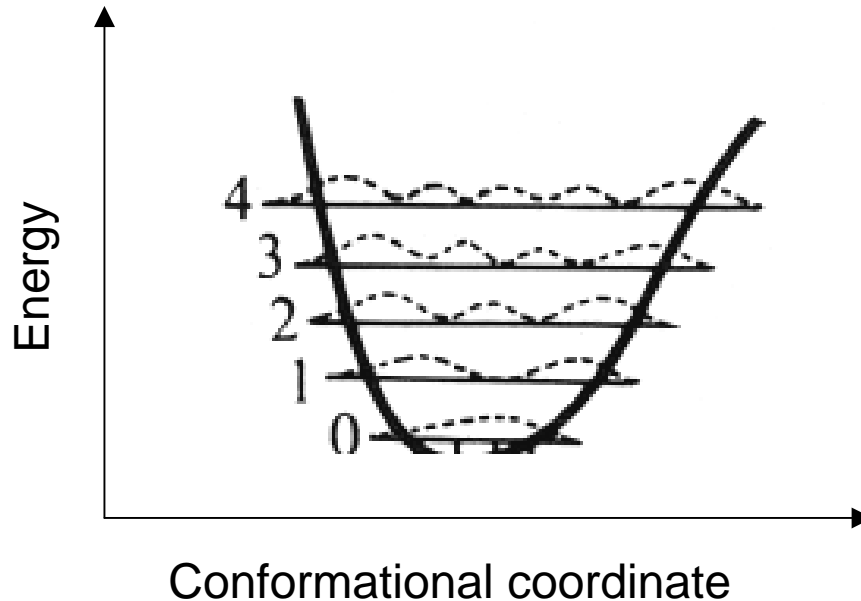
The number of molecules in each vibrational energy level is proportional to $e^{-E/kT}$. The spacing between levels is on the order of 0.2 eV, which is much greater than kT (0.0259 eV) at room temperature, so most of the molecules are in the vibrational ground state.

Absorption

Emission

These 3 arrows need to be shifted.

The excited electrons relax into the lowest vibrational energy level.

Conformational coordinate

Absorption and emission both involve electronic transitions. Electrons move much faster than nuclei, so the nuclei move by a negligible amount during the electronic transitions. For this reason, transitions connect points on the ground state (S_0) and excited state (S_1) curves that have the same conformational coordinate.

Pope, Swenberg, *Electronic Processes in Organic Crystals and Polymers*

Exciton migration to low energy sites
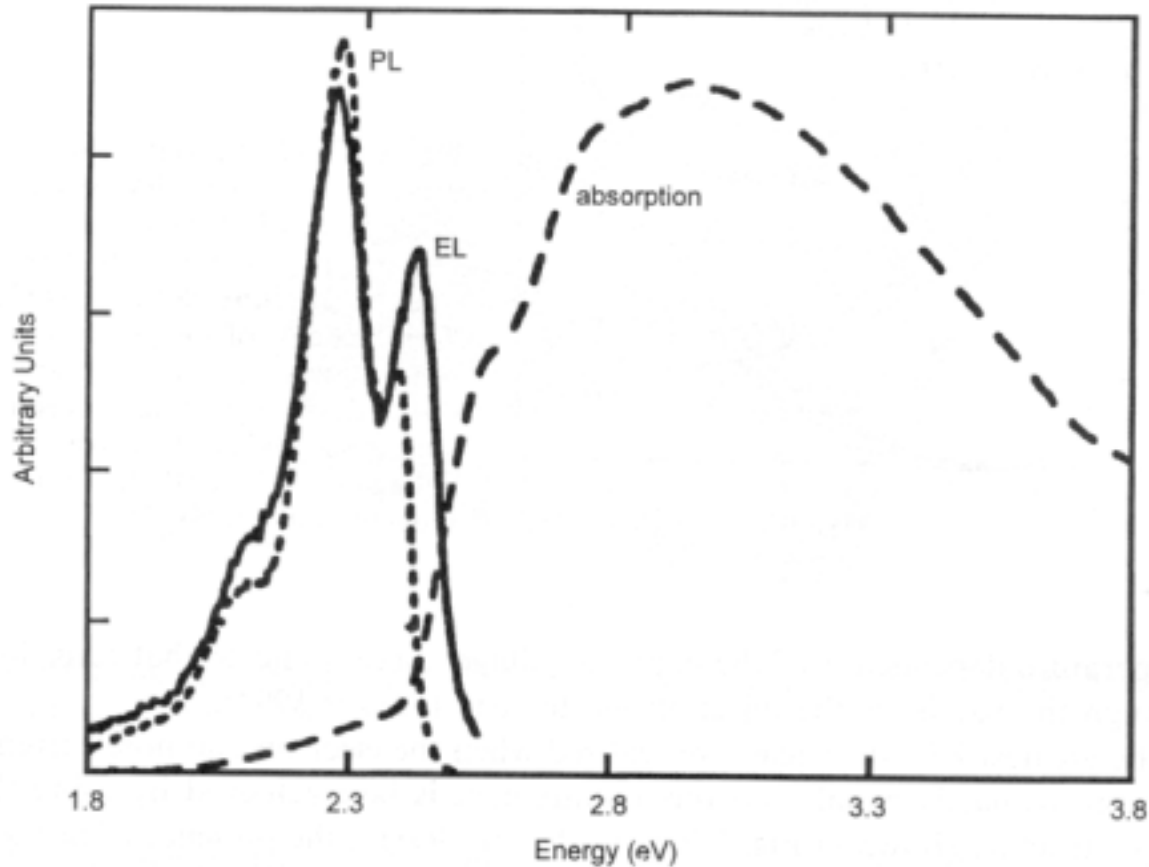
(The PL and EL spectra are typically slightly different because the emission occurs in different parts of the film and the electrodes affect the emission in ways we will discuss later.)

e⁻

h⁺
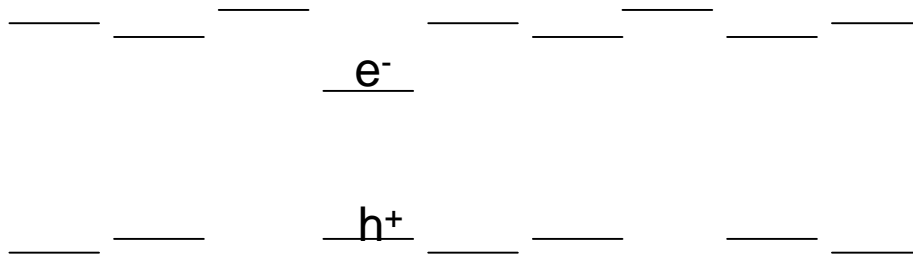
Explanation of the previous slide

For an individual molecule, the absorption spectrum has relatively sharp vibronic peaks.

In a disordered PPV film, there are variations in the conjugation length. Consequently, the band gap varies also.

The absorption spectrum shows absorption from all of the sites. All of the sharp peaks add together to create a smooth spectrum.

Excitons migrate from all of the different sites in a film to find the regions where the band gap is smallest. Consequently, most of the emission comes from a small number of sites with similar band gap. This explains why the emission spectra have sharp peaks.

Migration of energy is another mechanism for inducing a shift between the absorption and emission spectra.
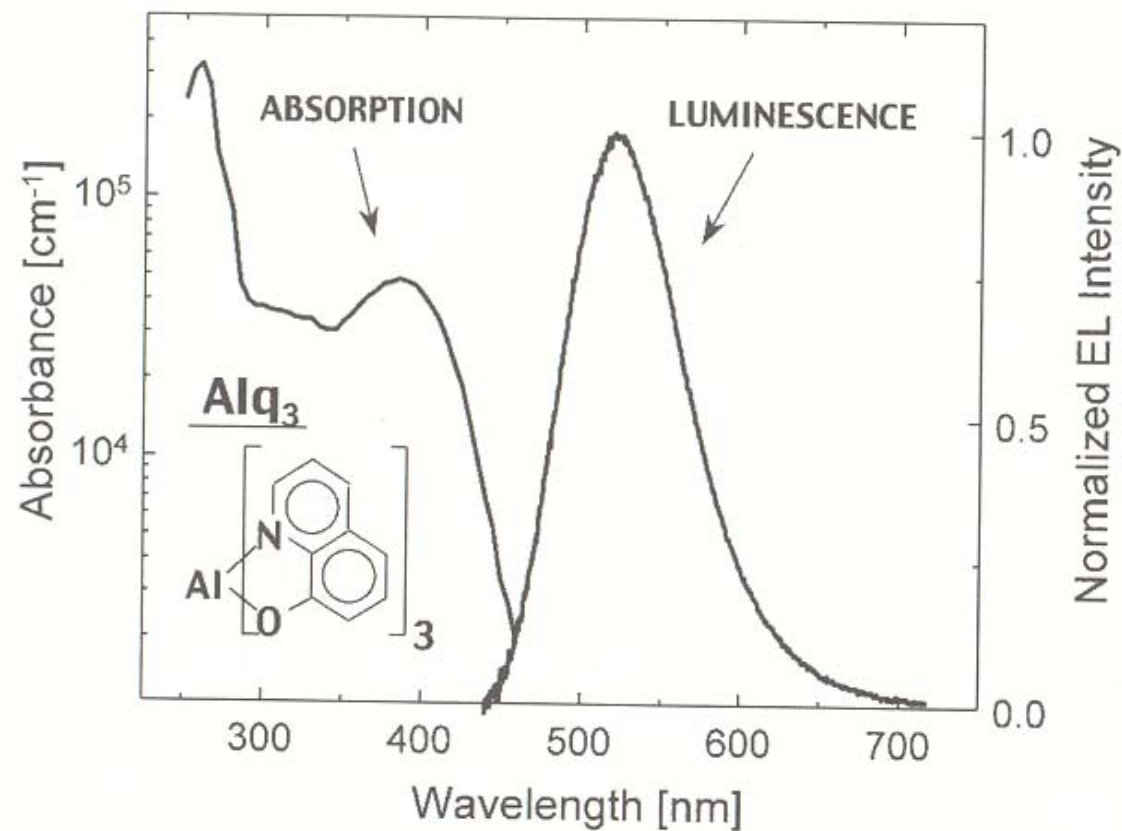
Fig. 11.3. Absorption and luminescence of aluminum *tris*-(8-hydroxyquinoline) (Alq3). Due to the Franck–Condon shift this material is transparent to its own radiation. Structural formula of Alq3 is also shown. (From [7])
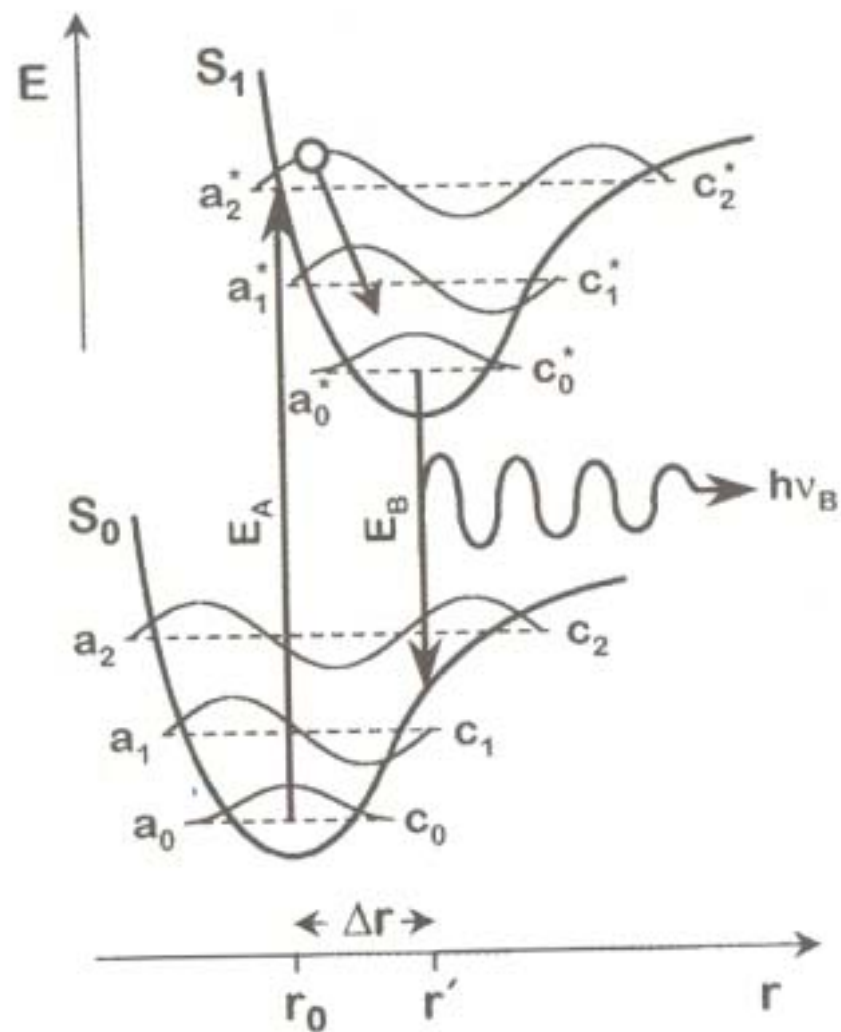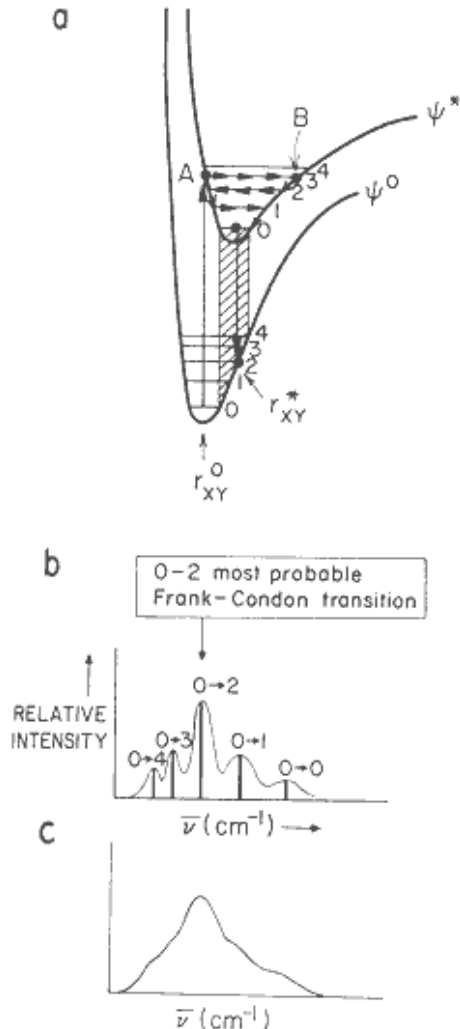
Fig. 11.2. Molecular configuration energy diagram of electronic states S_0 and S_1 for a diatomic molecule. *Dashed lines* indicate the vibrational energy levels on top of which the vibrational wavefunctions are drawn. The equilibrium distance, r_0, and nuclear displacement Δr are indicated

Franck-Condon & Emission

- The most probable transitions produce an elongated ground state, while absorption initiallly produces a compressed excited state

- In both cases of absorption and emission, transition occurs from the $\nu=0$ level of the initial state to some vibrational level of the final state $\rightarrow$ which level is dependent on the displacement between ψ^o and ψ^*

- Band spacing in the resulting spectrum is determined by the vibrational structure in the final state
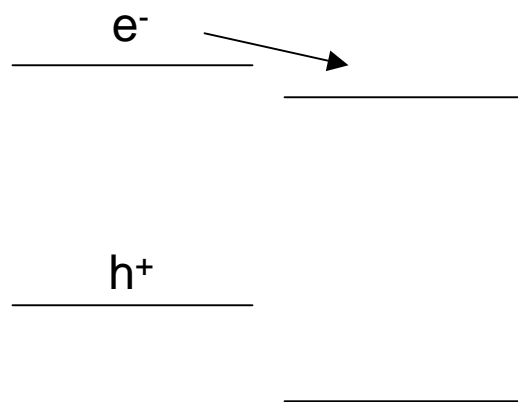
Energy and charge transfer

Energy transfer

e^-

h^+
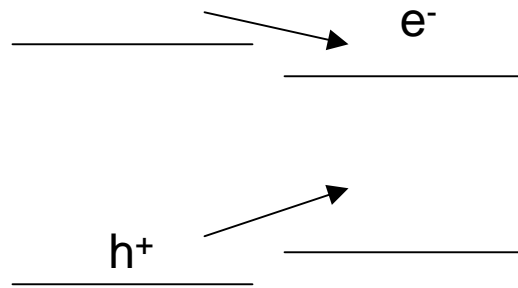
Energy transfer is very important for LEDs and lasers.

Charge transfer

e^-

h^+

Charge transfer is very important in photovoltaic cells and biosensors.

Some uses of energy transfer

Luminescence efficiencies can be improved
• Phosphorescent dyes harness triplets
• Luminescent molecules trap excitons before non-emissive traps do.
• Diluting chromophores can prevent concentration quenching (excimer formation)

Spectrum alteration
• Transferring energy can change the emission color.
• Some chromophores (e.g. rare earth complexes) have very sharp emission spectra.

Four-level systems for lasers
• If emission occurs at a different energy than absorption, then light is not reabsorbed.

Mechanisms of energy transfer

1. Emission and reabsorption

2. Förster (also called Dipole-dipole or energy resonance)

The excited molecule puts out a radiation field that couples with another dipole.

3. Dexter

The electron and hole transfer (hop) to another molecule at the same time. Wavefunction overlap is required.

See Chapter 9 in Nicholas Turro's *Modern Molecular Photochemistry* for a thorough discussion of this topic.

Emission and reabsorption
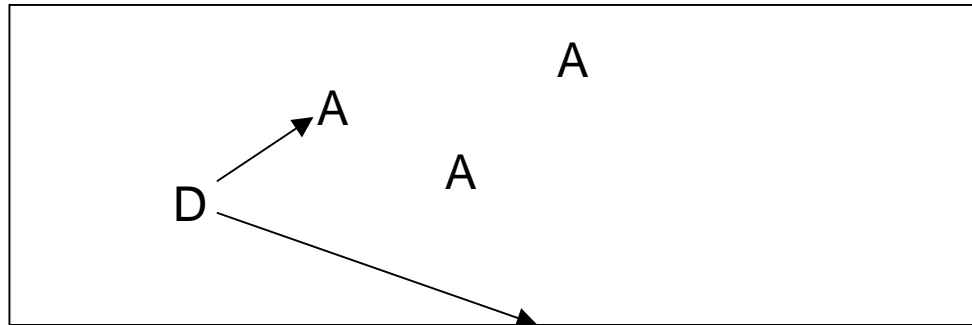
For energy to be efficiently transferred from a donor (D) to an acceptor by emission and reabsorption of photons:

• The donor must be an efficient emitter.
• The absorption spectrum of the acceptor must overlap the emission spectrum of the donor.
• There must be a significant number of acceptor molecules in the path of any photons emitted by the donor.

This process is rarely important, because Förster energy transfer will probably occur before the donor can emit a photon if the above conditions are satisfied.

Förster (resonance) energy transfer

D   A

The electric field near an excited molecule behaves like a field generated by a classical oscillating dipole. The dipole oscillates at frequencies corresponding to its emission frequencies.

The oscillating dipole can induce an oscillating dipole in the acceptor molecule.

If the acceptor absorbs light at the frequencies of the oscillation, then it can take the energy from the donor molecule.

The Nature of Light

The classical theory of light is a convenient starting point providing a pictorial and understandable physical representation of the interaction of light and molecules

classical theory can be improved by applying quantum interpretations of basic concepts (orbital, quantized energy etc.)

Dipoles as a model for interactions between electrons and light

oscillating electric dipole field of the electromagnetic wave
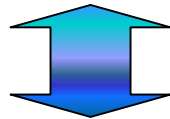
oscillating dipoles due to electrons moving in orbitals

→ Dipole-dipole interactions are through space and don't require orbital overlap

(Interactions requiring overlap are "exchange interactions")

Oscillating Electric Field

➤ Frequency (ν) of oscillating field must "match" a possible electronic oscillation frequency (conservation of energy)

➤ There must be an interaction or coupling between the field (oscillating dipoles) and the electron: Interaction strength depends on field dipole and induced dipole strength as well as distance between the two.

➤ Laws of conservation of angular momentum must be obeyed: Spin change is highly resisted in absorption due to time constraints

The most important interaction between the electromagnetic field and the electrons of a molecule can be modeled as the interaction of 2 oscillating dipole systems

Rate of Förster energy transfer

$$k_{ET} \propto \frac{\int I_D \varepsilon_A \, d\omega}{R_{DA}^6}$$

The integral quantifies the overlap of the emission of the donor (I_D) with the absorption of the acceptor (ε_A). Strong emitters put out stronger radiation fields. Strong absorbers are excited more easily.

R_{DA} is the separation between the donor and acceptor.

Förster (resonance) energy transfer

The radiation field from an excited dipole can transfer energy to another dipole that oscillates at the same frequency. This occurs when:

1.) There is some spectral overlap. →
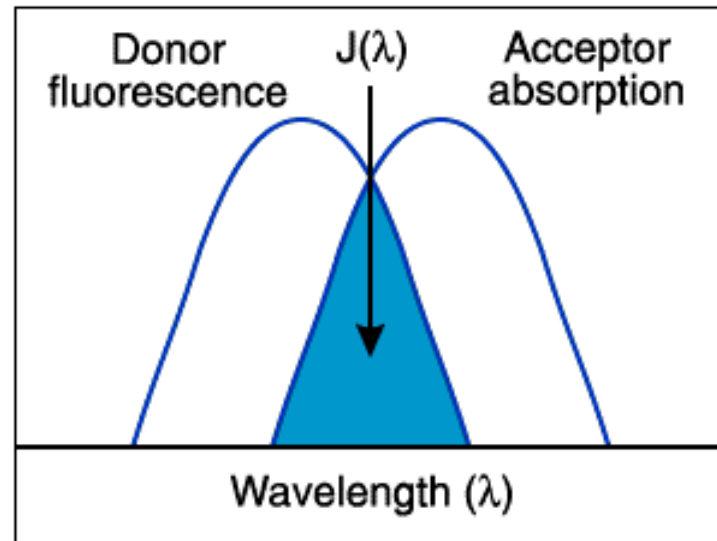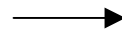
2.) The donor and acceptor transition dipole orientations are approximately parallel.

3.) The donor and acceptor molecules are within ~ 10 nm of each other.
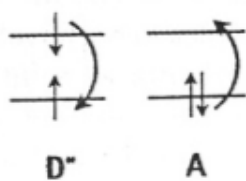
Dexter energy transfer

If there is some wavefunction overlap, an exciton can hop from one molecule to another.

Dexter transfer is usually only substantial for molecules that are touching or separated by just one molecule.

If the donor can emit strongly, the acceptor can absorb strongly and all of the conditions for Förster transfer are satisfied, then energy transfer will occur mostly by the Förster mechanism.

If however, triplets are involved, Förster transfer will be slow and Dexter transfer will dominate.
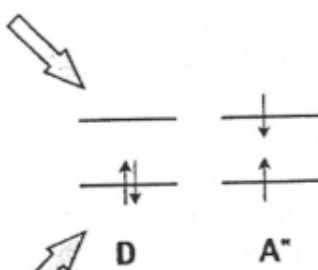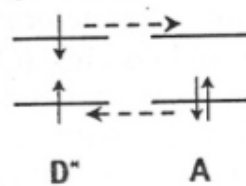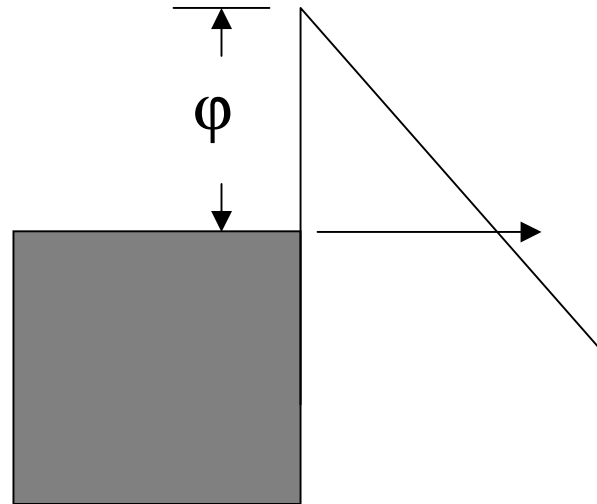
Fig. 11.6. Representation of the Förster and the Dexter processes in singlet–singlet energy transfer

Electrodes & Charge injection

Fowler-Nordheim tunneling

φ

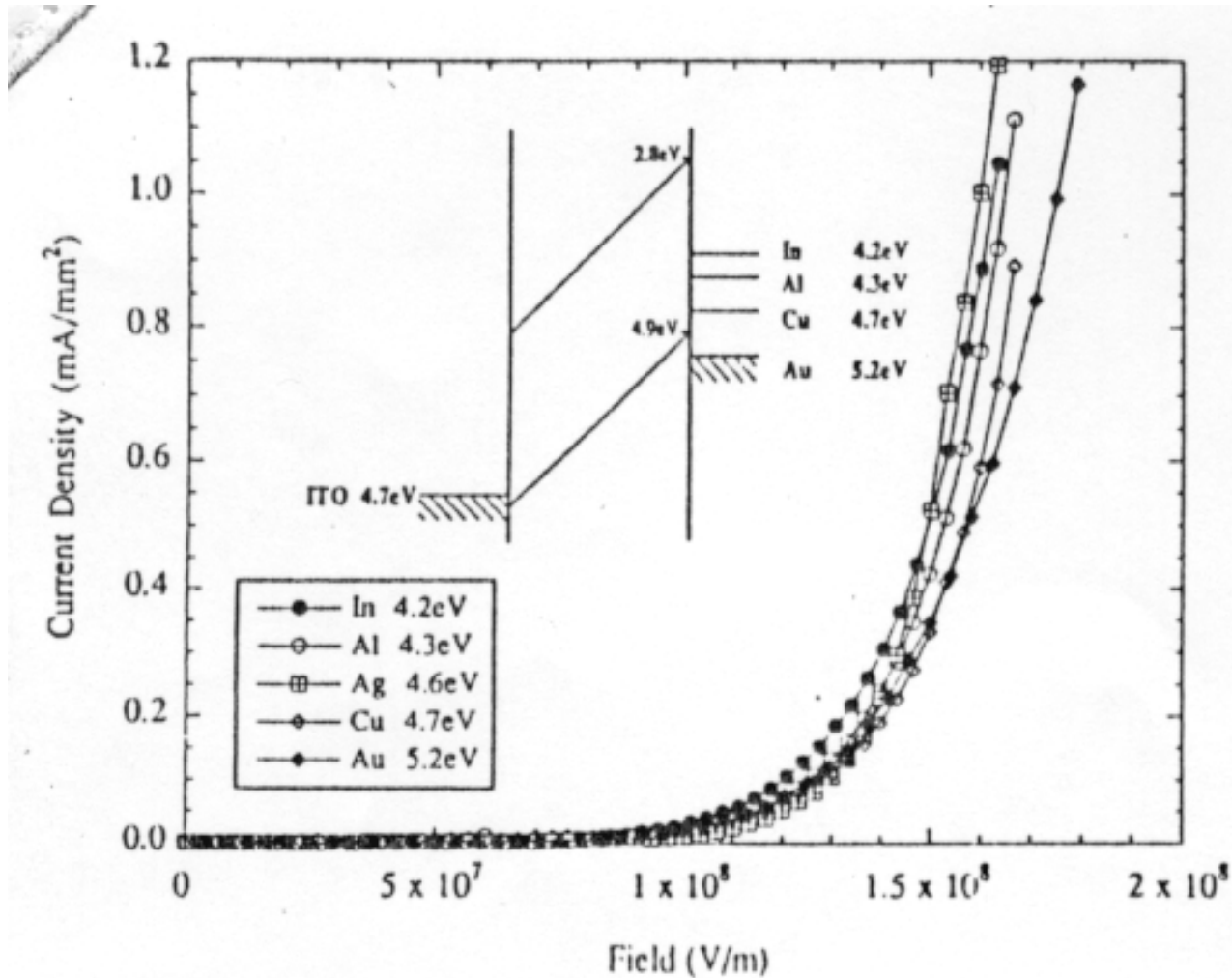Electrons tunnel through the triangular barrier. The width of the barrier depends on the electric field.

$$J \propto E^2 \exp(\frac{-\kappa}{E})$$

$$\kappa = \frac{8\pi\sqrt{2m^*\varphi^{3/2}}}{3qh}$$
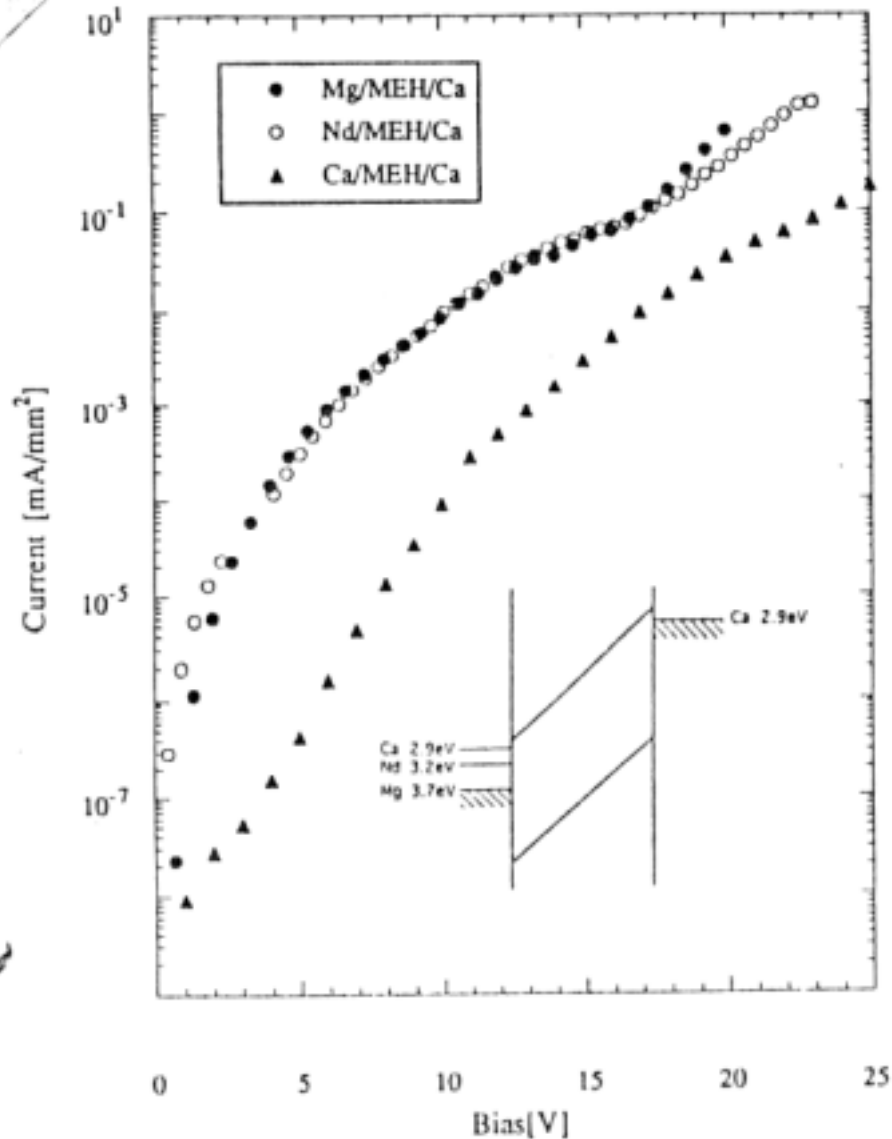
J = current density
E = electric field

m* = effective mass
φ = barrier height

Hole-only diodes

Since J doesn't depend at all on the work function of the cathode, we know that all of the current is due to holes. The absence of light emission supports this claim.

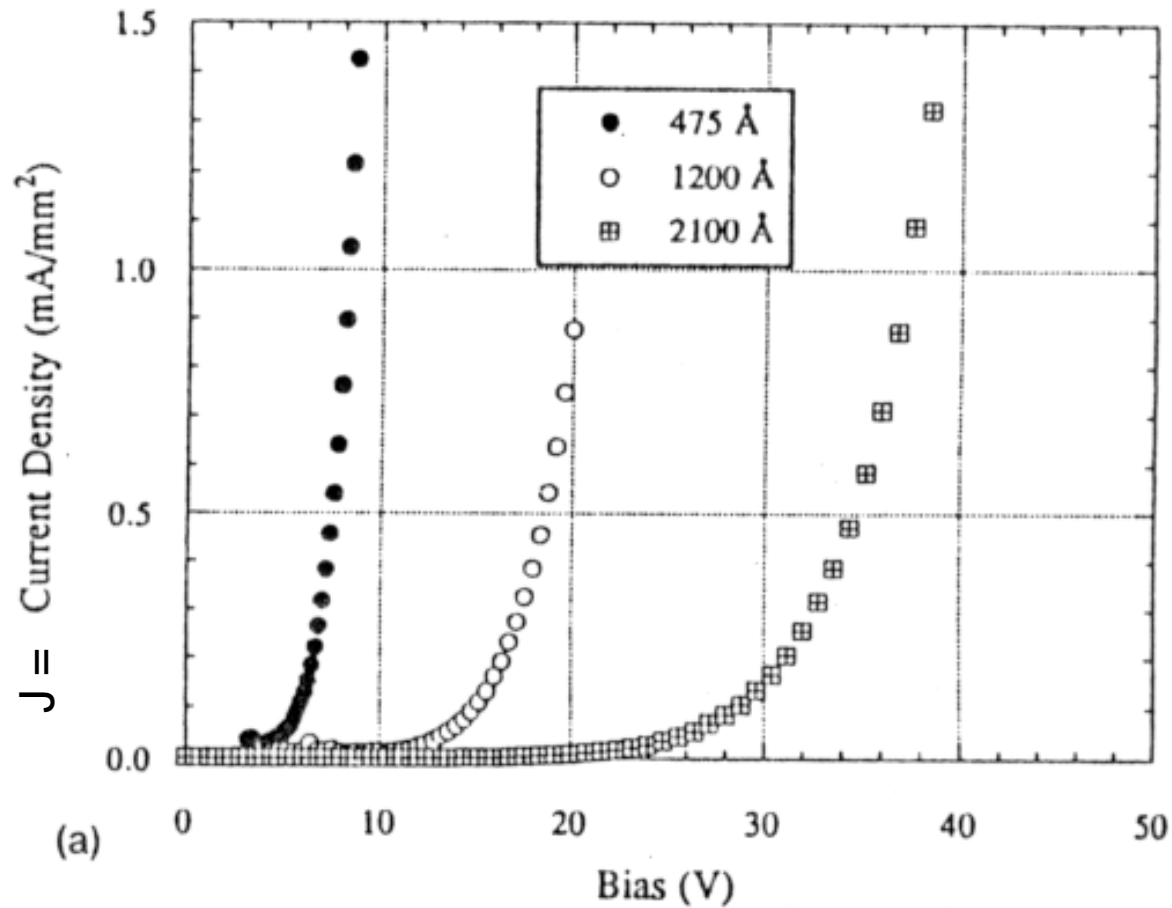Ian Parker, *J. Appl. Phys.* **75** (1994)1656.

Electron-only diodes

Since the barrier for hole injection is so high, no holes are injected. The current only depends on injection at the cathode.
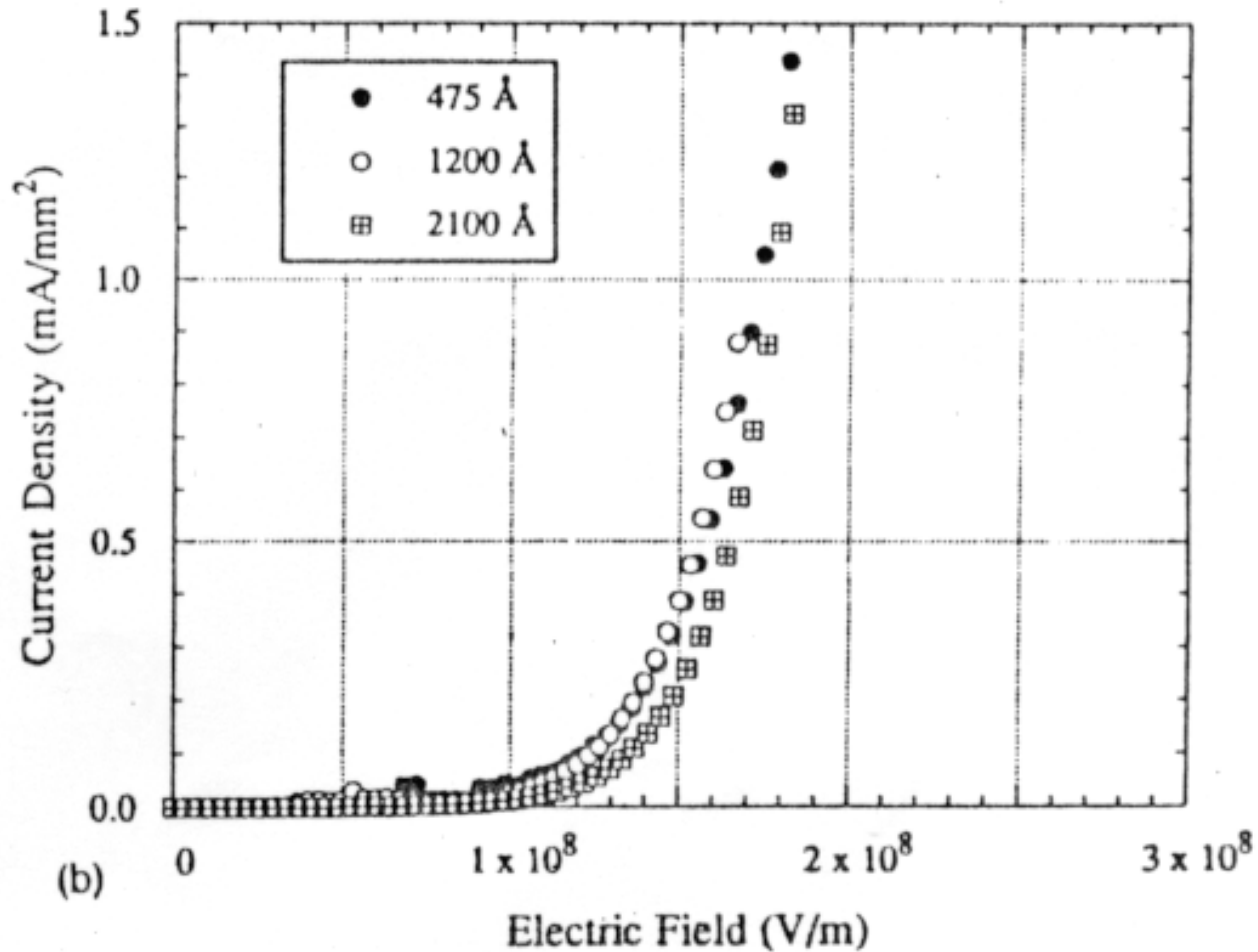
The experiment didn't work well with a Ca anode, because the Ca reacted with the solvent during spin casting.

Ian Parker, *J. Appl. Phys.* **75** (1994)1656.

J vs V in hole only (ITO/MEH-PPV/Cu) diodes

(a)

Legend:
- ● 475 Å
- ○ 1200 Å
- ⊞ 2100 Å

x-axis: Bias (V)
y-axis: J = Current Density (mA/mm²)

V clearly affects J, but J must depend on something else as well.
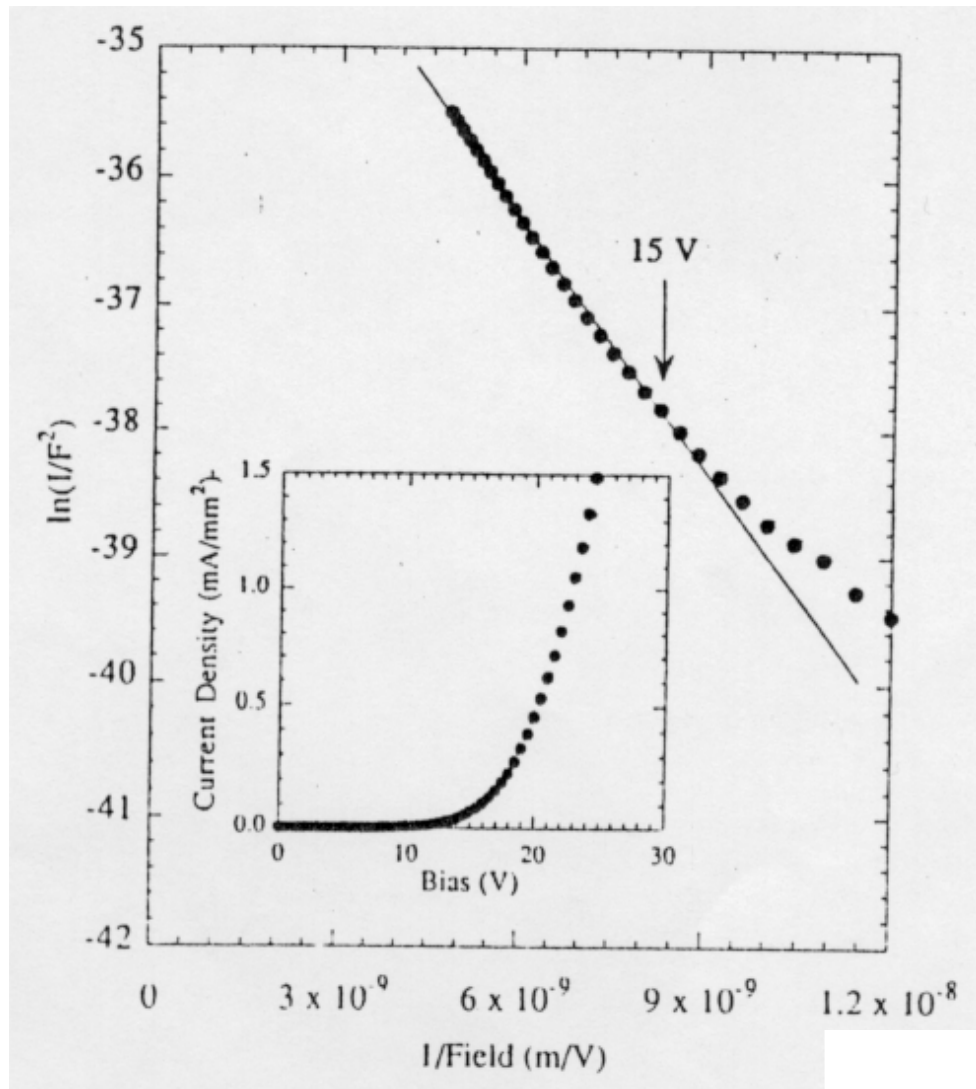
Ian Parker, *J. Appl. Phys.* **75** (1994)1656.

J vs E in the same hole-only diodes

The electric field determines the hole current.

The semiconducting layer must be thin so that the operating voltage can be kept low.

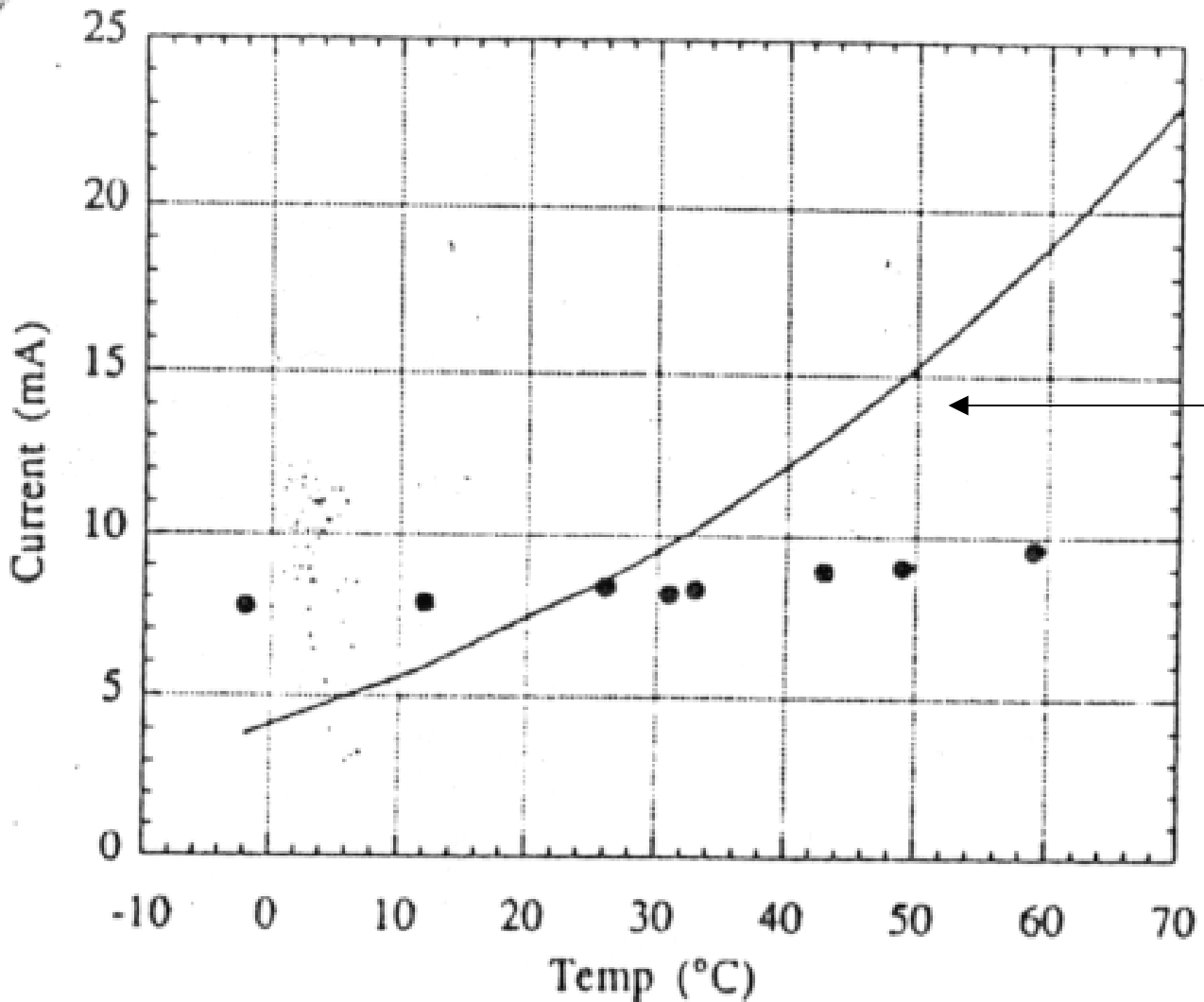Ian Parker, *J. Appl. Phys.* **75** (1994)1656.

Fowler-Nordheim plot

$$J \propto E^2 \exp(\frac{-\kappa}{E})$$

$$\kappa = \frac{8\pi\sqrt{2m*\varphi^{3/2}}}{3qh}$$

By finding the value of κ that gives the best fit to the data, one can find the barrier height, φ. In this case $\varphi = 0.2$ eV.

At high voltage, the data fits the Fowler-Nordheim curve nicely.

Ian Parker, *J. Appl. Phys.* **75** (1994)1656.

Temperature dependence

Prediction for a 0.2 ev Schottky barrier device

The lack of temperature dependence supports the tunneling model.

Ian Parker, *J. Appl. Phys.* **75** (1994)1656.