전자물리특강
Electronic Structure of Organic Semiconductors
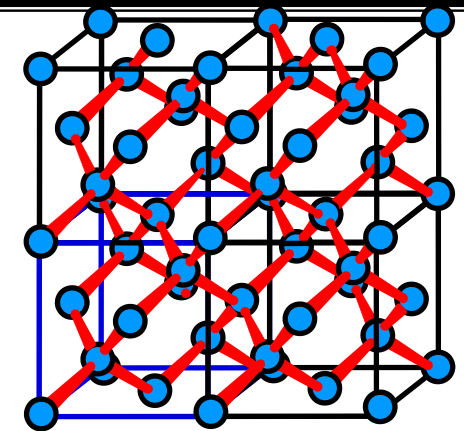
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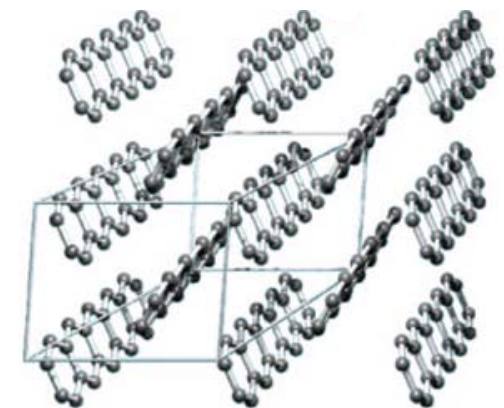chlee7@snu.ac.kr

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Organic *vs* inorganic semiconductors

Inorganic Semiconductor		Organic Semiconductor
Covalent (2 ~ 4 eV)	Interaction Energy	Weak Van der Waals ($10^{-3} \sim 10^{-2}$ eV)
Band	Transport Mechanism	Hopping
100 ~ 10,000	Mobility (cm^2/Vs), RT	$10^{-6} \sim 1$
$l \sim (100 \sim 1000)\, a_o$	Mean free path	$l \sim a_o$ = lattice constant
$m_{eff} \leq m_e$	Effective mass	$m_{eff} = (10^2 \sim 10^3) m_e$, (Polaron)
Wannier-Mott	Exciton	Frenkel

E. A. Silinsh and V. Capek, Organic Molecular Crystals,(AIP, NY, 1994)

Inorganic Crystals
Strong covalent bond
(Diamond structure)

Organic Crystals
Weak Van der Waals interaction
(Herring bone structure)

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Electronic Configuration of carbon: C=1s²2s²2p²

2p

~4 eV

2s

Covalent bonding energy for the s orbital:
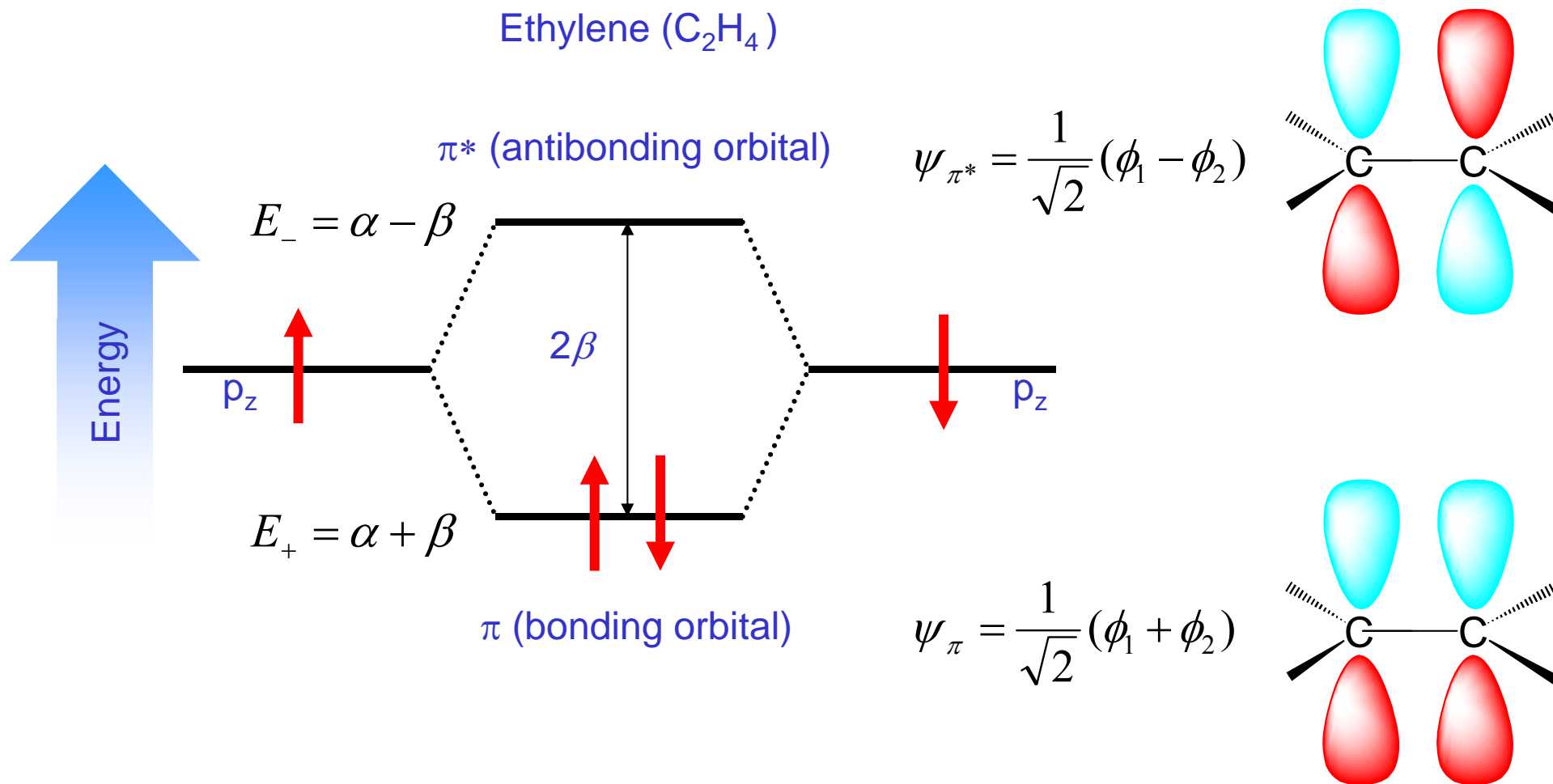3~4 eV per bond

hybridization: sp, sp², sp³

"In carbon, three possible hybridizations occur: sp, sp², and sp³ ; other group IV elements such as Si, Ge exhibit primarily sp³ hybridization. Carbon differs from Si and Ge insofar as carbon does not have inner atomic orbitals except for the spherical 1s orbitals, and the absence of nearby inner orbitals facilitates hybridizations involving only valence s and p orbitals for carbon."
Ref. R. Saito *et al.* "Physical Properties of Carbon Nanotubes" (Imperial College Press, 1998, Singapore) p.5.
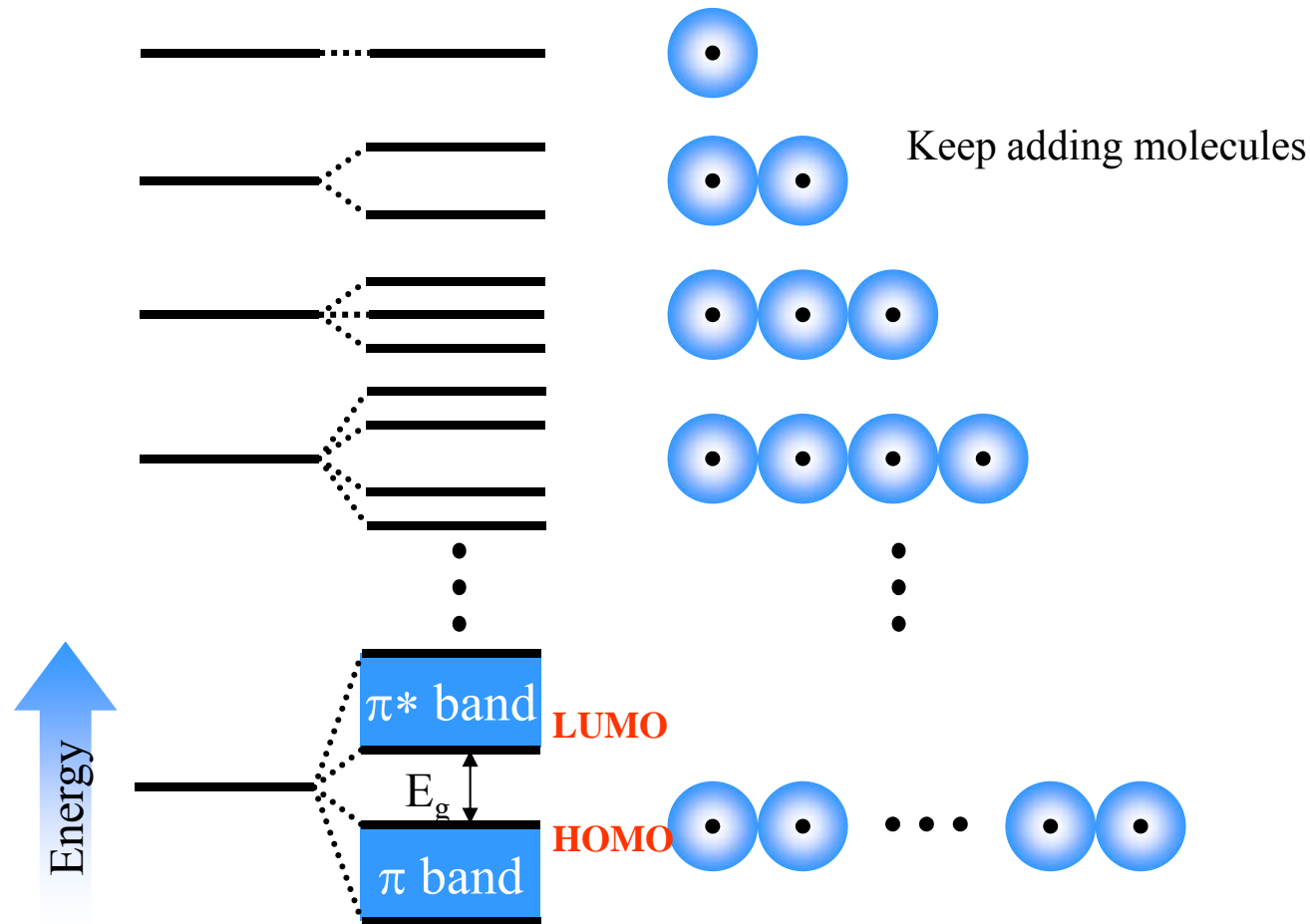
$$\varphi_1 = \frac{1}{\sqrt{2}}(\phi_s + \phi_{p_x})$$

$$\varphi_2 = \frac{1}{\sqrt{2}}(\phi_s - \phi_{p_x})$$

Orthonormality : $\langle \varphi_1 | \varphi_1 \rangle = 1, \langle \varphi_2 | \varphi_2 \rangle = 1, \langle \varphi_1 | \varphi_2 \rangle = 0, \langle \varphi_2 | \varphi_1 \rangle = 0$
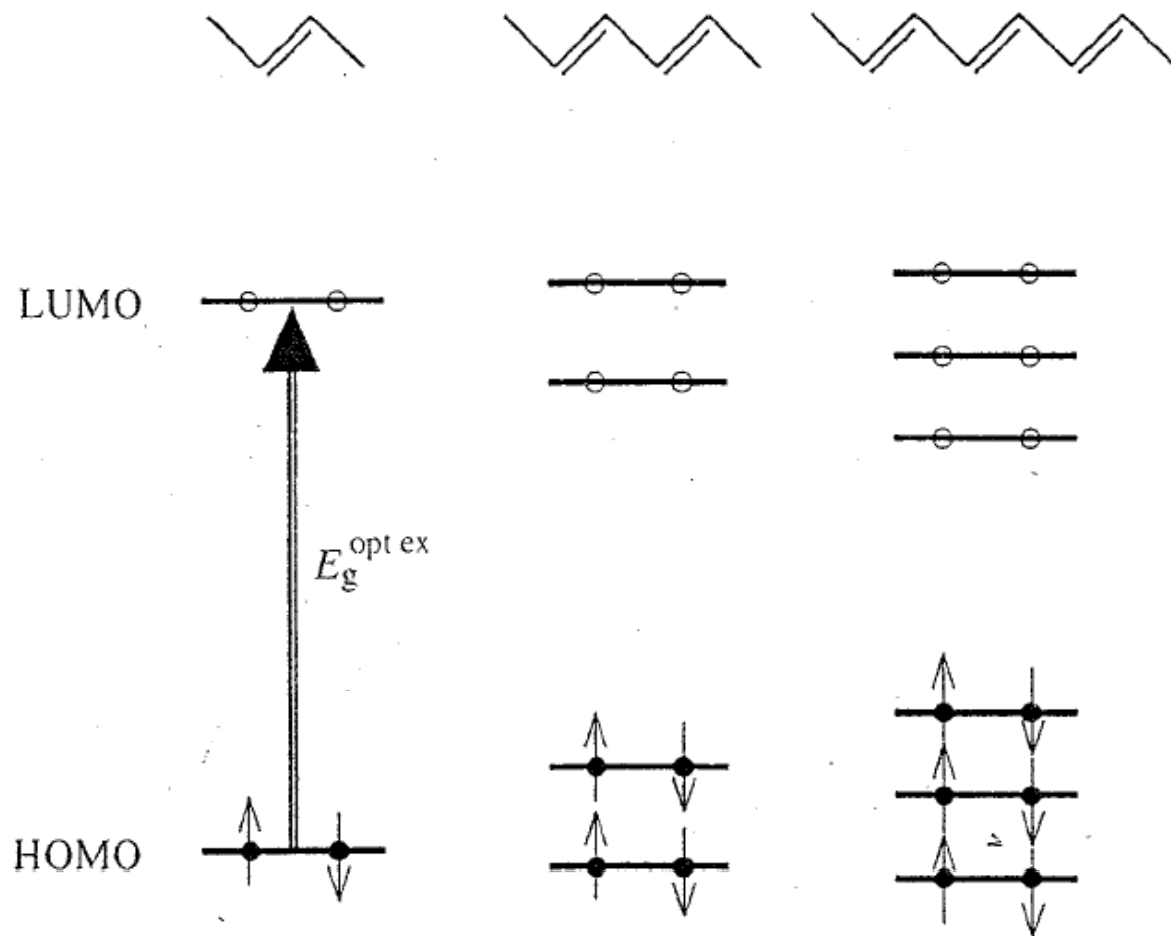
sp hybridization

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Ethylene (C_2H_4)

$\pi*$ (antibonding orbital)

$$\psi_{\pi*} = \frac{1}{\sqrt{2}}(\phi_1 - \phi_2)$$

$E_- = \alpha - \beta$

2β

Energy

p_z p_z

$E_+ = \alpha + \beta$

π (bonding orbital)

$$\psi_\pi = \frac{1}{\sqrt{2}}(\phi_1 + \phi_2)$$

Keep adding molecules

Energy

$\pi*$ band   **LUMO**

E_g

π band   **HOMO**
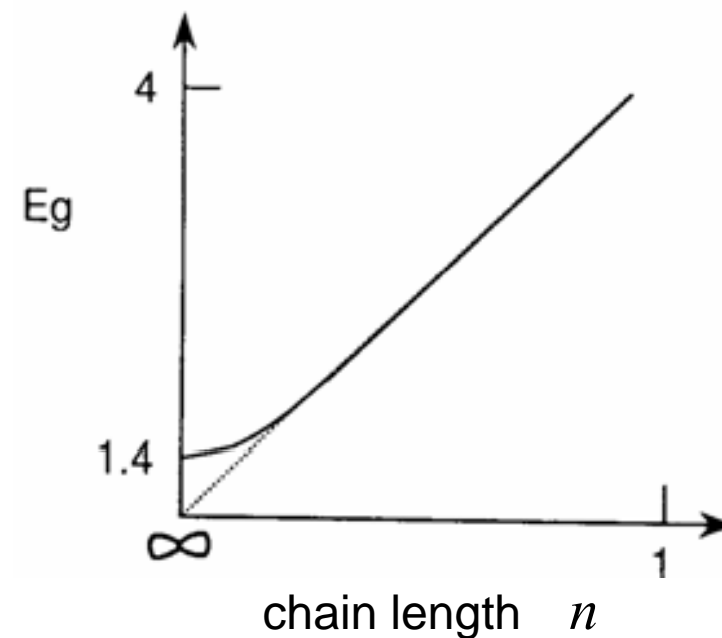
- The average energy separation between MOs decrease as n increases → Formation of bands.
- The HOMO-LUMO separation, ΔE = EHOMO – ELUMO, decreases as n increases.
- Energetically favored electron excitation is from the HOMO to the LUMO
- The interchain transfer integral (t) expresses the ease of charge transfer between two interacting chains: The larger the band-width (the magnitude of transfer integral), the higher the mobility.

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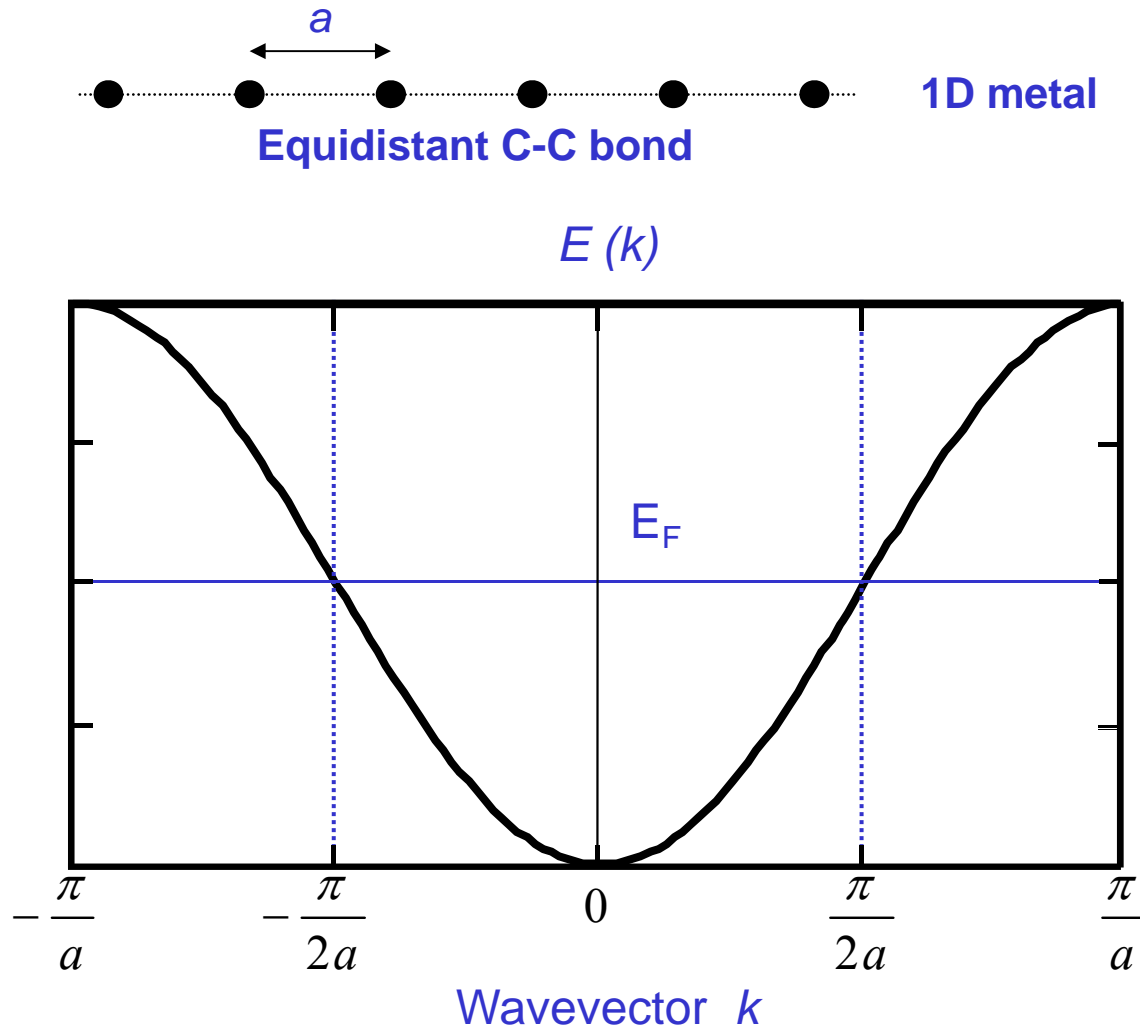$$E_g^{opt}(n) = E_g^{opt}(\infty) - \frac{K}{n}$$

LUMO

$E_g^{opt\ ex}$

HOMO

Eg

4

1.4

∞

1

chain length n

Energy gap (HOMO-LUMO) decreases with increasing π-conjugation.

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a

● ----- ● ----- ● ----- ● ----- ● ----- ●   **1D metal**

Equidistant C-C bond

E (k)

E_F

$$-\frac{\pi}{a} \qquad -\frac{\pi}{2a} \qquad 0 \qquad \frac{\pi}{2a} \qquad \frac{\pi}{a}$$

Wavevector *k*

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Peierls instability →Energy Band gap

**Sir Rudolf E. Peierls
1907-1995**

a

1-D metal

Equidistant C-C bond

2a

semiconductor

Bond alternation (dimerization)

$E = E_{pz} - \beta - 2\,t\,\cos ka$

$(CH)_x$

$E(k)$

E_F

E_g **Peierls Gap**

$-\pi/a$ $\quad -\pi/2a$ $\quad 0 \quad$ $\pi/2a$ $\quad \pi/a$

Wavevector k

π^*

π

M. Rohlfing and S. G. Louie,
Phys. Rev. Lett. **82**, 1959
(1999)

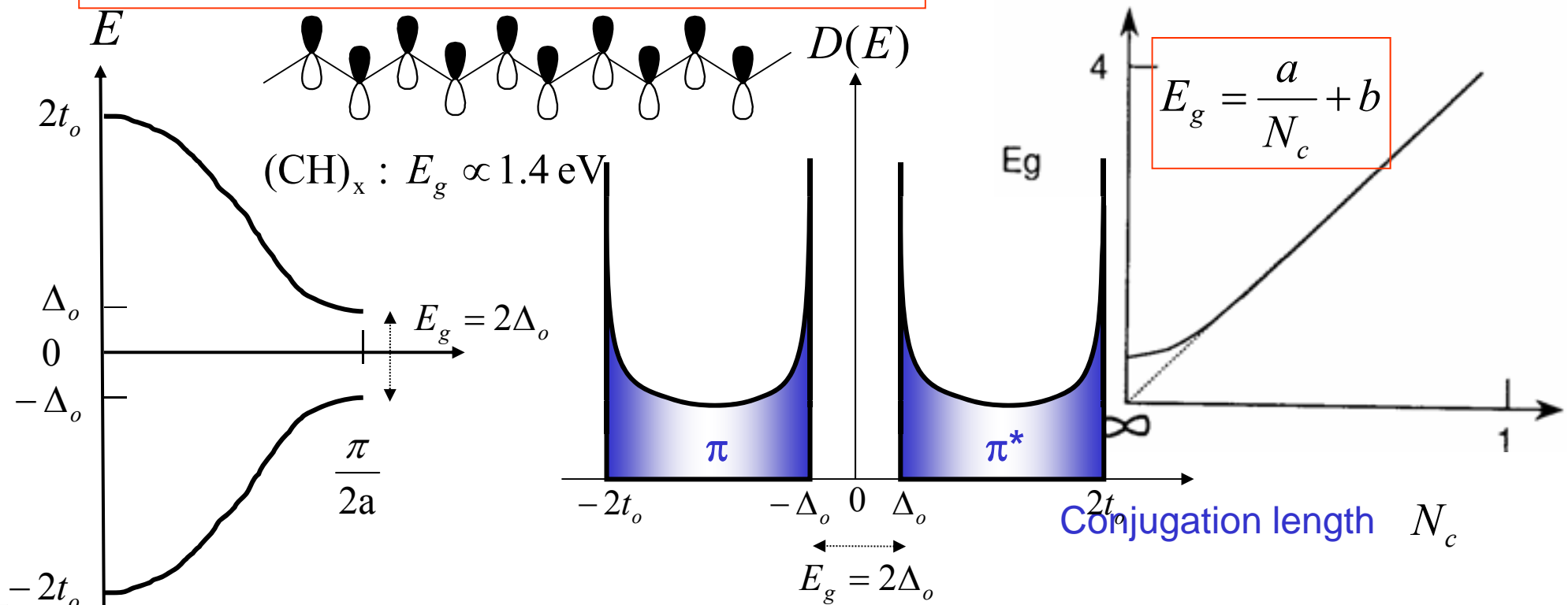R.E. Peierls *Quantum Theory of Solids* (Oxford University, London Chap.5(1955).

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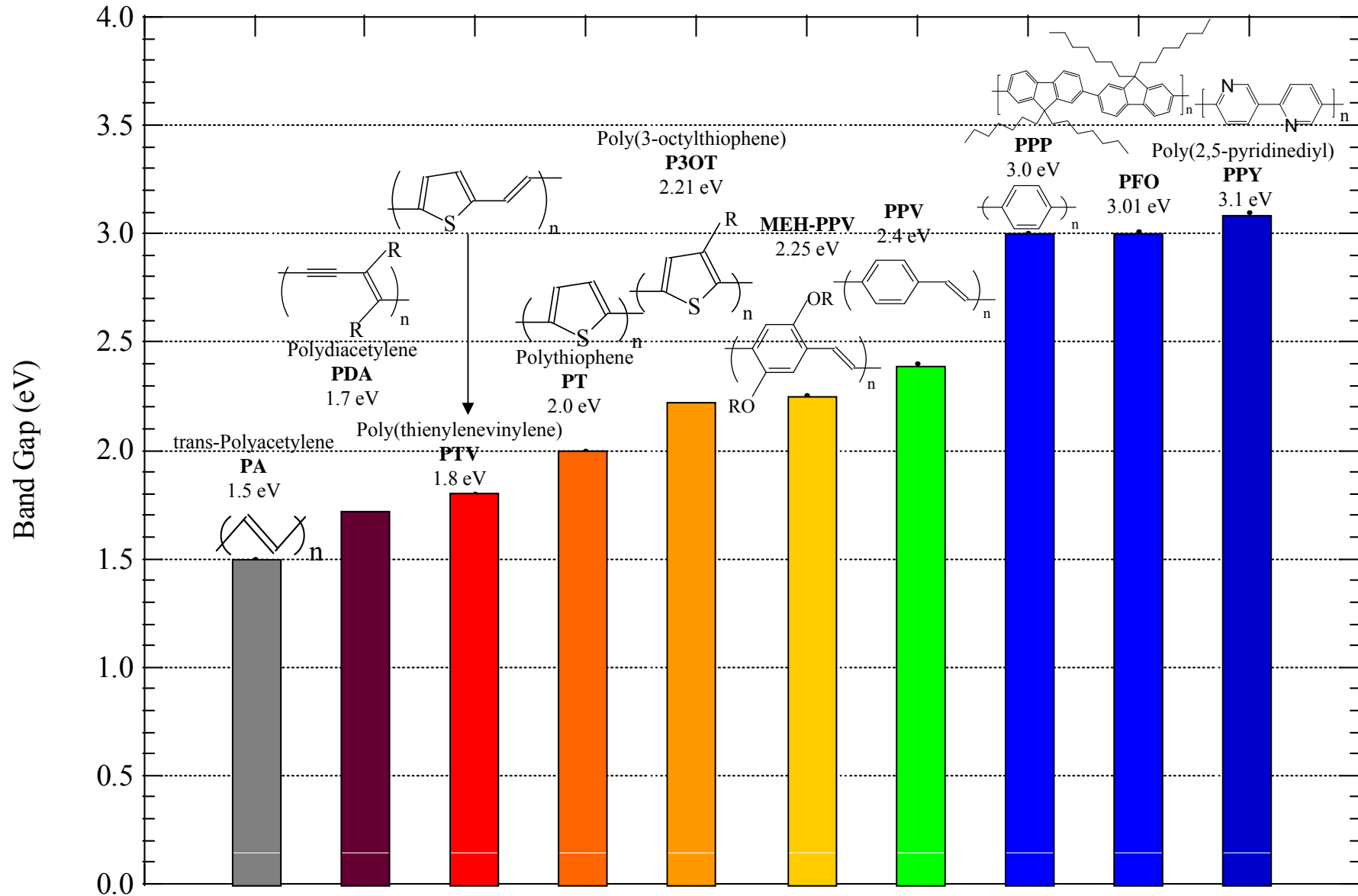# Polyacetylene: SSH Hamiltonian

Su-Schrieffer-Heeger Hamiltonian

$$H = H_{kinetic} + H_{elastic} + H_{electronic}$$

$$= \frac{M}{2}\sum \dot{u}_n^2 + \frac{K}{2}\sum_n (u_n - u_{n+1})^2 - \sum_{n,s}[t_0 + \alpha(u_n - u_{n+1})](c_{n+1,s}^+ c_{n,s} + c_{n,s}^+ c_{n+1,s})$$

Peierls gap : $2\Delta = 16t_o \exp[-(1 + \frac{1}{2\lambda})]$, where $\lambda = \frac{2\alpha^2}{\pi t_o K}$.

E

$D(E)$

$E_g = \frac{a}{N_c} + b$

$2t_o$

$(CH)_x : E_g \propto 1.4 \text{ eV}$

Eg

Δ_o

0

$E_g = 2\Delta_o$

$-\Delta_o$

$\frac{\pi}{2a}$

π

π^*

$-2t_o$

$-\Delta_o \ 0 \ \Delta_o$

$2t_o$

Conjugation length N_c

$-2t_o$

$E_g = 2\Delta_o$

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π- π* Energy Gap of Conjugated Polymers
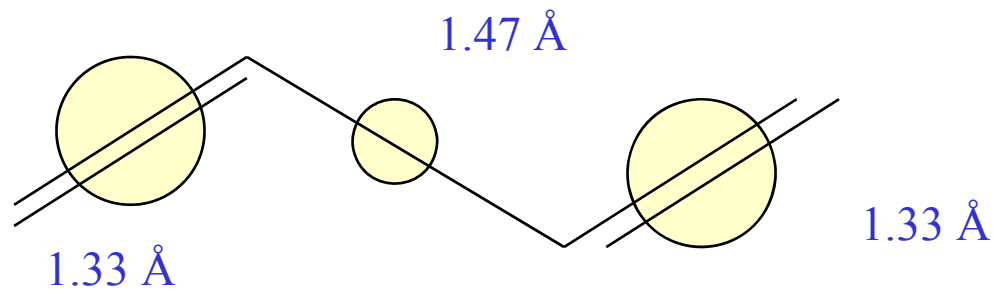
Ref. N. C. Greenham and R. H. Friend, Solid State Physics **49**, 1 (1995) p.13; A. Monkman et al., Phys. Rev. Lett. **86**, 1358 (2001)
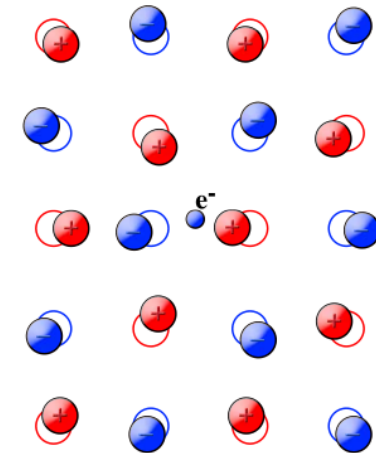
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Electron-Phonon coupling – Polaron

• Strong electron-phonon coupling:
π-electron bond densities directly determine the geometric structure,

e.g., butadiene, C4H6.

1.47 Å

1.33 Å

1.33 Å

• **Vibronic progressions** in optical absorption and photoluminescence spectra

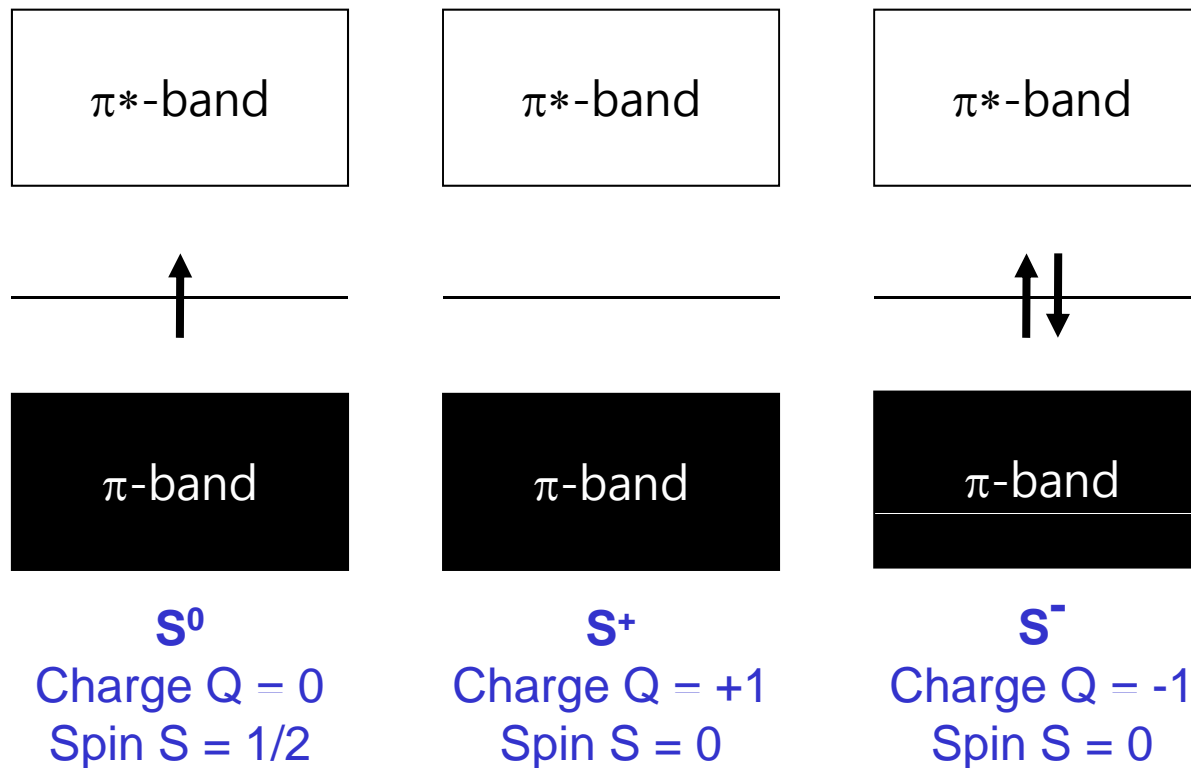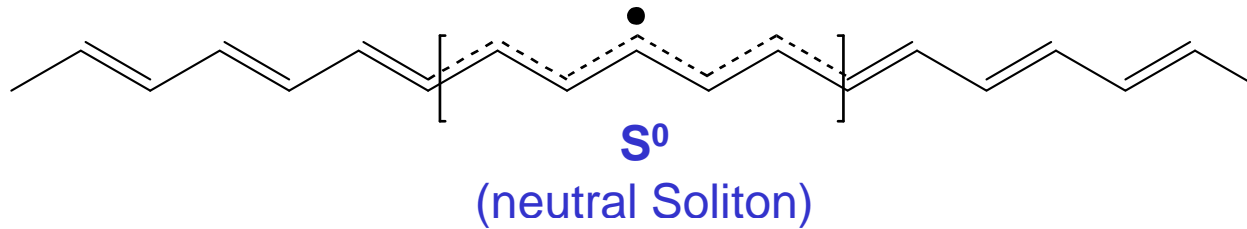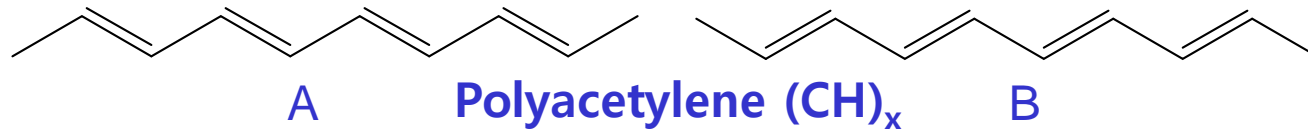• **Stokes shift** between optical absorption and emssion.
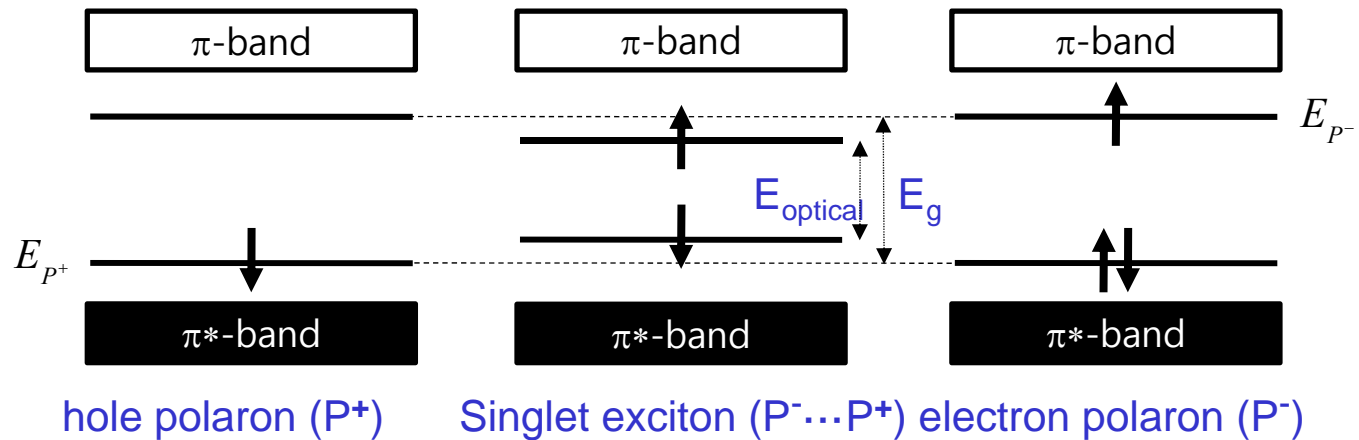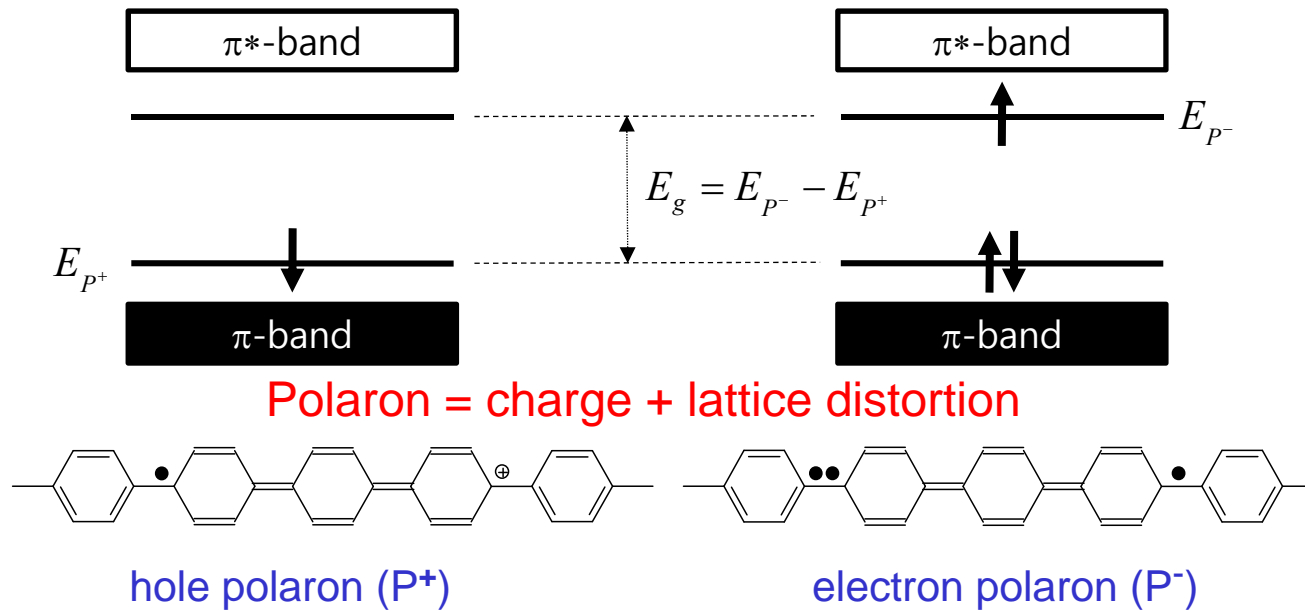
• **Polaron** formation

A **polaron** is a quasiparticle composed of a charge and its accompanying polarization field. Moving through the crystal, the electron carries the lattice distortion with it. The resulting lattice polarization acts as a potential well that hinders the movements of the electron, thus decreasing the electron mobility.
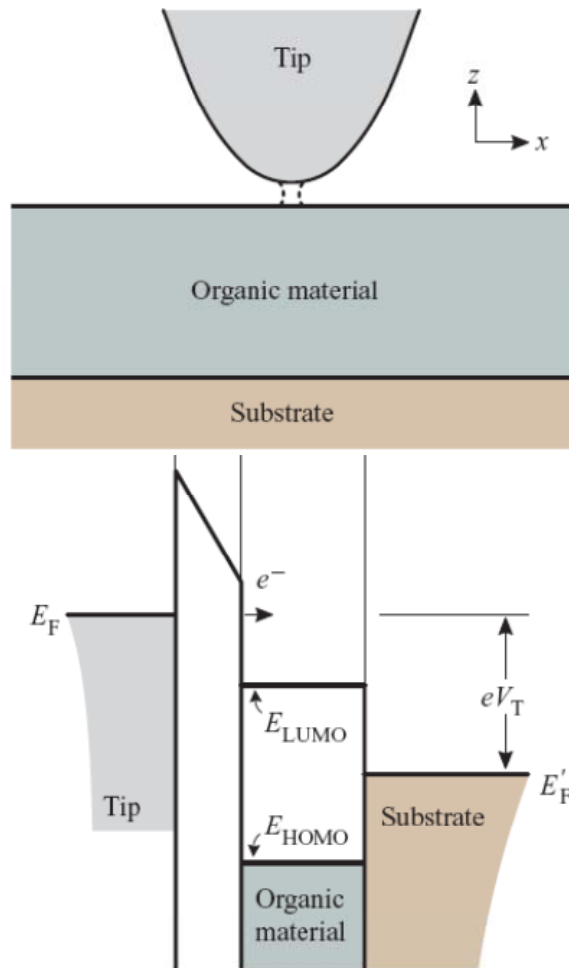
From Wikipedia: http://en.wikipedia.org/wiki/Polaron

Charge transfer or low energy charge-excitations (via dong or photoexcitation) strongly affects the π-electron bond densities $\rightarrow$ geometric structure.

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Soliton

A   **Polyacetylene (CH)$_x$**   B

S^0
(neutral Soliton)

$\pi*$-band	$\pi*$-band	$\pi*$-band

$\uparrow$ | | $\uparrow\downarrow$

π-band	π-band	π-band

S^0
Charge Q = 0
Spin S = 1/2

S$^+$
Charge Q = +1
Spin S = 0

S$^-$
Charge Q = -1
Spin S = 0

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Energy gap

$$E_g = E_{P^-} - E_{P^+}$$

Polaron = charge + lattice distortion

hole polaron (P$^+$)   electron polaron (P$^-$)

$E_{optical}$ E_g

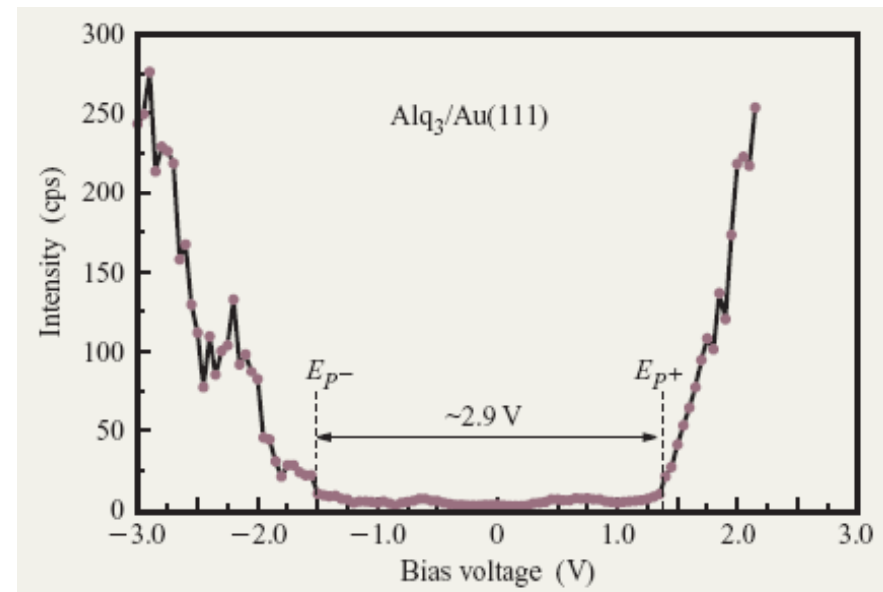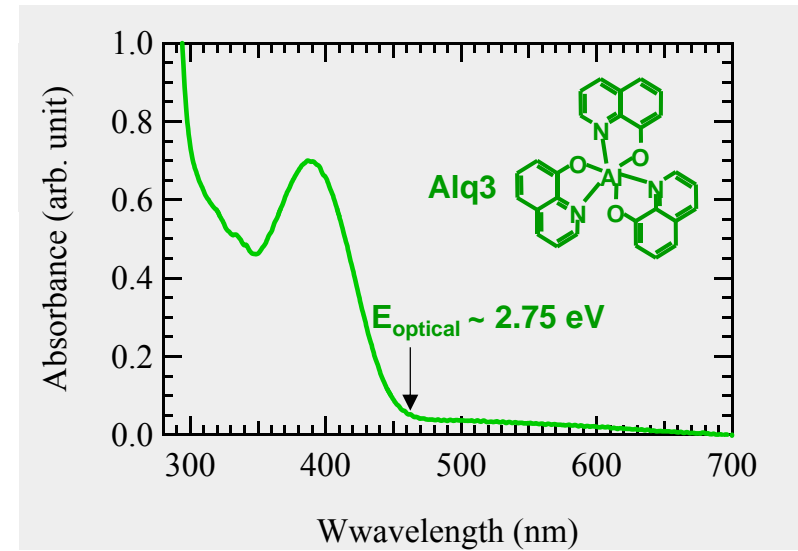hole polaron (P$^+$)   Singlet exciton (P$^-$···P$^+$) electron polaron (P$^-$)

Bandgap, Exciton binding energy

Alq3

From z–V measurements, $E_{gsp} = 2.96 \pm 0.13$ eV.

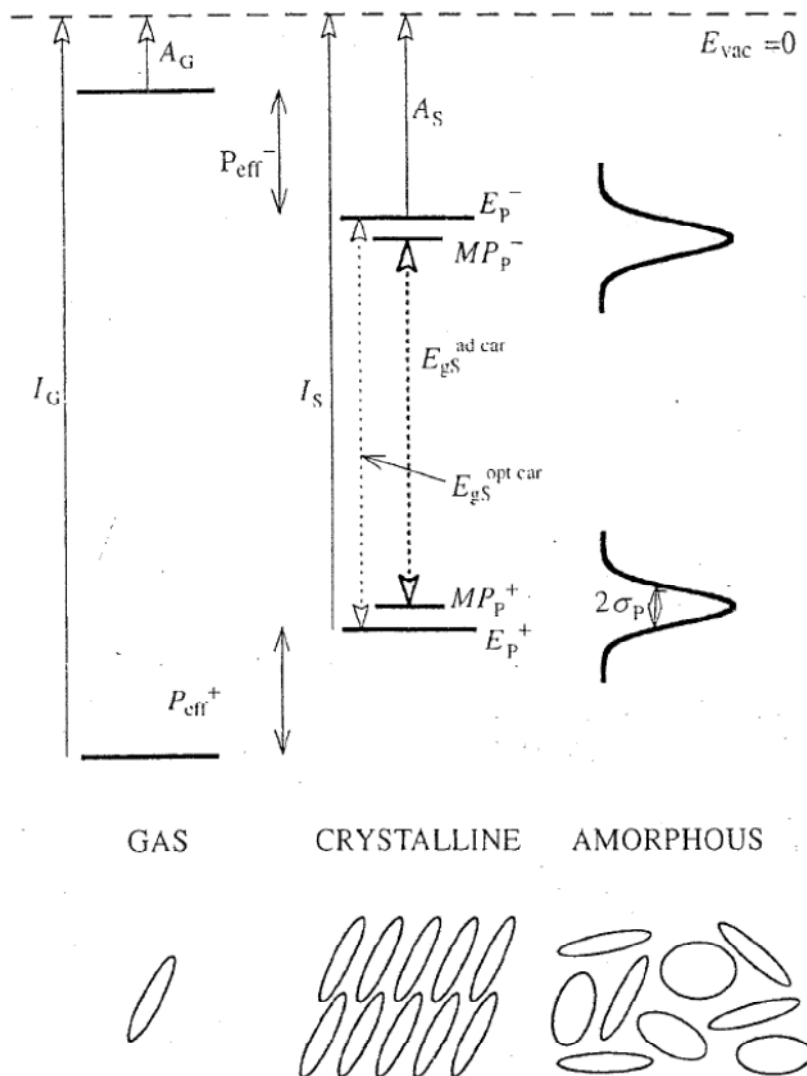Threshold for optical absorption: $Ea = 2.75$ eV,

→ $E_b = 220 \pm 130$ meV.

S. F. Alvarado, L. Rossi, P. Muller, P. F. Seidler, W. Riess, IBM J. Res. Dev. **45,** 89 (2001)

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• **Weak van der Waals interaction between molecules** → Each molecule keep its molecular levels which are shifted due to the interaction with surrounding molecules in the solid-state.

Solid-state ionization potential

$$I_S = I_G - P_{eff}^{\ +} - (E_b^{\ +})_{eff}$$

Solid-state electron affinity

$$A_S = A_G + P_{eff}^{\ -} + (E_b^{\ -})_{eff}$$

Gaussian density of localized states

FWHM: ~ 200 meV

transport states

impurity trap states

trap states

Energy level

Density of state

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