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**WINTER COLLEGE ON  
SPECTROSCOPY AND APPLICATIONS**

( 8 - 26 February 1999)

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***"Ultrafast Spectroscopy in Polymers"***

presented by:

**Guglielmo LANZANI**

Dipartimento di Matematica e Fisica  
Università di Sassari  
Sassari  
Italy

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These are preliminary lecture notes, intended only for distribution to participants.

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**Winter College  
on  
Spectroscopy and Applications**

Trieste, 8-26 February 1999

**ULTRAFAST SPECTROSCOPY IN  
POLYMERS**

*Guglielmo Lanzani*

*Dip. di Matematica e Fisica, Università di Sassari*

- Introduction on Conjugated Polymers
- Basic physics of conjugated polymers
- The pump-probe technique
- Photophysics in a model compound
- Electric field-assisted pump-probe spectroscopy: the charge generation mechanism in conjugated polymers

## Chains of conjugated carbon atoms

...C-C=C-C=C- -C= C-C=C-C=C-C-C=C-C=C-C=C...

*Electronic properties of semiconductor + Mechanical properties of plastic*

### *Advantages*

Molecular Engineering

Synthesis  $\leftrightarrow$  Chemical Tailoring gives infinite possibilities

Self-assembly

Conductivity/mass ratio

Processability

Soluble

Thin films of large area

Inexpensive technology (e.g. Spin coating)

### *Drawback*

Air degradation (mainly due to oxygen)

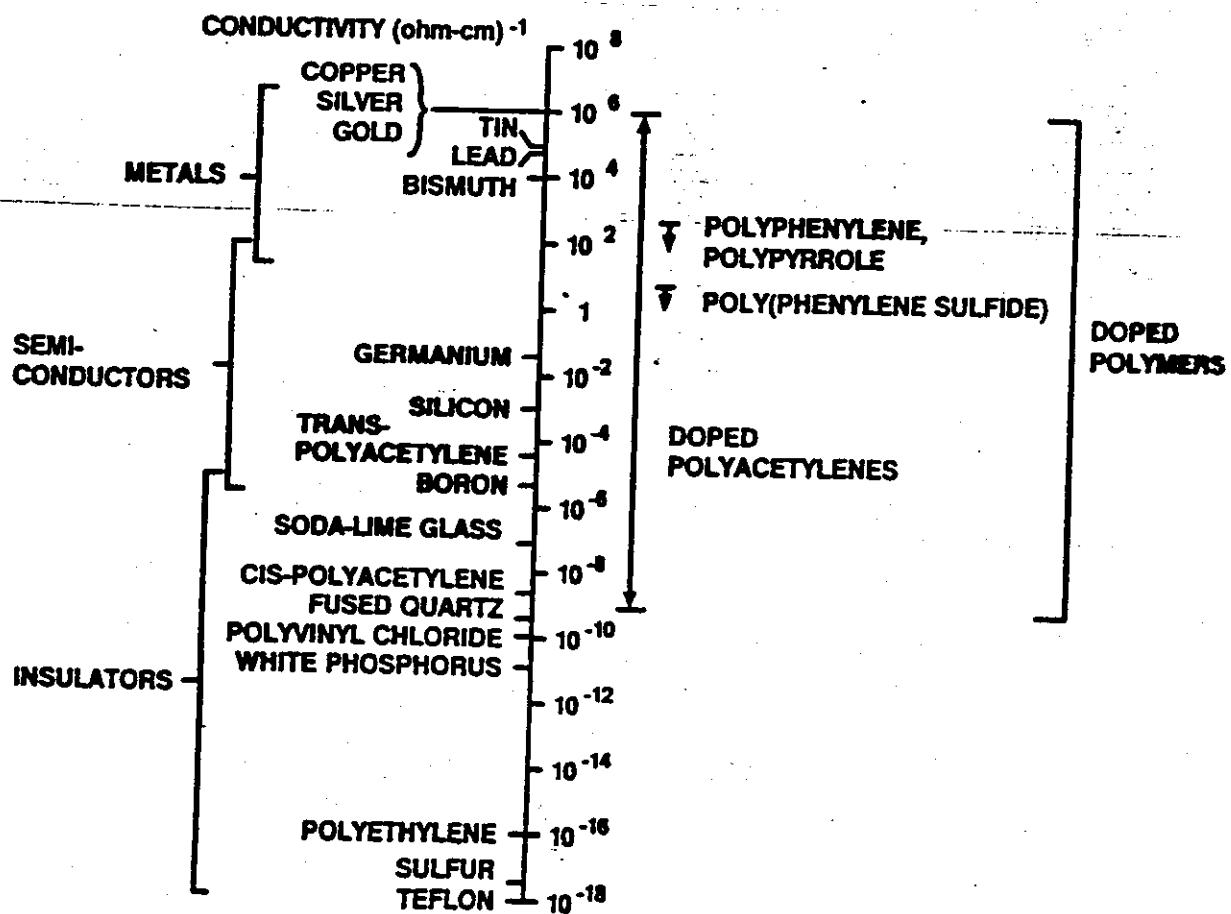
Short lifetime

Limited performances

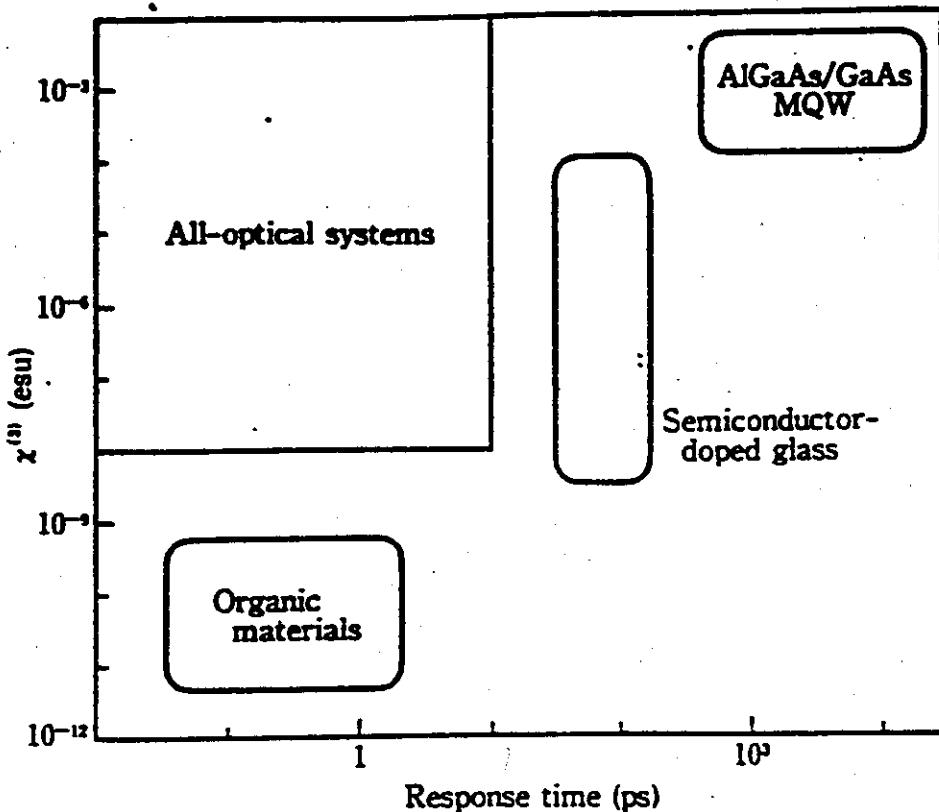
Subject	No	Material	No	Country	No	Institution	No
<u>LED</u>	27	Pani	19	Japan	19	Government	71
<u>Schottky junction</u>	6	PPy	12	USA	17	UNIAX	4
<u>Conductivity</u>	5	PPV	9	Korea	8	Philips	3
<u>Battery</u>	5	Phthalocyanine	5	Russia	6	Power Plus	2
<u>Synthesis</u>	5	PPP	4	UK	6	Schnapp & Co	1
<u>Photoluminescence</u>	3			Germany	5	RICOH	1
<u>Actuator</u>	3			China	5	Samsung	1
<u>Photovoltaics</u>	3			Netherlands	4	NEC	1
<u>Biophysics</u>	2			Sweden	3	CSIRO	1
<u>Polyblends</u>	2			France	3	DSM	1
<u>Gas sensor</u>	2			Israel	3	Dae Young	1
<u>Electrochromism</u>	2			Italy	2	Sumitomo	1
<u>Glucose Sensor</u>	2			Brasil	1	Goldstar	1
<u>Capacitor</u>	2			Austria	1	Bahador Res.	1
<u>Membranes</u>	2			Uzbekistan	1	IBM	1
<u>Patterning</u>	1			Ukraine	1	Zipperling Kessler	1
<u>Electroplating</u>	1			Australia	1	Americhem	1
<u>MIS</u>	1			Portugal	1	Milliken	1
<u>Neuronal Net</u>	1			Spain	1		
<u>Transistors</u>	1						
<u>LCPs</u>	1						
<u>Molecular Electronics</u>	1						
<u>Drug Delivery</u>	1						
<u>Corrosion Protection</u>	1						

Table 5: Statistical data concerning the application-oriented contributions to the *International Conference on Science and Technology of Synthetic Metals, July 24<sup>th</sup>-29<sup>th</sup> 1994, Seoul/South Korea.*

Polymer	Structure	Typical Methods of Doping	Typical Conductivity ( $\Omega \text{ cm}$ ) $^{-1}$
Polyacetylene	$\left[ -\text{CH}=\text{CH}- \right]_n$	Electrochemical, chemical (AsF <sub>3</sub> , I <sub>2</sub> , Li, K)	$500-1.5 \times 10^5$
Polyphenylene	$\left[ -\text{C}_6\text{H}_4- \right]_n$	Chemical (AsF <sub>3</sub> , Li, K)	500
Poly(phenylene sulfide)	$\left[ -\text{C}_6\text{H}_4-\text{S}- \right]_n$	Chemical (AsF <sub>3</sub> )	1
Polypyrrole	$\left[ -\text{CH}_2-\text{CH}(\text{N})-\text{CH}_2- \right]_n$	Electrochemical	600
Polythiophene	$\left[ -\text{CH}_2-\text{CH}(\text{S})-\text{CH}_2- \right]_n$	Electrochemical	100
Poly(phenyl-quinoline)	$\left[ \text{C}_6\text{H}_5-\text{C}_6\text{H}_4-\text{N}=\text{C}_6\text{H}_4-\text{C}_6\text{H}_5 \right]_n$	Electrochemical, chemical (sodium naphthalide)	50



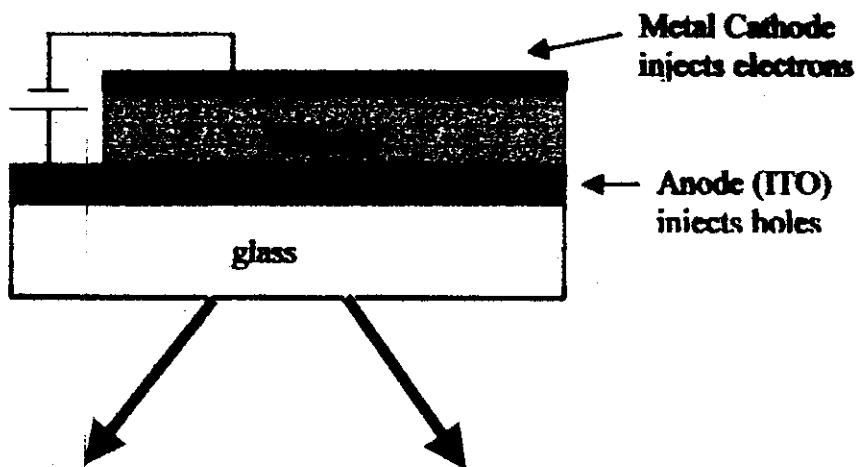
NLO<sup>3</sup>



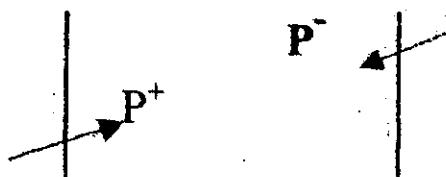
$$\gamma \sim \frac{L^{10}}{N^3} \xrightarrow[N \sim L]{1-D} \gamma \sim L^7 [\gamma \sim L^4]$$

$$\tau \sim \frac{h}{\Delta E} \approx 10^{-14} - 10^{-15} \text{ s}$$

## *Light Emitting Diode*



### 1. Injection



### 2. Transport



### 3. Recombination



### 4. Migration and Decay



# STRUCTURAL MODIFICATIONS IN LIGHT EMITTING POLYMERS

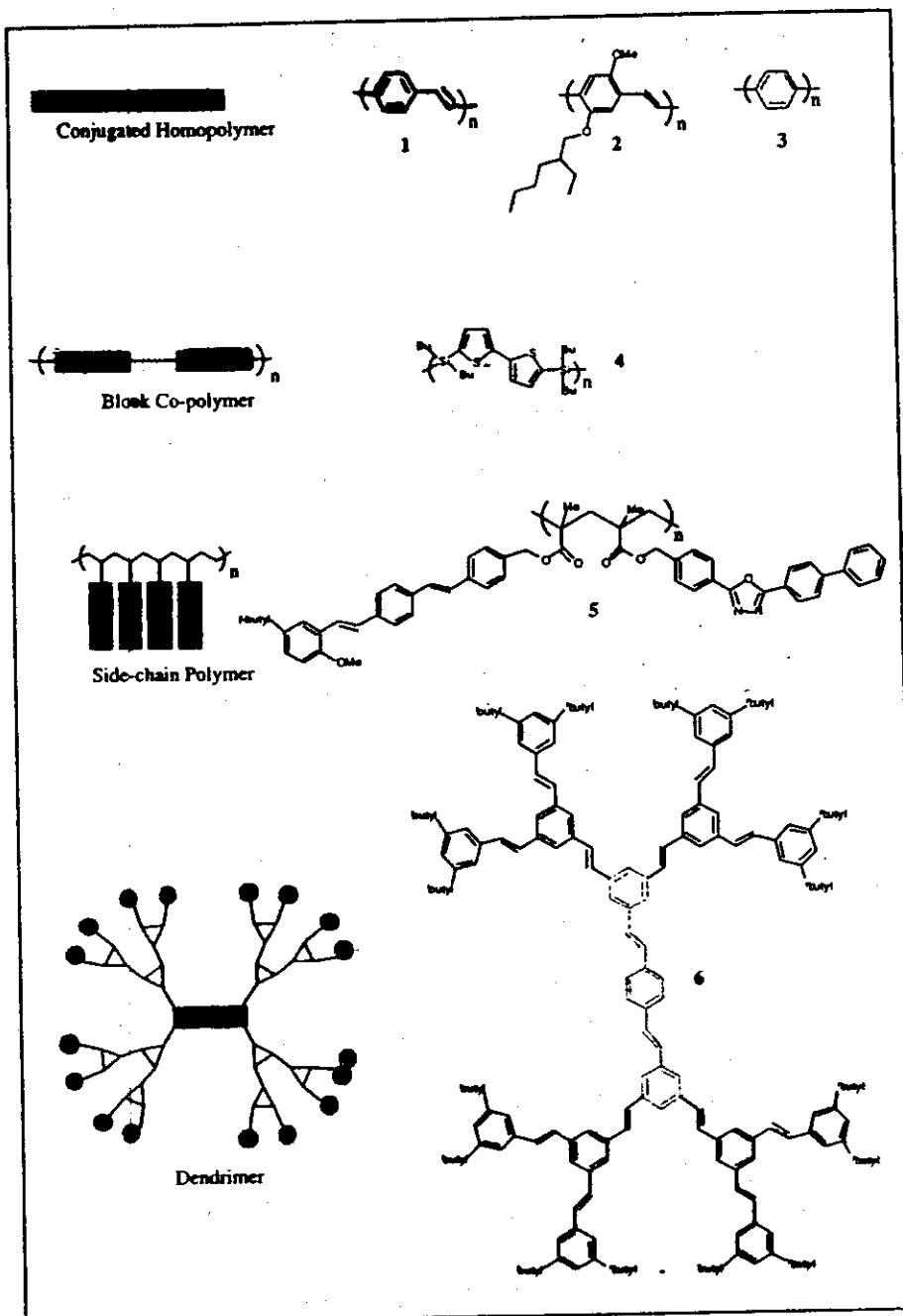
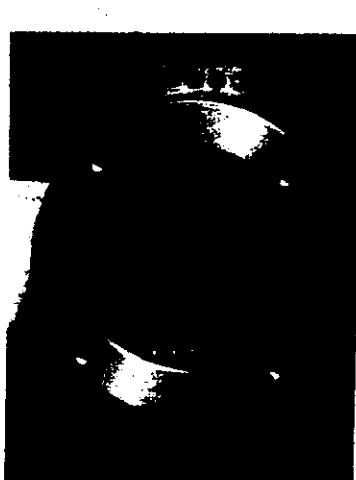
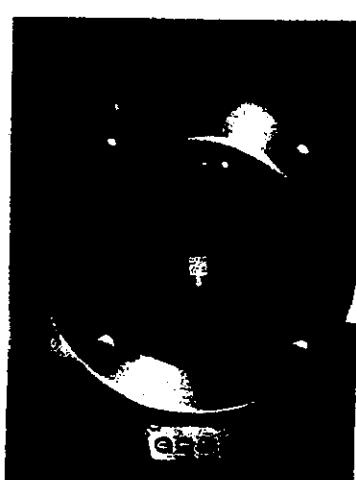
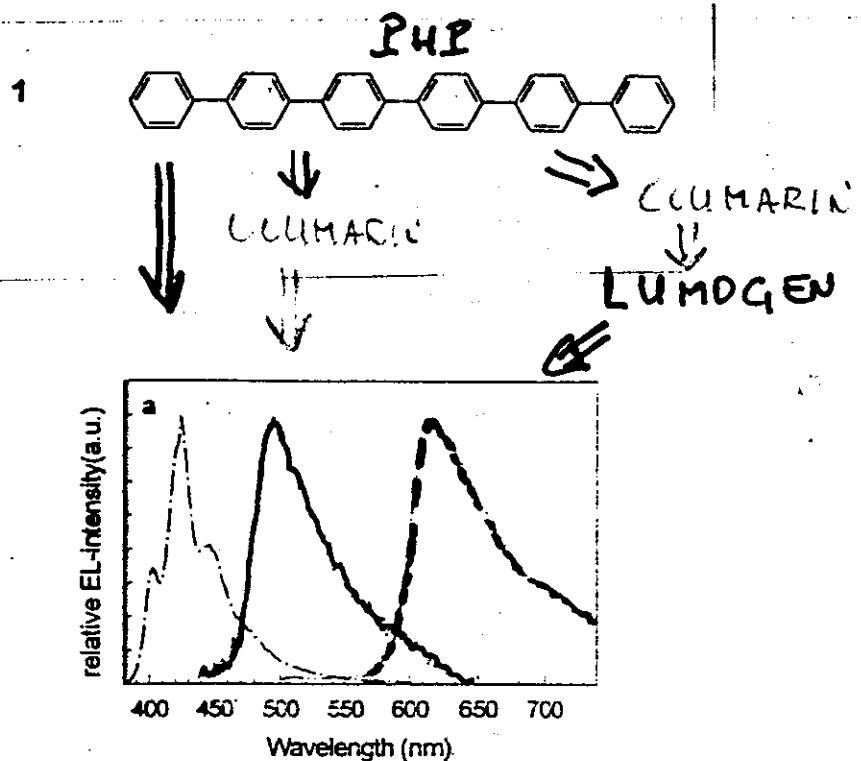
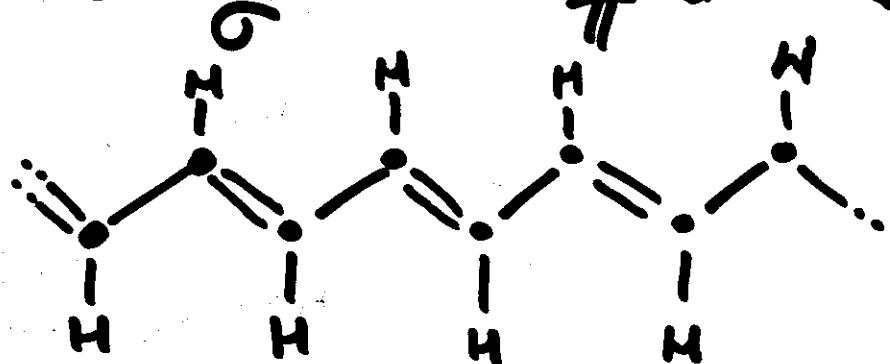
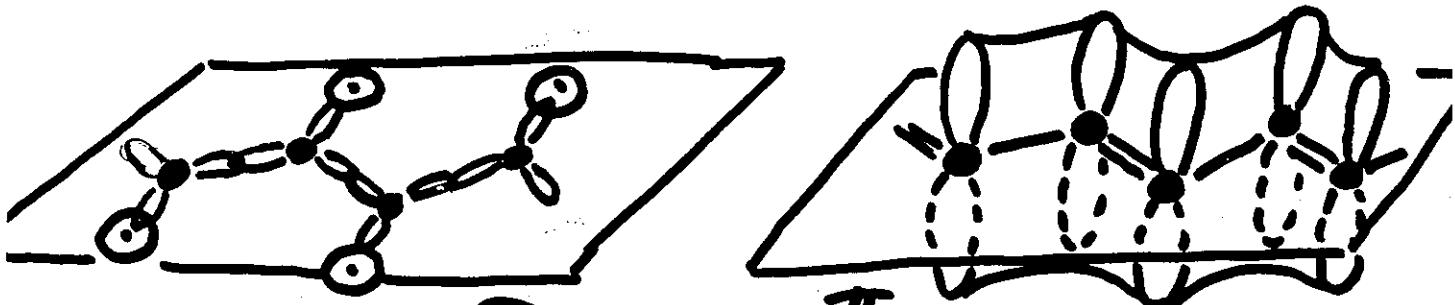
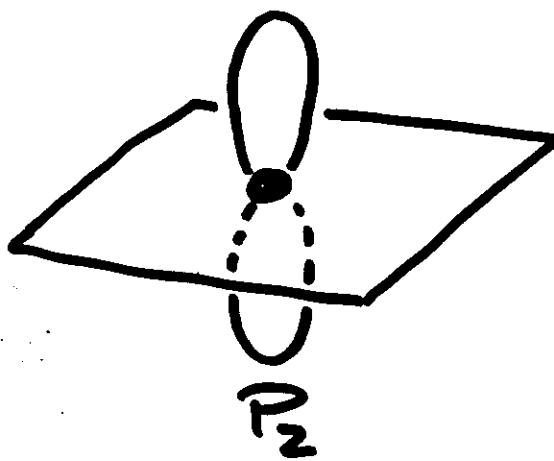
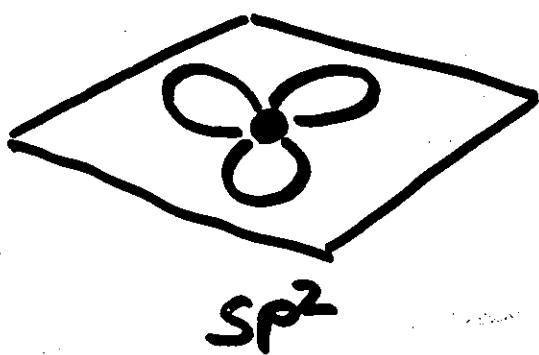


Figure 2: General polymer structures. AFTER P.L.BURN et AL.  
MATERIALS TODAY '98

# "DOWN CONVERSION"

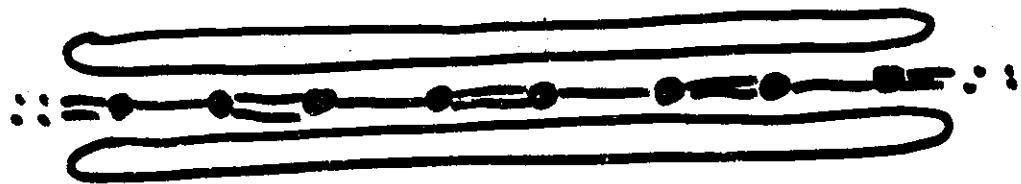


# BASIC ON CHEMICAL BONDING

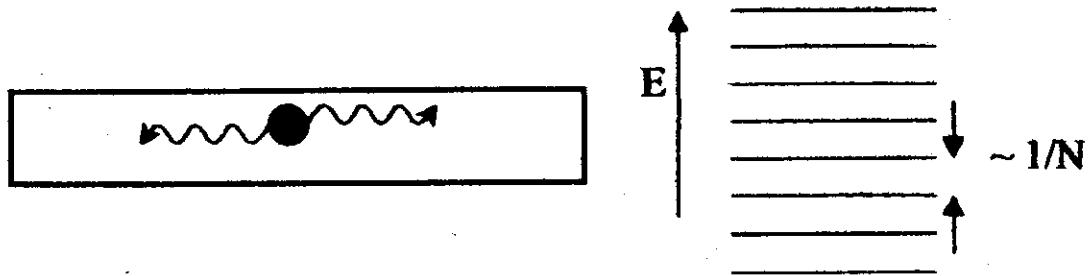


$\bullet = C$

## DELOCALIZED MOLECULAR ORBITAL



## Free electron in a 1-D box



- $E_g$  (HOMO-LUMO Gap)  $\sim 1/N \Rightarrow$  Redshift of the optical spectra with N

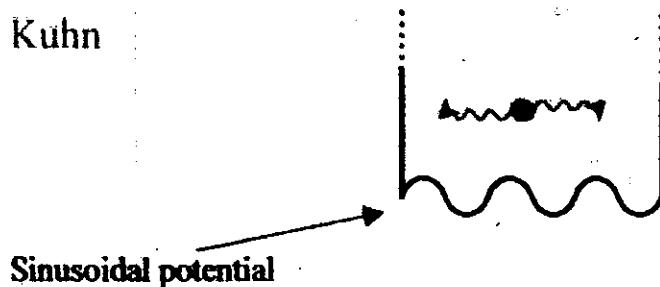
**TRUE!**

- Metallic limit

$$N \rightarrow \infty \quad E_g \rightarrow 0$$

**FALSE!**

Kuhn

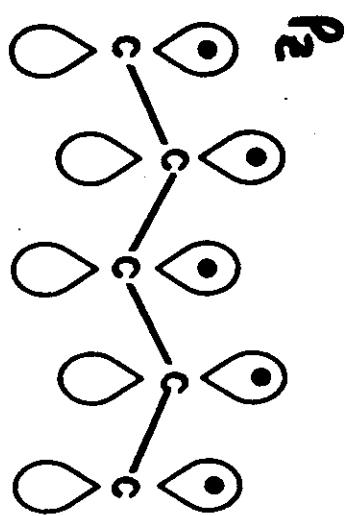


$$E_g = A + B/N$$

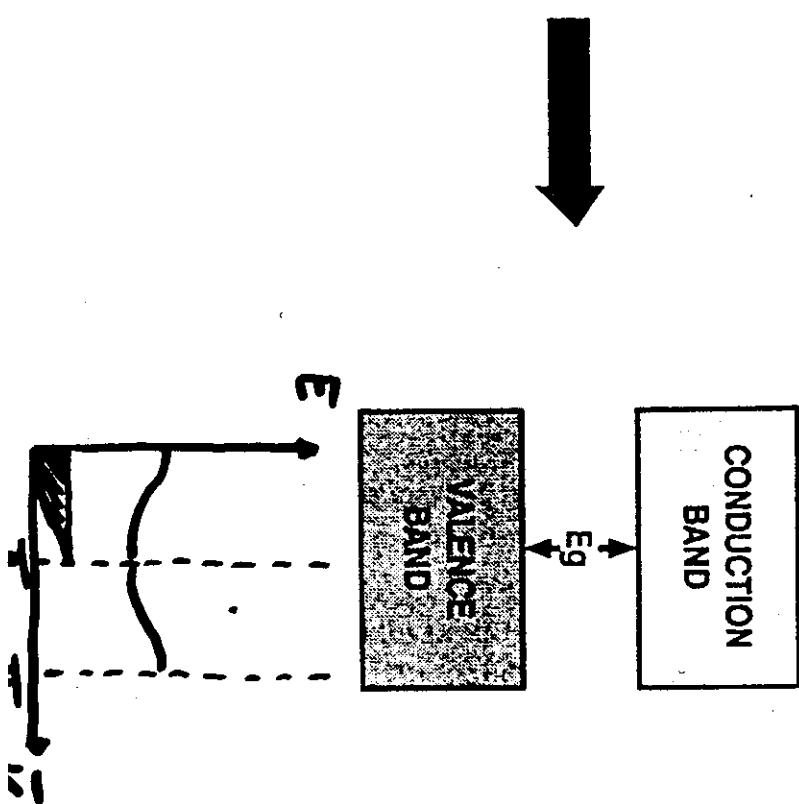
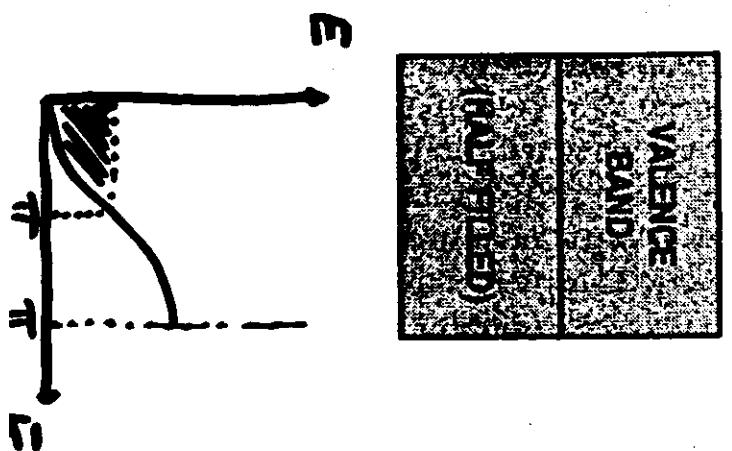
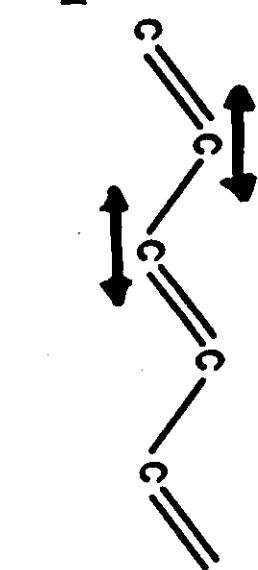
$N = \# \text{ double bonds};$

$A = 14520 \text{ cm}^{-1}; \quad B = 5500 \text{ cm}^{-1}$  (Lichtman, From Experiments)

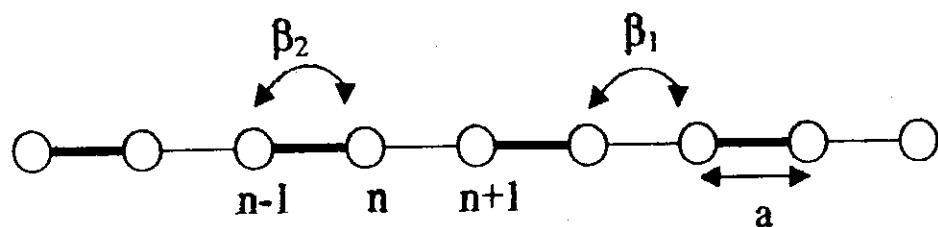
# METAL - SEMICONDUCTOR TRANSITION



$\downarrow$



The ideal model of an infinite chain in the tight-binding approximation (Hückel) [Cojan et al]



$$\alpha = \langle n | H | n \rangle \quad \beta_i = \langle n | H | m \rangle \quad n = m \pm 1$$

$n>$  = atomic wavefunction

$\alpha$ =on site Coulomb integral

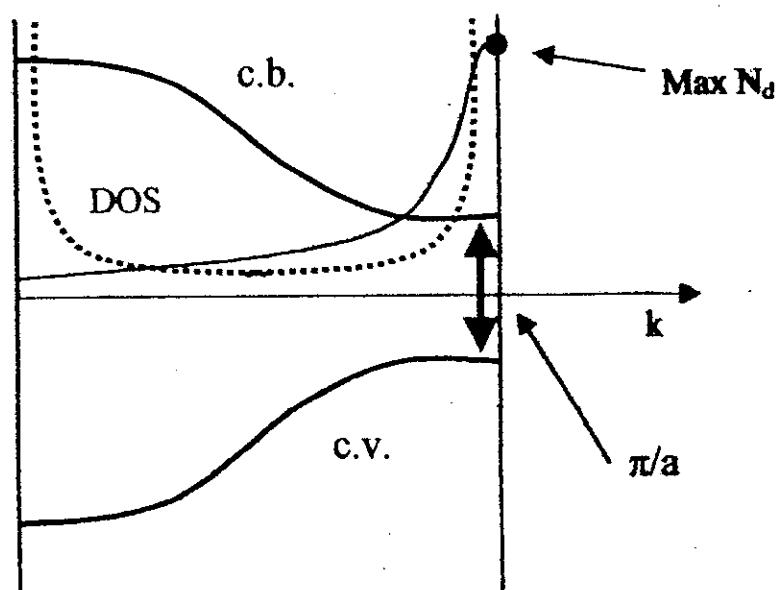
$\beta$ =n.n. hopping (resonance) integral

The "MO" is a linear combination of atomic orbitals (LCAO)

Results:

$$E_g = 2(\beta_2 - \beta_1)$$

$$L_d = N_d a = |(\beta_2 + \beta_1)/(\beta_2 - \beta_1)| a \quad \text{Optical delocalization length}$$



## Finite chain with bond alternation

$L_d$  is still valid. If  $L$  is the real chain length:

### 1. $L_d < L \Rightarrow$ Semiconductor behaviour

- $E_g = 2(\beta_2 - \beta_1) \sim 1/L_d$
- First order polarizability  $\alpha \sim (L_d)^2$

### 2. $L_d > L \Rightarrow$ Free electron behaviour

In any case the whole optical properties depend on  $L_d$  ( $\sim$  optical dipole moment).

One electron Excited States (MO picture) are labelled following:

spin multiplicity (Singlet, Doublet, Triplet, ...).

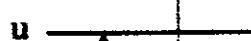
spatial symmetry of the total wavefunction.

### Dipole Transition Selection Rules

$$\langle g | \mu | g \rangle = 0$$



$$\langle g | \mu | u \rangle \neq 0$$



$$\Delta S = 0$$



$\Rightarrow$  This theory fails to predict the correct level ordering.

# SIZE DEPENDENCE IN $\text{f}(\text{---S---})_m$

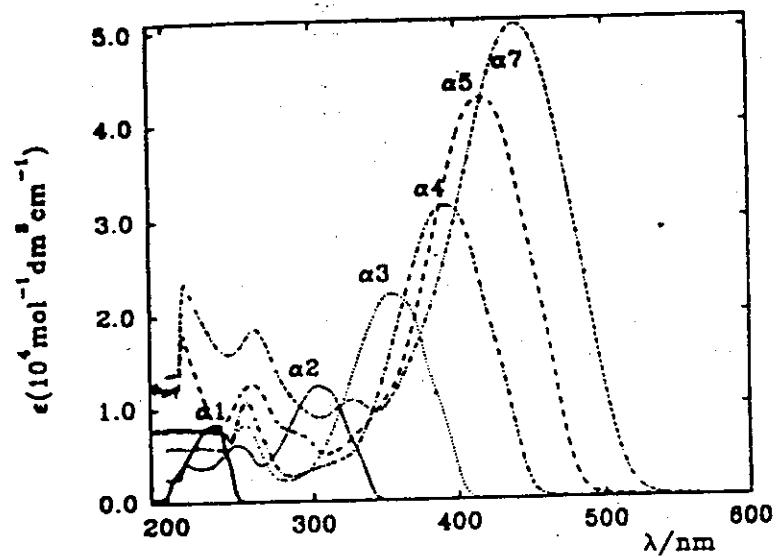


Fig. 3 Absorption spectra of oligothiophenes  $n=5, 7$ .

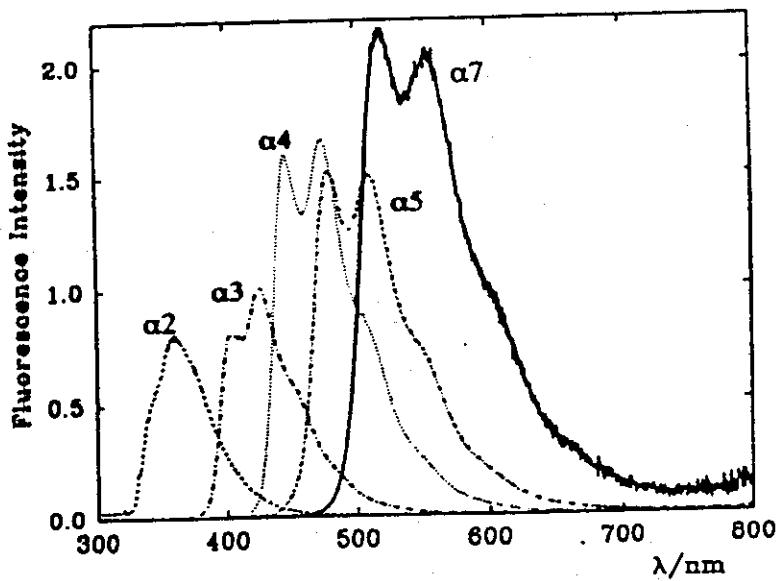


Fig. 5 Fluorescence spectra of oligothiophenes  $n=2-5, 7$ .

## **Band-like picture (Heeger et al. '88)?**

It predicts:

1. Primary excitations are charge carriers with high quantum yield ( $\approx 1$ ).
2. Strong electron-phonon coupling (within the Hückel model) leads to SELF-TRAPPED STATES. There is a large Intrachain Stokes Shift.
3. Exciton binding energy should be small (Wannier-like).

*"Within a few years researchers found evidences that contradict the basic premise and feature of the band-model":*

1. *Very small Stokes shift for isolated chains (site-selective and high resolution spectroscopy in polymer blends);*  
[R. Lécuiller et al., Rauscher, U. et al.]
2. *Long chains do not exist. Defects and impurities break the conjugation. Polymers are modelled as ensemble of short conjugated segments;*
3. *Large inhomogeneous broadening mask single chain behaviour. Raw data should not be taken as indicative of 1-D Joint density of states;*
4. *Oligomers ( $n=6-8$ ) are good model compound that mimic long chain behaviour, hence band-like states are not needed to reproduce the observations; [C. Taliani et al.]*
5. *Several experiments indicate large exciton binding energy (0.1-1 eV).*
6. *ElectroAbsorption experiments are well understood in terms of Stark shift of molecular (localized) level, in contrast with Franz-Keldish signatures proper of continuum states.*

# ELECTRO ABSORPTION

mLPPP

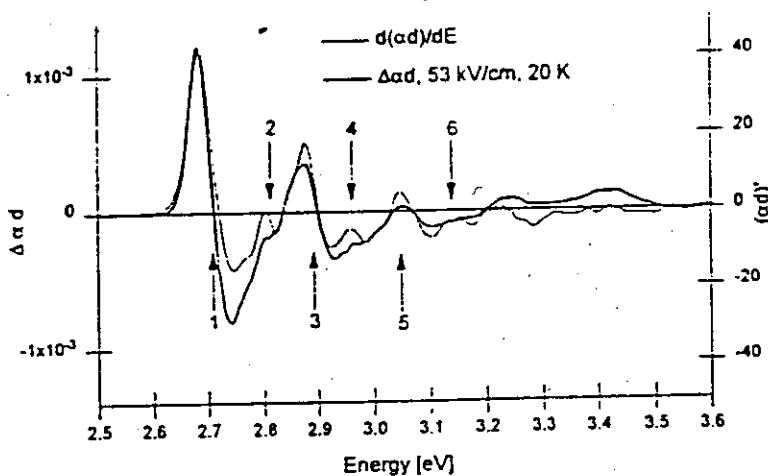
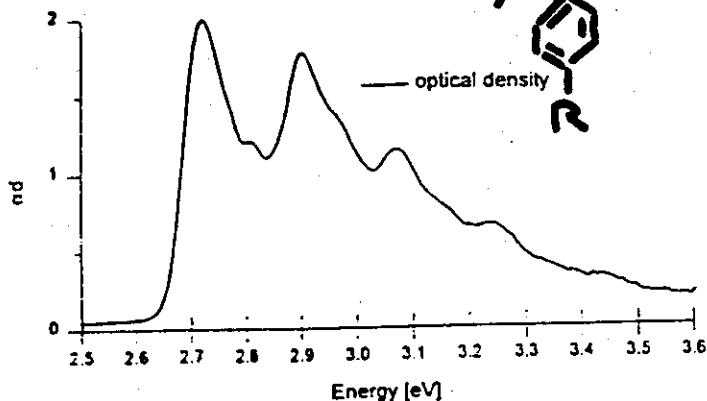
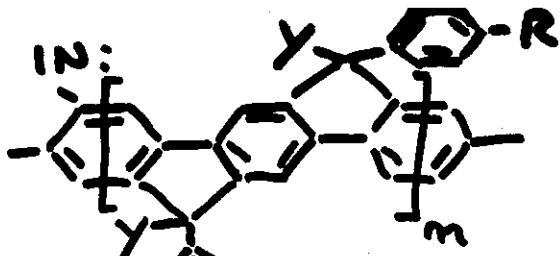


FIG. 1 : Optical density of mLPPP and EA-spectrum at 20K,  $F=53 \text{ kV/cm}$ , field parallel to polarization of light

$$\Delta E_{1B_u} = \frac{\left| \langle nA_g | \vec{\mu} \cdot \vec{F} | 1B_u \rangle \right|^2}{E_{1B_u} - E_{nA_g}} = \frac{p}{2} F^2$$

# SITE SELECTIVE SPECTROSCOPY IN PDT

$R = C_{12}H_{26}$

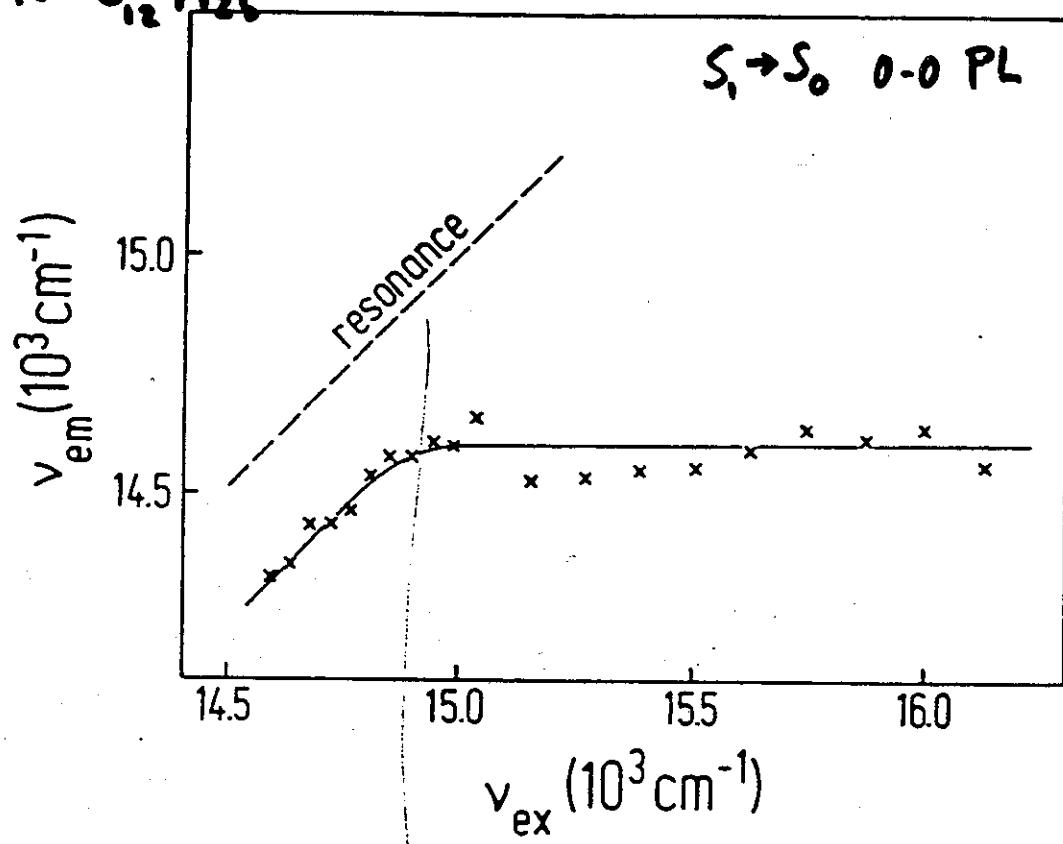
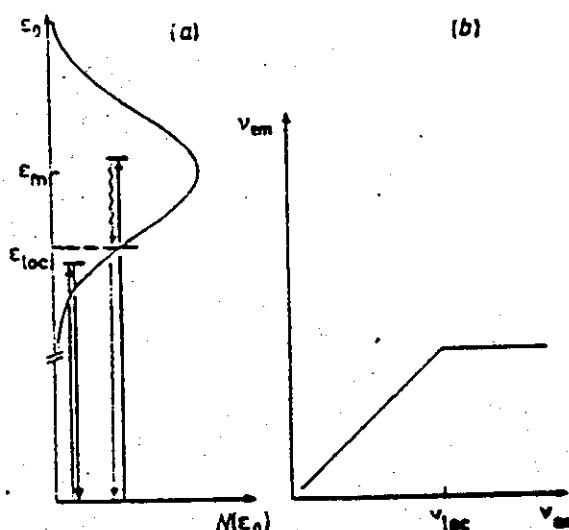


Figure 1. (a) Density-of-states profile of a random organic solid. States above the localisation threshold  $\epsilon_{loc}$  are subject to incoherent random walk leading to energetic relaxation. States below  $\epsilon_{loc}$  emit resonantly. (b) Schematic variation of the emission energy with excitation energy. To comply with spectroscopic convention, energies are denoted by wavenumber symbols.



RAUSCHER et al.

# SPECTRALLY RESOLVED TEMPORAL DECAY OF PHOTOLUMINESCENCE IN

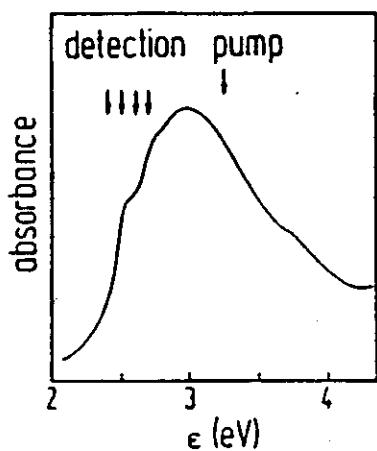
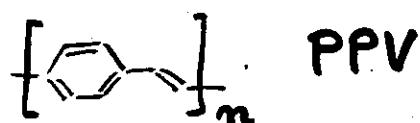


FIG. 1. Absorption spectrum of a PPV film. Arrows indicate luminescence excitation and detection energies, respectively.

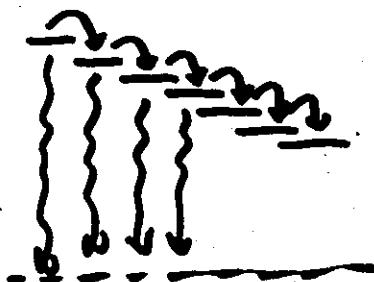
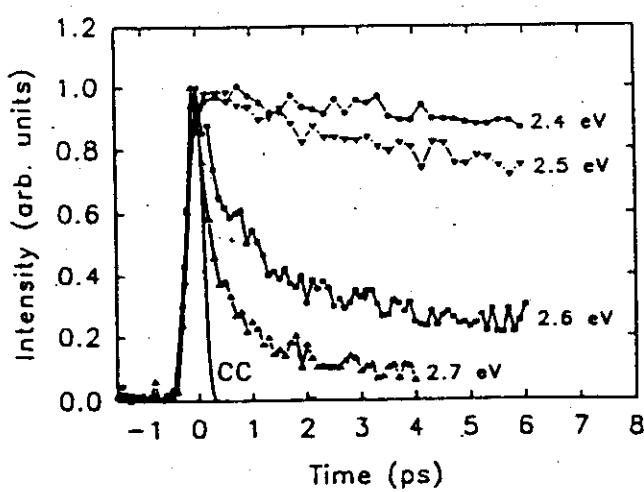


FIG. 3. Temporal decay of the photoluminescence of a PPV film probed at variable detection energies at 295 K. CC (solid line) denotes the cross correlation of exciting and reference pulse.

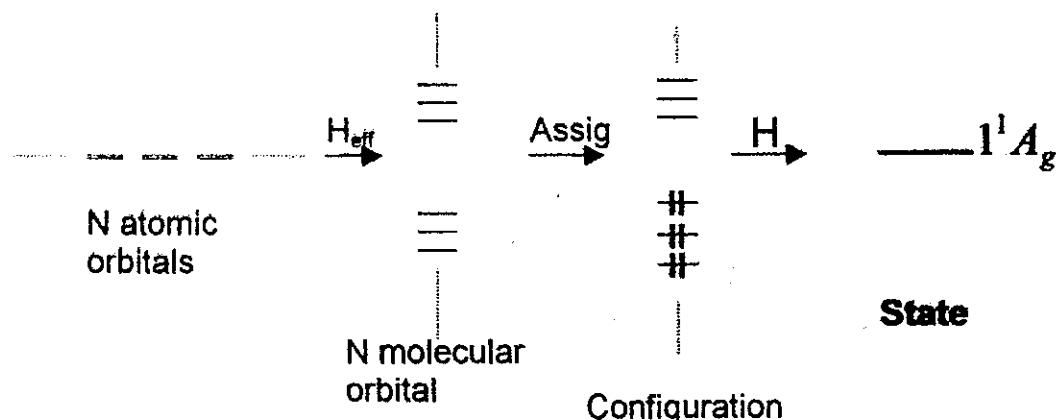
## Beyond independent particle models

*"The motion of conjugated  $\pi$  electrons is governed by two opposing interactions:*

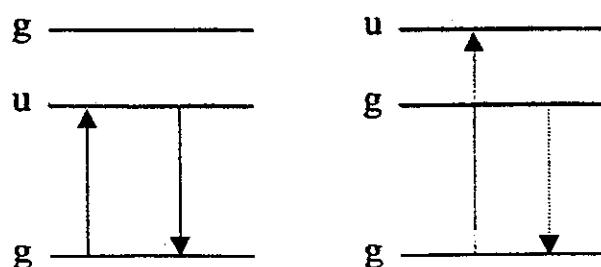
- i) *the Hückel resonance interaction, which tends to delocalize the  $\pi$ -electrons over the whole molecular frame and induces frequent encounters of the  $\pi$ -electrons on common atomic sites;*
- ii) *and the Coulomb repulsion interaction, which tends to prevent close encounters and thereby induces localisation of  $\pi$ -electrons at different atomic sites (correlated motion).*

Hudson, Kohler and Schulten 1982

- Electron correlation is accounted for by linear combination of one-electron configurations.
- States are classified following the molecular language according to the spatial symmetry of the dominant configuration ( $A_g$ ,  $B_u$ , ecc.) and the spin multiplicity (Singlet, Doublet, Triplet, ...)



⇒ Coulomb correlated models predict correctly the level ordering in linear polyenes



## Extended Hubbard model

$$H = U \sum_i n_{i,\uparrow} n_{i,\downarrow} + V \sum_i (n_i - 1)(n_{i+1} - 1) - t \sum_{i,\sigma} \left[ 1 - (-1)^i \delta \right] c_{i,\sigma}^+ c_{i+1,\sigma} + c_{i+1,\sigma}^+ c_{i,\sigma}$$

$c_{i,\sigma}^+$  creates an electron of spin  $\sigma$  on site  $i$ ,  $t$  one electron hopping integral,  $\delta$  bond alternation parameter,  $U$  on-site Coulomb interaction,  $V$  nearest-neighbour Coulomb interaction.

**Strong coupling limit:**  $U \gg V \gg 1$

ground state ( $1A_g$ ): ...111111111111...

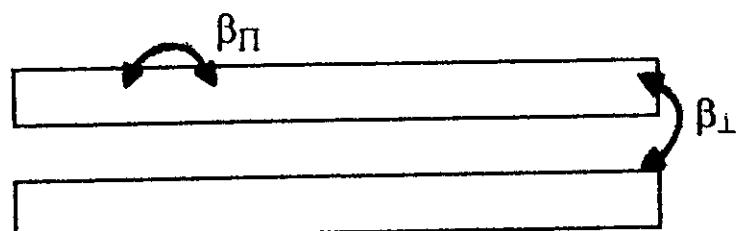
exciton ( $1B_u$ ): .....111111**20111111**.....  $U-V$

1e-1h continuum: .....111**211**.....**11011**.....  $U$

Bi-exciton ( $14A_g$ ): .....111111**20201111**.....  $2U-3V$

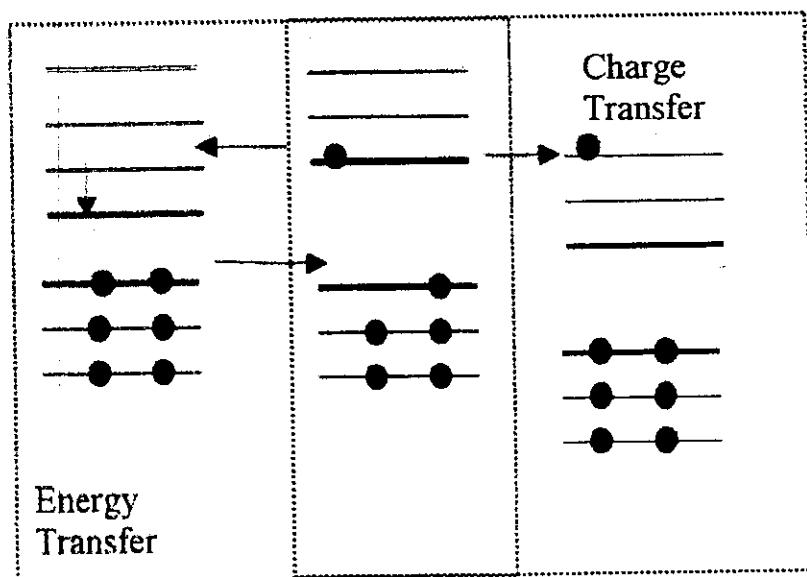
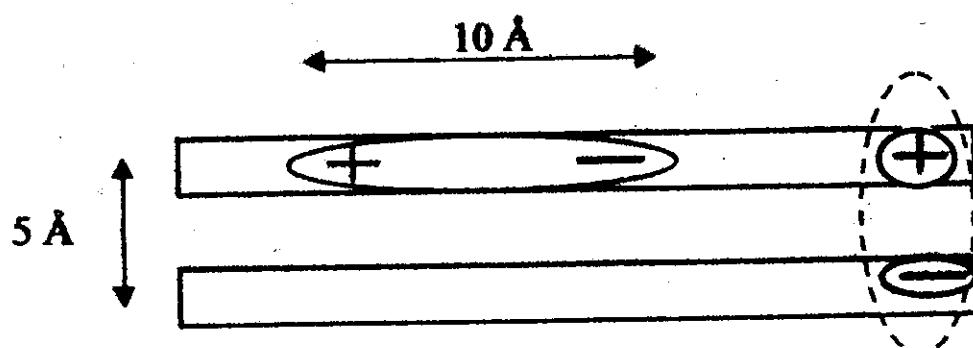
2 ex continuum: .....112**011**....**120111**.....  $2U-2V$

## Inter Chain Interactions

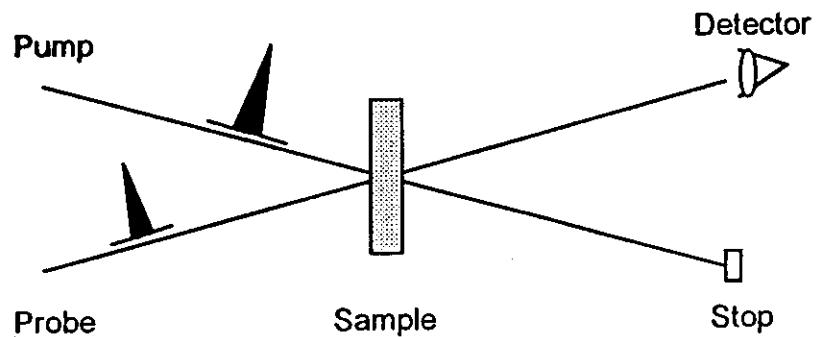


$$\beta_{\Pi} \gg \beta_{\perp}$$

## Polaron-Pairs



## PUMP AND PROBE TECHNIQUE



- STEP 1:

Saturation of sample absorption by the pump pulse

- STEP 2:

Change in probe energy transmission ( $\Delta E_p$ ) as a function of probe time delay  $\tau$ :

$$\Delta E_p(\tau) \propto \int_{-\infty}^{+\infty} A(\tau - t) G(t) dt$$

$A(t)$  → impulsive response of the sample

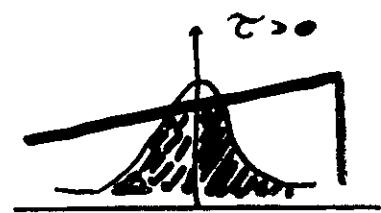
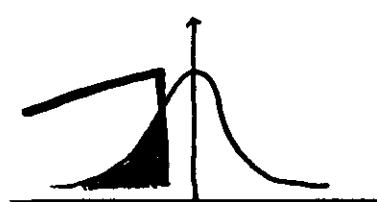
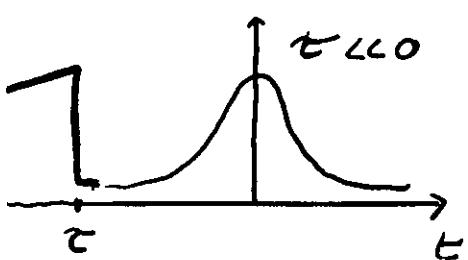
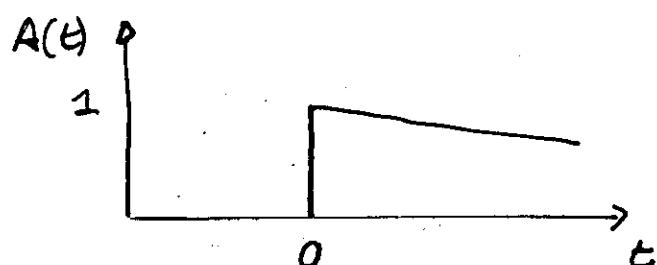
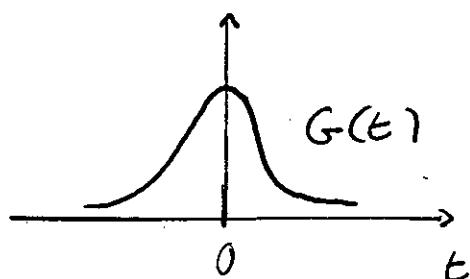
$G(t)$  → intensity cross-correlation of pump and probe pulses

# TIME BEHAVIOUR IN PROBE DIRECTION

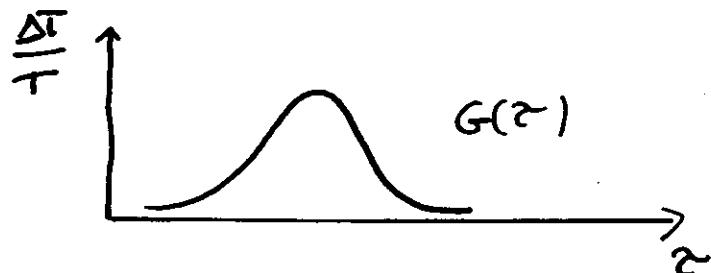
$$\frac{\Delta T}{T}(z) \sim \int_{-\infty}^z A(z-t) G(t) dt$$

$$G(t) = \int |E_p(t'-t)|^2 |E_e(t')|^2 dt'$$

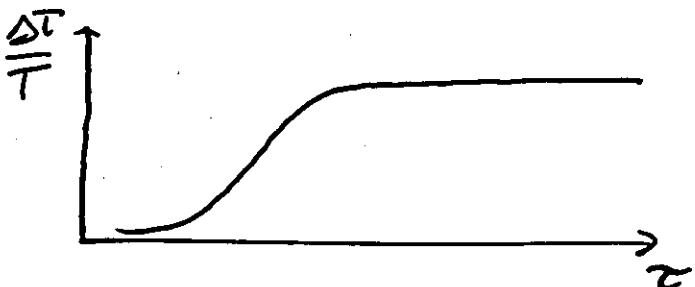
FWHM OF  $G \sim$  TIME RESOLUTION



$$A(t) = \delta(t)$$



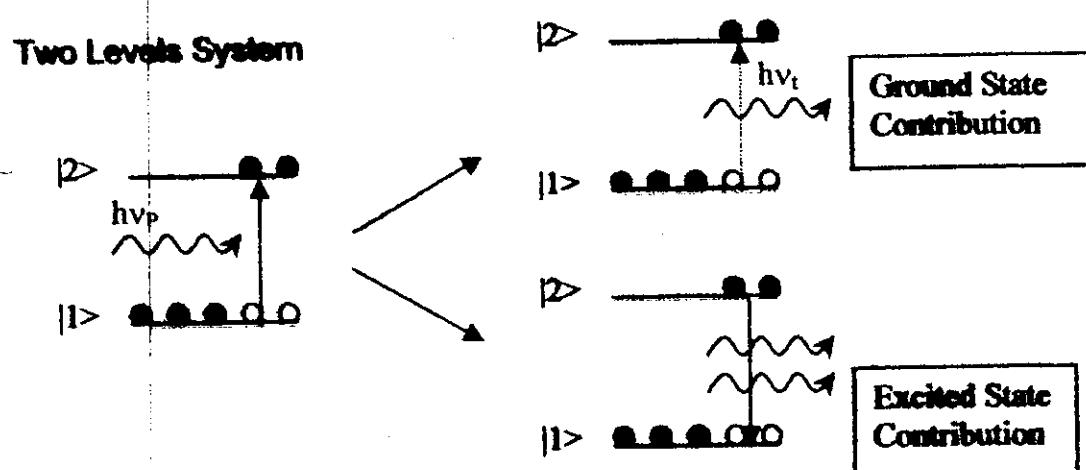
$$A(t) = \begin{cases} 1 & t \geq 0 \\ 0 & t < 0 \end{cases}$$



### Interpretation of the Pump-Probe experiment:

#### 1. Photobleaching (Photoinduced increase of Transmission)

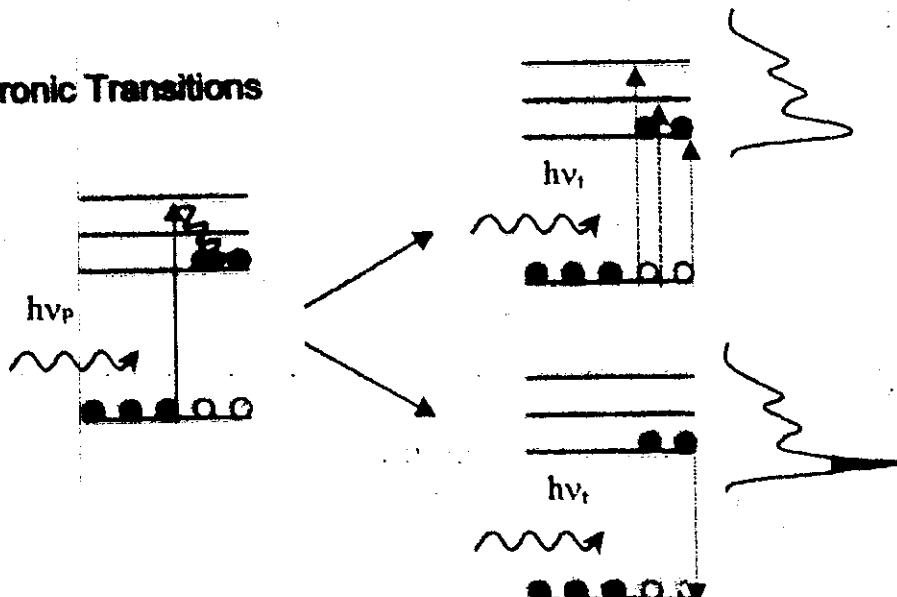
##### Two Levels System



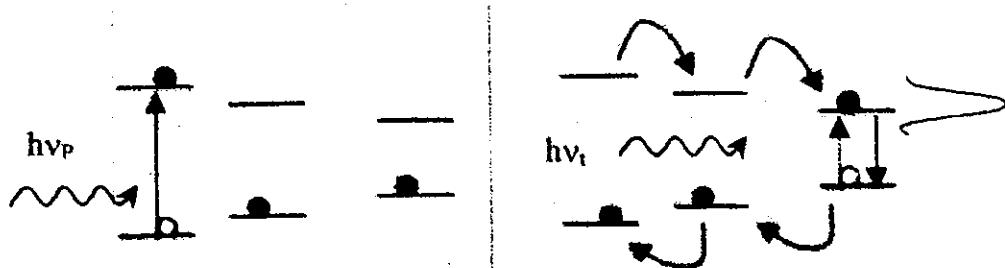
**Obs.1** Never net gain in Two Level Systems!

**Obs.2**  $-\Delta\alpha(\tau) = PB = -2\sigma_{12}N_2(t)$

##### Vibronic Transitions

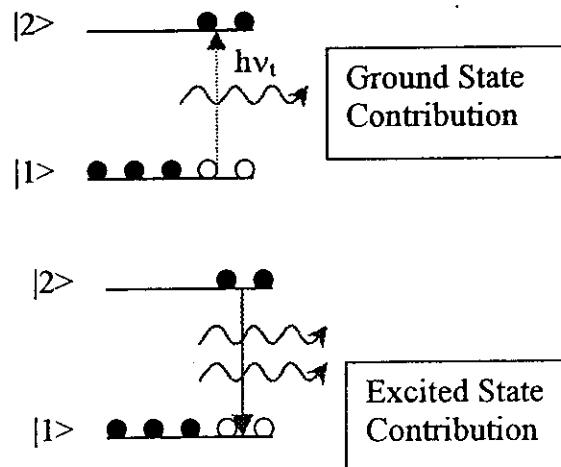
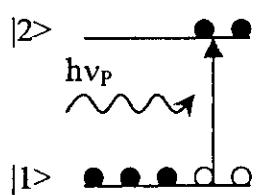


##### Inhomogeneous Broadening



## Photobleaching (Photoinduced increase of Transmission)

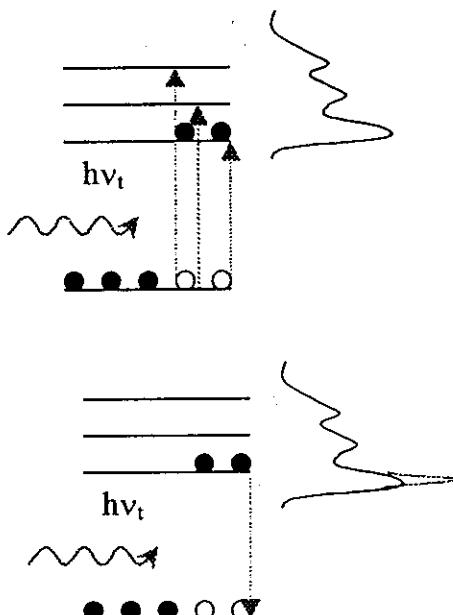
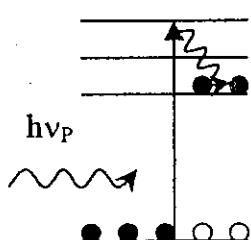
### Two Levels System



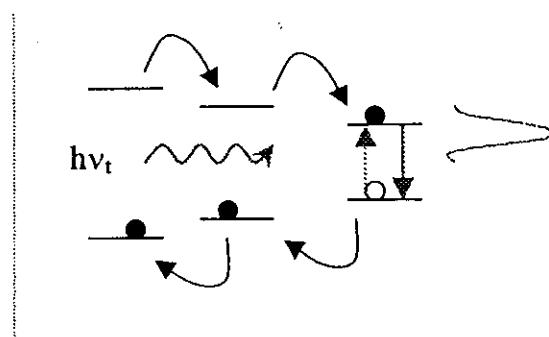
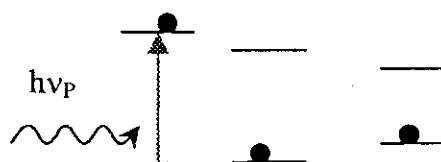
Obs.1 Never net gain in Two Level Systems!

Obs.2  $-\Delta\alpha = PB = -2\sigma_{12}N_2$

### Vibronic Transitions



### Inhomogeneous Broadening



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