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**WINTER COLLEGE ON
SPECTROSCOPY AND APPLICATIONS**

(8 - 26 February 1999)

"Ultrafast Spectroscopy in Polymers"

presented by:

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

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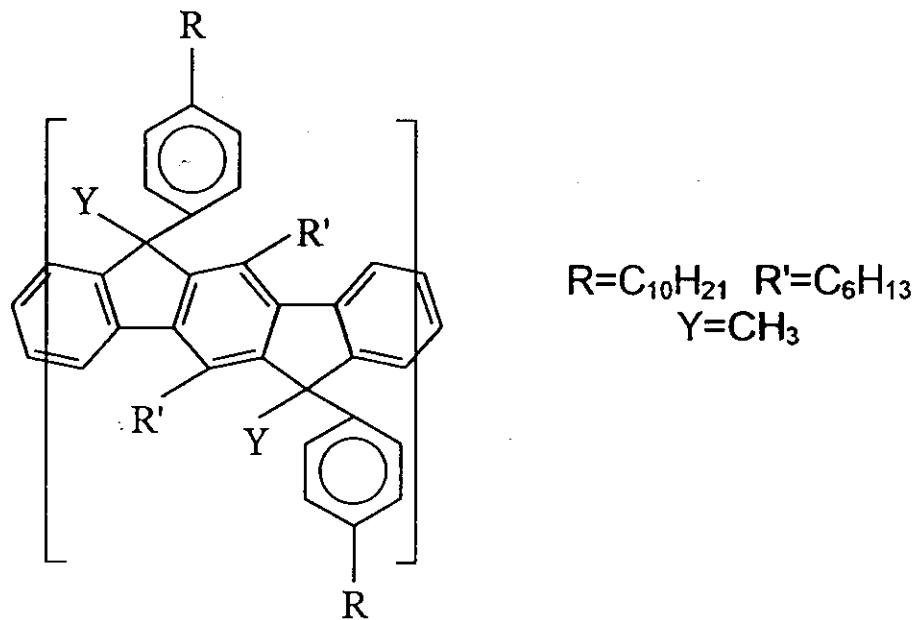
• GENERAL OVERVIEW ON MLPPP PHOTOPHYSICS

- W.Graupner, G.Leising, G.Lanzani, M.Nisoli, S.De Silvestri, U.Scherf, Phys.Rev.Lett.**76**, 847(1996)
- W.Graupner, G.Leising, G.Lanzani, M.Nisoli, S.De Silvestri, U.Scherf Chem.Phys.Lett. **246**, 95(1995)
- G. Kranzelbinder, M. Nisoli, S. Stagira, S. De Silvestri, G. Lanzani, W. Graupner, G. Leising Applied. Phys. Lett. **71**, 2725(1997)
- G. Cerullo, S. Stagira, M. Nisoli, S. De Silvestri, G. Lanzani, G. Kranzelbinder, W. Graupner, G. Leising, Phys. Rev. **B57**, 12806(1998).
- S. Stagira, M. Nisoli, G. Cerullo, M. Zavelani-Rossi, S. De Silvestri, G. Lanzani, W. Graupner, G. Leising, Chem. Phys. Lett., in press
- G. Kranzelbinder, H. J. Byrne, S. Hallstein, S. Roth, G. Leising, U. Scherf, Phys. Rev. **B56**, 1632(1997)
- G. Leising, O. Ekström, W. Graupner, F. Meghdadi, M. Moser, G. Kranzelbinder, T. Jost, S. Tasch, B. Winkler, L. Athouel, G. Froyer, U. Scherf, K. Müllen, G. Lanzani, M. Nisoli, S. De Silvestri "Non Linear Optical Properties of Organic Materials IX" Vol. **2852**, p.189, SPIE, Denver 1996

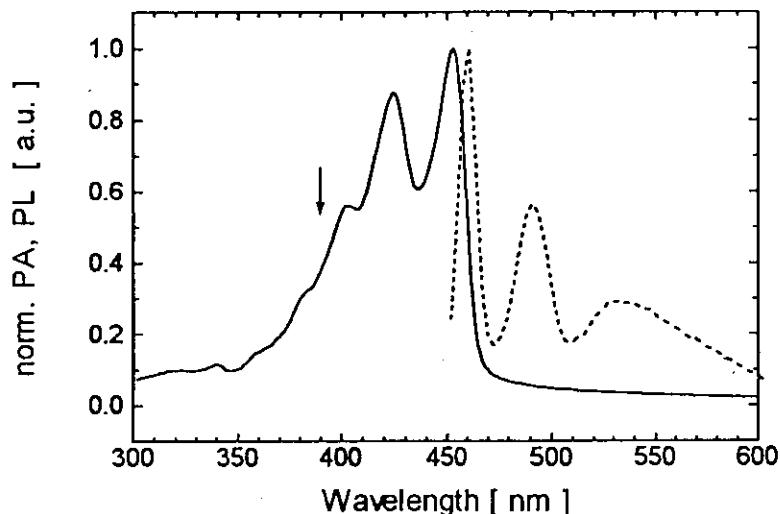
LADDER POLYMER m-LPPP

- Chemical structure

(U. Scherf, K. Müllen, Polymer 33, 2443(1992))



- Optical properties

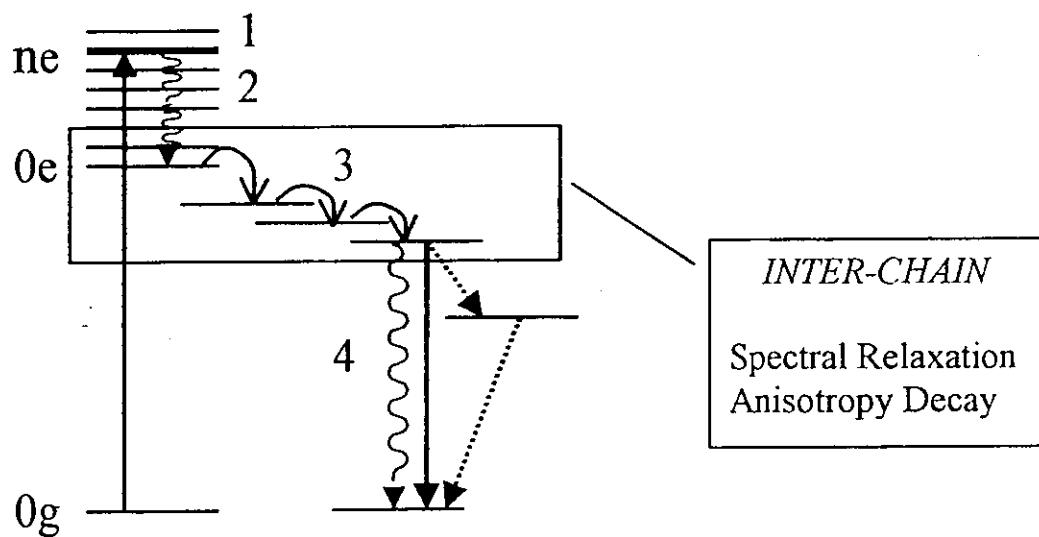


⇒ Highly ordered (J. Stampfl et al. Synth. Met. 71, 2125(1995)).

⇒ High blue electroluminescence. S. Tasch et al. Appl.Phys. Lett. 68, 1090(1996)

⇒ Lasing (CThC4)

Photoexcitation in Conducting Polymers

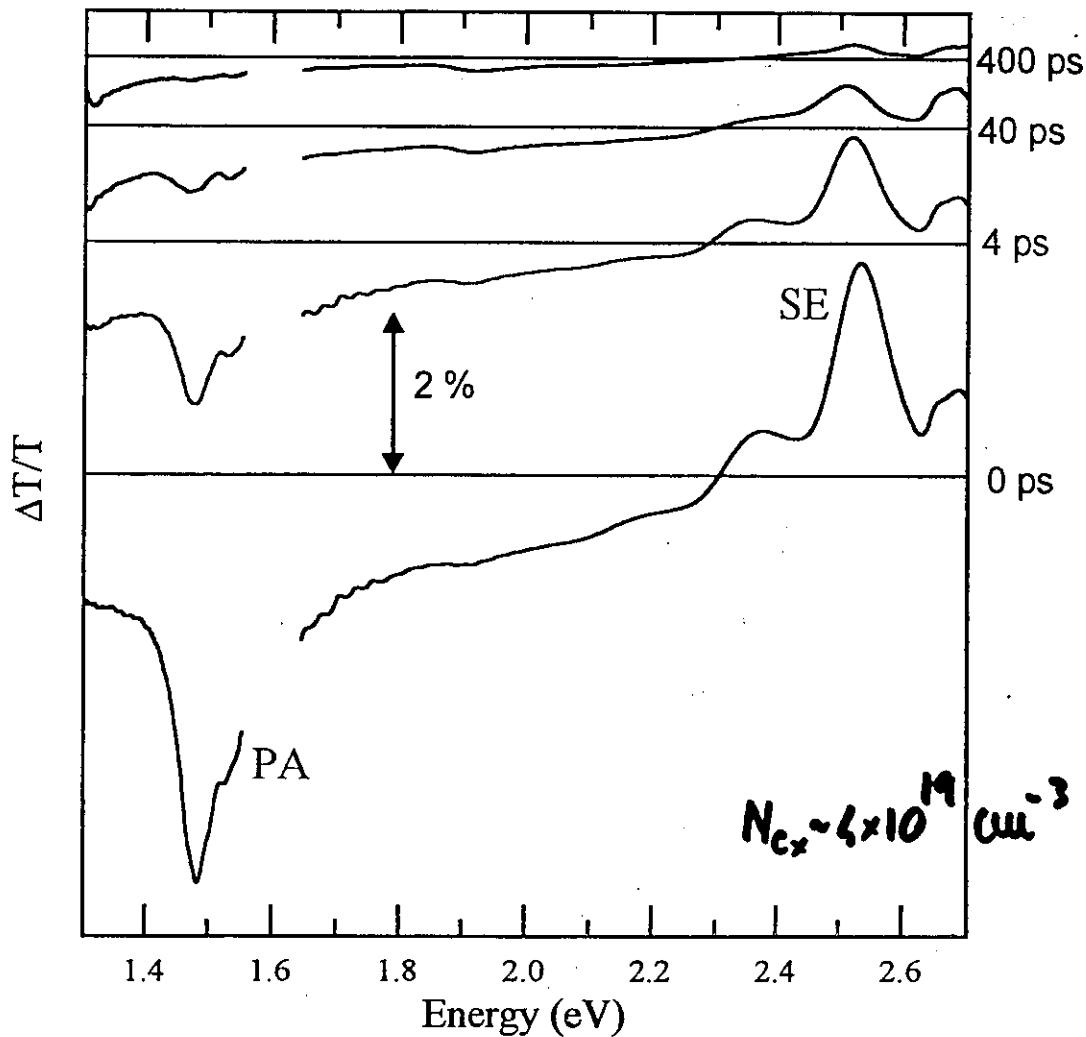


- 1 Dephasing ≈ 10 fs
- 2 Energy redistribution ≈ 100 fs
- 3 Energy migration $\approx 1 - 10$ ps
- 4 Deactivation $\approx 10 - 100$ ps

WHAT ABOUT CHARGE GENERATION ?

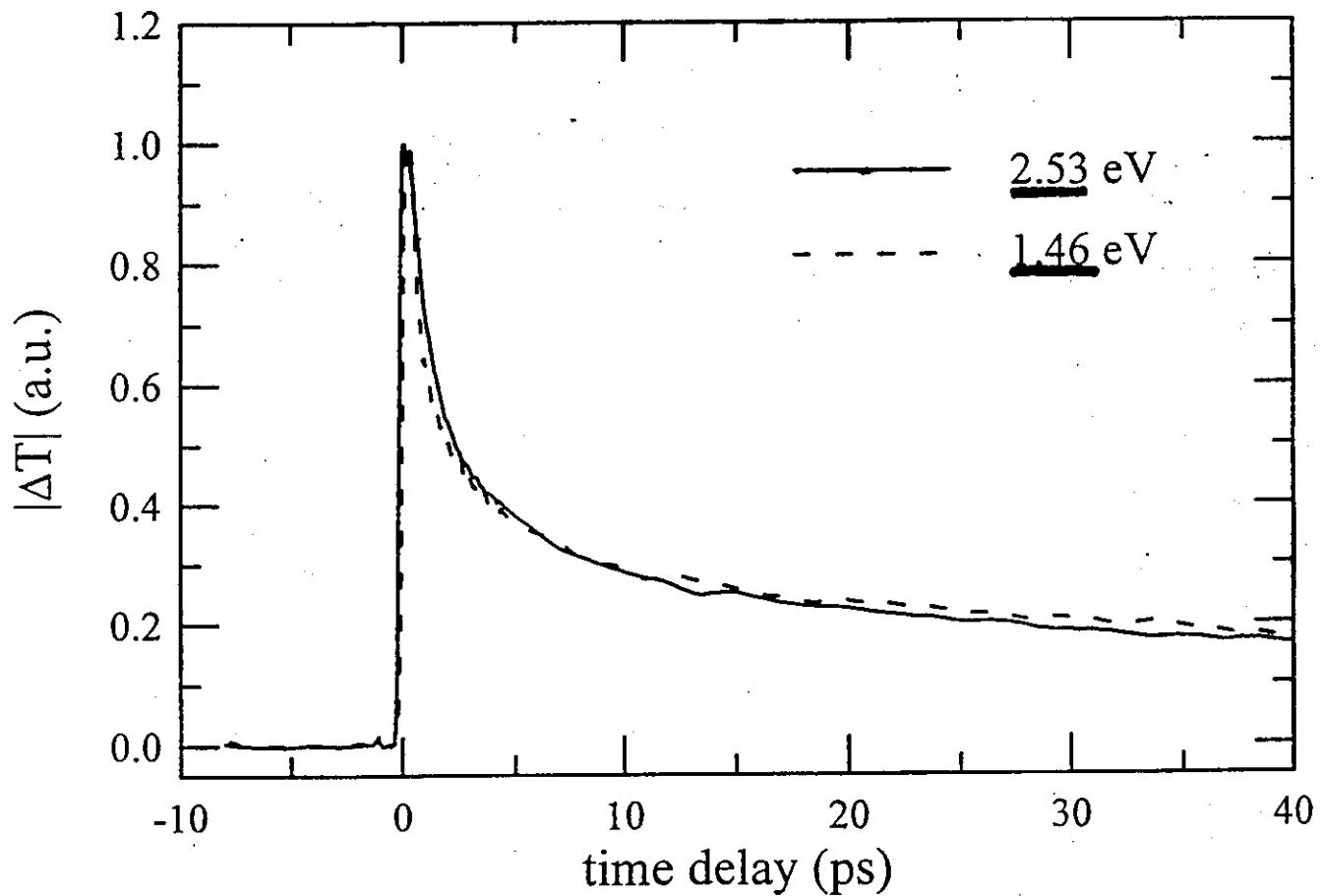
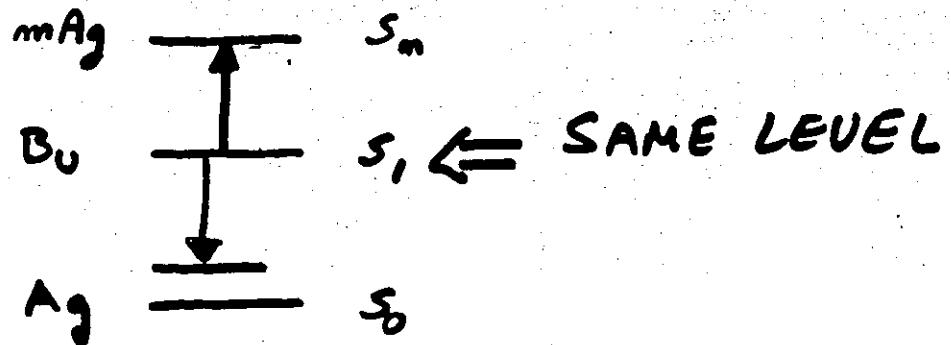
EXCITED STATE DYNAMICS IN m-LPPP

- Pump @ 3.2 eV, white light probe (150 fs time resolution):



- Singlet exciton:
 - ⇒ Stimulated Emission (SE) @ 2.5 eV
 - ⇒ Photoinduced Absorption (PA) @ 1.5 eV
- Singlet exciton decay with a time constant of ~ 10 ps.

COMPARISON SE - PA

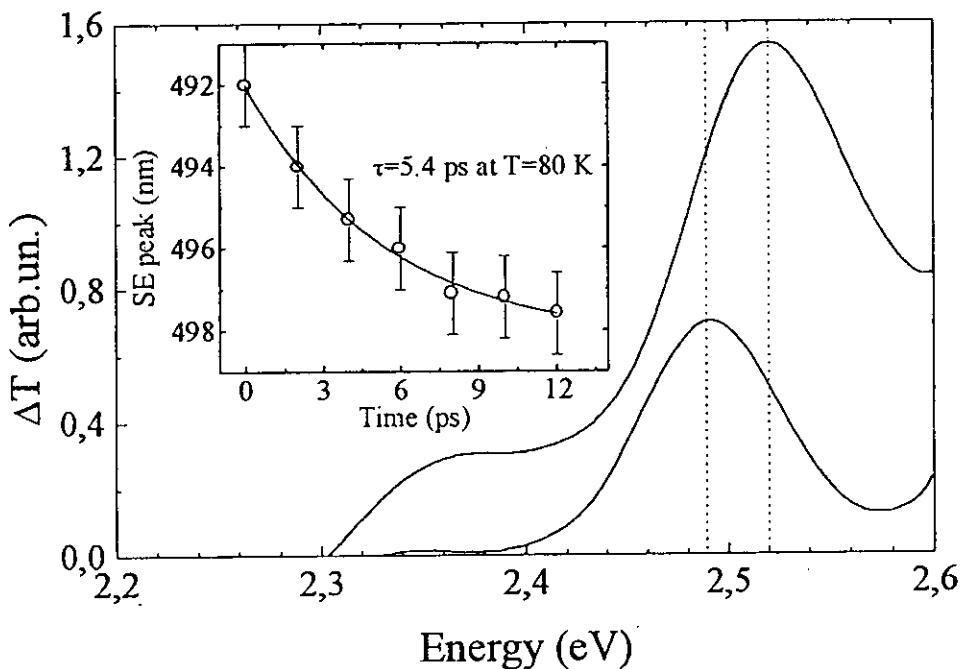


G. Lanzani et al.: "Photophysics of m-LPPP..."

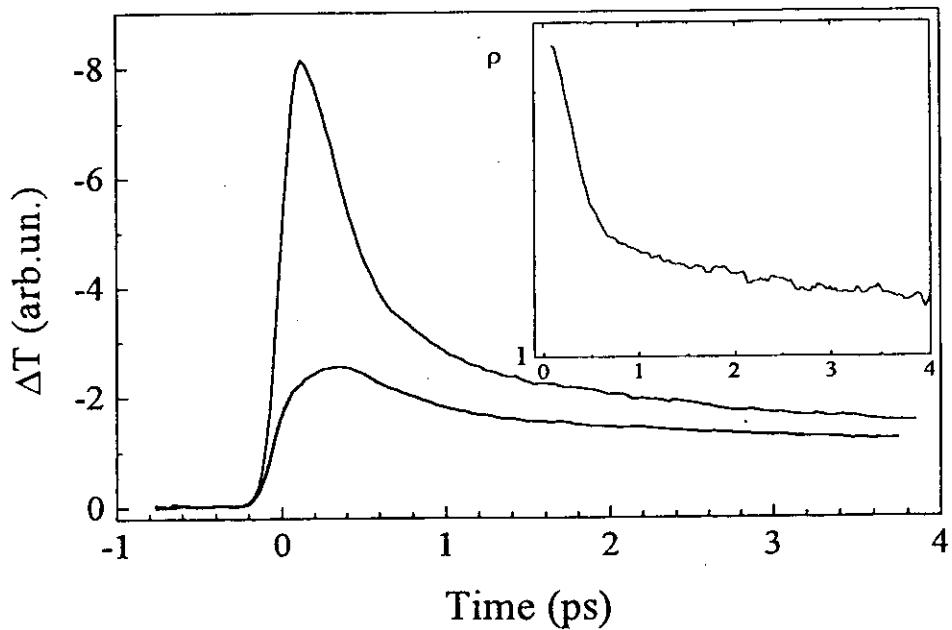
Figure 9

Experimental Evidences of Ultrafast Exciton Migration in m-LPPP

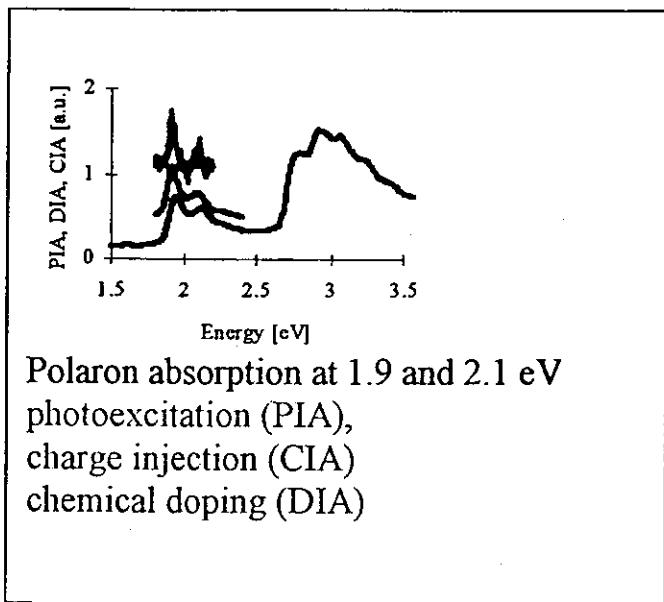
- Stimulated Emission Spectral Relaxation



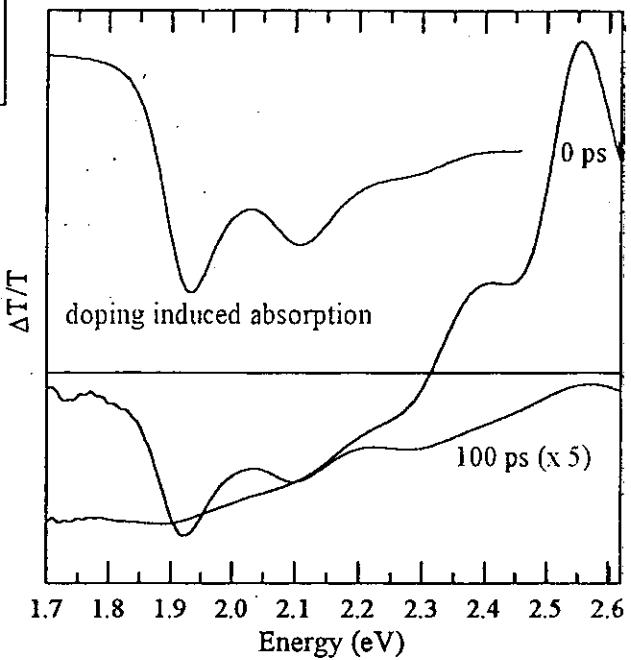
- Polarization Memory Loss



Charged states in m-LPPP

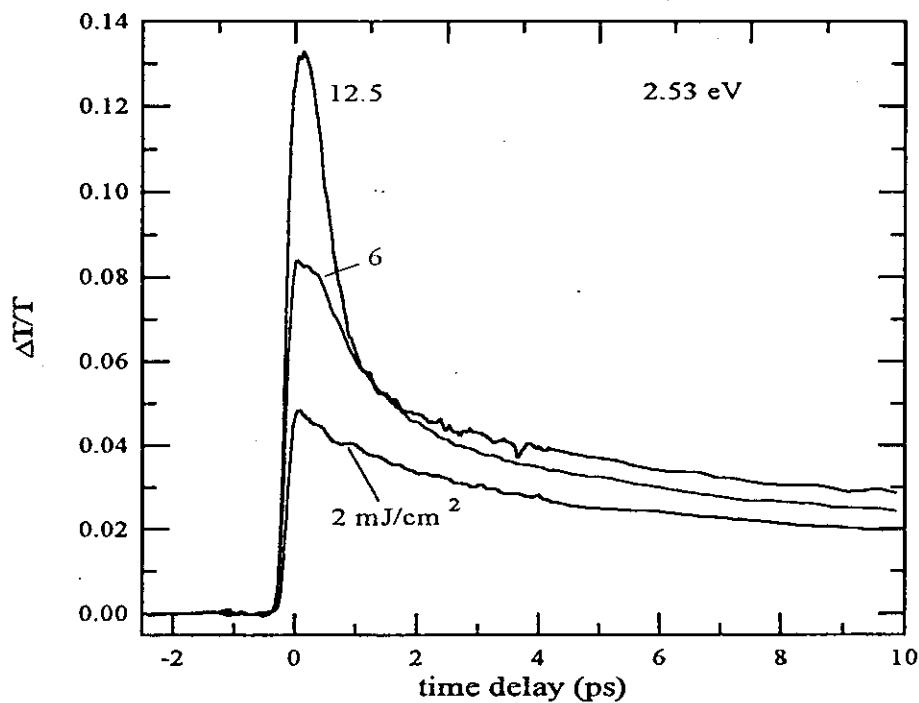


Long lived PA @ 1.9 eV, (with vibronic replica at 2.1 eV), assigned to charged species (polarons).

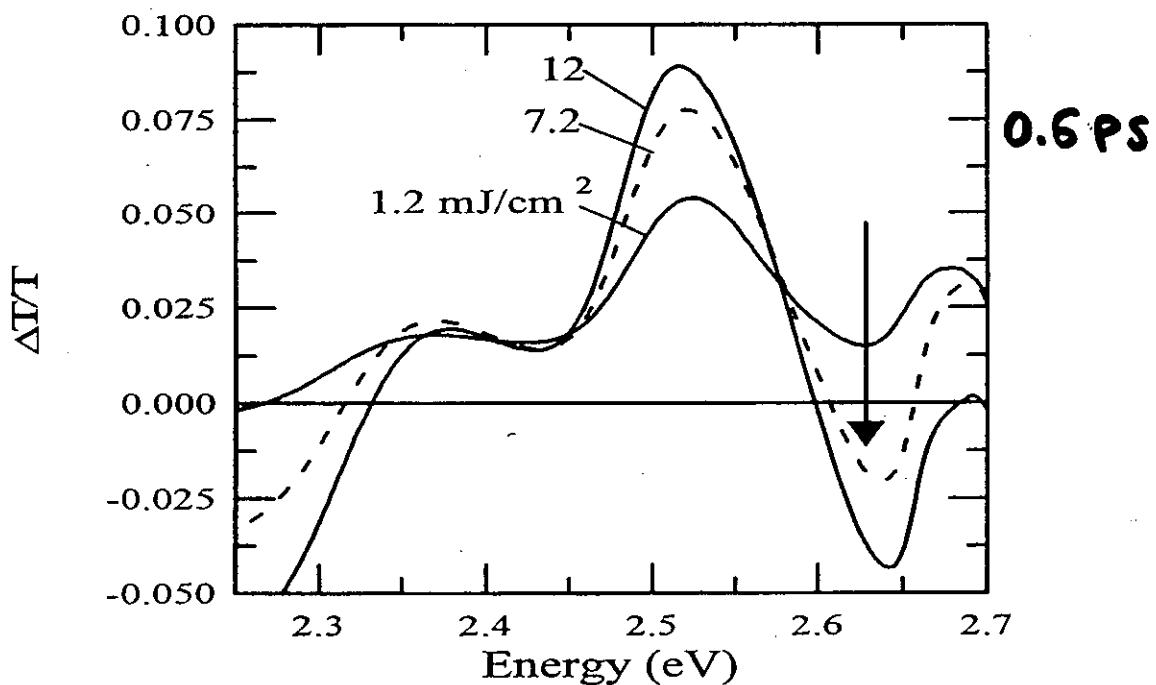


PA @ 1.9 eV is a fingerprint of charge states in m-LPPP.

Photoexcitation at high density



- Ultrafast exciton depopulation due to ASE



- Condensation reactions \Rightarrow Interchain Excitonic Molecules
- G. Cerullo et al., Phys. Rev. B57, 12806(1998).

HYPERLINEAR EMISSION

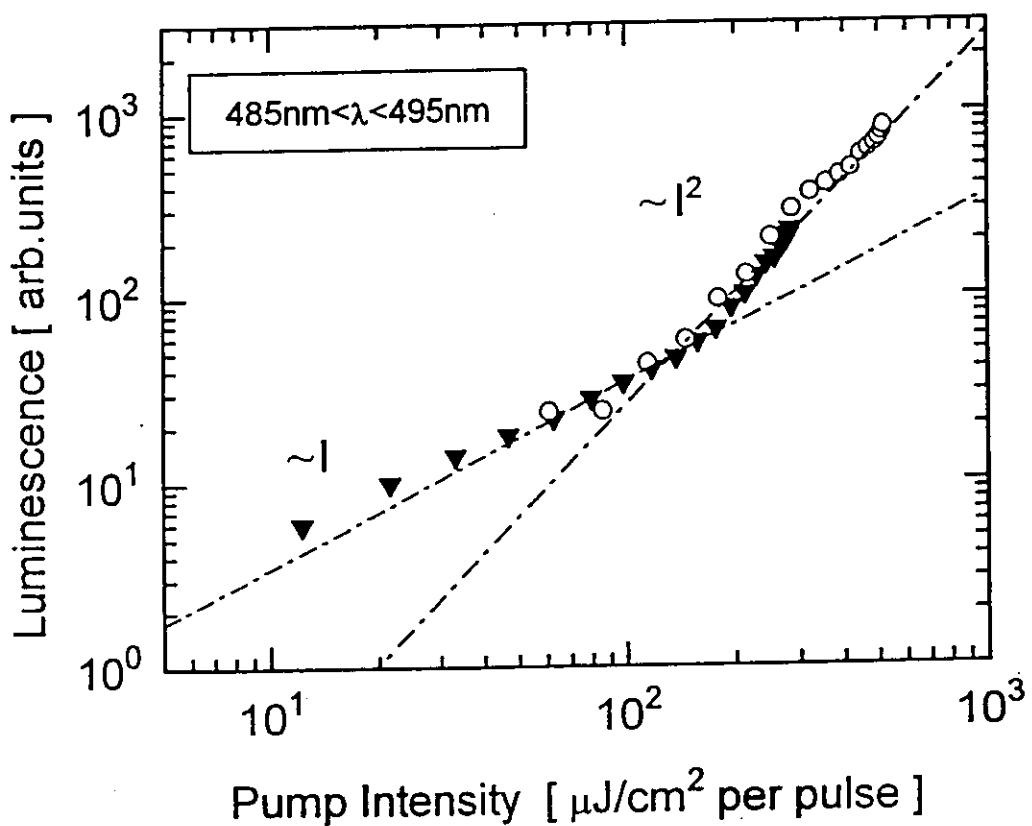
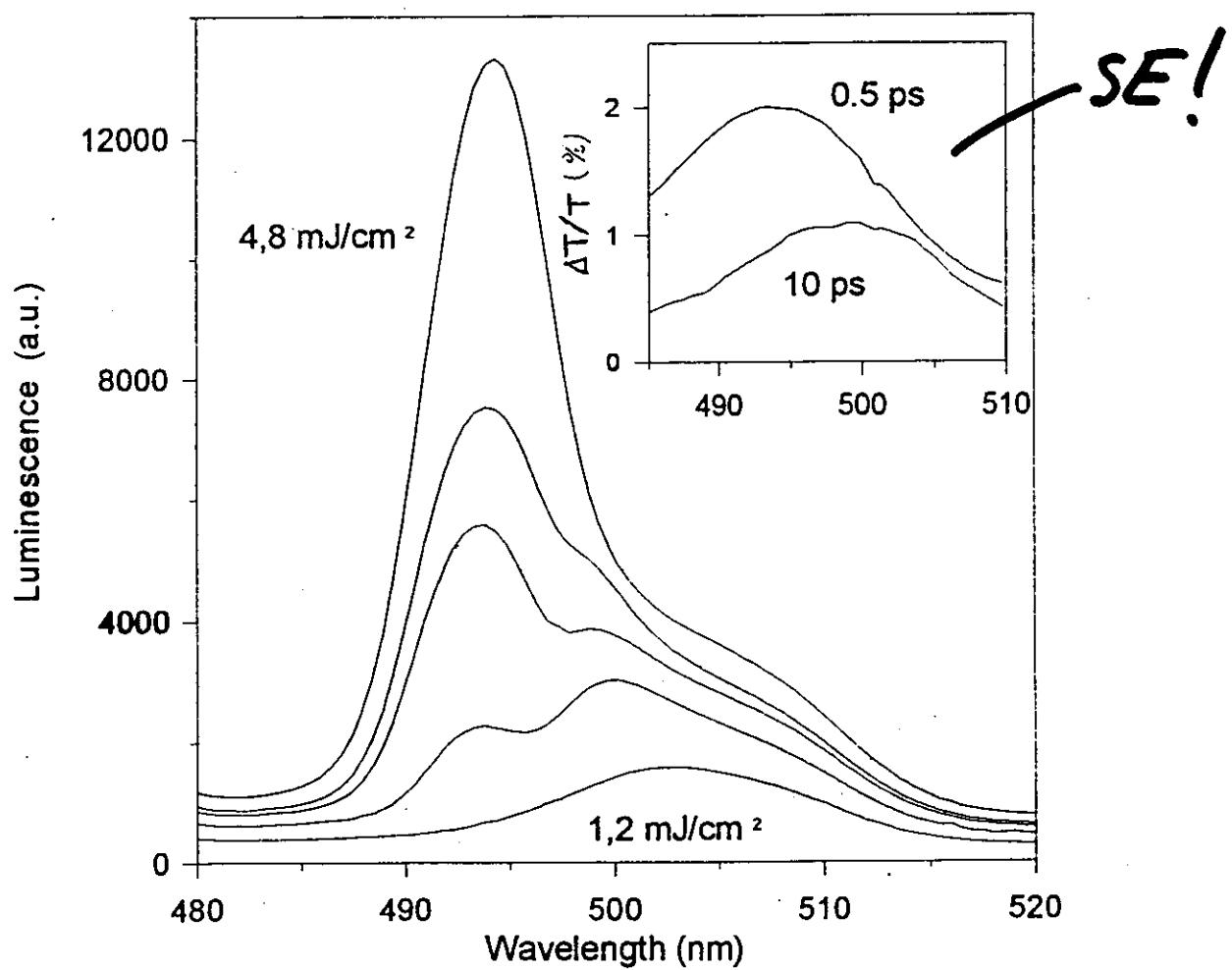


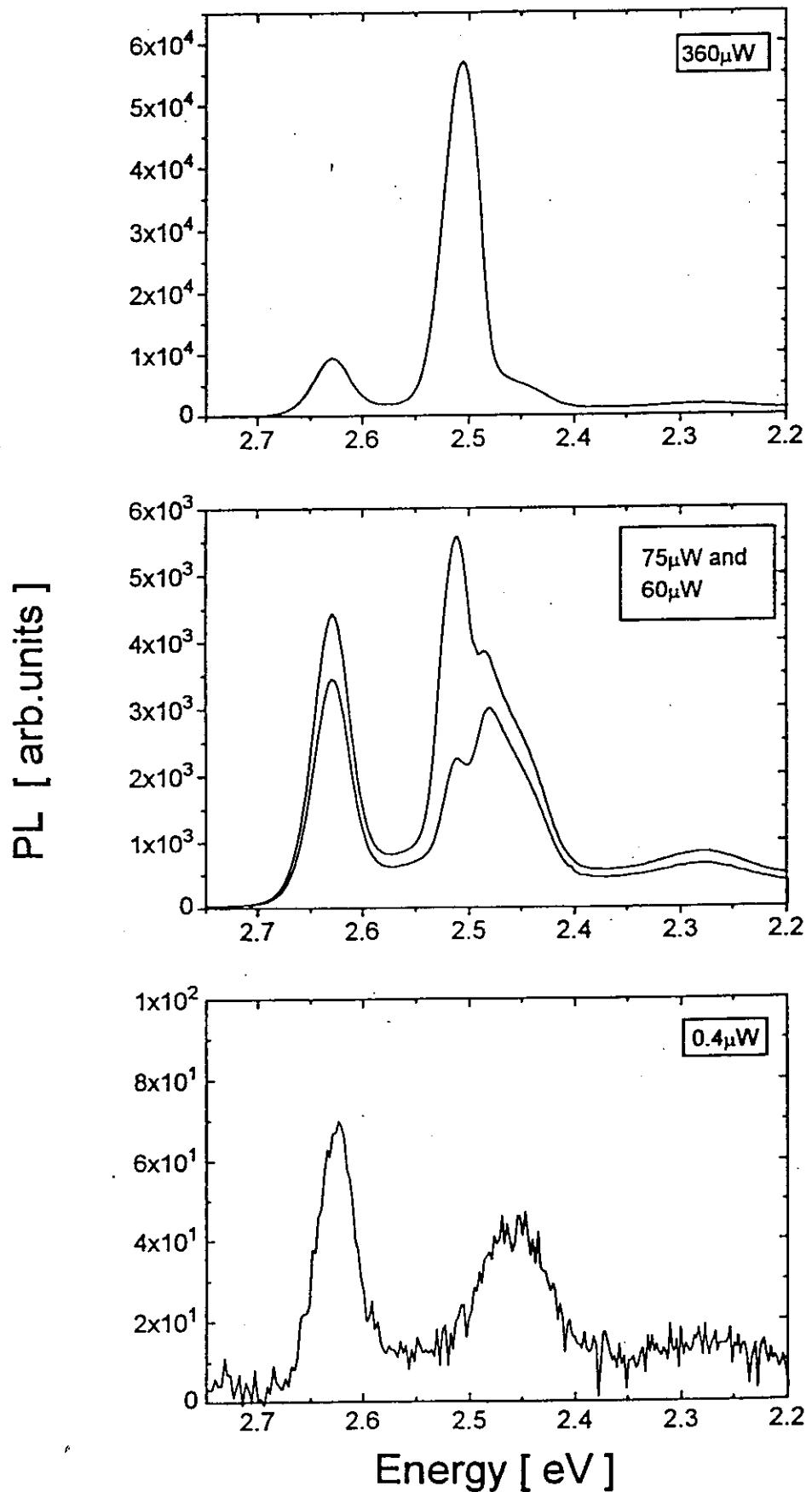
Fig.2 : Luminescence vs. Intensity in PPP-type Ladderpolymer,
($T=80\text{K}$, Excitation: $\lambda_{\text{exc}}=390\text{nm}$, $t_{\text{pulse}}=190\text{fs}$)

Fig 1

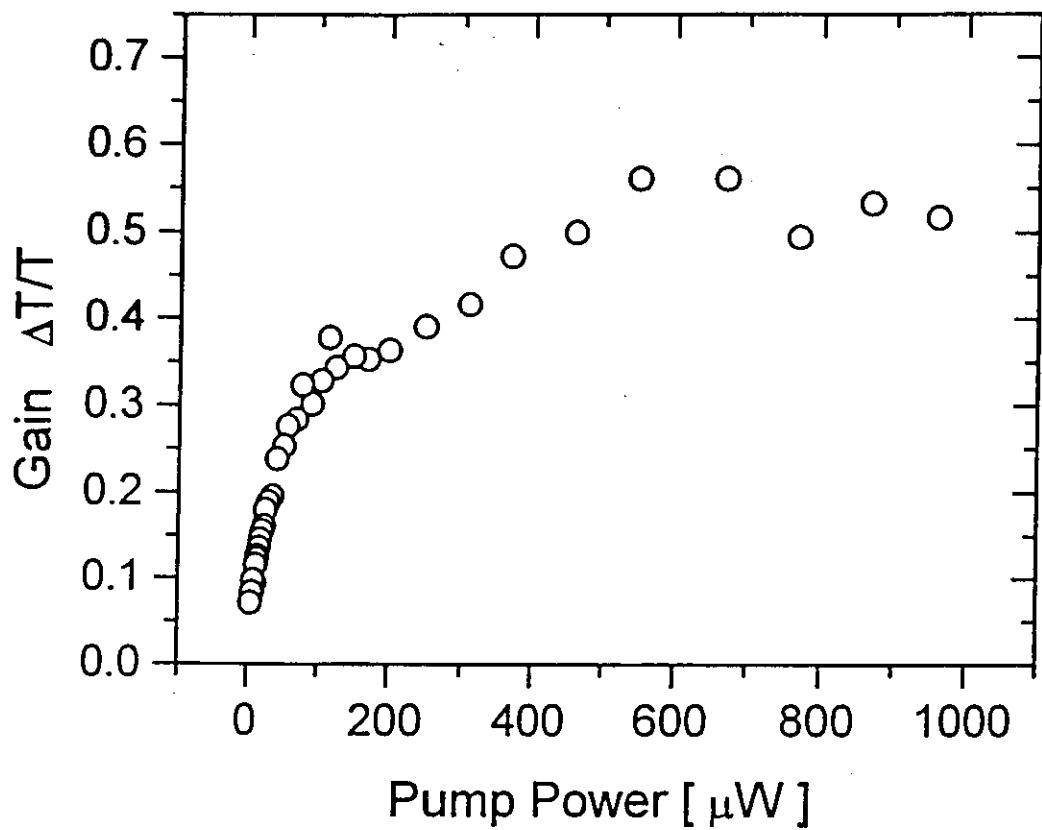
PL vs I_{ex} in m-LPPP films
 $T = 80 K$ PUMP @ 390 nm; 100 fs



PL EMISSION SPECTRA AT DIFFERENT EXCITATION DENSITIES



STIMULATED EMISSION AT 490 NM (± 5 NM)



INTENSITY DEPENDENT SATURATION OF NON RADIATIVE DECAY?

i)

$$\tau = \left(\frac{1}{\tau_R} + \frac{1}{\tau_{NR}} \right)^{-1} \xrightarrow{\tau_{NR} \rightarrow \infty} \tau_R$$

$$\tau_R \propto \langle \psi_G | \mu | \psi_E \rangle \approx 10^2 - 10^3 \text{ ps}$$

ii)

PL spectrum does not change

Cooperative emission

Manybody phenomena leading to the emission of a coherent pulse I_p with
peak intensity $\sim N^2$
pulse width $\tau_c \sim N^{-1}$

Super-radiance:

the ensemble of emitters is initially excited into a correlated state with a Giant dipole moment.

Super-fluorescence:

the emitters are initially uncorrelated and spontaneously develop a cooperative macroscopic dipole moment.

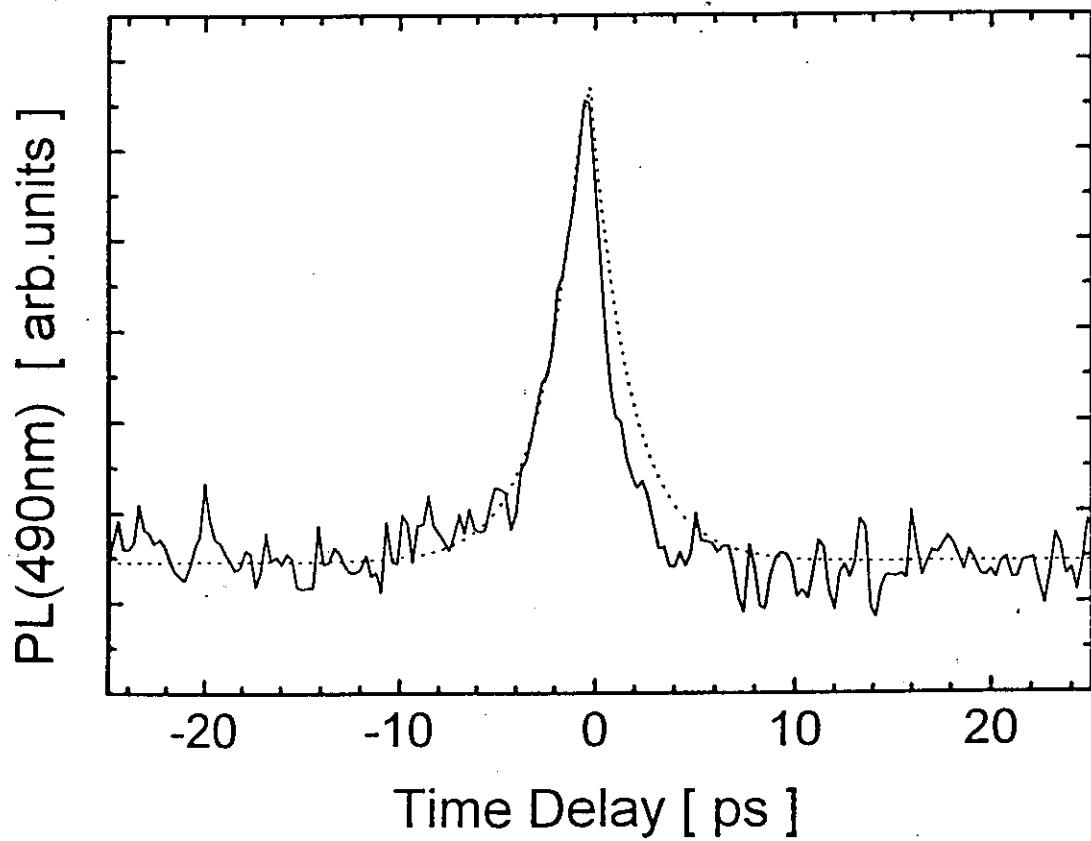
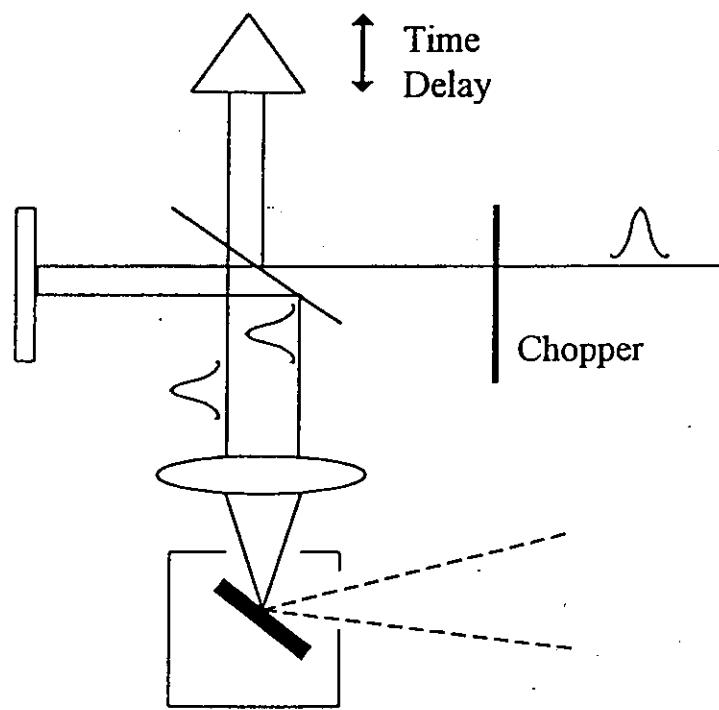
$$L/c = \tau \ll \tau_c \ll T_2, T_1$$

In both cases:

1. there is a distinct threshold
2. the length of the material should be smaller than some characteristic length
3. the time evolution of the emitted light is non-exponential (light burst)
4. light propagation is diffraction limited

• DOUBLE EXCITATION CROSS-CORRELATION

PL excitation cross-correlation



COLLECTIVE EMISSION

(Amplified Spontaneous Emission)

The spontaneous emission originating from an ensemble of emitters is linearly amplified by the same group of emitters with a large gain

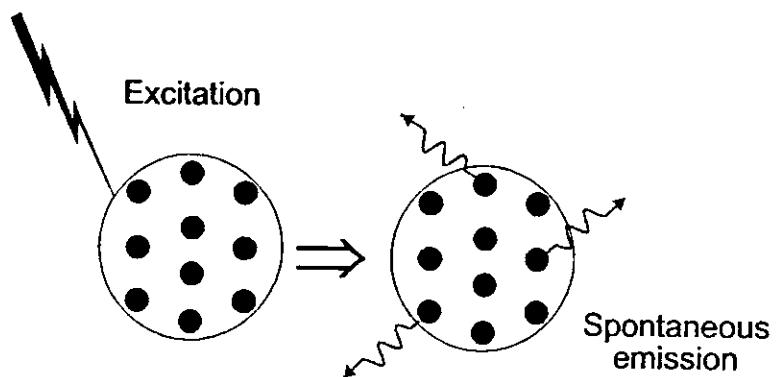
⇒ pulsed emission

there is no threshold for ASE
no limitations on the length of the active medium
light divergence is determined by geometrical condition

SR, SF, ASE lead to a dramatic spectral narrowing

AMPLIFIED SPONTANEOUS EMISSION

□ Spontaneous Emission



□ Amplified Spontaneous Emission

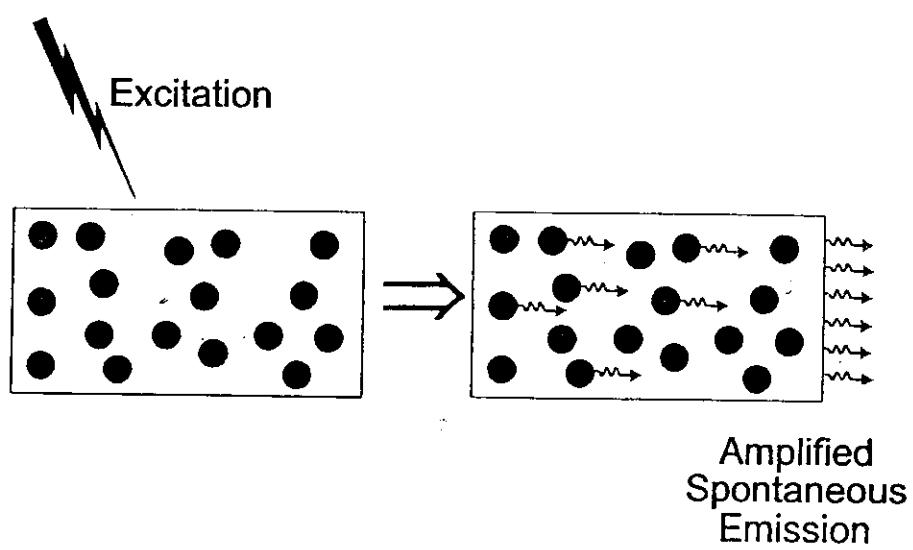
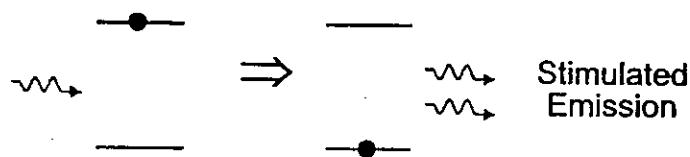


Fig. 4

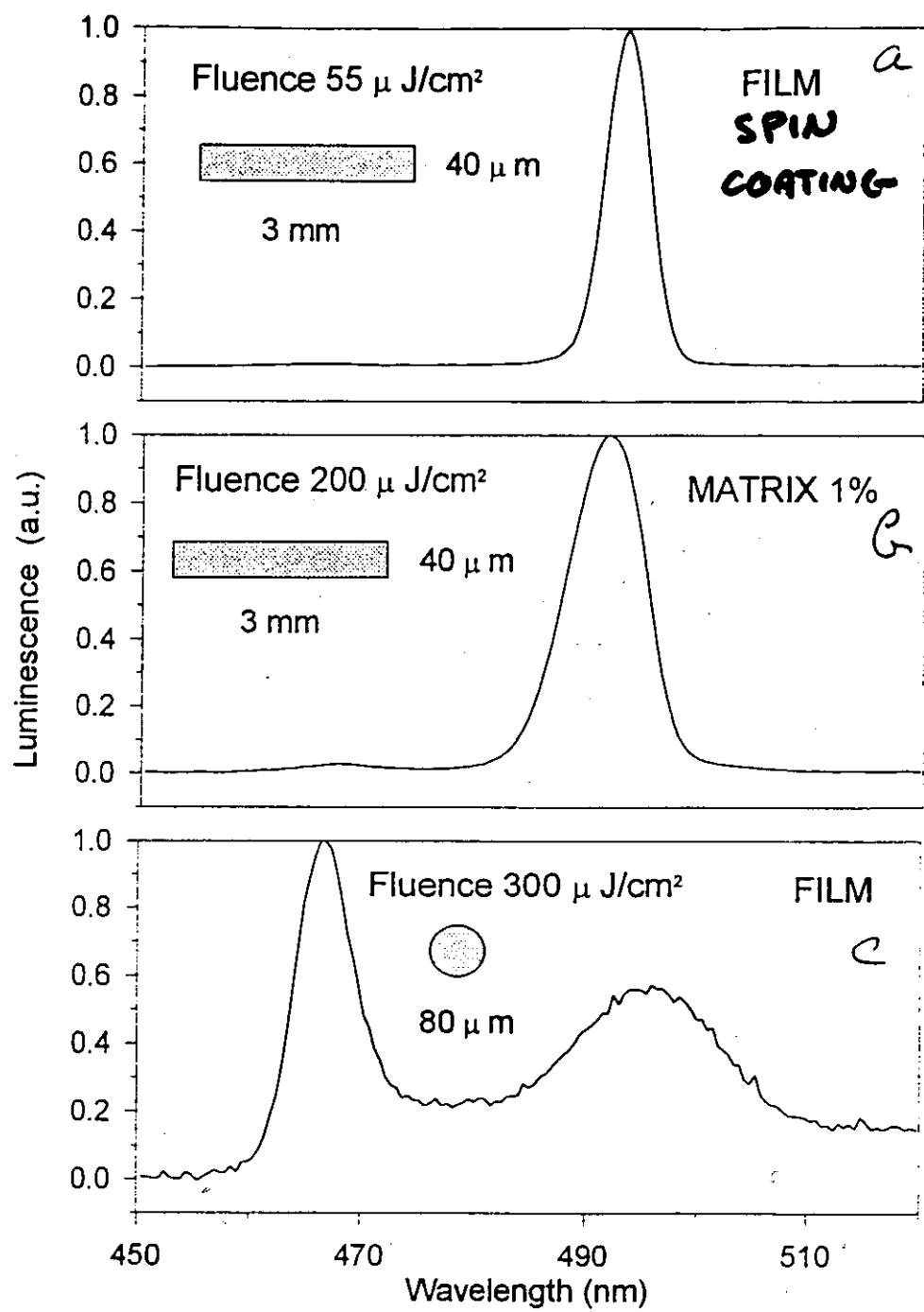
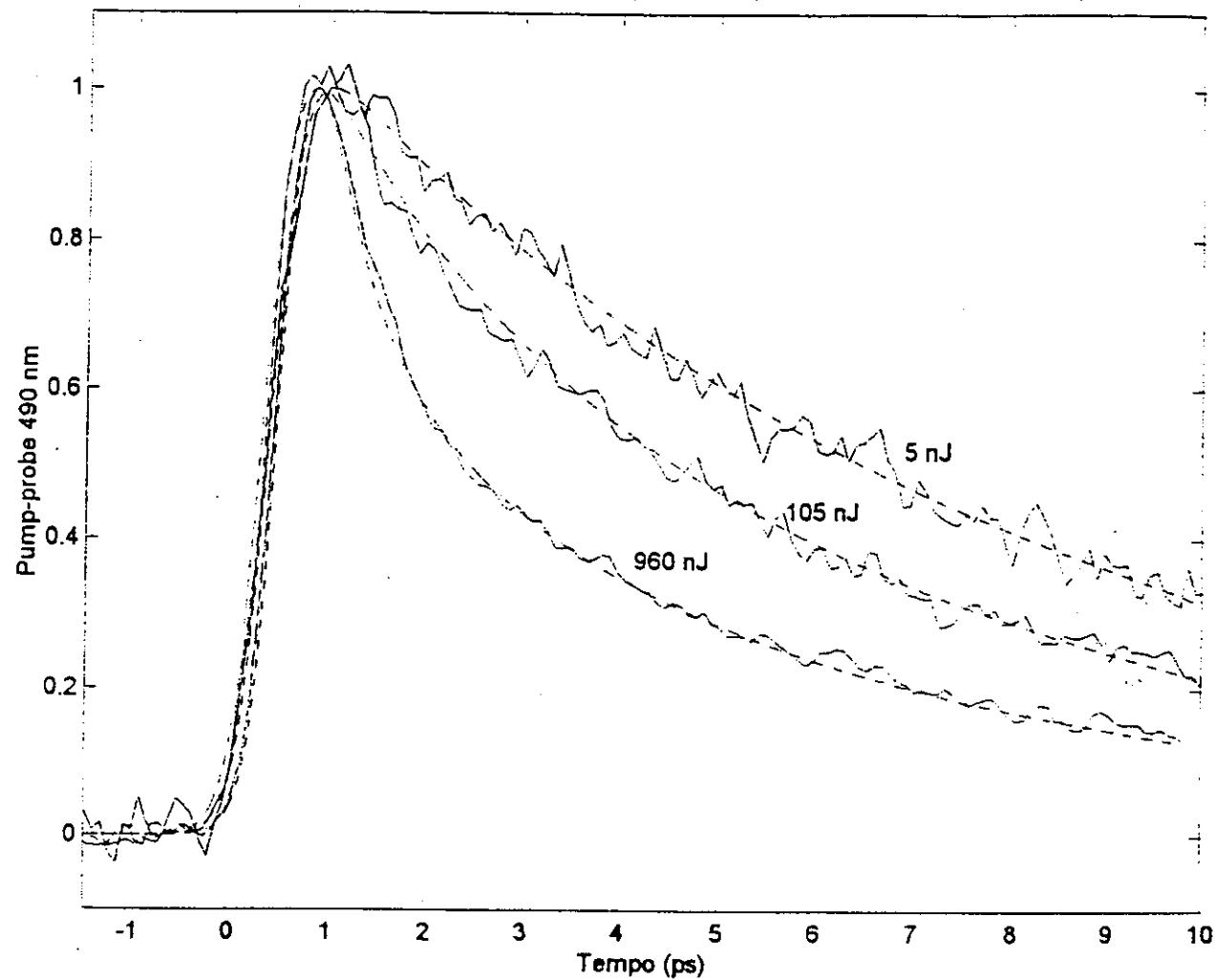


Fig 3

SE DYNAMICS @ 490 nm

Linea continua = Misura; Linea tratteggiata = Fit (ASE + annichilazione eccitoni)



$$\dot{N}(\bar{r}, t) = G - \kappa N - \delta N^2 - \frac{d\phi}{dV}(\bar{r}, t) [G(\bar{r}, t) - 1]$$

$SE (P_{0.5\mu m} = 300 \mu J)$

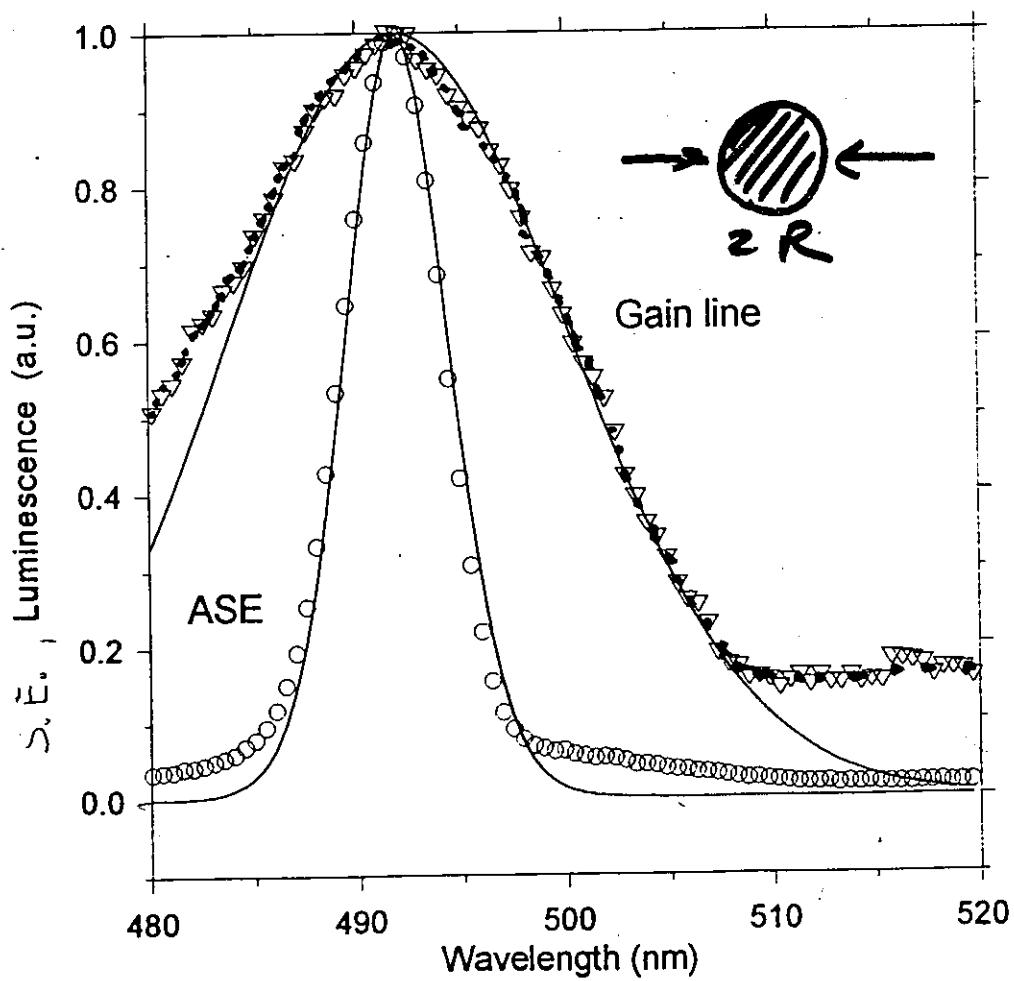


$$N \approx 2.8 \times 10^{19} \text{ cm}^{-3}$$

Fig 2

$$\sigma_{GAIN} = 1.15 \times 10^{-16} \text{ cm}^{-2}$$

$$R = 40 \mu m$$



- THE FIELD-ASSISTED PUMP-PROBE TECHNIQUE

AIM

- To provide new experimental results on the early stage of charge photogeneration in π -conjugated semiconductors;

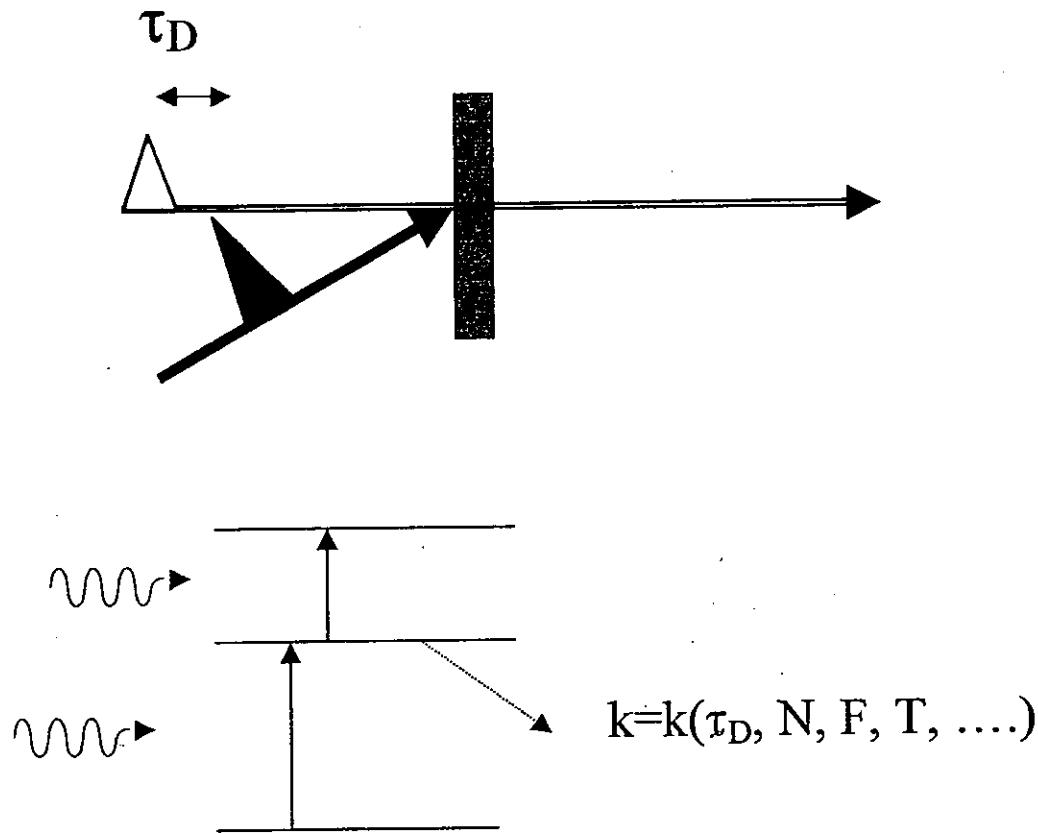
Tool:

- Electric field assisted fs *pump-probe* spectroscopy
 - ⇒ understanding of the basic physics of conjugated polymers
 - ⇒ relevant for applications (LED efficiency, photovoltaics,...)
- So far, time dynamics of field induced charge generation was investigated via
 - ⇒ photoluminescence quenching (R. Kersting et al., Phys. Rev. Lett. **73**, 1440 (1994)).
 - ⇒ photobleaching quenching (G. E. O'Keefe et al., Chem. Phys. Lett. **276**, 78 (1997)).
 - ⇒ photoconductivity (D. Moses et al., Phys. Rev. Lett. **58**, 2710 (1997)).

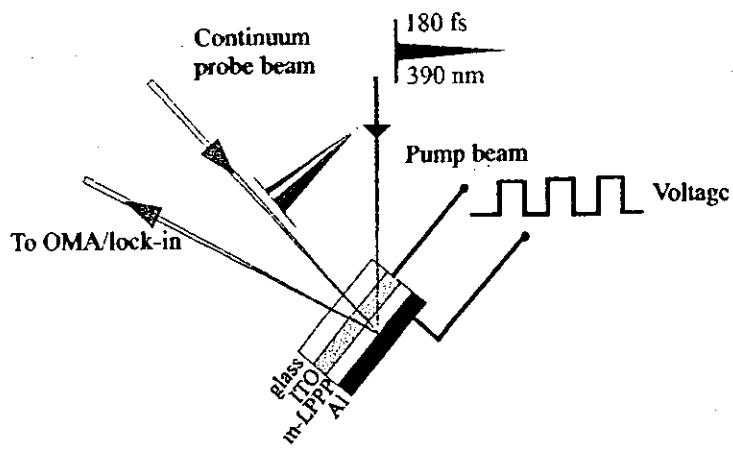
THIS WORK

- ⇒ First **direct** observation, with femtosecond time resolution, of charge generation in a methyl substituted ladder type poly(*para*-phenylene) (m-LPPP) polymer.

Pump-Probe



Field-assisted Pump-Probe



Definitions

No Applied Voltage ($F=0$) $\Rightarrow \Delta T/T = \sigma_i N_i L$

Biased LED($F \neq 0$) $\Rightarrow (\Delta T/T)_F = \sigma_i(F) N_i(F) L$

Modulated electric field (MF) $\Rightarrow (\Delta T/T)_{MF}$

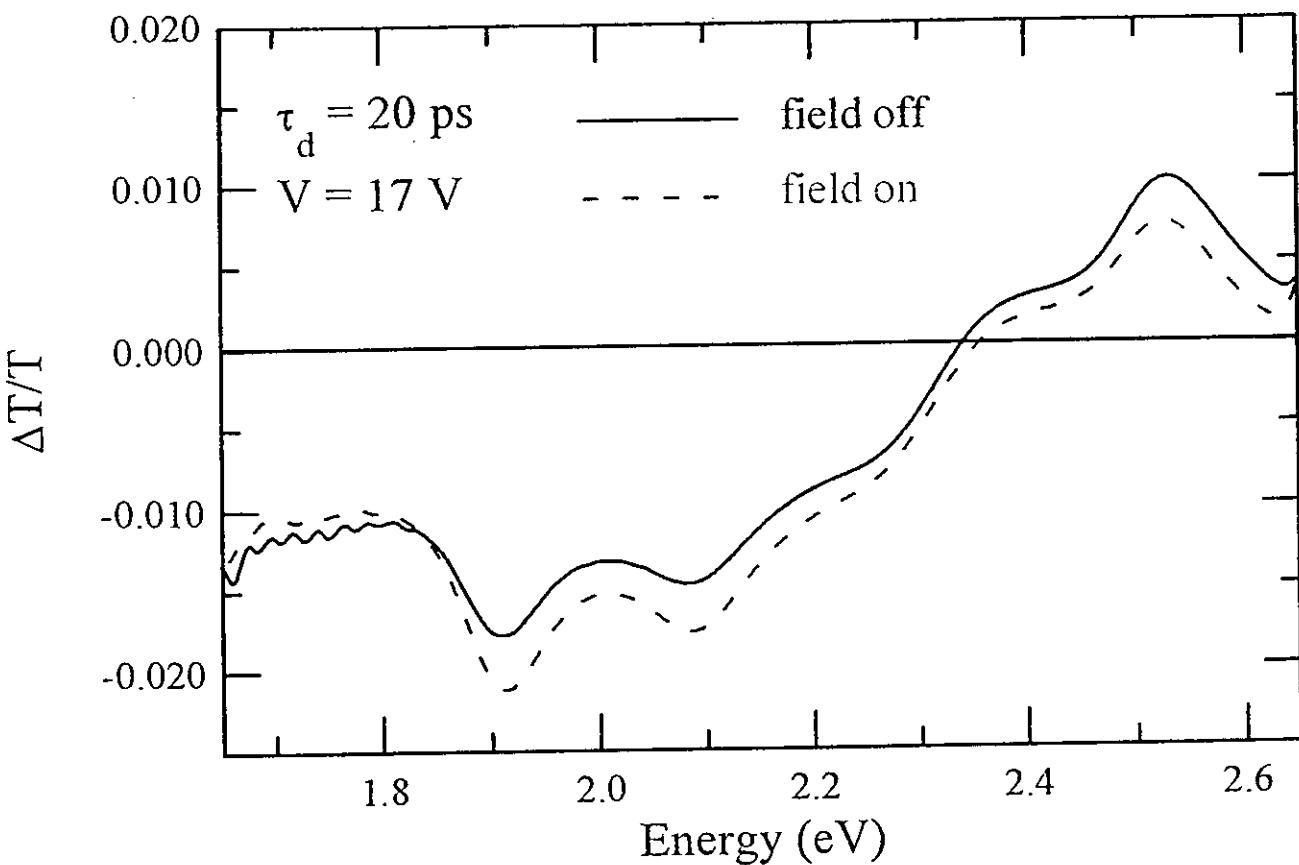
$$(\Delta T/T)_{MF} = (\Delta T/T)_F - \Delta T/T = \Delta(\sigma_i N_i) L$$

if $\sigma_i(F) = \sigma_i$ (check time dynamics!)

$$(\Delta T/T)_{MF} = \sigma_i \Delta N_i L$$

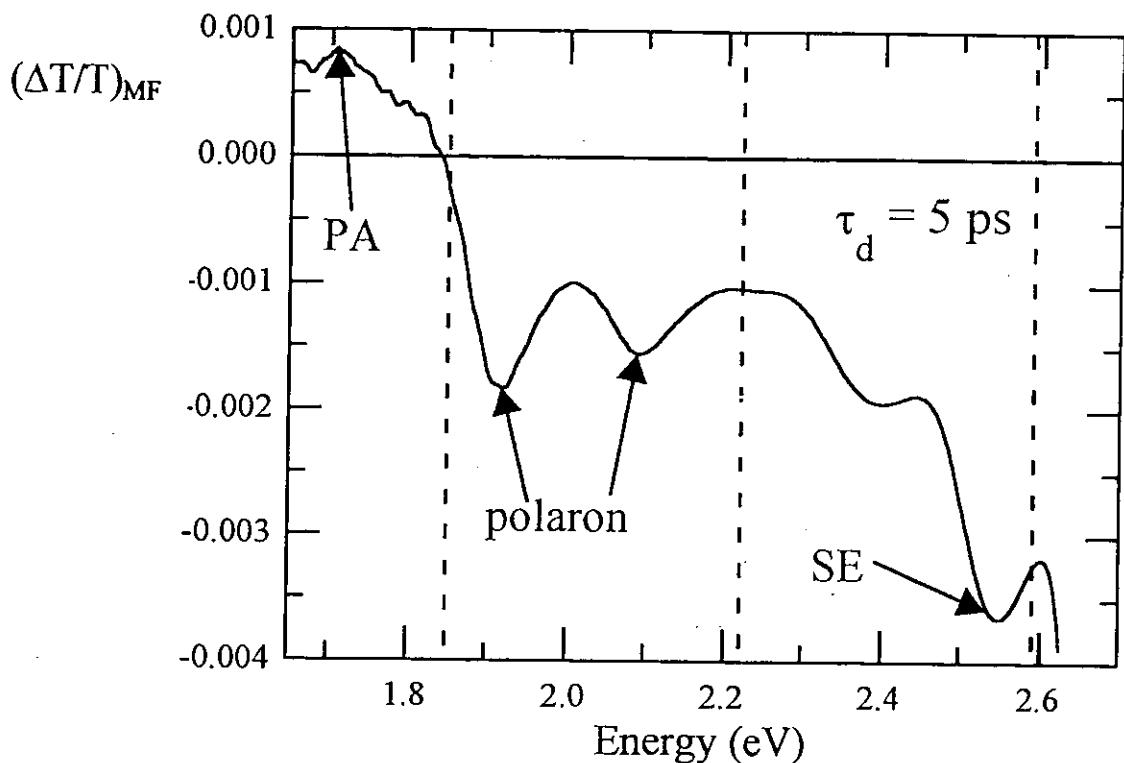
$$\Delta\sigma \quad \longleftrightarrow \quad \text{Stark Shift}$$

EFFECT OF AN ELECTRIC FIELD ON THE DIFFERENTIAL SPECTRUM



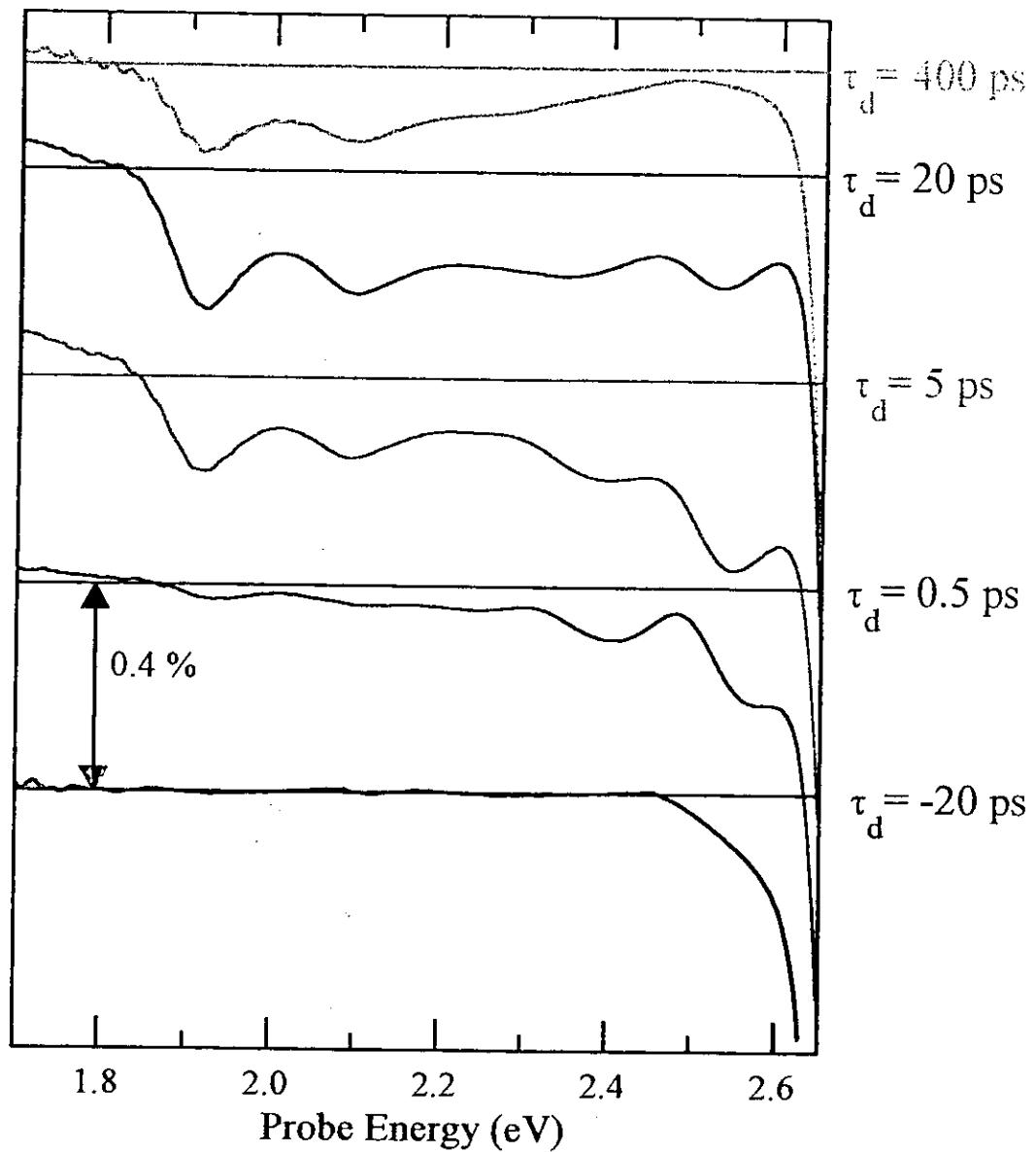
- Reduction of singlet exciton SE (@ 2.5 eV)
 - Reduction of singlet exciton PA (@ 1.5 eV)
 - Increase of polaron absorption (@ 2.1 eV)
- ⇒ field induced dissociation of singlet excitons into polaron pairs

EFFECT OF AN ELECTRIC FIELD ON THE DIFFERENTIAL SPECTRUM



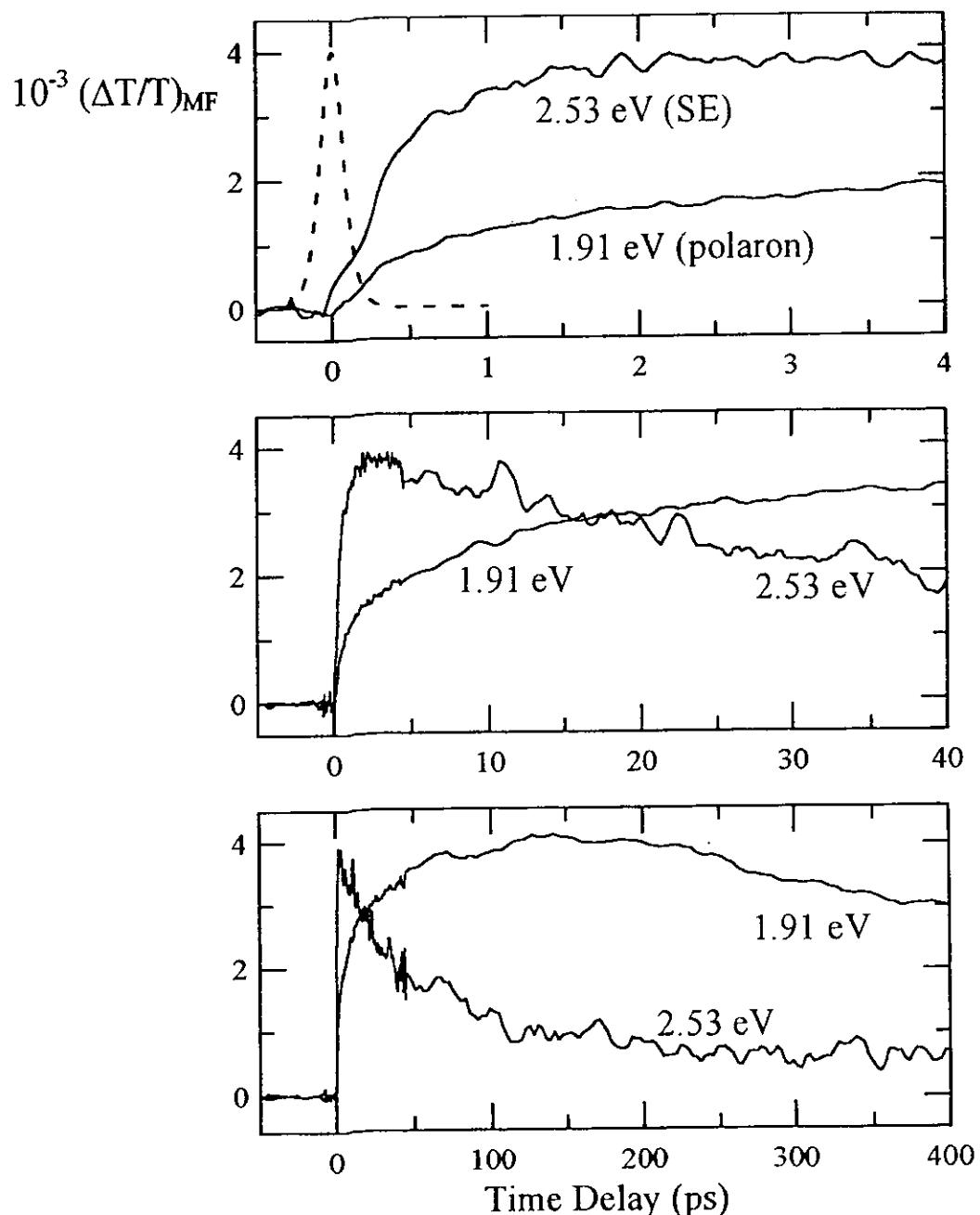
- Reduction of singlet exciton SE (@ 2.5 eV)
- Reduction of singlet exciton PA (@ 1.5 eV)
- Increase of polaron absorption (@ 1.9 and 2.1 eV)

TEMPORAL EVOLUTION OF $(\Delta T/T)_{MF}$



- Negative delays \Rightarrow Stark shift of the HOMO-LUMO transition
- Early time delays \Rightarrow quenching of singlet exciton features
 \Rightarrow increase of polaron absorption
- Long time delays \Rightarrow long-lived polaron absorption

KINETICS AT SELECTED WAVELENGTHS



- Formation time for singlet SE quenching signal
⇒ field induced dissociation is **noninstantaneous**
- Polaron absorption has an initial fast rise (≈ 2 ps) followed by a slower increase (40 ps timescale).

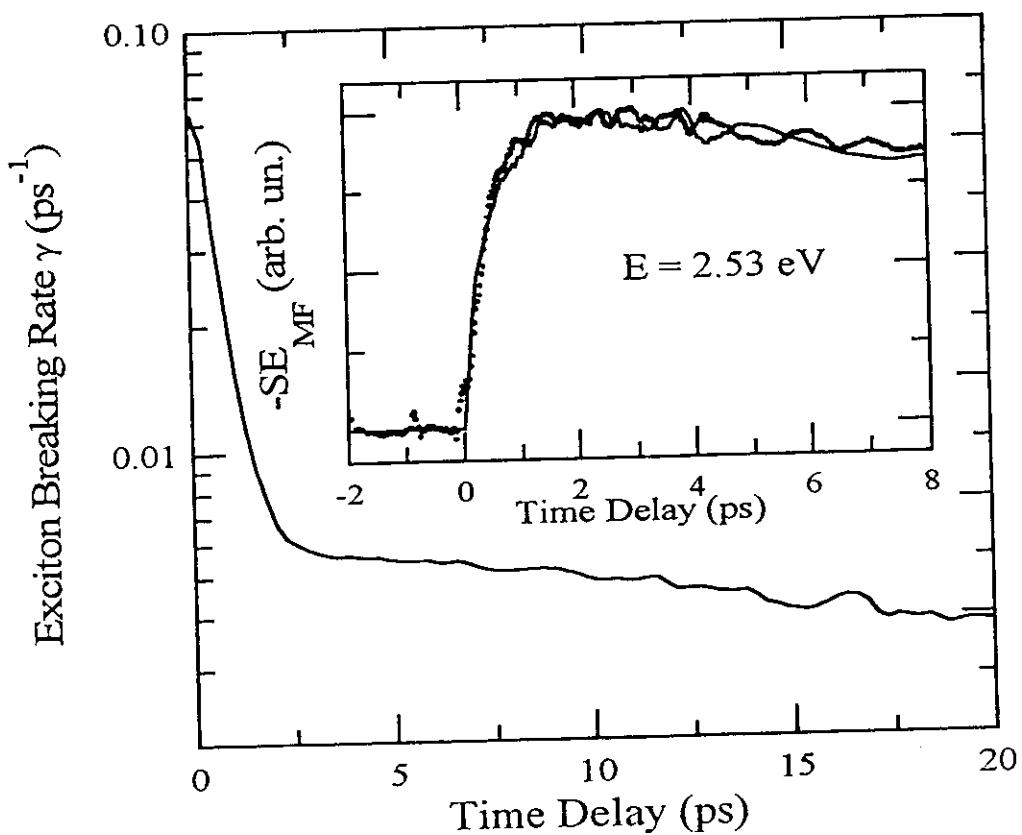
EXCITON BREAKING vs POLARON FORMATION

- Phenomenological field-induced charge generation rate:

$$\gamma(t) = \frac{1}{N_{SF}} \frac{dN_{PMF}}{dt} = \frac{\sigma_S}{\sigma_P} \frac{1}{SE_F} \frac{dPA_{MF}}{dt}$$

where N_S and N_P are singlet and polaron populations;

$SE_F = (\Delta T/T)_F$ @ 2.53 eV; $PA_{MF} = (\Delta T/T)_{MF}$ @ 1.9 eV

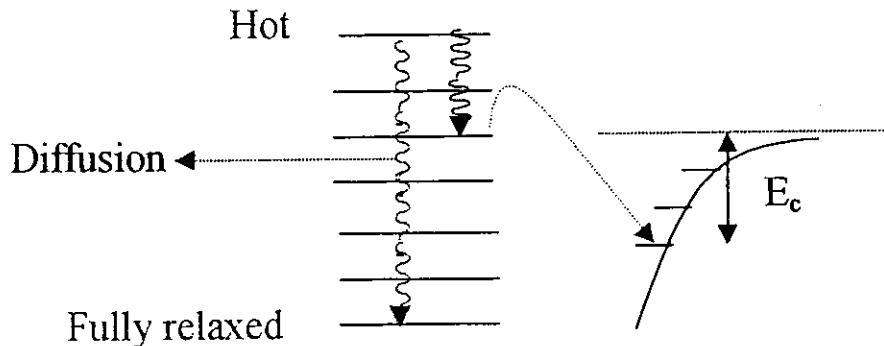


- If exciton dissociation directly results into polarons \Rightarrow

$$\Delta N_S(t) = N_S(t) \left(1 - \exp \left(- \int_0^t \gamma(t') dt' \right) \right)$$

Charge Photogeneration Dynamics

*We propose a diffusion-limited mechanism
driven by hot exciton thermalization*



- There is a fraction “ α ” of the sites on which dissociation can take place either on-chain or by an inter-chain process.
- “ α ” is enhanced by the electric field \Rightarrow *microscopic* models
- Exciton diffusion allows population of the dissociating sites.



Approaching the localization edge (at the bottom of the DOS)
exciton diffusion becomes slower and slower

\Rightarrow the process fades off.

The Potential Box model for tunneling in organic semiconductors

Gutmann & Lyons "Organic Semiconductors" J. Wiley & Sons, 1967

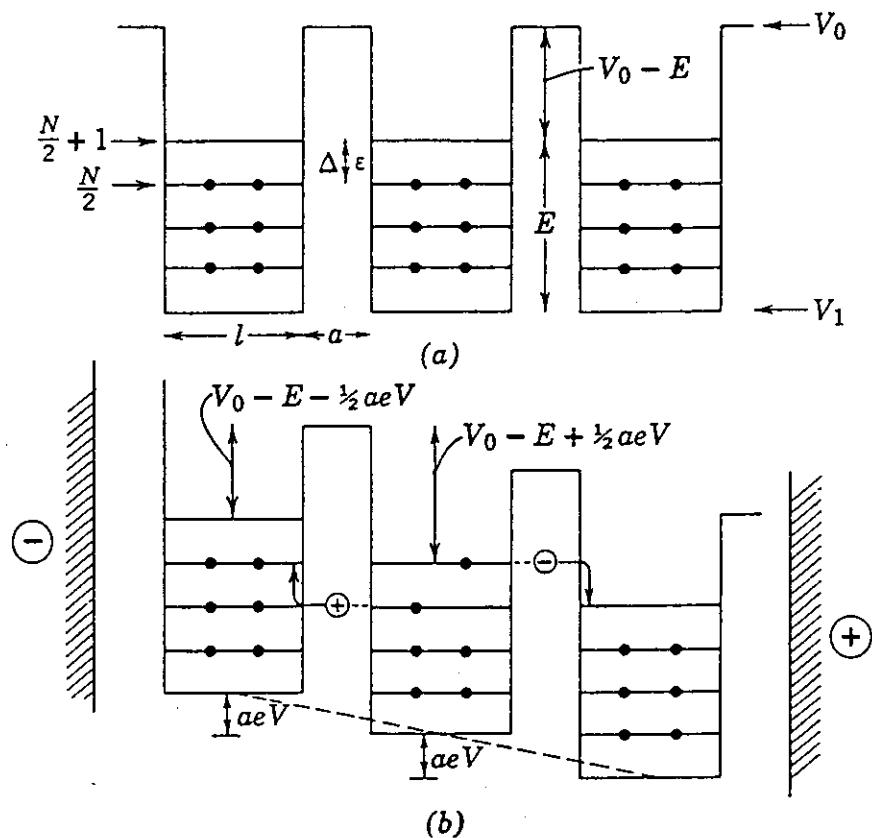


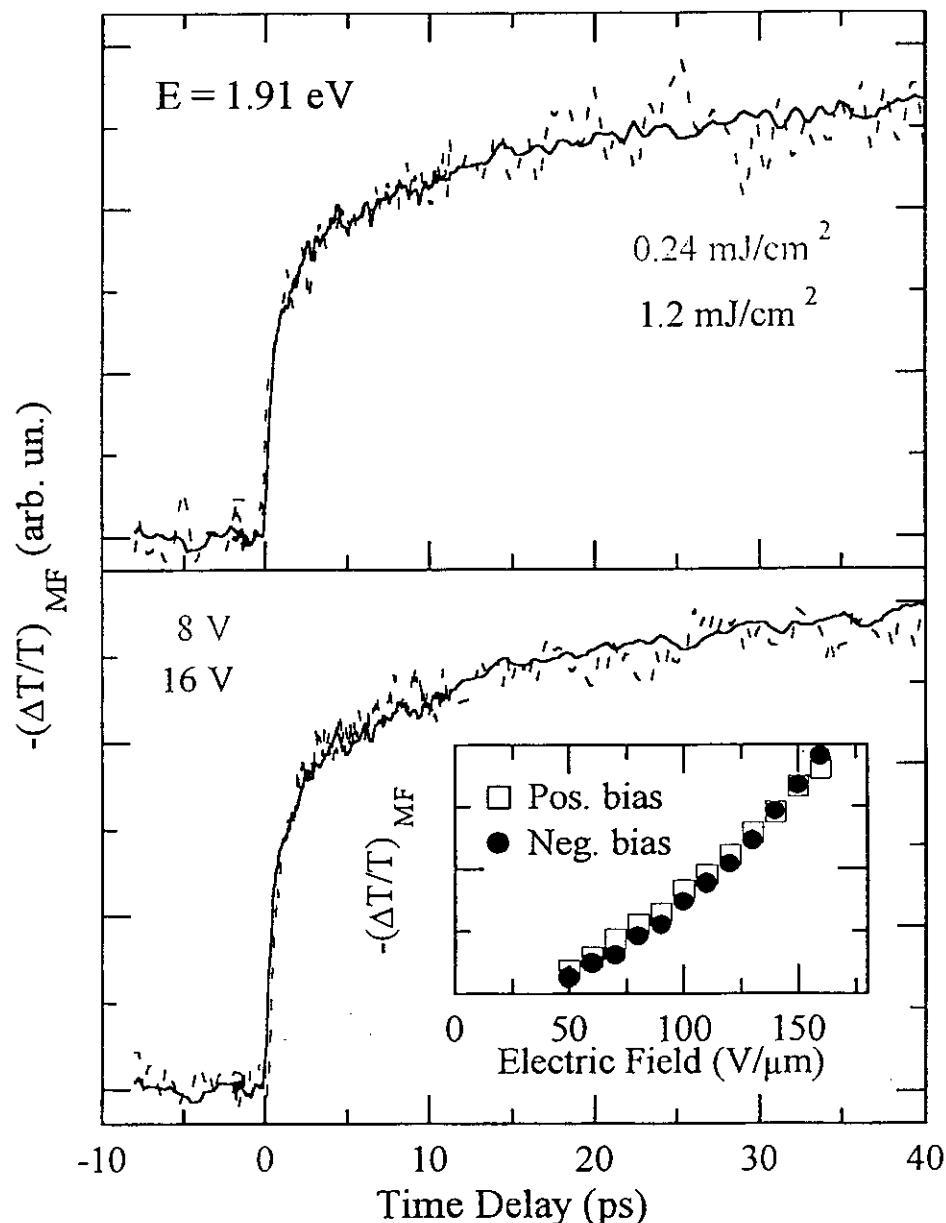
Fig. 7.9 Potential box model (tunnel model) of an organic semiconductor. After Eley and Parfitt.³ By permission of The Faraday Society.

$$\text{Field kick} = e a F \approx 0.1 - 0.01 \text{ eV}$$

Disorder and Polaronic effects help dissociation

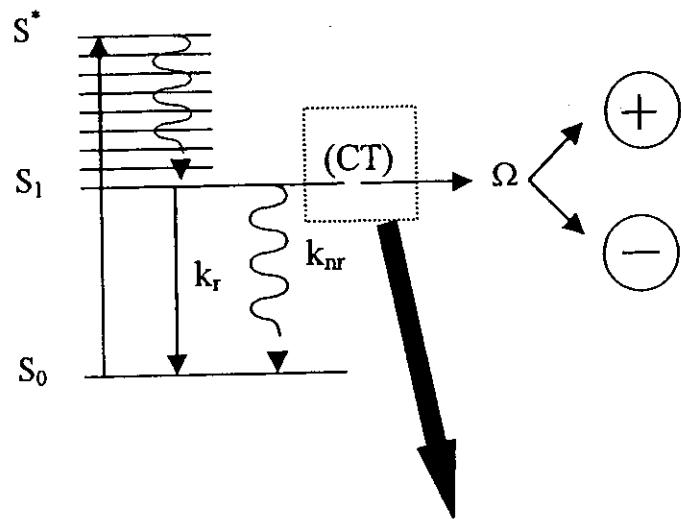
CHARGE GENERATION DEPENDENCE ON EXCITATION DENSITY AND VOLTAGE

- Field-induced polaron absorption vs. excitation intensity and applied field.

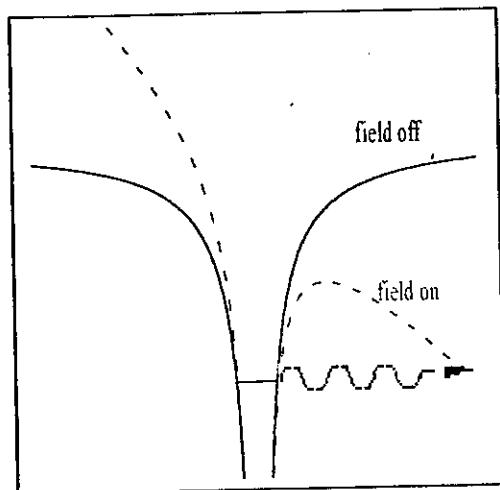


- Symmetry with respect to LED bias voltage \Rightarrow space charge effects and exciton-carrier interactions are ruled out.

2. The cold process



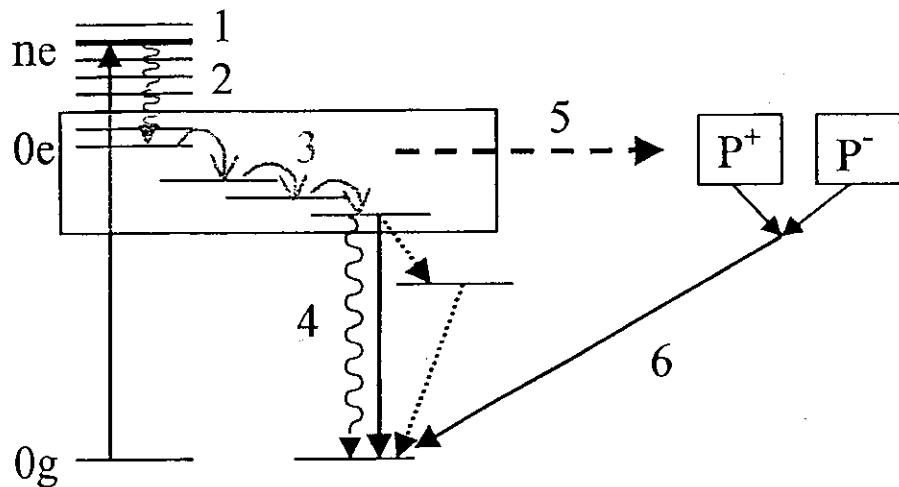
1-D Wannier Exciton



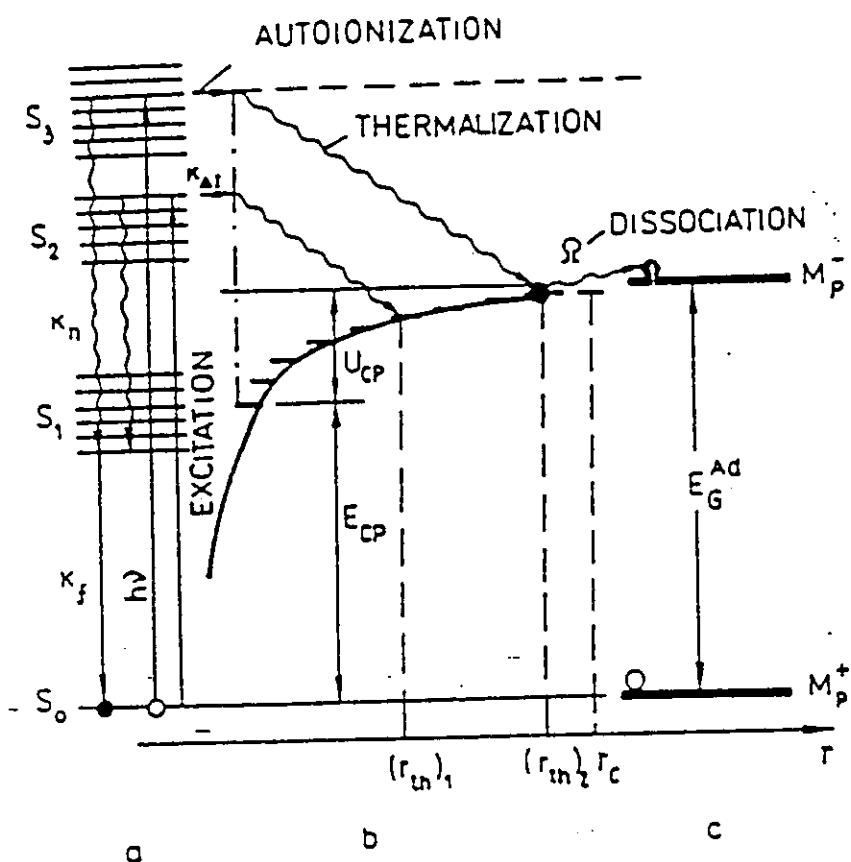
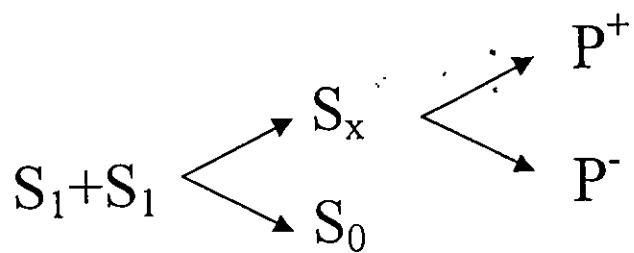
- Z. D. Popovic Chem. Phys. **86**, 311(1984)
- H. Tachibana et al. Phys. Rev. **B47**, 4363(1993)

Conclusions

- The electric field assisted pump-probe technique is a fruitful tool for studying charge photogeneration phenomena with sub ps time resolution.
- Field-induced exciton breaking in m-LPPP directly results into polarons. We find no evidence for intermediate states.
- The build-up kinetics of polaron population suggests that dissociation be driven by exciton migration during inter-chain thermalization.



Exciton Collision ?



PUMP - PROBE

SOME APPLICATIONS :

1. ENERGY MIGRATION
(KERR-SHUTTER)
2. STRUCTURAL RELAXATION
3. COLLECTIVE VIBRATIONAL COHERENCE
LOOKING AT NUCLEAR MOTION
IN REAL TIME

KERR-GATE

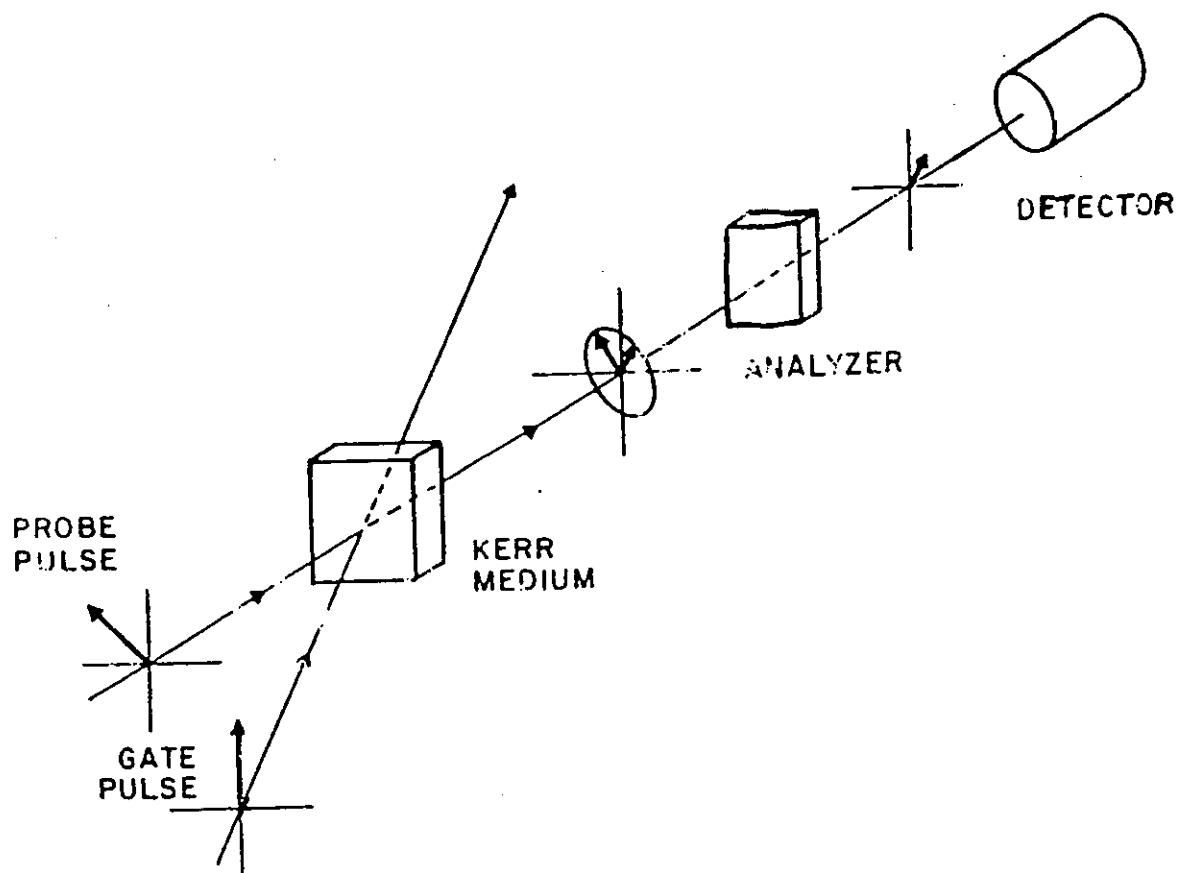


PHOTO INDUCED ANISOTROPY

~~Re~~

~~Im~~

BIRIFRINGENCE (Δn) DICHROISM ($\Delta \alpha$)

CHANGE IN PROBE POLARIZATION STATE

. THERMAL EFFECTS UNOBSERVABLE

. BACKGROUND FREE SIGNAL

. BOTH REAL AND IMAGINARY NL.

BIRIFRINGENCE

- NON RESONANT EXCITATION
- PROBE POLARIZATION GETS ELLIPTICAL.

$$\Delta n = \Delta n_{||} - \Delta n_{\perp} \sim \frac{\pi}{m_e} (\chi_{2222}^{(3)} - \chi_{22xx}^{(0)})$$

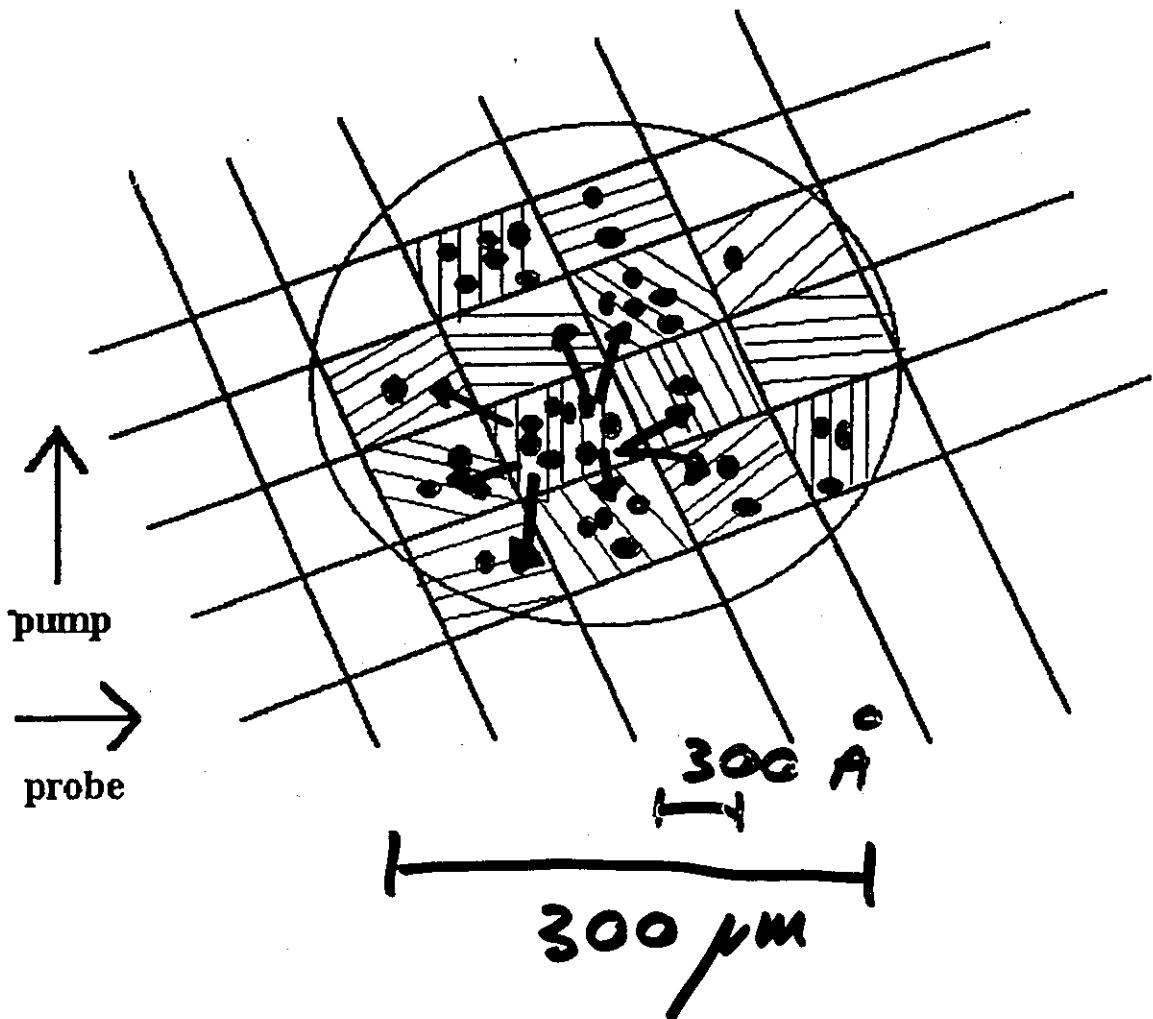
$$T_K \sim \left(\frac{\pi L}{\lambda} |n_z'' - n_z'| I_c \right)^2$$

DICHOISM

- PREFERENTIAL SATURATION OF MOLECULES ALIGNED PARALLEL TO THE PUMP BEAM
- PROBE POLARIZATION ROTATION (LINEAR)
- ORIENTATIONAL RELAXATION

$$T_K = \frac{1}{8} e^{-\alpha_0 L} G^2 (N_{||}(t) - N_{\perp}(t))^2 L^2$$

DEPHASING



$$m_D = 10^8$$

DIFFUSION $J = -D \nabla m$

BOLTZMANN $\frac{\partial m}{\partial t} \Big|_{\text{cell}} = - \frac{m - m_0}{\tau_D}$

$$\Delta m = \Delta m(0) e^{-t/\tau_D} \quad (\text{Gaussian Transport})$$

$$D = \frac{R^2}{\tau_D} = 6 \times 10^{-3} \frac{\text{cm}^2}{\text{s}}$$

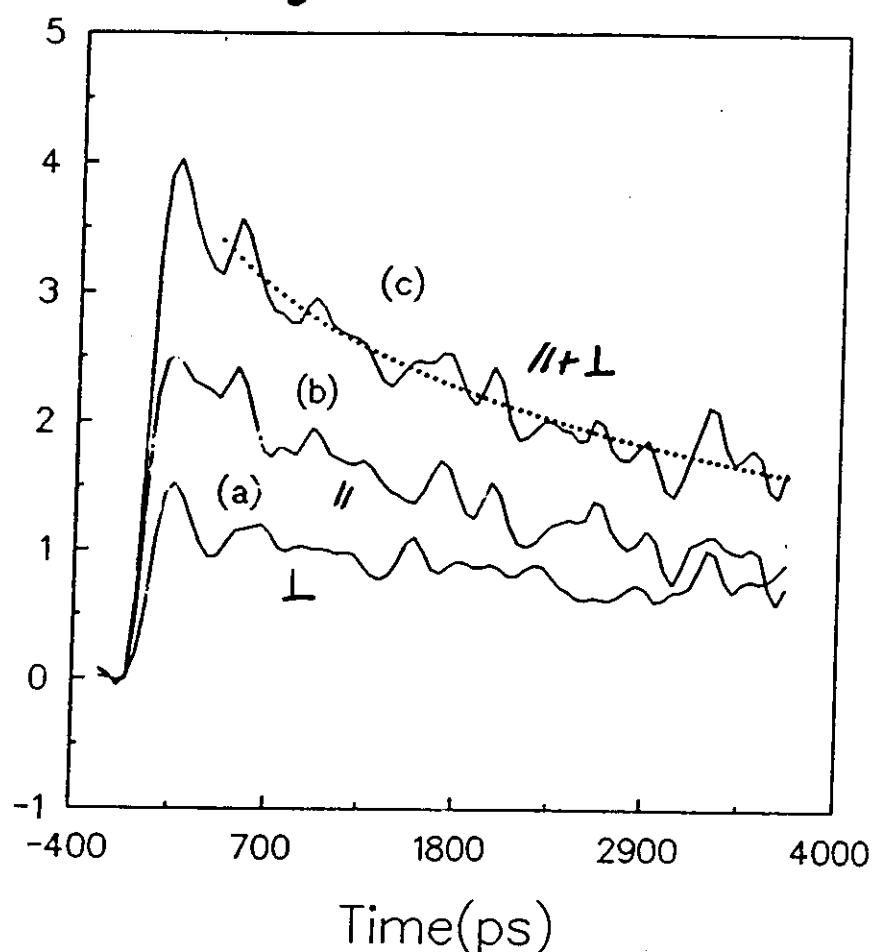


$$N(t) \sim e^{-(\frac{t}{\tau})^\alpha}$$

$$\tau = 3.5 \text{ ms}$$

$$\alpha = 0.51$$

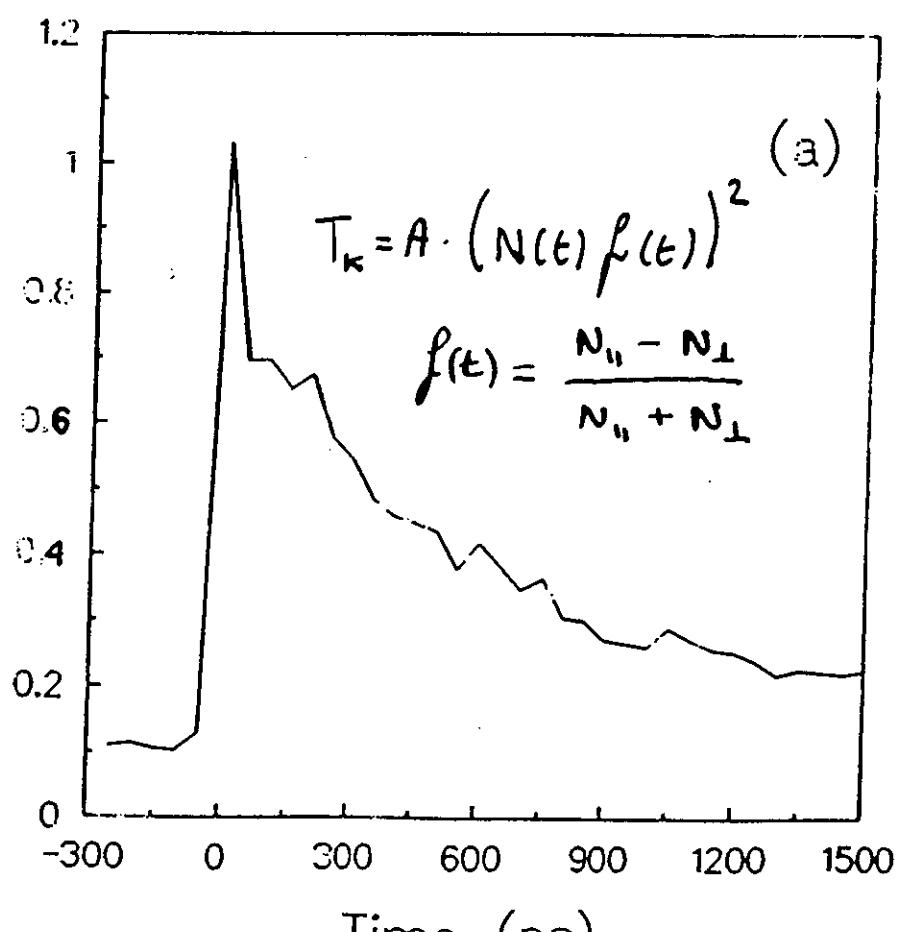
$\Delta T/T$ (Arb. Un.)



$$f(t) \sim e^{-t/\tau_D}$$

$$\tau_D = 1.4 \text{ ms}$$

T_K (Arb. Un.)



$$I_{\text{KERR}} \sim (N'' - N^\perp)^2$$

$$\Delta T = \Delta \alpha'' + \Delta \alpha^\perp = N_0(t)$$

$$\Delta P = \frac{\Delta \alpha'' - \Delta \alpha^\perp}{\Delta \alpha'' + \Delta \alpha^\perp} \sim \frac{N'' - N^\perp}{N_0} = f(t)$$

$N_0(t)$ = EX POPULATION ; γ_{EX}

$f(t)$ = DEPHASING ; γ_d

$$I_{\text{KERR}} \sim [N_0(t) f(t)]^2$$

1) SINGLE EXP

$$K_{ERR} \sim e^{-\frac{t}{\tau}} \quad \Delta T \sim e^{-\frac{t}{\tau_{Ex}}}$$

$$\frac{1}{2\tau} = \frac{1}{\tau_0} + \frac{1}{\tau_{Ex}}$$

$$\tau_0 = 1011 \text{ ps}; \tau_{Ex} = 4743 \text{ ps}$$

$$D = \frac{e^2}{2\tau_0} = 9 \times 10^{-3} \frac{\text{cm}^2}{\text{s}}$$

2) STRETCHED EXP + SINGLE EXP

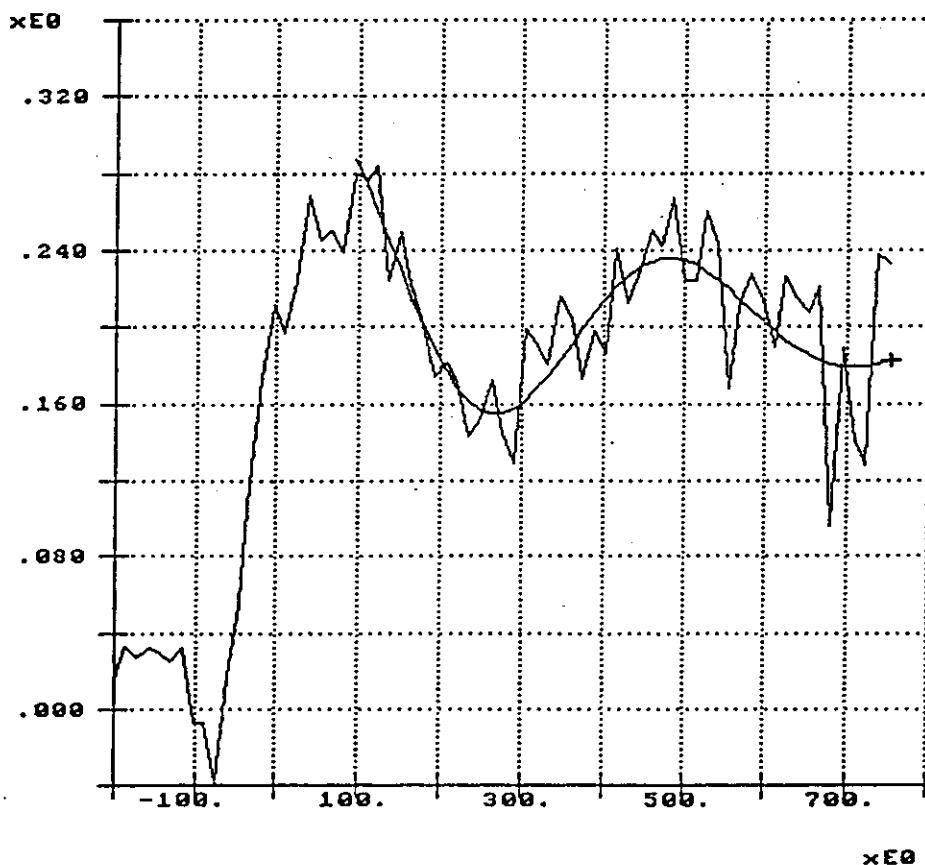
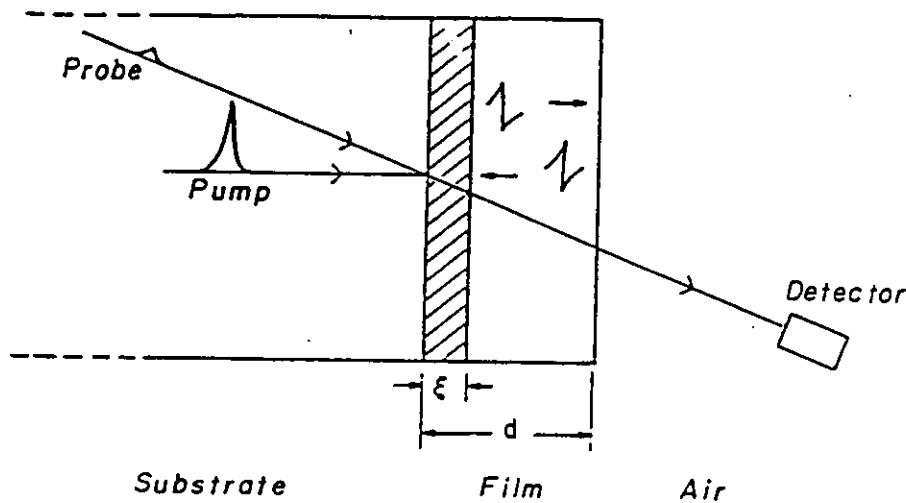
$$\tau_{Ex} = 3500 \quad \tau_0 = 1343$$

$$D = 6 \times 10^{-3} \frac{\text{cm}^2}{\text{s}}$$

PT(VARDENY) $D = 2 \times 10^{-2} \frac{\text{cm}^2}{\text{s}}$

Am (POPE) $D = 2.5 \times 10^{-3} \frac{\text{cm}^2}{\text{s}}$ (s')

PHOTO ACOUSTIC

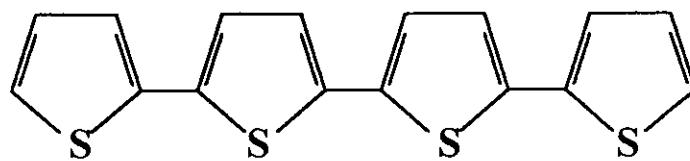


$$\frac{\Delta T}{T} = \frac{d}{\pi} \frac{\partial \alpha(\omega)}{\partial \omega} \frac{\partial E_g}{\partial \eta} \langle \eta(t) \rangle$$

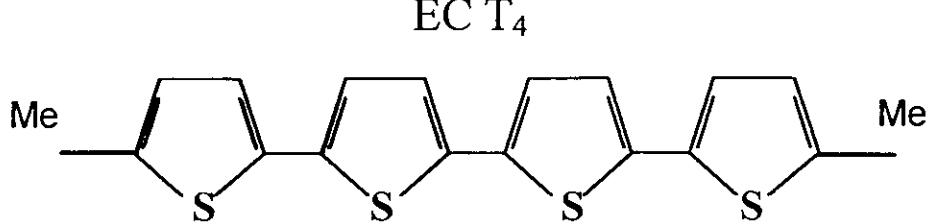
$$\tau = \frac{4d}{\sqrt{s}}$$

STUDIED MOLECULES

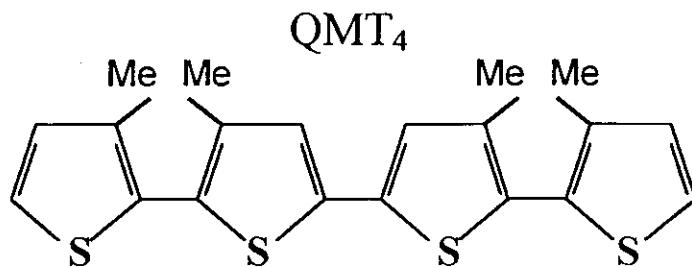
P



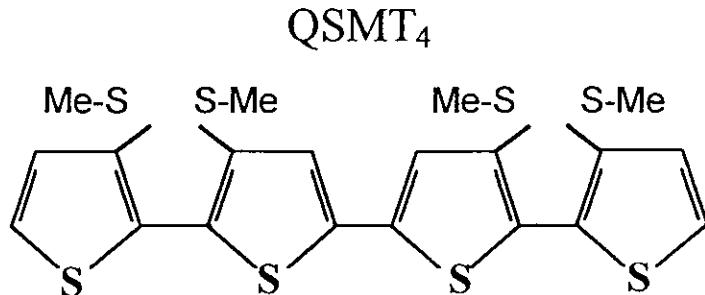
P



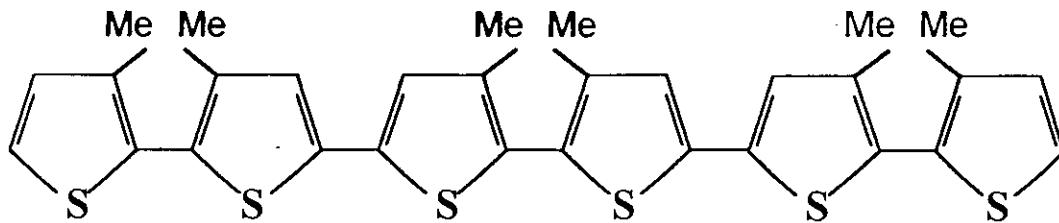
T



F

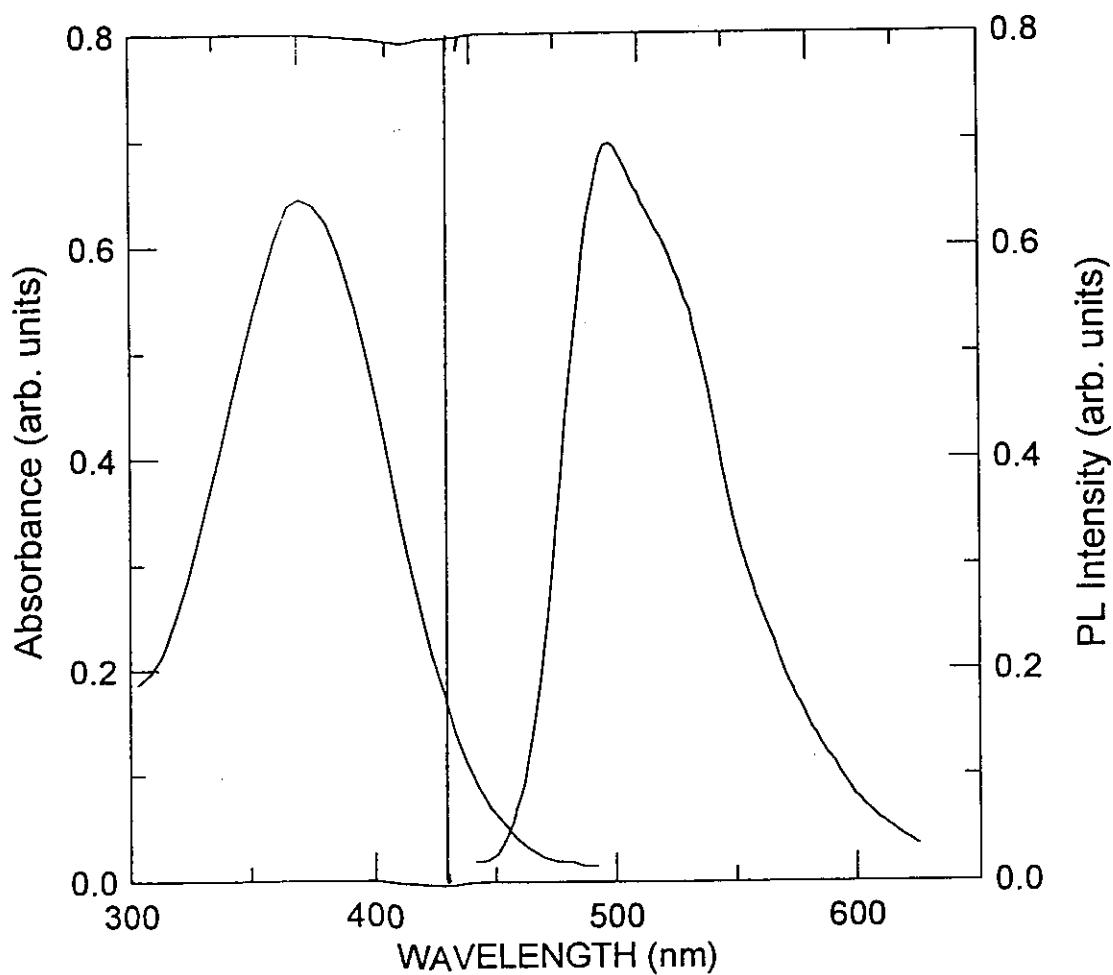


F



IM: UNDERSTANDING THE ROLE OF INTER-RING TORSIONS IN THE EXCITED STATE KINETICS.

HMT6 LINEAR OPTICAL PROPERTIES

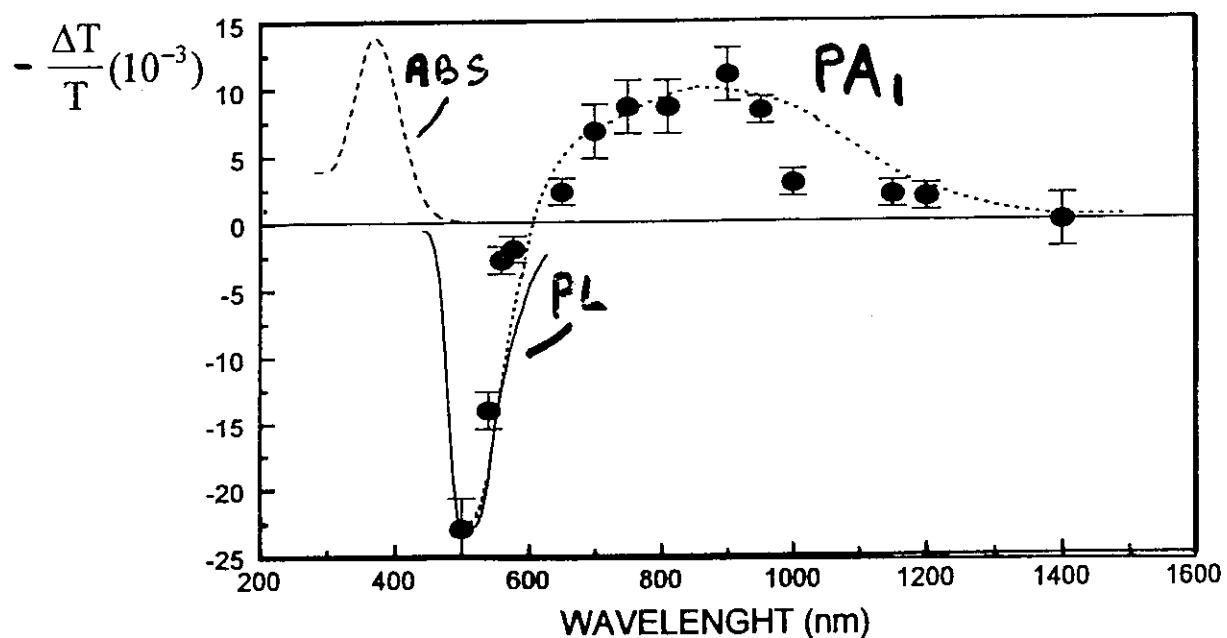


- Absorption blu-shift:
⇒ Twisted ground state
- Large apparent Stokes shift:
⇒ Planarization of the excited state

TRANSIENT PHOTOEXCITED SPECTRUM OF HMT6 IN CHLOROFORM SOLUTION

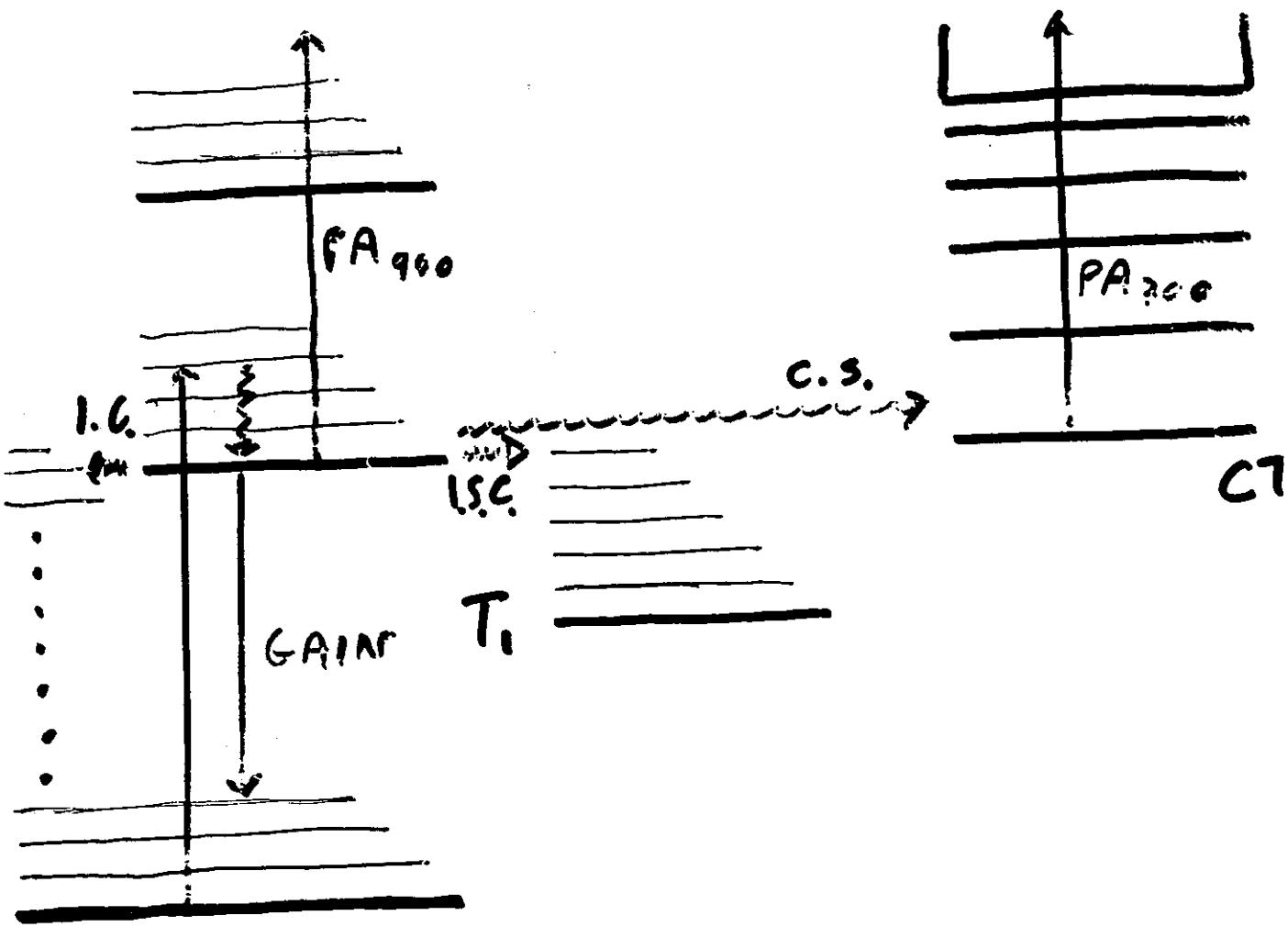
$\lambda_{\text{Pump}} = 390 \text{ nm}$; $E_{\text{pump}} = 10 \text{ nJ}$ ($\varnothing \approx 250 \mu\text{m}$);

$\Delta t = 10 \text{ ps}$ *C.C. $\approx 200 \mu\text{s}$*



- Stimulated Emission (500 - 600 nm)
- Photoinduced Absorption "PA₁" (600 - 1500 nm)

HOTO EXCITATION SCENARIO

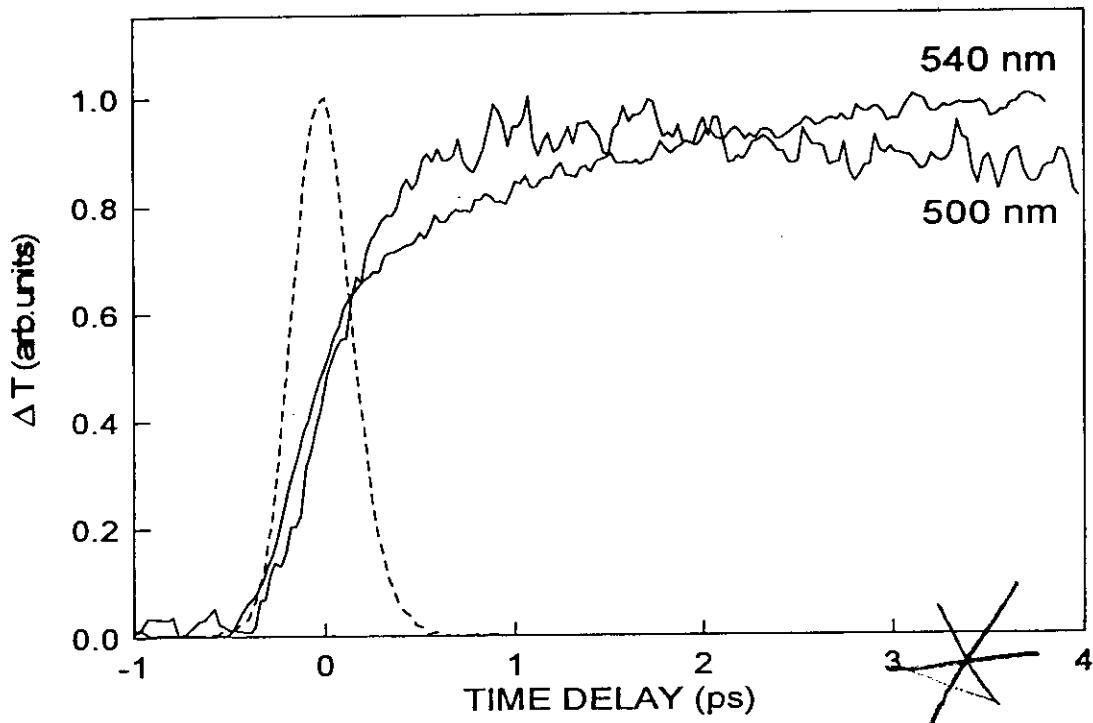


THE OBSERVED DYNAMICS:

$\lambda(\text{nm})$	DECAY	PARAMETERS
540	SINGLE EXP	$\tau = 160 \text{ ps}$
900-1000	SINGLE EXP	$\tau = 160 \text{ ps}$
700	SINGLE EXP	$\tau = 8 \text{ ps} + \text{PRATER}$

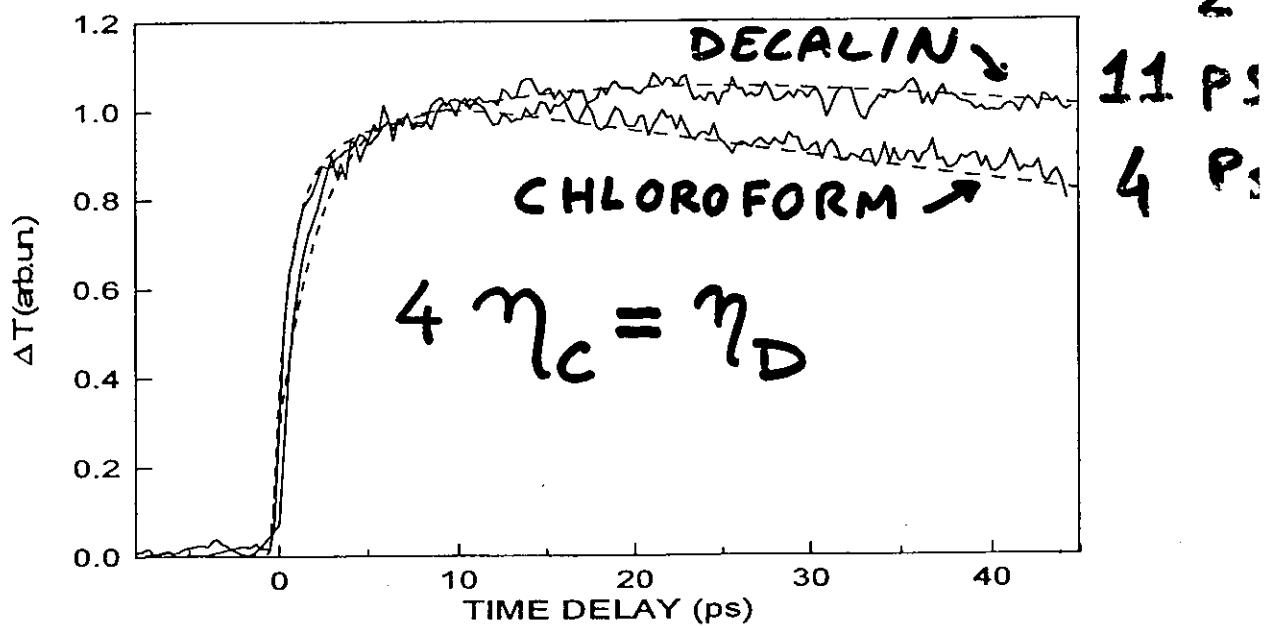
$$\tau_{S_1(\text{HMT}_6)} < \tau_{S_1(T_6)} = 900 \text{ ps}$$

- PROBE WAVELENGTH DEPENDENCE



→ Red Shift of the SE Band

- SOLVENT EFFECT



→ Conformational Readjustment

EXCITED STATE ENERGY REDISTRIBUTION

- 2-D Frank-Condon

- Excess Energy ($E_x = \hbar\omega_p - E_g$):

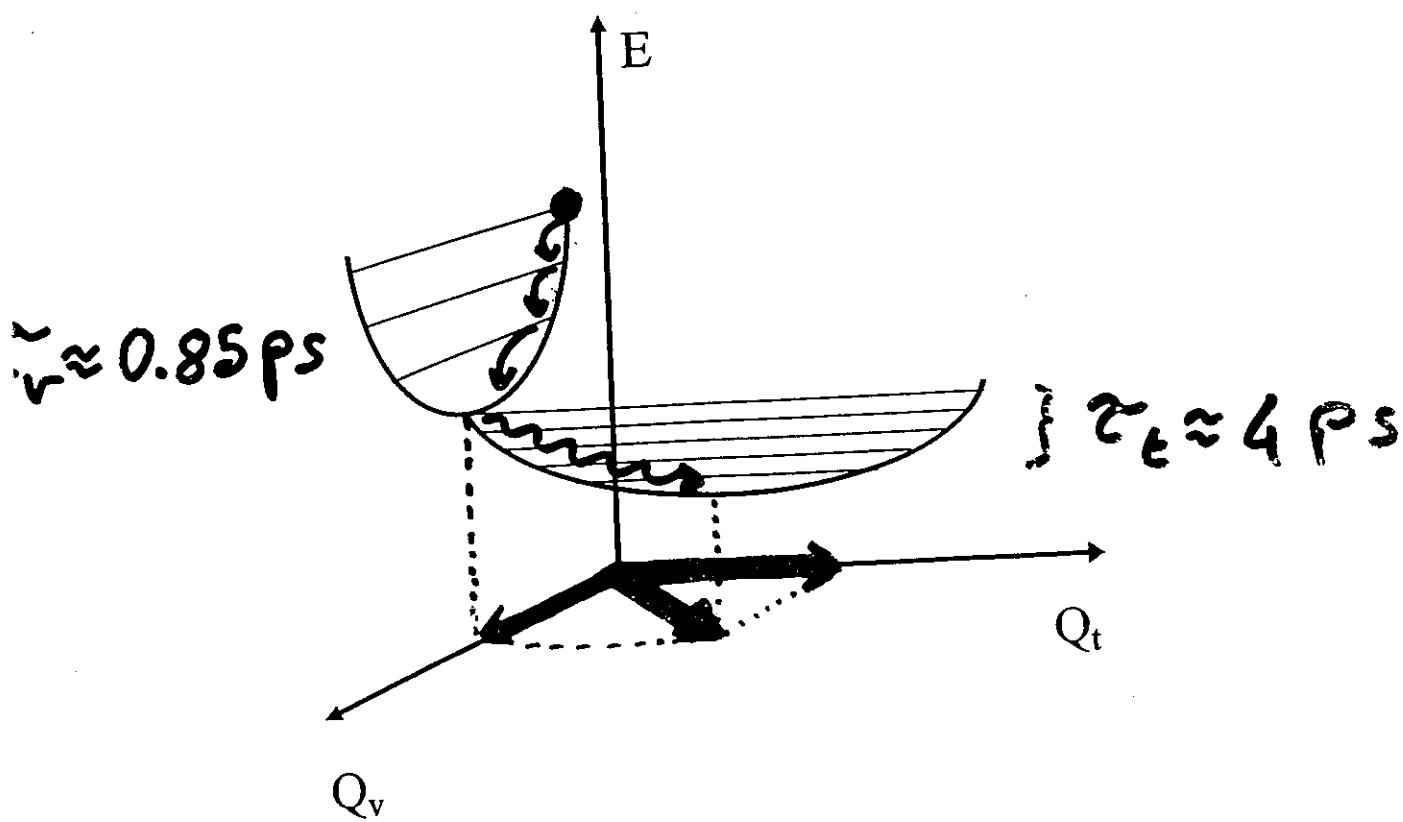
$$E_x = n_v \hbar\omega_v + n_t \hbar\omega_t$$

$$\hbar\omega_v = 0.15 \text{ eV}$$

$$t_v \geq 28 \text{ fs}$$

$$\hbar\omega_t = 0.04 \text{ eV}$$

$$t_t \geq 110 \text{ fs}$$



Excess energy is dissipated through emission of vibrational quanta (t being the emission time of a single vibrational quantum) of two types:

$\omega_v = 0.15 \text{ eV}$ C-C stretching

$\omega_t = 0.04 \text{ eV}$ torsion