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Ultrafast processes in organic semiconductors

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ISTITUTO ITALIANO DI TECNOLOGIA
CENTER FOR NANO SCIENCE AND TECHNOLOGY

Ultrafast processes in organic semiconductors

Guglielmo Lanzani

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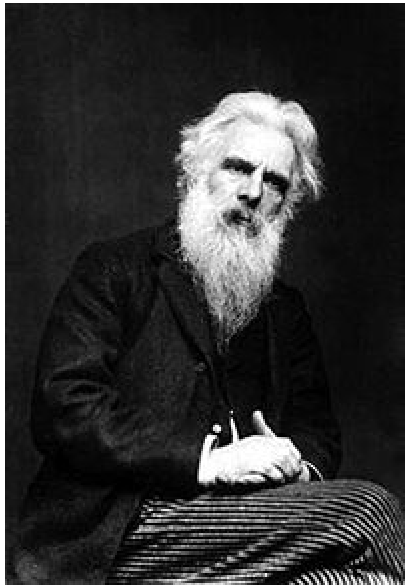
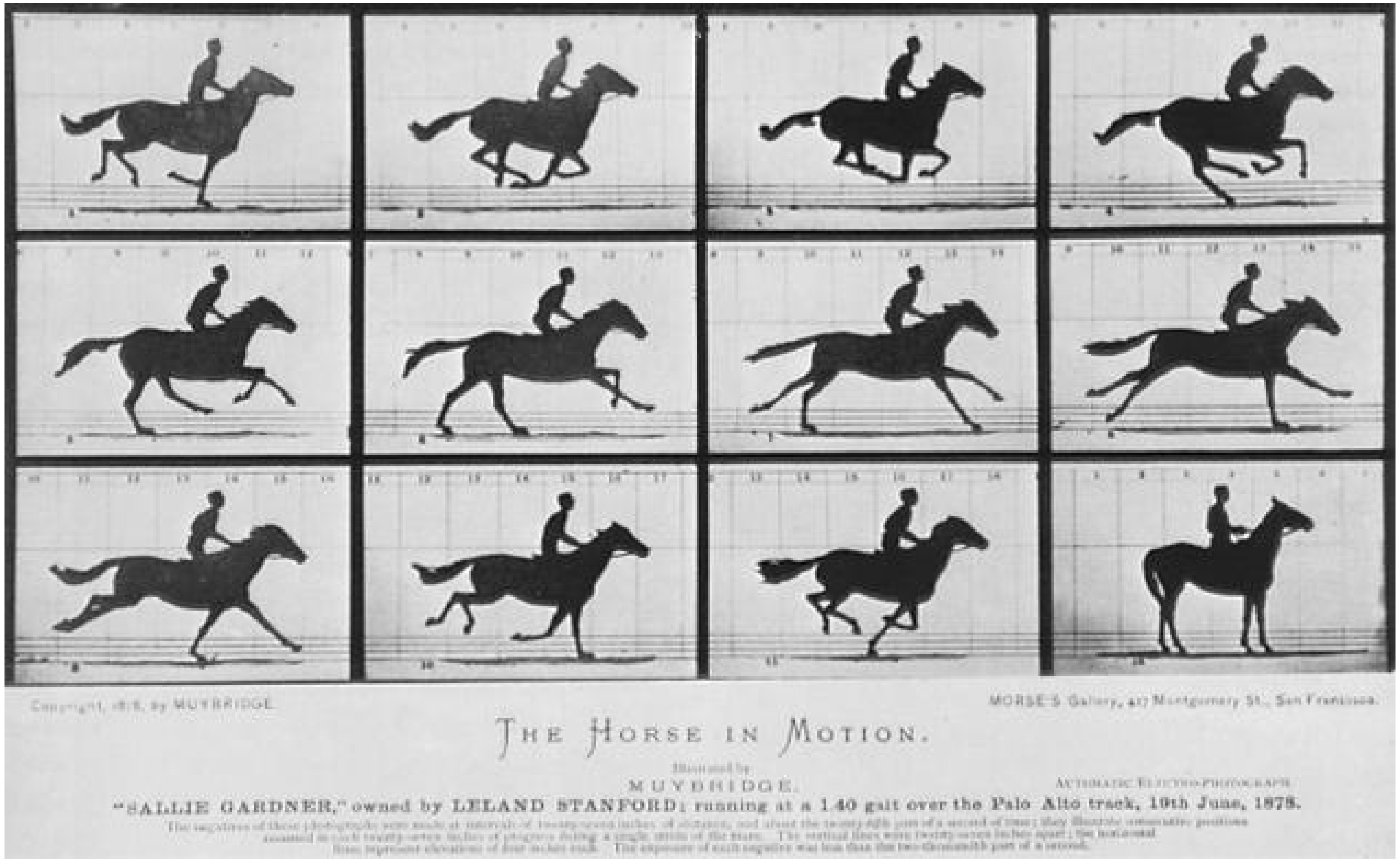
When time matters:

- Carrier cooling
- Excited state lifetime
- Recombination
- Electron injection
- Carrier transit

The aerial phase of the galloping horse





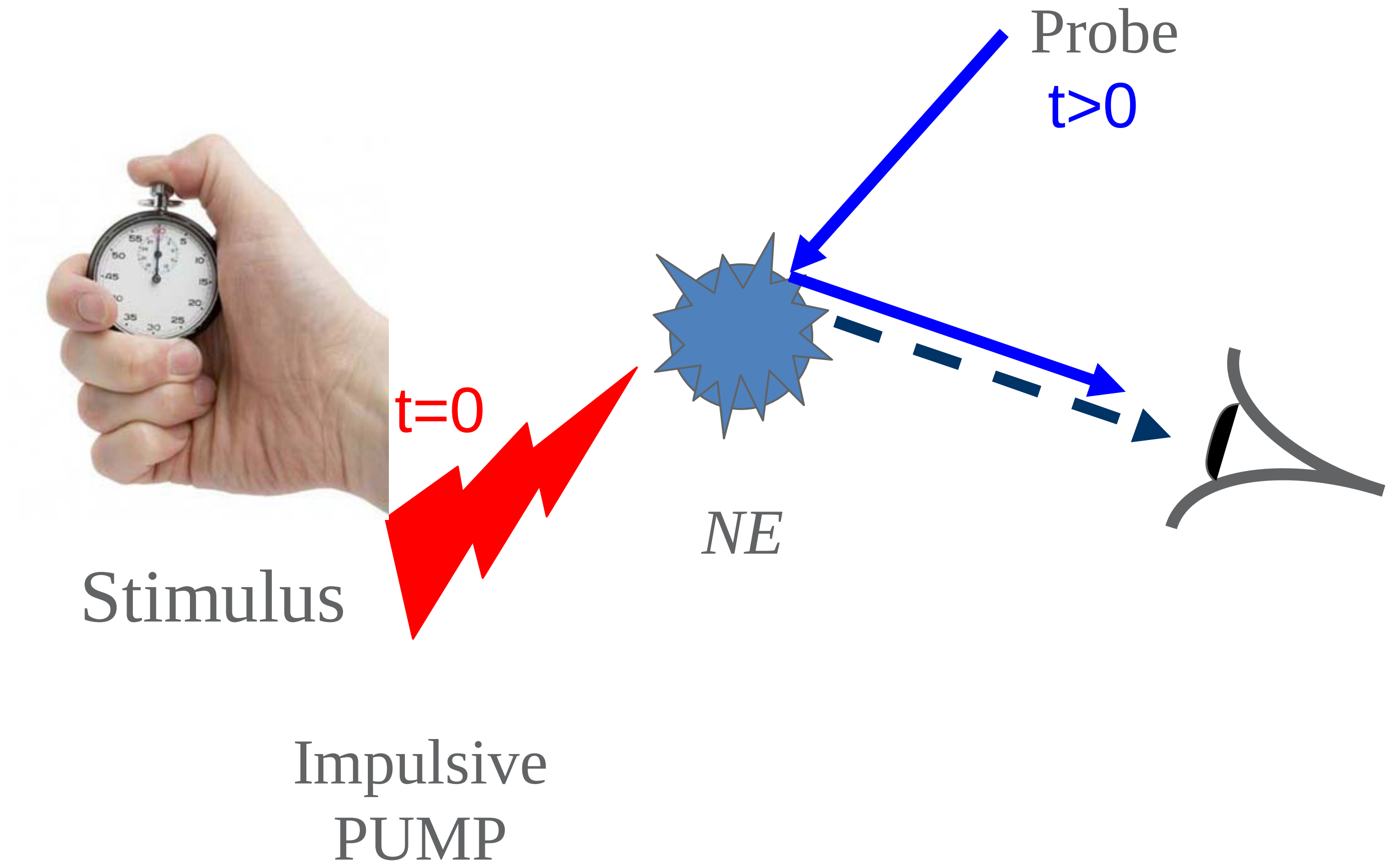
Not so for the elephant!

Figure 1 An Asian elephant marked with dots for gait analysis.

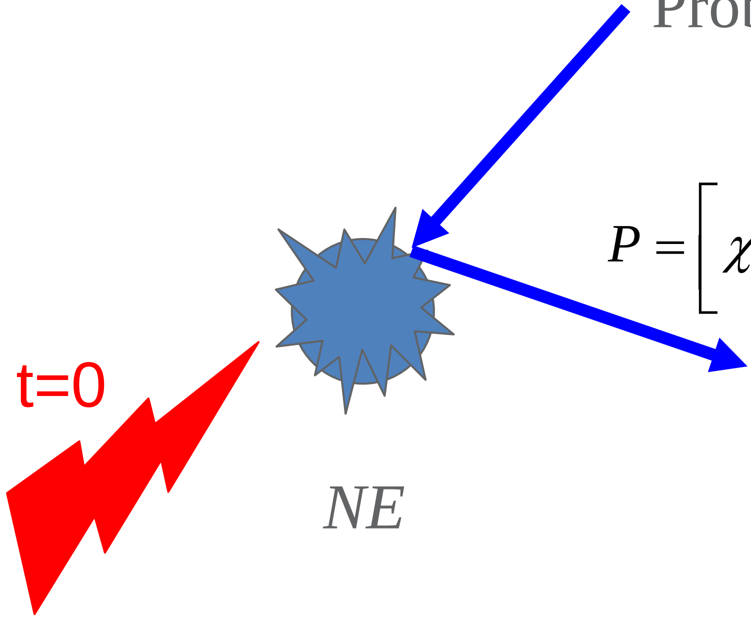
Nature422, 493(2003)

Observation Time << then typical phenomenon time scale

Pump-Probe:
Start and Stop



Pump-Probe



$$P = \chi^{(1)}(\omega)E(\omega_t)$$

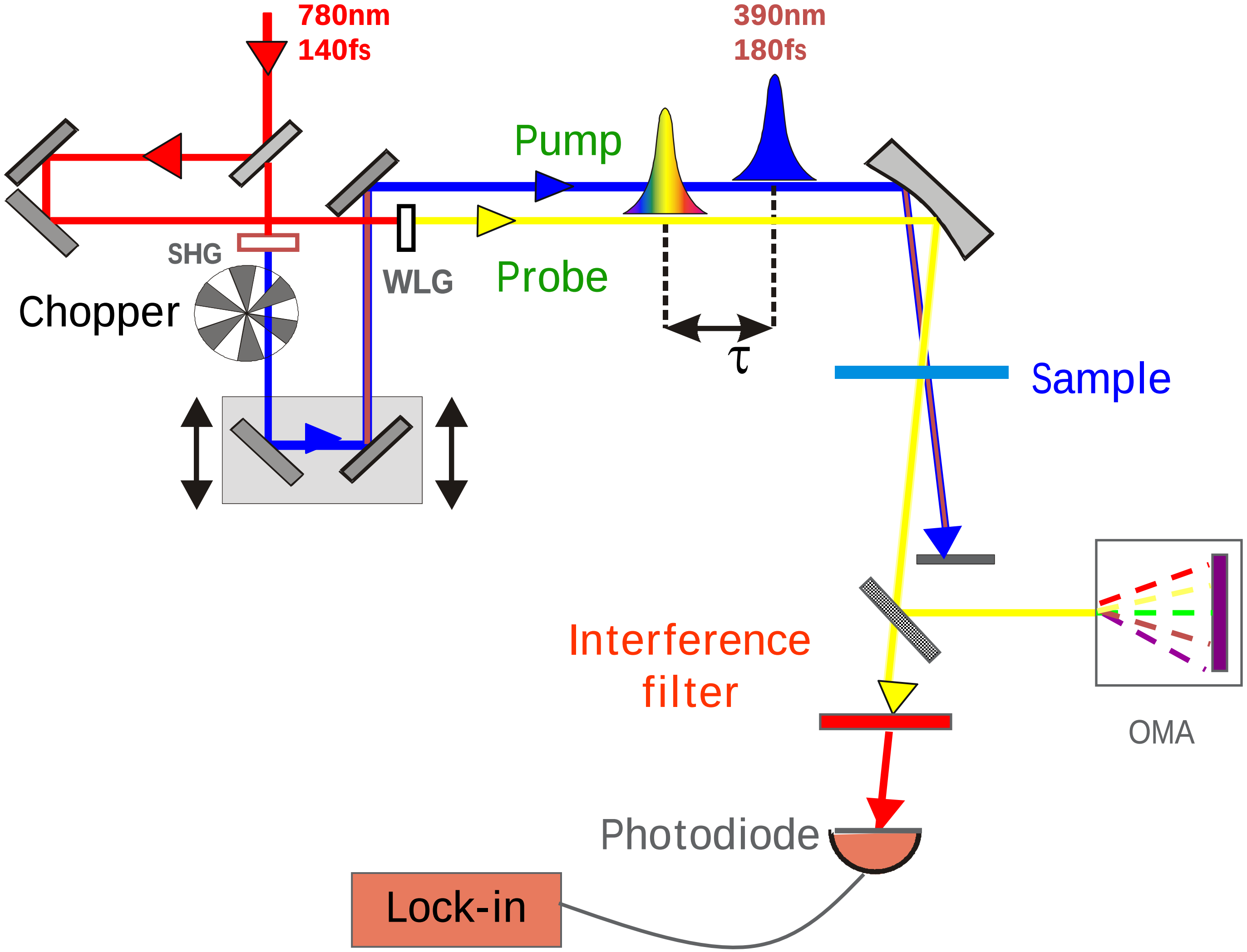
$$P = \left[\chi^{(1)}(\omega) + \frac{\Delta N}{N}\chi^{(1)}(\omega)\right]E(\omega_t)$$

$$\chi^{(3)}(\omega,\omega,\omega)$$

$$P = \chi^{(1)}(\omega_P)E(\omega_P) \Rightarrow \Delta N(E_P E_P^*)$$

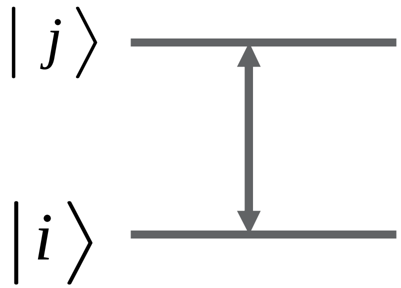
$$P \cdot E$$

Experimental Layout



Transmission

$$I_t = I_0 e^{-\alpha D}$$



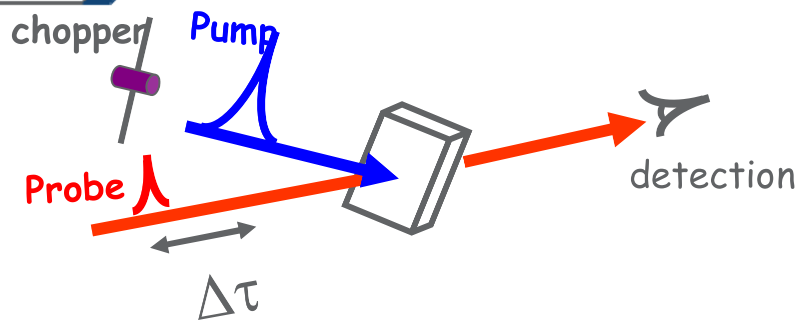
$$T = \frac{I_t}{I_o}$$

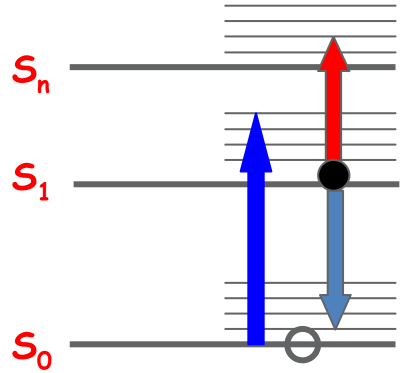
$$\alpha_{ij}(\omega) = \sigma_{ij}(\omega)(N_i - N_j)$$

$$A = -\log_{10} T$$

$$\alpha = \sum_{i,j} \sigma_{ij}(\omega)(N_i - N_j)$$

Pump-Probe



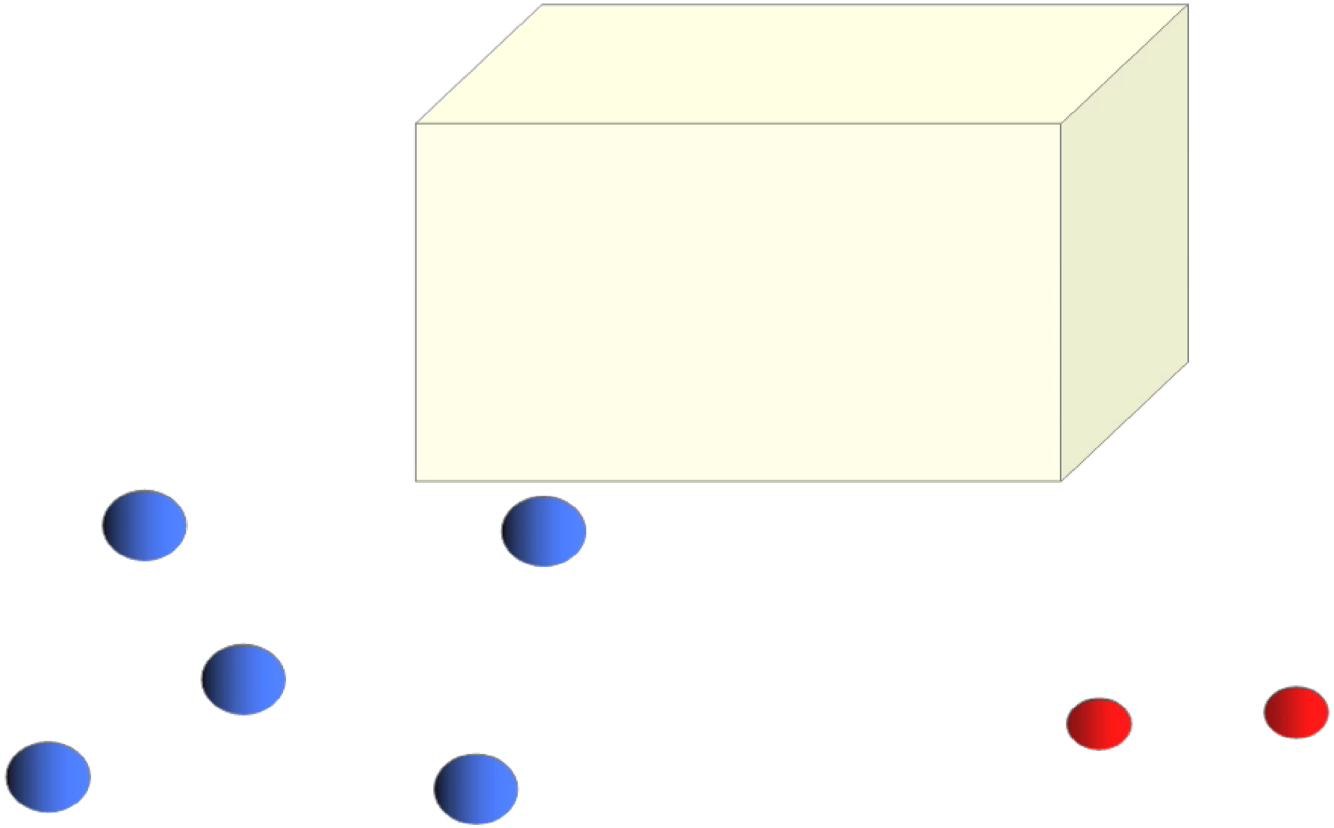


$$\frac{\Delta T}{T}(\omega,\tau) \cong -\sum_{i,j} \sigma_{ij}(\omega)\left[\Delta N_i(I_{Pu},\tau) - \Delta N_j(I_{Pu},\tau)\right]D$$

$$\frac{dN_i}{dt} = G_i(t) - R_i(t)$$

Direct Pumping: $G_i(t) = \sigma_{0i} N_0(t) \frac{F(t)}{t_P}$

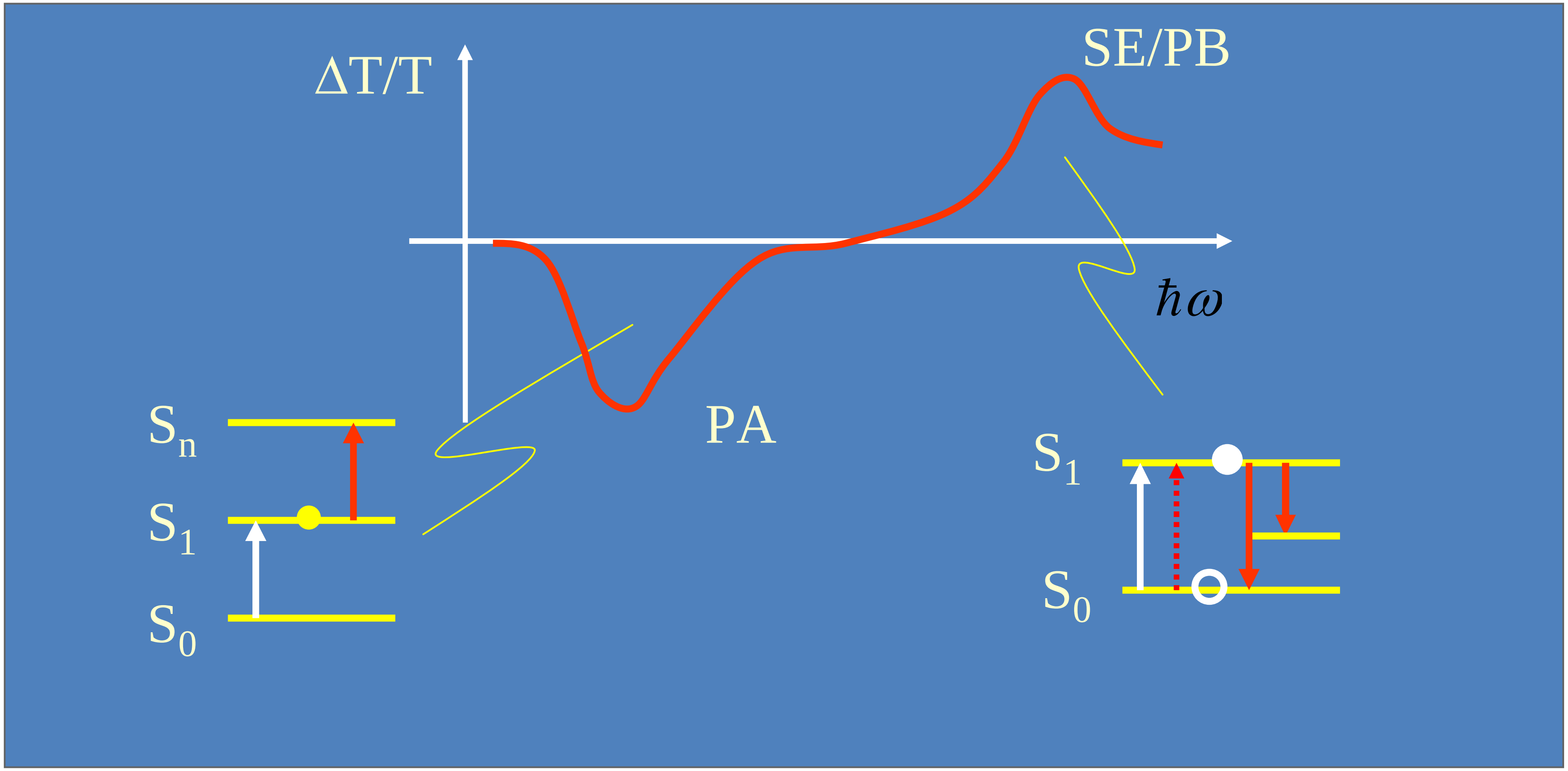
The Pump-Probe Experiment



movie

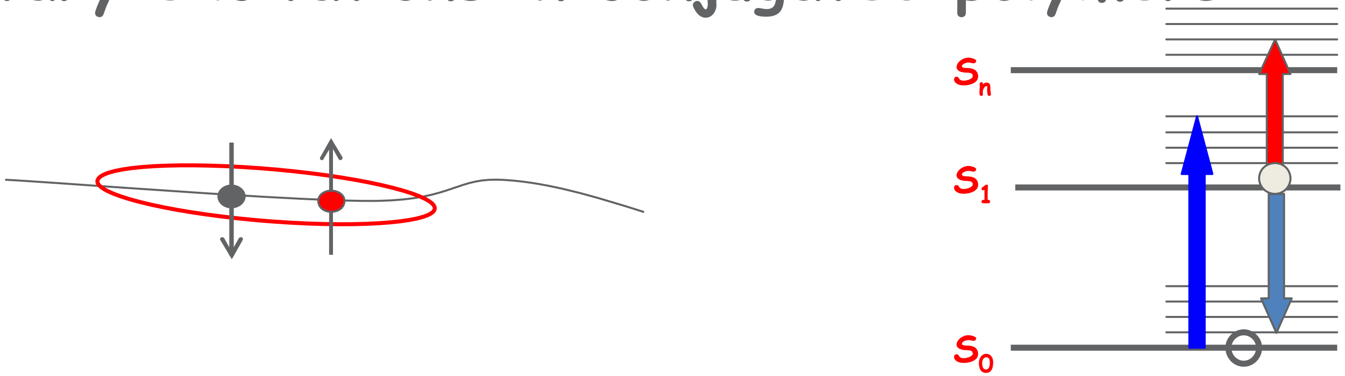
Transmission difference spectra (ΔT/T)

$$\frac{\Delta T}{T}(\omega,t) \approx -\sum_{ij} \tilde{\sigma}_{ij}(\omega)\Delta N_j(I_{Pu},t)\, d$$

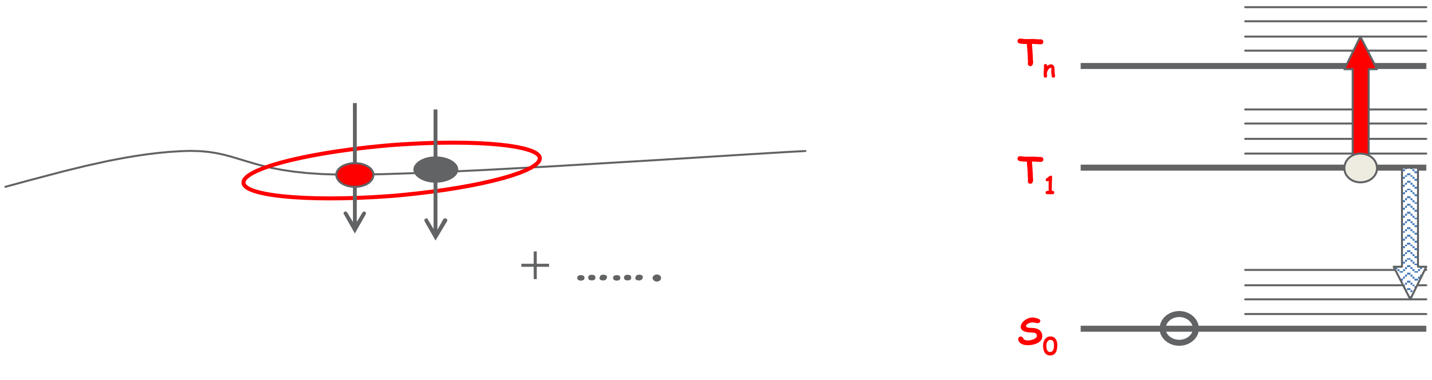


Elementary excitations in conjugated polymers

Singlet State S_1

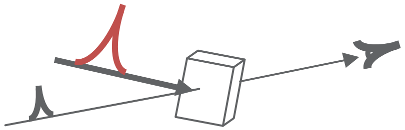


Triplet State T_1



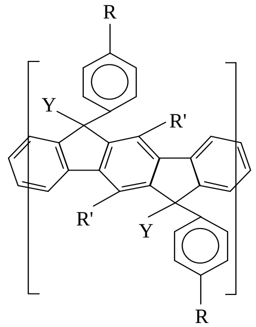
Doublet State D_0

The excitations in mLPPP films

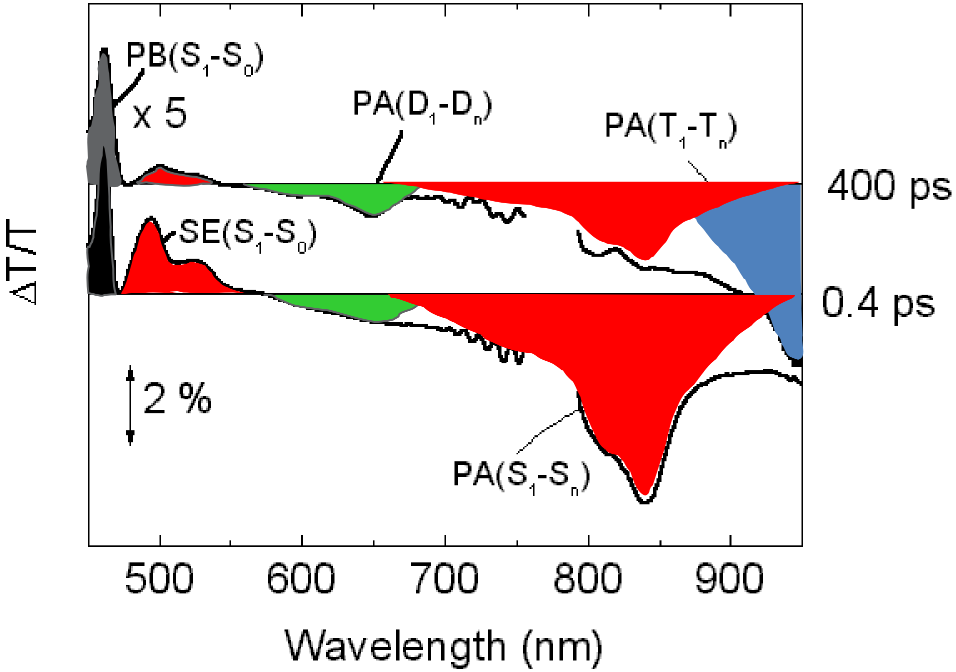


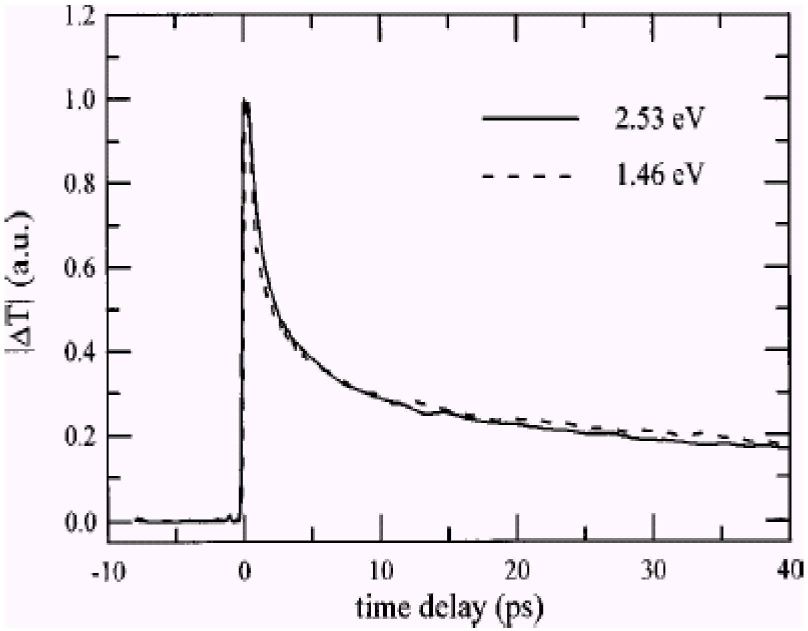
Pump @ 390 nm

White Probe



$R=C_{10}H_{21}$
$R'=C_6H_{13}$
$Y=CH_3$





Phys.Rev.Lett.**76**, 847(1996)

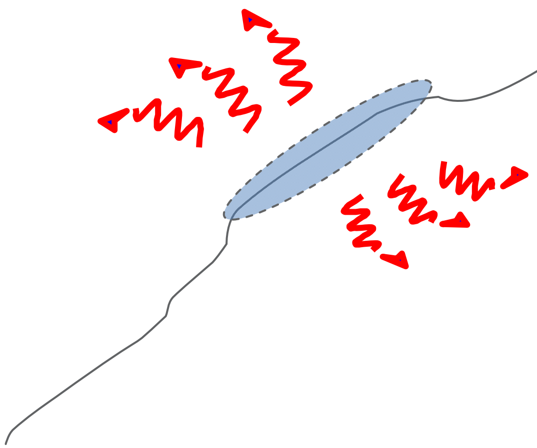
Singlet depopulation mechanisms in conjugated polymers

$$\frac{dN_{S_1}}{dt} = G(t) - f(N_{S_1})$$

$$f = -\left(k_m(t)N_{S_1} + \gamma(t)N_{S_1}^2 + ...\right)$$

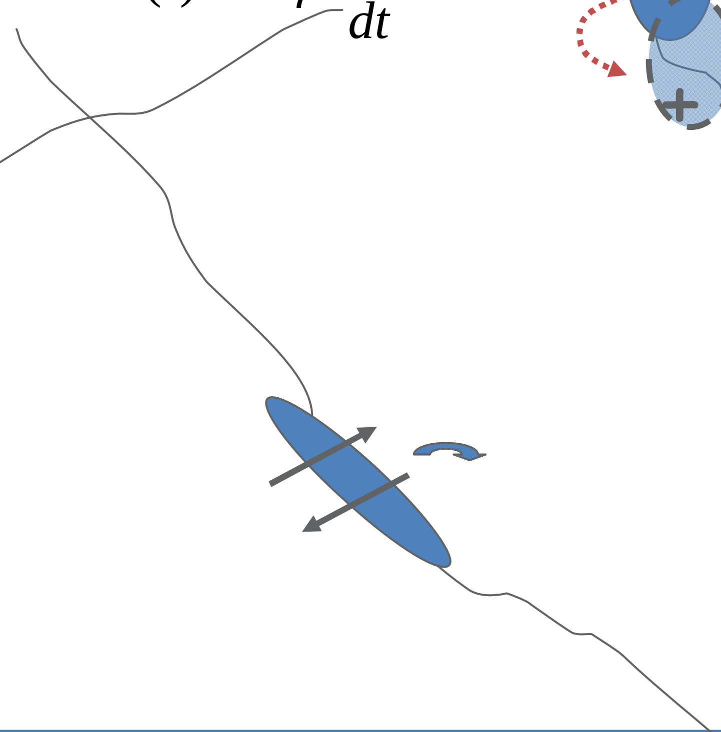
External

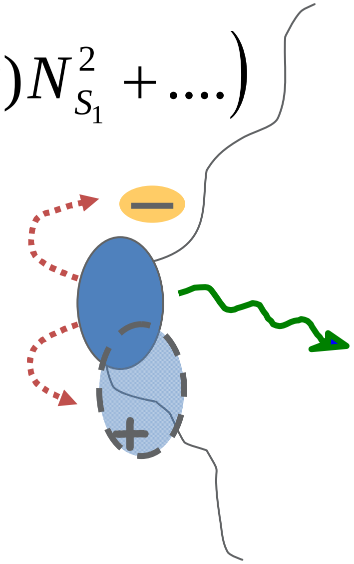
$$G(t) = \sigma_{01}(\omega_{pump})F(t)N_0(t)$$



Internal

$$G(t) = +\eta\frac{dN_k}{dt}$$





MONOMOLECULAR decay

$$\frac{dN_{S_1}}{dt} = -k_m(t)N_{S_1}$$

$k_m = k_{mo}$

$k_m = k_0 t^{a-1}$

$$N_{S_1} = N_{S_1}(0)\exp(-k_{m0}t)$$

$$N_{S_1} = N_{S_1}(0)\exp\left\{-\left(\frac{k_0}{a}t\right)^a\right\}$$

Kinetics does not depend on excitation density

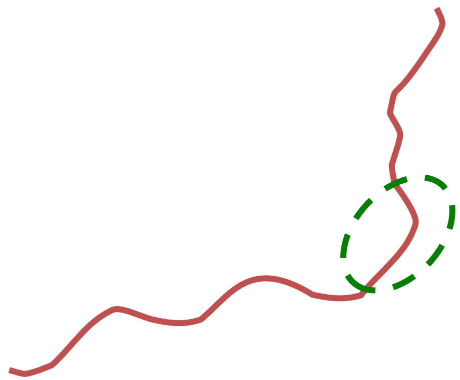
Possible mechanism:

PL $S_1 \rightarrow S_0 + h\nu$

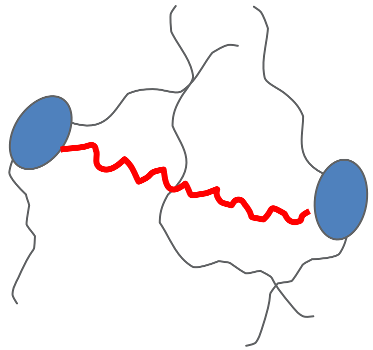
ISC $S_1 \rightarrow T_n$

IC $S_1 \rightarrow S_0 + \text{heat}$

quenching $S_1 + X \rightarrow$........



BI-MOLECULAR delay



$$\frac{dN}{dt} = -\gamma(t) N^2$$

$\gamma = C_0$

$\gamma = C_3 t^{-\frac{1}{2}}$

$$N_{S_1} = \frac{1}{N_{S_1}(0)^{-1} + C_0 t}$$

$$N_{S_1} = \frac{1}{N_{S_1}(0)^{-1} + 2C_3 t^{1/2}}$$

Yeas, but….what is really taking place?

→ Bi-molecular annihilation may proceeds via:

energy transfer reaction

→ or the formation of

"encounter" complex, that further decay to the products

Pump-Probe

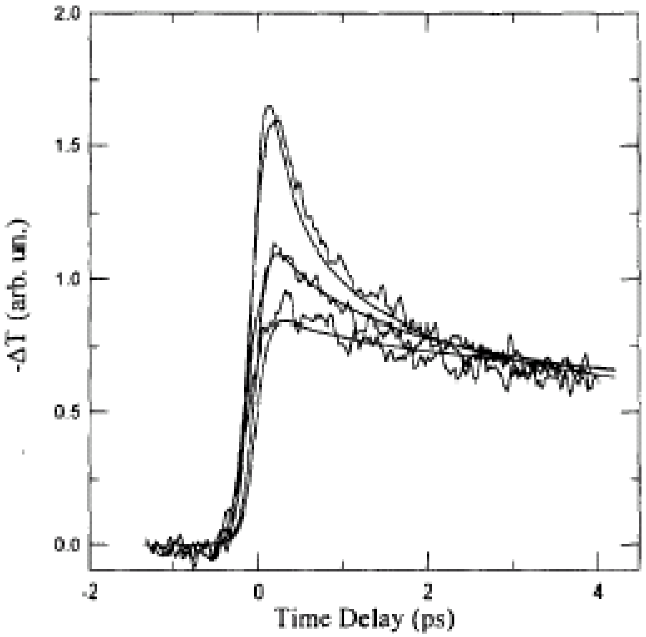


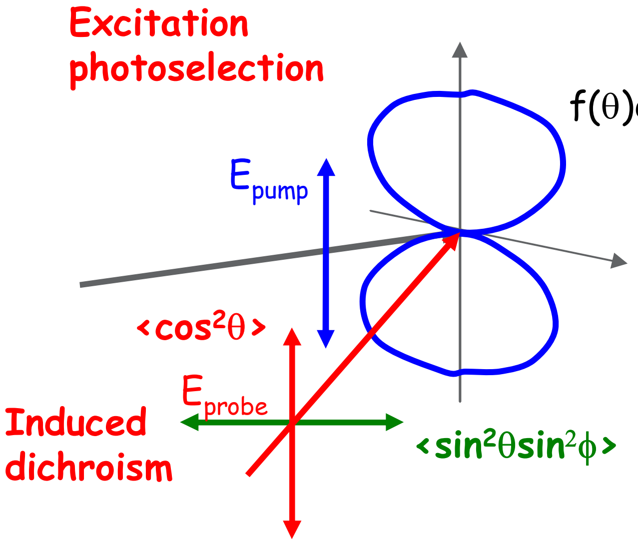
Fig. 3. Induced changes in transmission of the T6 film versus delay time for an excitation density of 8×10^{19} cm^{-3} (upper), 7×10^{18} cm^{-3} (center), 3.5×10^{18} cm^{-3} (lower).

$$\frac{\mathrm{d}n}{\mathrm{d}t} = -\gamma t^{-1/2} n^2 - kn\,.$$

$$n(t) = n_0 \frac{\exp(-kt)}{1 + \left(2 n_0 \gamma / k^{1/2}\right)\mathrm{erf}\left[(kt)^{1/2}\right]}$$

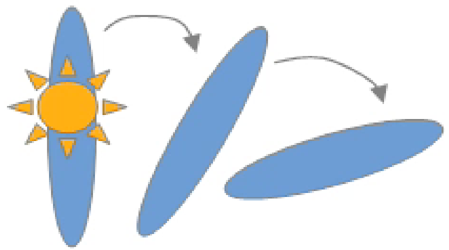
G. Lanzani et al. / Chemical Physics Letters 264 (1997) 667–672

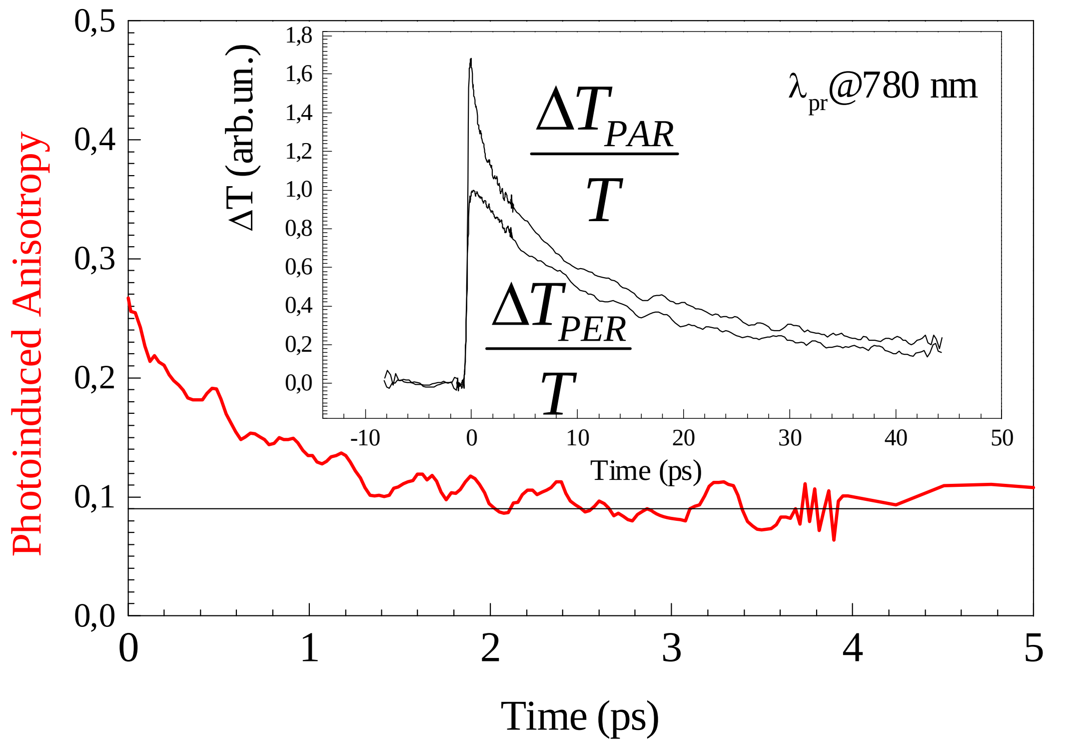
Probing Hot Singlet Migration



$$r = \frac{par - per}{par + 2\,per}$$

Photoinduced dichroism decay in mLPPP films

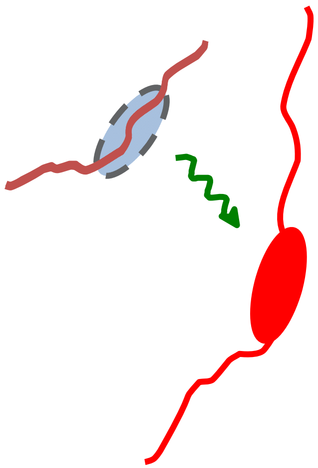


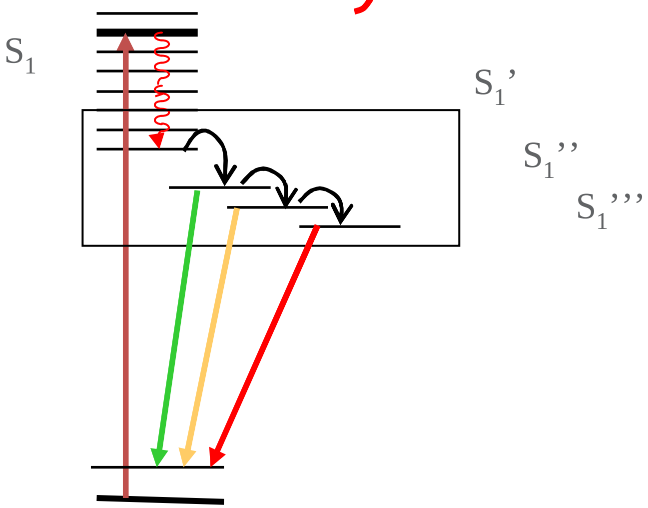


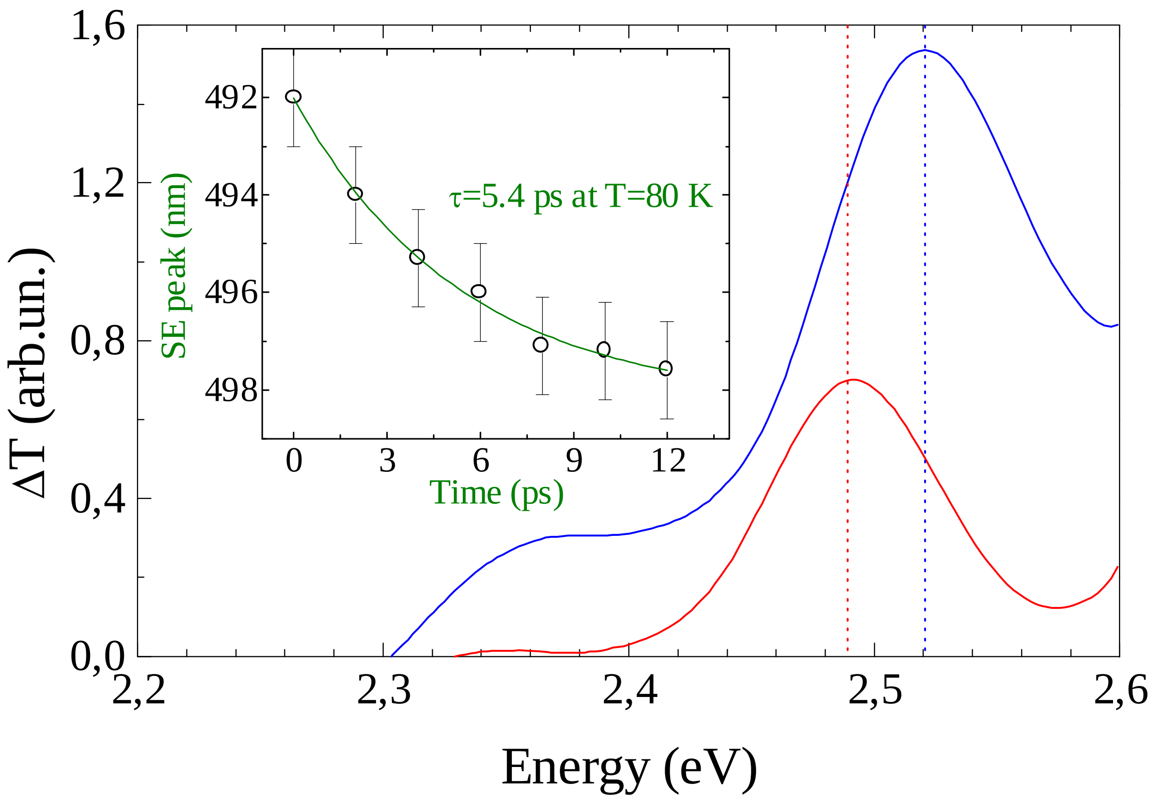
movie

Probing Hot Singlet Migration

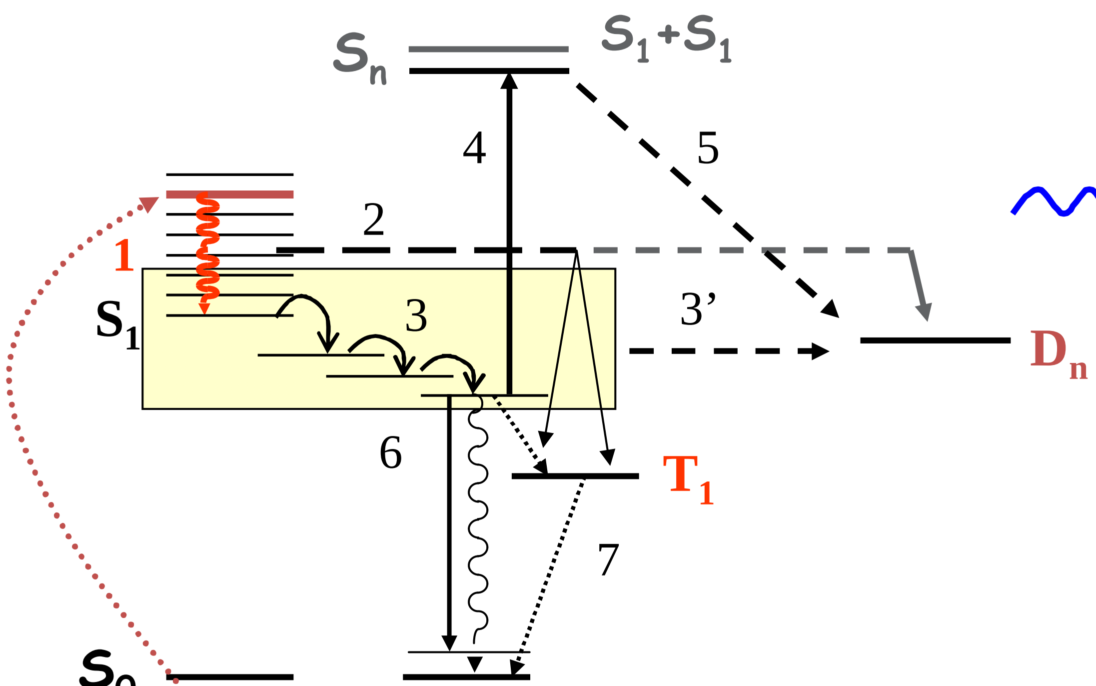
Stimulated Emission red-shift in mLPPP films

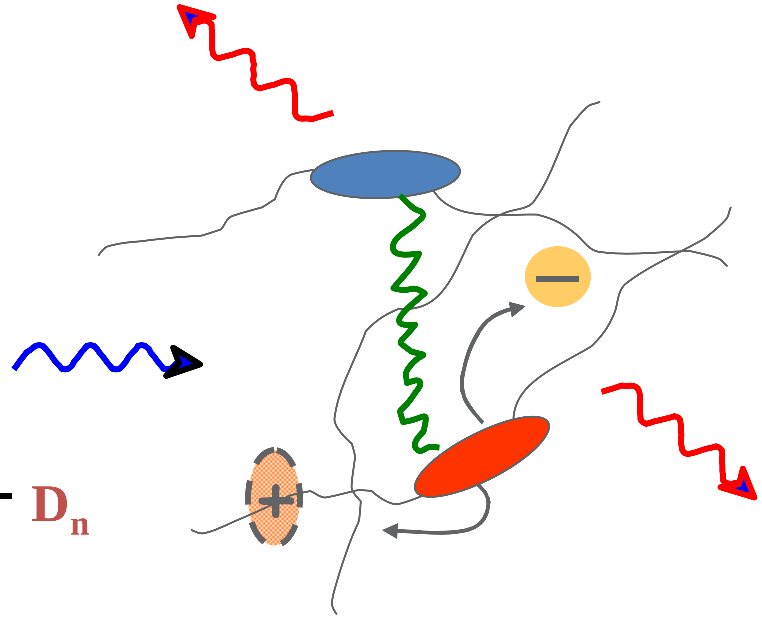






Excitation scenario in conjugated chains

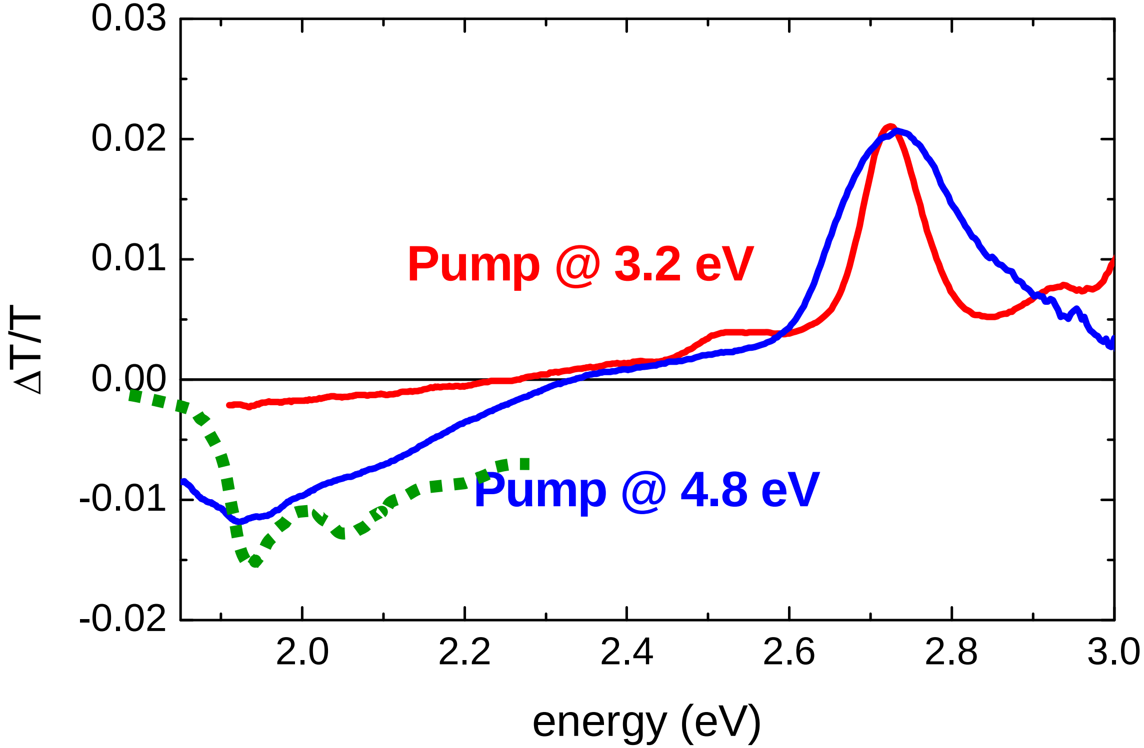


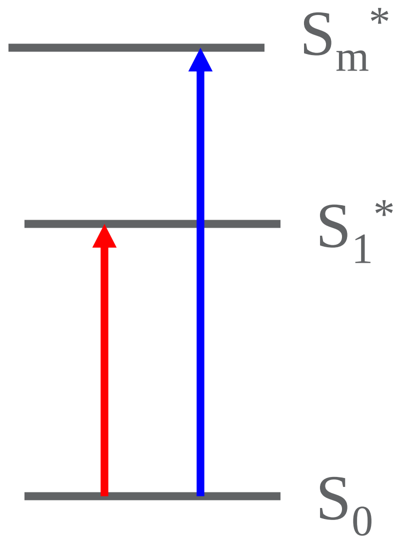


Time Scales:

1) 0.150 ps
2) 0.1 ps
3) 1-10 ps
5) 0.1 ps
6) $10-10^2$ ps
7) $10^{-6}-10^{-3}$ s

The role of high lying states, 1 (mLPPP)

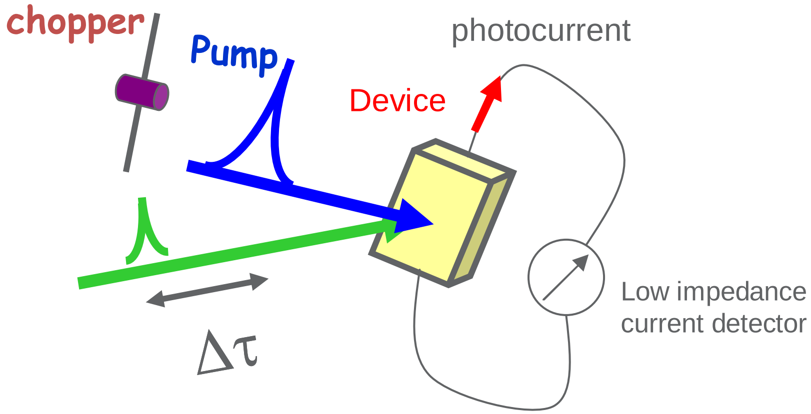




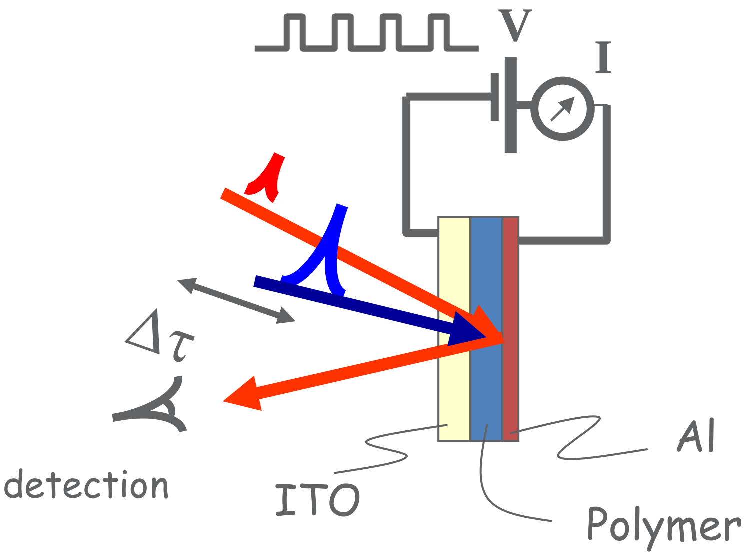
Curves normalised to PB: Polaron PA is stronger for 4.8 eV than 3.2 eV

→ enhanced polaron formation from S_m

Ultrafast Optoelectronic Probing



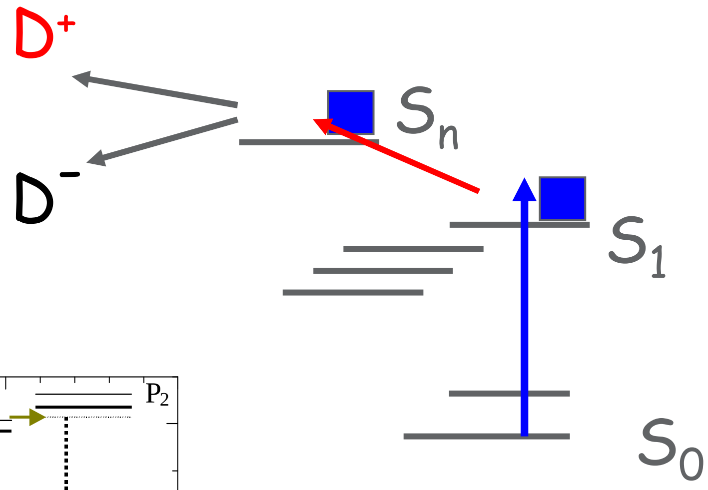
$$\Delta j = q\mu F \Delta N(I_1, I_2, \tau)$$

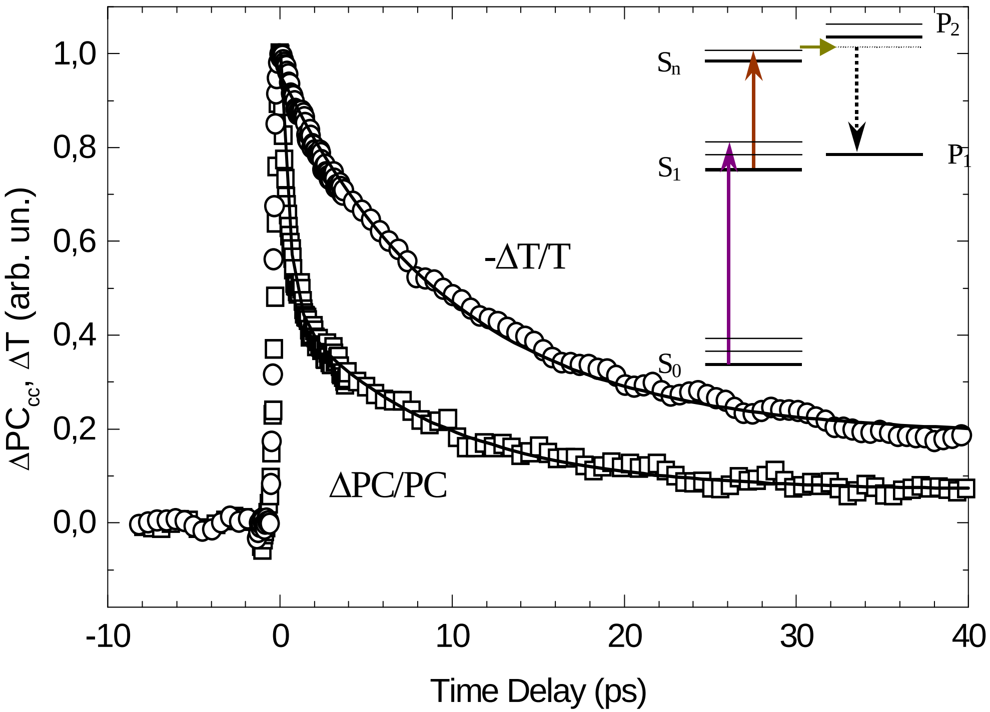


$$\Delta^2 T/T = -d\sum_{i,j}\Delta\sigma_{ij}(\omega, F)\Delta N_J \otimes f_p$$

$$-d\sum_{i,j}\sigma_{ij}(\omega)\Delta^2 N_J(F)\otimes f_p - \sum_{i}\Delta\sigma_{io}(F)N_o$$

Hot state signature 2:
Photocurrent excitation cross-correlation dynamics





C. Zenz *et al.* Chem. Phys. Lett. **341**, 63(2001).

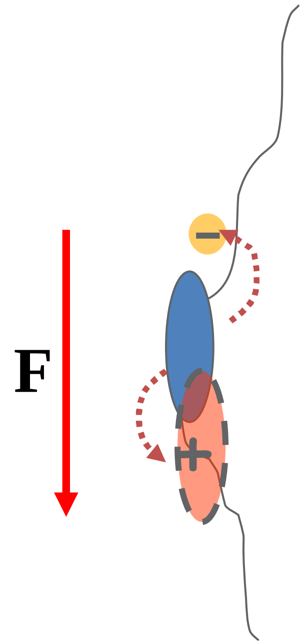
- dynamics of S_1 population:
  τ ~ 10 ps
- change in carrier generation efficiency:
  τ_1 ~ 0.5 ps, τ_2 ~ 10 ps
- positive signal:
  S_n state higher dissociation probability than S_1
- dynamics of carrier generation faster than S_1 population:
  additional mechanism

Electric-Field assisted Pump-probe

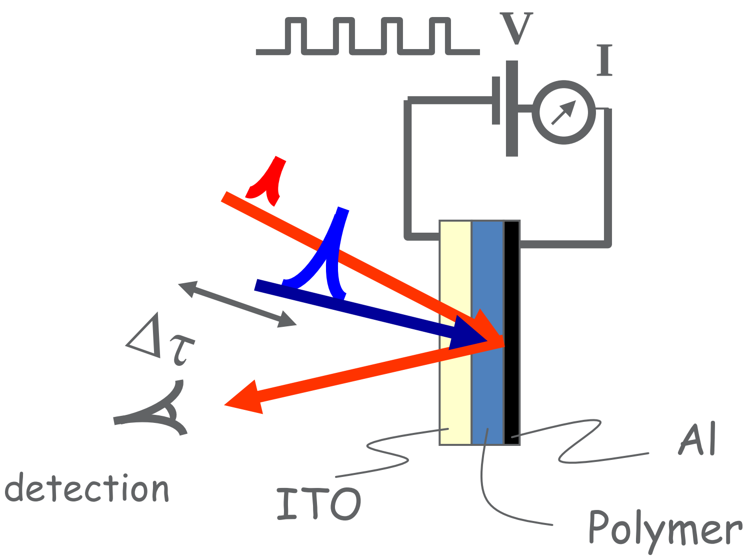
1. Perturbation of energy states provides Info on their Nature and Dynamics

2. Study of polymer films at condition typical of an active layer into a biased device

3. Creating in Lab artificial situations for investigating elementary processes (not otherwise detectable)



Electric field pump – probe setup



Electric field pump – probe signal:

$$\Delta^2 T/T = -d\sum_{i,j}\Delta\sigma_{ij}(\omega,F)\Delta N_J \otimes f_p$$

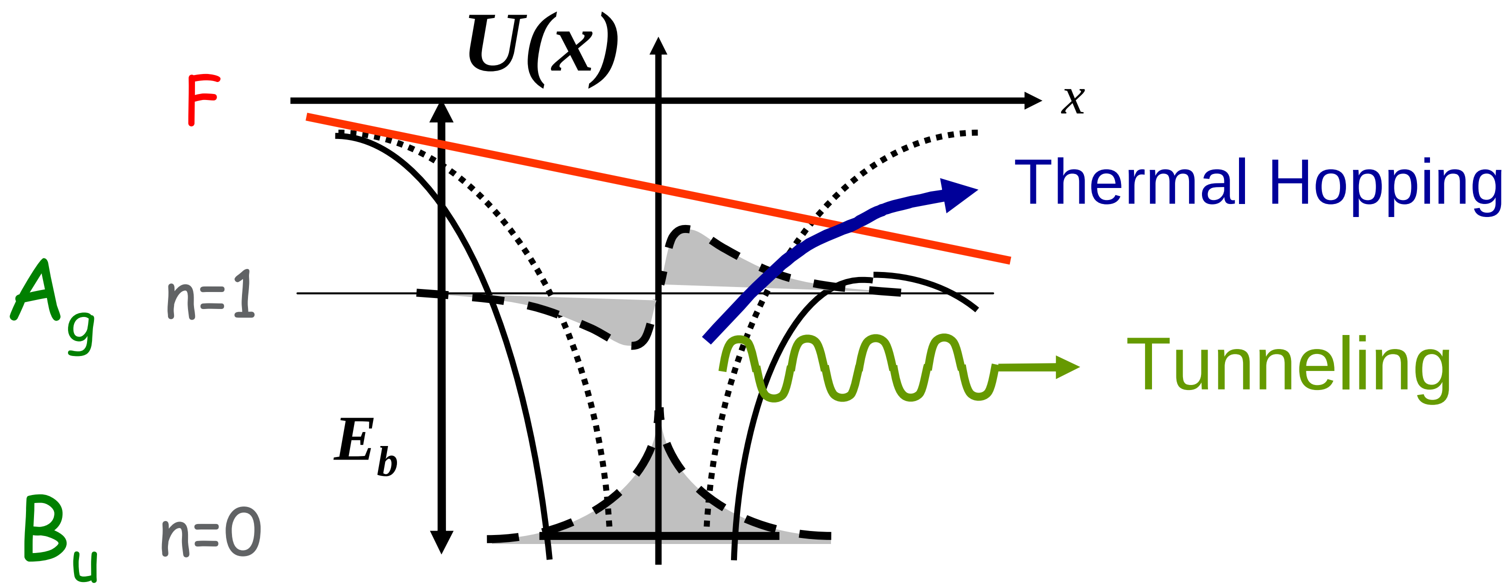
$$-d\sum_{i,j}\sigma_{ij}(\omega)\Delta^2 N_J(F)\otimes f_p - \sum_i \Delta\sigma_{io}(F)N_o$$

$\Delta\sigma_{io}$ = ground state Stark shift

$\Delta\sigma_{ij}$ = excited state Stark shift

$\Delta^2 N$ = change in population

1-D Exciton Ionization



1. Down shift in energy (~ F^2)
2. Change Oscillator Strength
3. Ionization

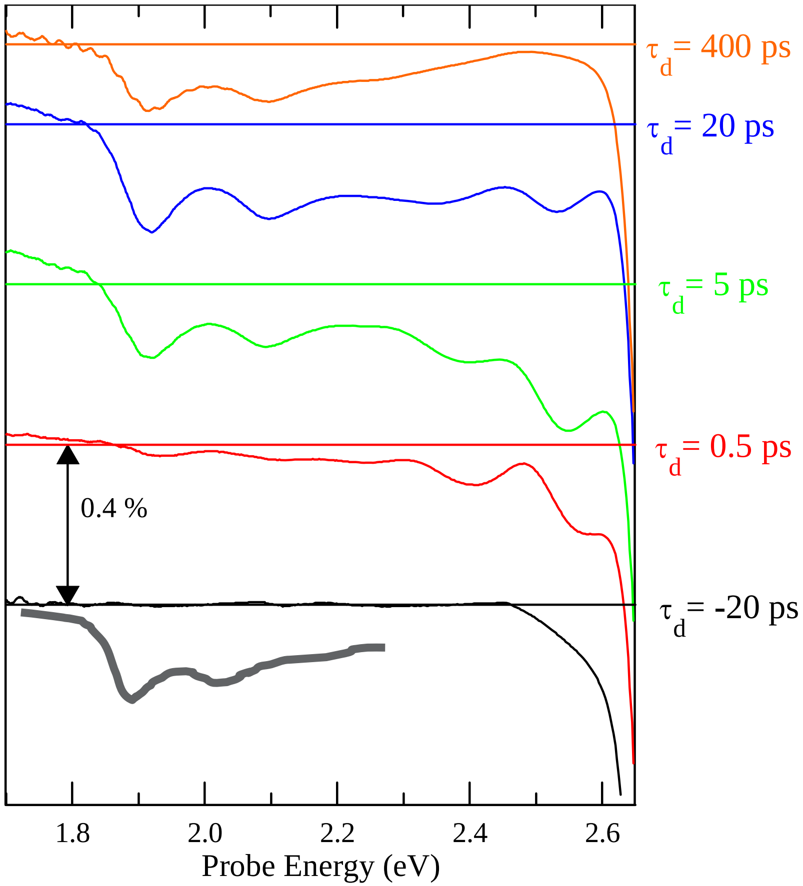
Order of magnitude of the involved quantities

The electric field is typically between 10^5-10^6 V/cm

The available electrostatic energy onto a 1 nm size is 10^{-2}-10^{-1} eV

The estimated time for carriers sweep with 1MV/cm field is 10 ns

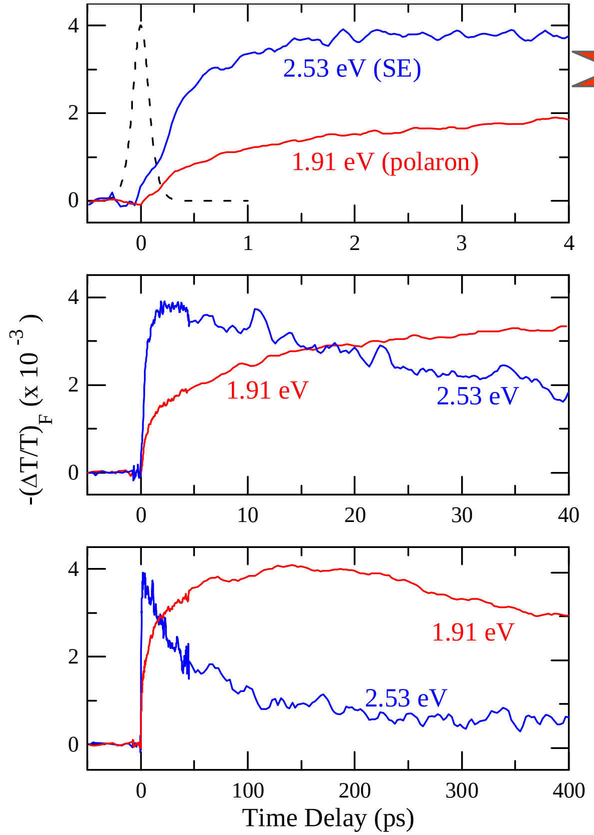
Electric field induced dissociation of neutral states in mLPPP



movie

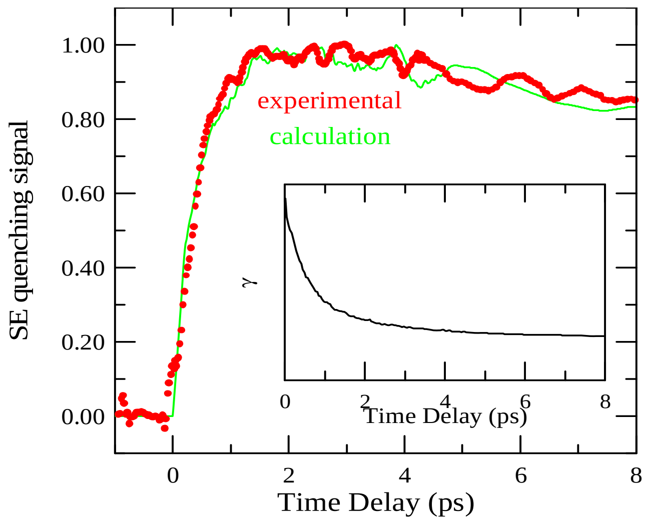
(W. Graupner et al.Phys. Rev. Lett. ***81****, 3259(1998))*

Singlet state dissociation into charged doublets



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

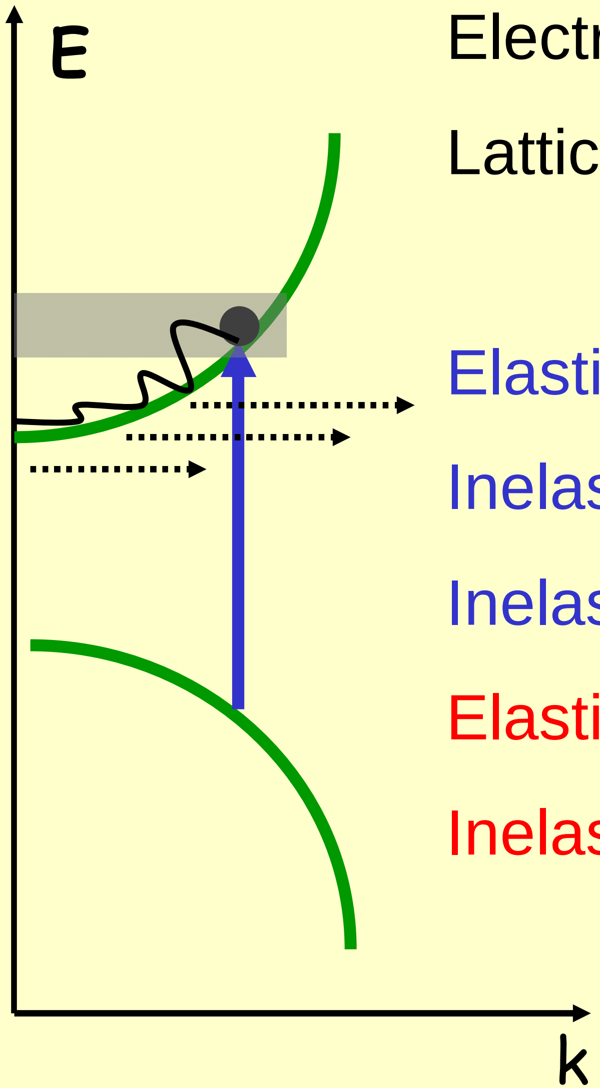
$$\Delta N_S(t) = N_S(t)\left(1 - \exp\left(-\int_0^t \gamma(t')dt'\right)\right)$$



Phys. Rev. Lett. **81**, 3259(1998)

Thermalization

Early events of scattering in semiconductors



Electrons have kinetic energy

Lattice is “frozen”

Elastic e-e (100 fs) k-vector distribution

Inelastic e-e (500 fs) hot Electron Distribution

Inelastic e-ph (1 ps) [rate ~ $h(1/t_{ph})^2$]

Elastic ph-ph (1 ps)

Inelastic ph-ph (10 ps) hot Phonon Distribution

AS Transient Raman Scattering in GaAS

Phonon Lifetime (T_1)

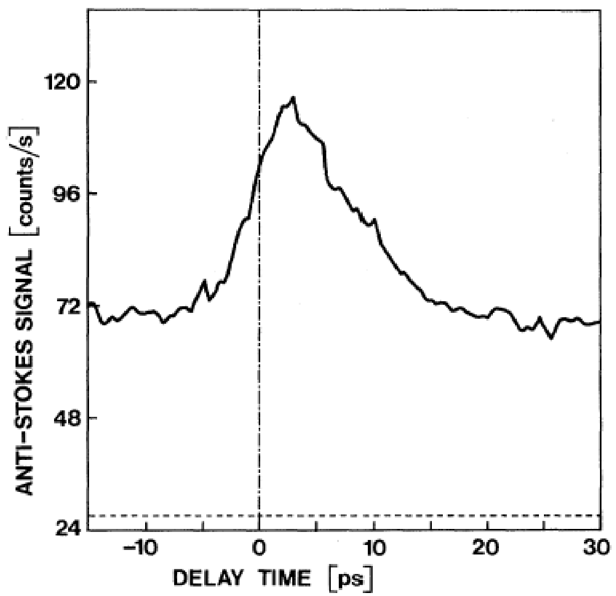


FIG. 1. Anti-Stokes Raman signal vs delay time Δt for the LO-phonon mode of GaAs at 77 K. The zero of the time scale is given by the maximum of the excitation pulse. The dashed horizontal line marks the background counting rate due to residual laser light and dark current of the detector.

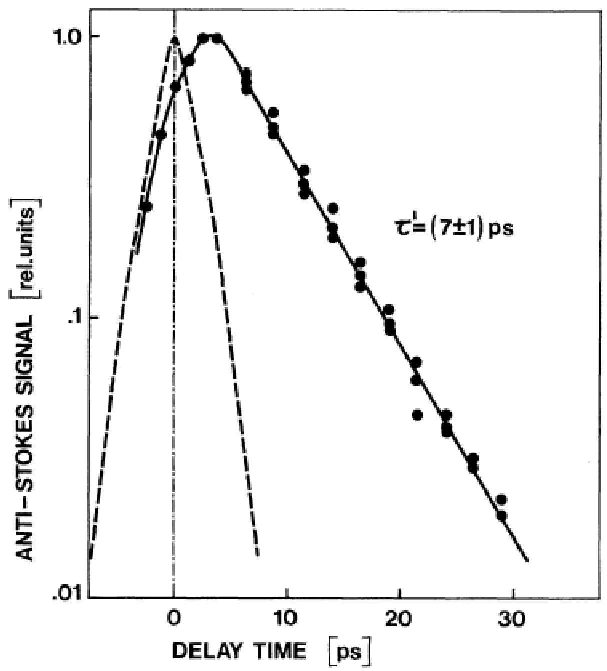
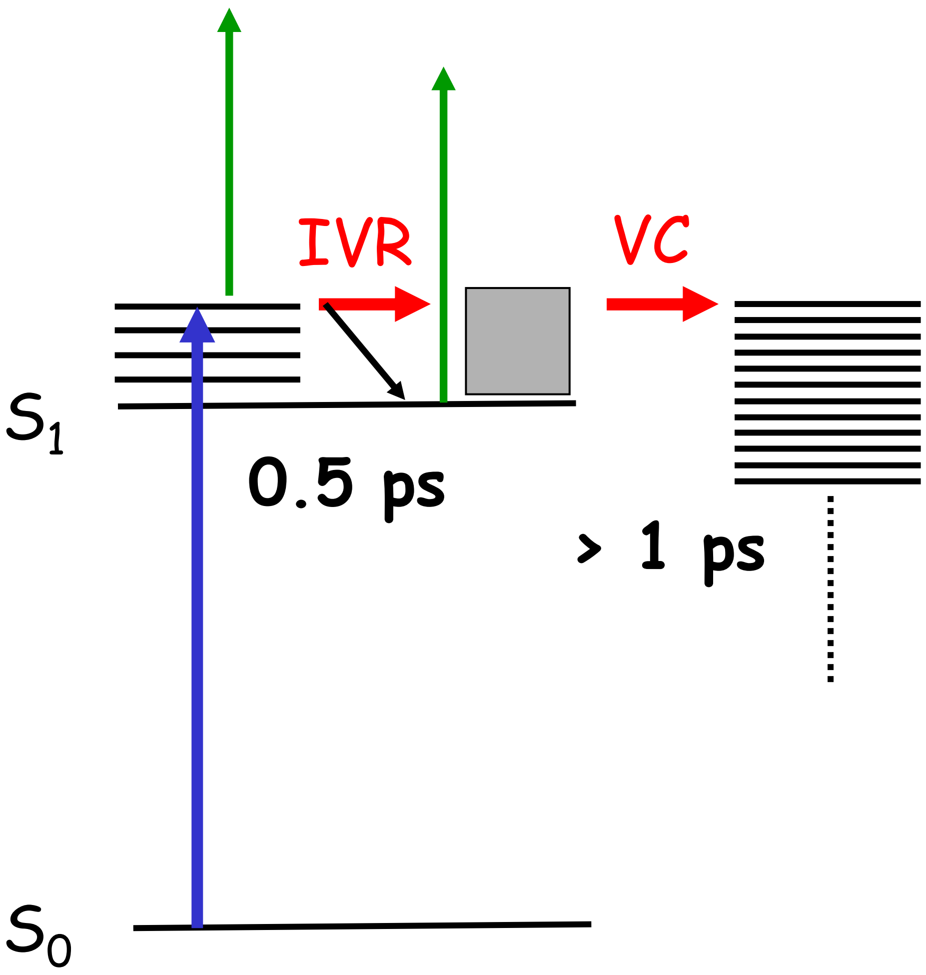
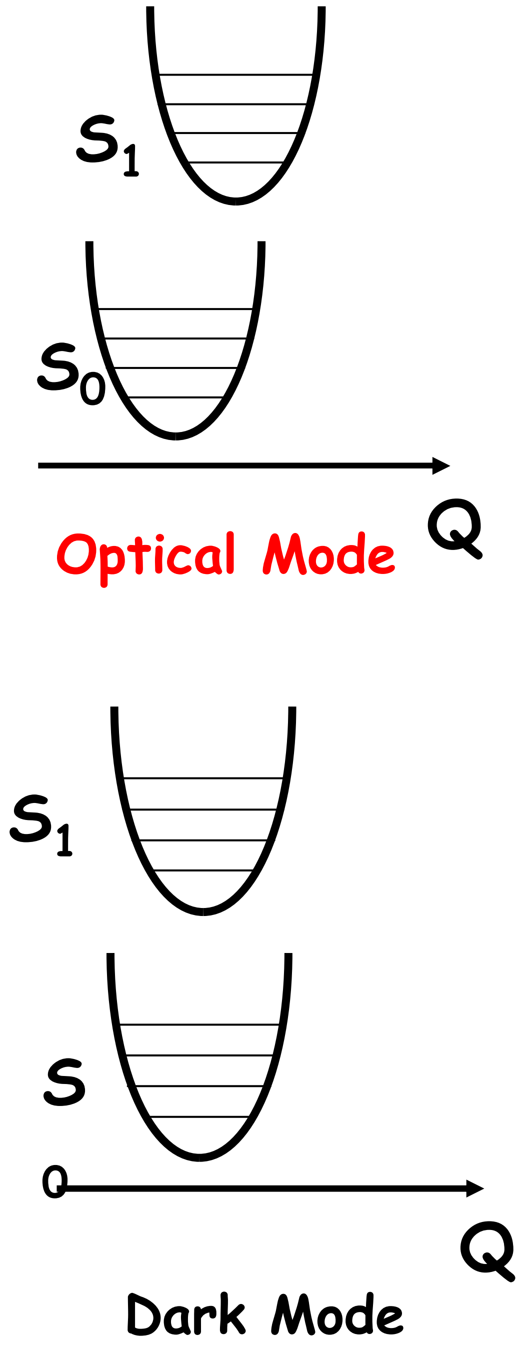


FIG. 2. Semilog representation of the anti-Stokes signal showing the decay of the LO-phonon population. The dashed curve is the measured autocorrelation function of the pulses. The solid curve is calculated.

Hot State Relaxation

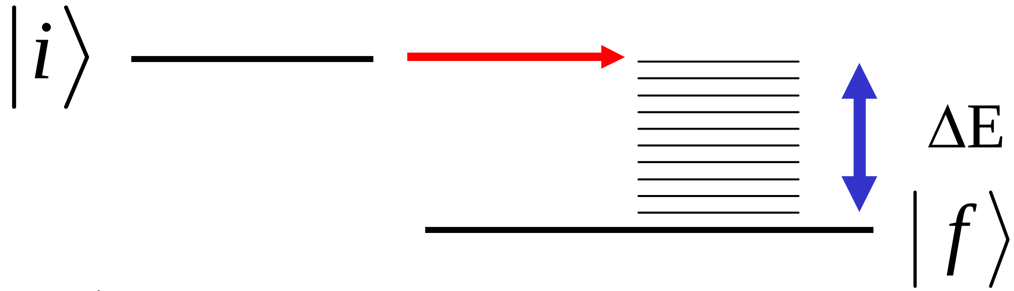




Radiationless transitions (IC)

Iso-energetic

ΔE ≃ E(i)-E(f)



$$H_{fi} = \langle \psi_f \phi_f(\Delta E) | \hat{J}_N | \psi_i \phi_i(0) \rangle$$

$$k_{nr} \propto |H_{fi}|^2 \rho_{\Delta E} \cong \left| \langle \psi_f | \hat{J}_N | \psi_i \rangle \langle \phi_f(\Delta E) | \phi_i(0) \rangle \right|^2 \rho_{\Delta E}$$

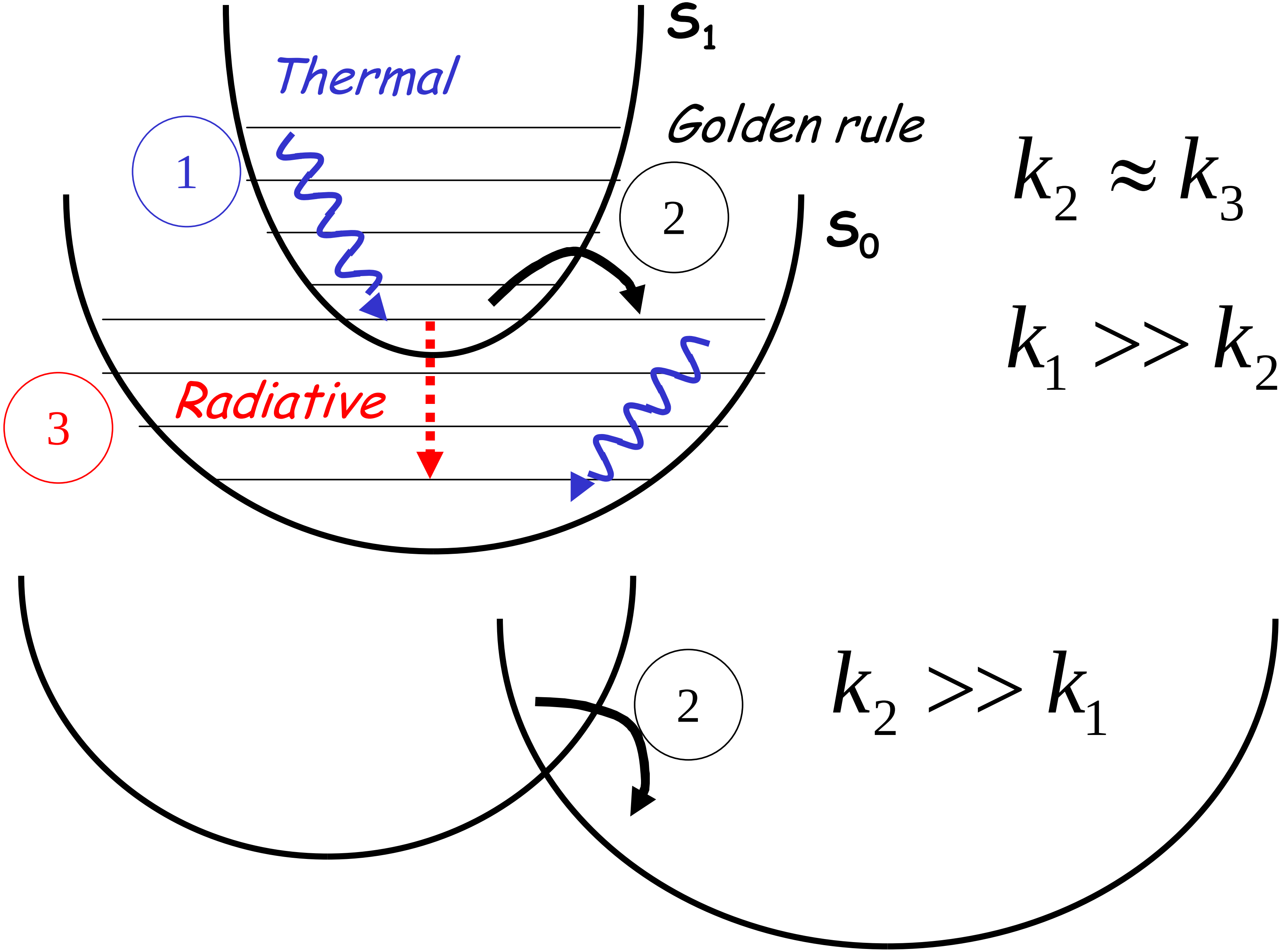
$$k_{nr} \propto J_{fi}^2 \, FC \, \rho_{\Delta E}$$

$$FC = \sum_p P \left[\prod_{k=1}^{N} \left| \langle \phi_{f,n}(n_k) | \phi_{i,k}(0) \rangle \right| \right]^2$$

Energy conservation:

$$\sum_k n_k \hbar \omega_{f,k} = \Delta E \pm \frac{1}{2\rho_{\Delta E}}$$

Conical intersection and "diabatic" path



$$k_2 \approx k_3$$

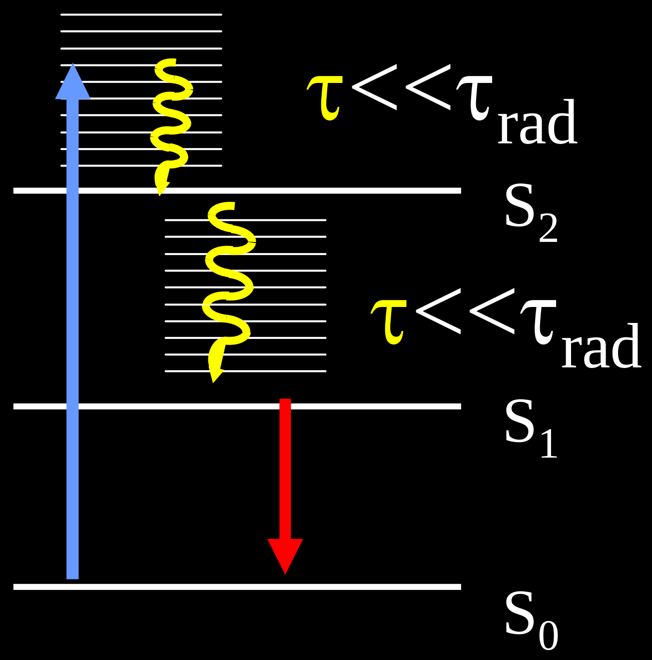
$$k_1 >> k_2$$

$$k_2 >> k_1$$

The Kasha rule (Discuss. Faraday Soc. 9, 14(1950))

"Fluorescence is observed exclusively from the lowest electronic excited state"

$\rightarrow$ *IC is much faster than radiative decay*



Exception: Azulene (S_2-S_0 emission) due to ultrafast S_1 deactivation.

[M. Beer, H. C. Longuet-Higgins JCP**23**, 1390(1955) C. V. Shank ret al. CPL**46**, 20('77)]

The Kasha rule

(M. Kasha, Discuss. Faraday Soc. 9, 14(**1950**))

"Fluorescence is observed exclusively from the lowest electronic excited state"

This is a statement on Dynamic Rates:

→ *IC and VR are much faster than radiative decay*

A.M.Weiner, E. P. Ippen [Chem. Phys. Lett.114, 456(**1985**)]

using 70 fs pulses...

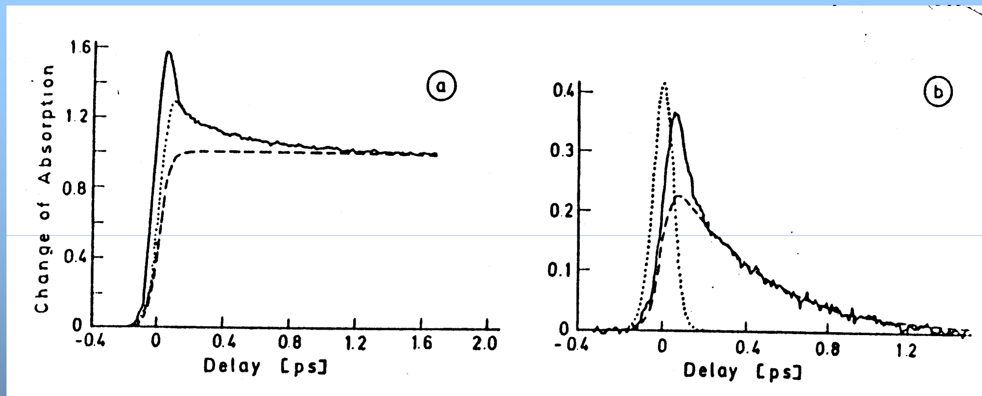


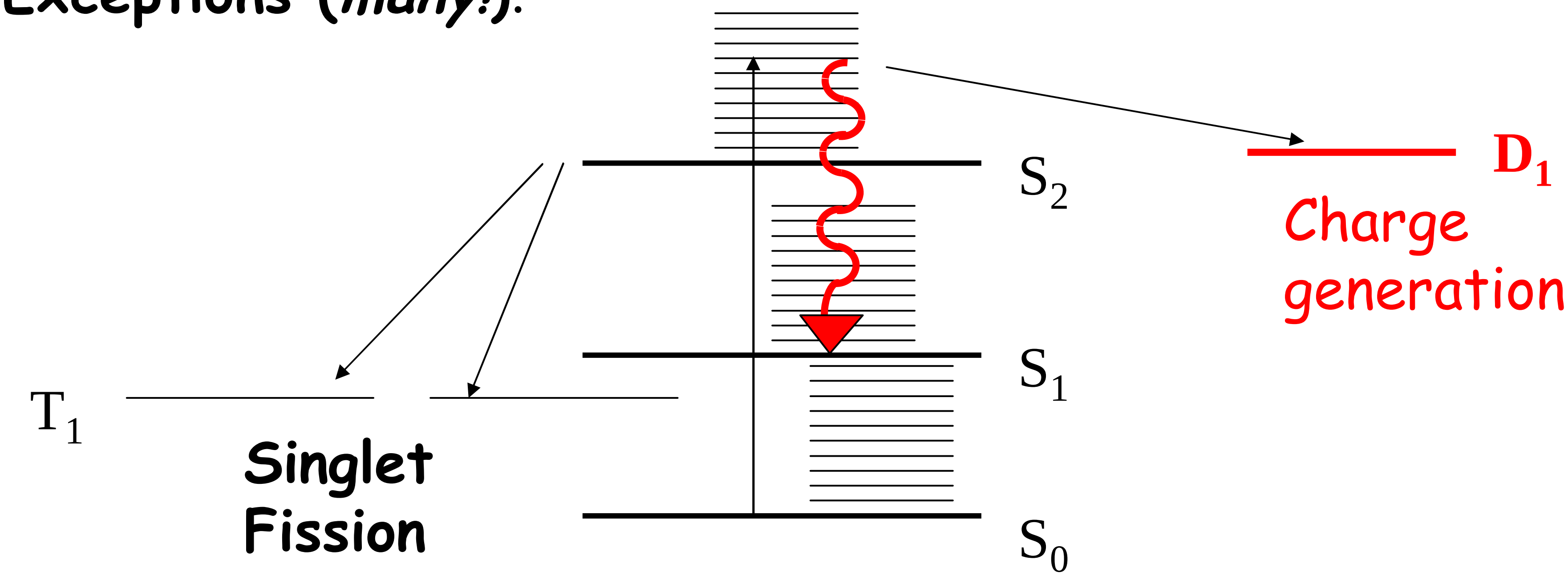
Fig. 7.22a, b. Vibrational relaxation in the S_1 state of nile-blue in methanol. Bleaching is plotted as a function of time. **(a)** The original data (——), the data after removal of the coherent artifact (····), and the integral of the intensity autocorrelation (– – –). **(b)** Portion of the probe signal due to fast molecular dynamics (——); fit assuming a single exponential response with a 410 fs time constant (– – –); intensity autocorrelation curve of the pulses (····) [7.73]

The Vavilov rule

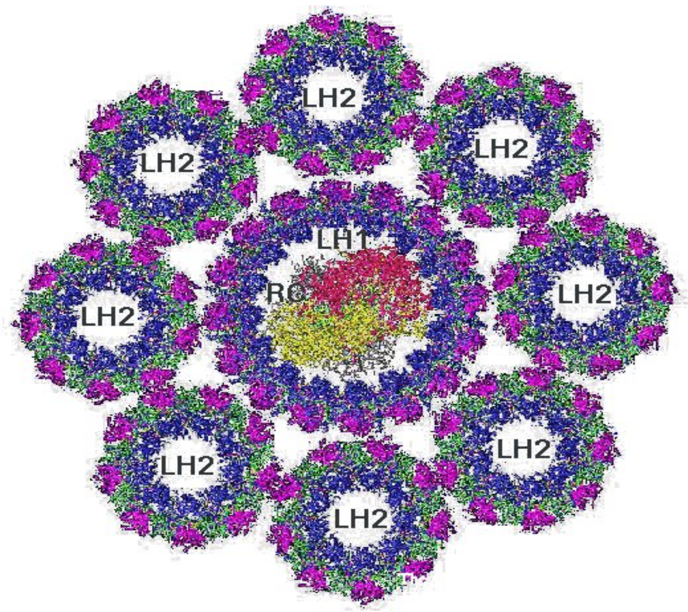
fluorescence quantum efficiency is independent of the excitation wavelength (for non ionizing radiation)

implies IC occurs with quantum efficiency of unity

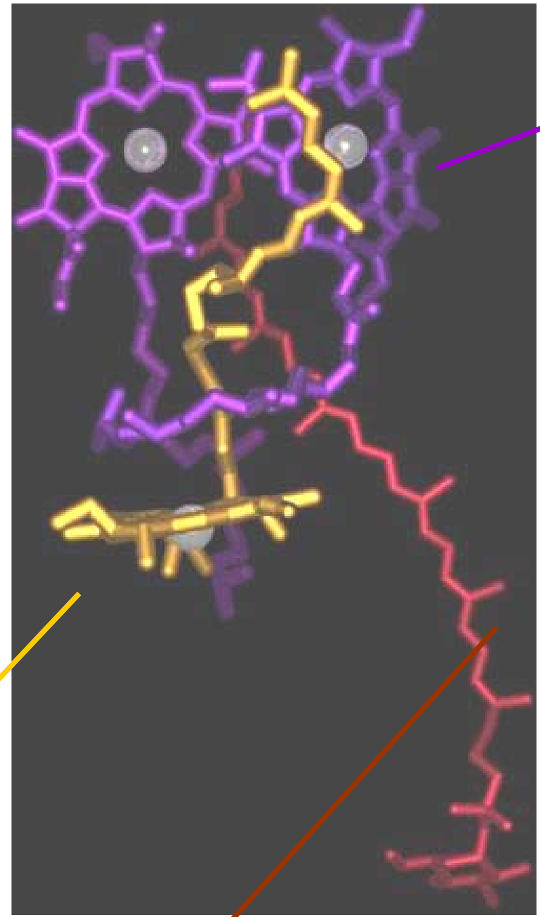
Exceptions (*many!*):



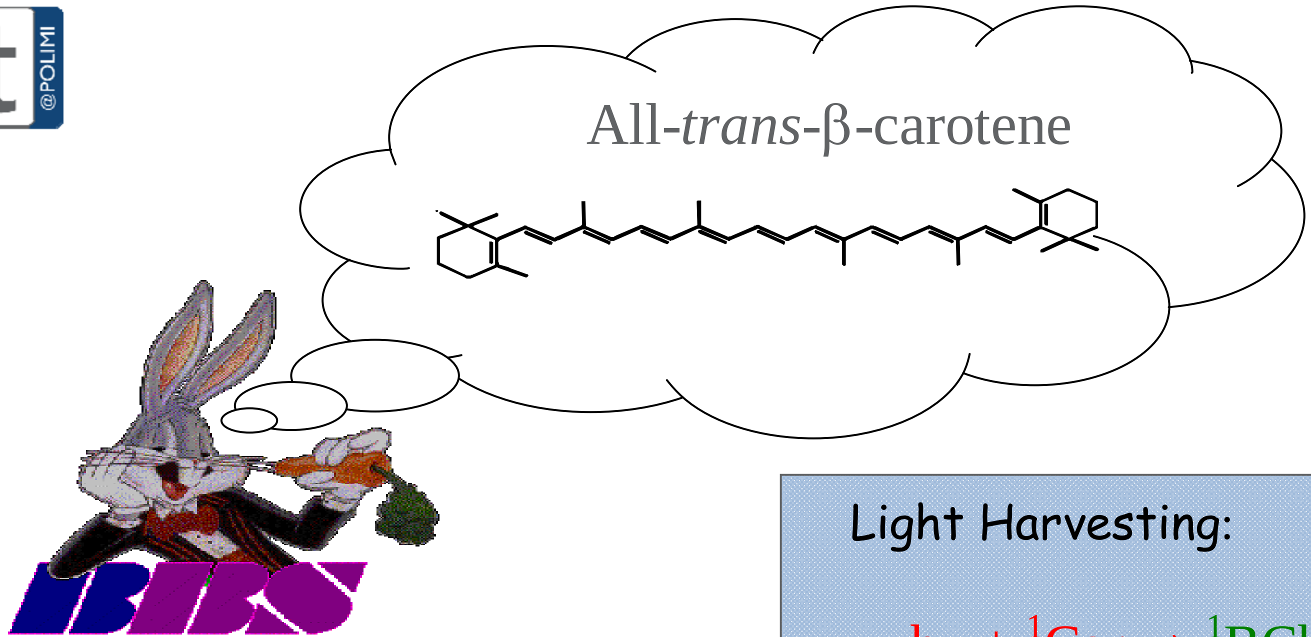
The Photosynthetic Unit



After Richard Cogdell - Univ. Glasgow



Antenna Complex in Rhodopseudomonas Acidophila 10050



$$h\nu + BChl \rightarrow {}^{1}BChl$$

$$\downarrow$$

$${}^{1}O_2 + BChl \leftarrow {}^{3}O_2 + {}^{3}BChl$$

Light Harvesting:

$h\nu + {}^{1}Car \rightarrow {}^{1}BChl$

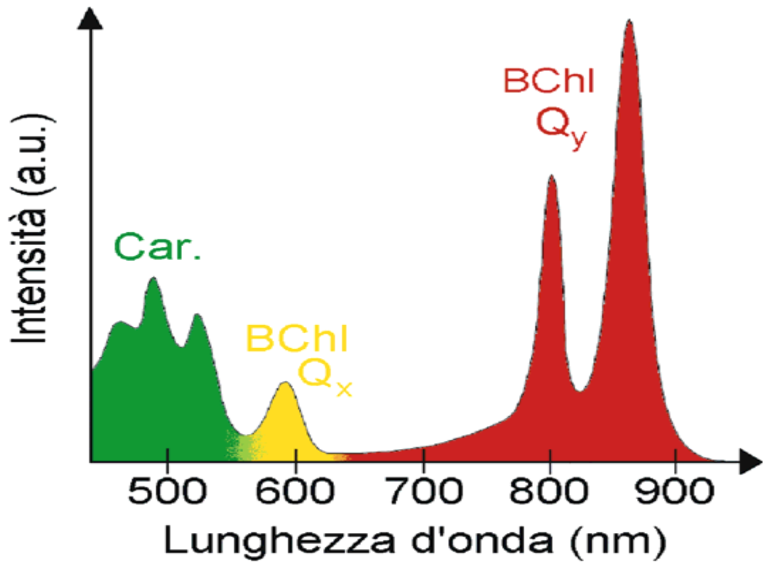
Photoprotection:

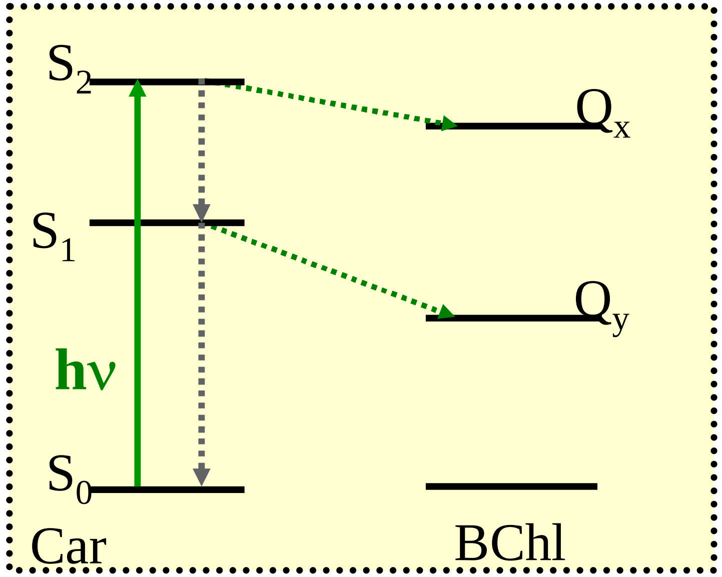
1) UV filter

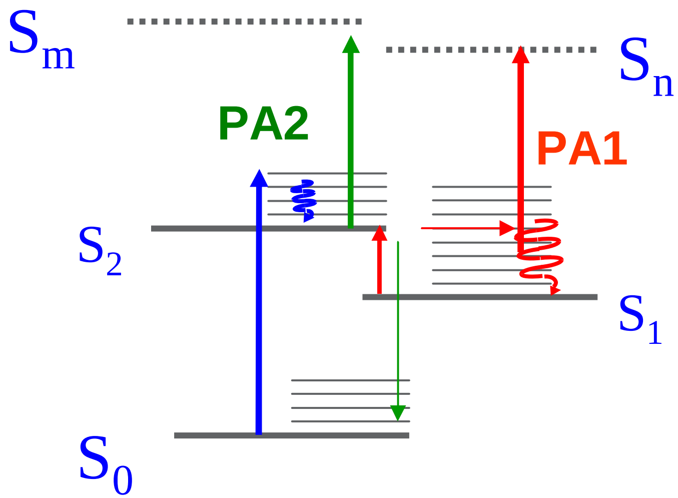
2) ${}^{1}O_2^{*} + Car \rightarrow {}^{3}Car^{*} + {}^{3}O_2$

3) $3BChl^{*} + Car \rightarrow BChl + {}^{3}Car^{*} + {}^{1}Car \rightarrow {}^{1}BChl + {}^{3}Car^{*}$

Energy Transfer Process





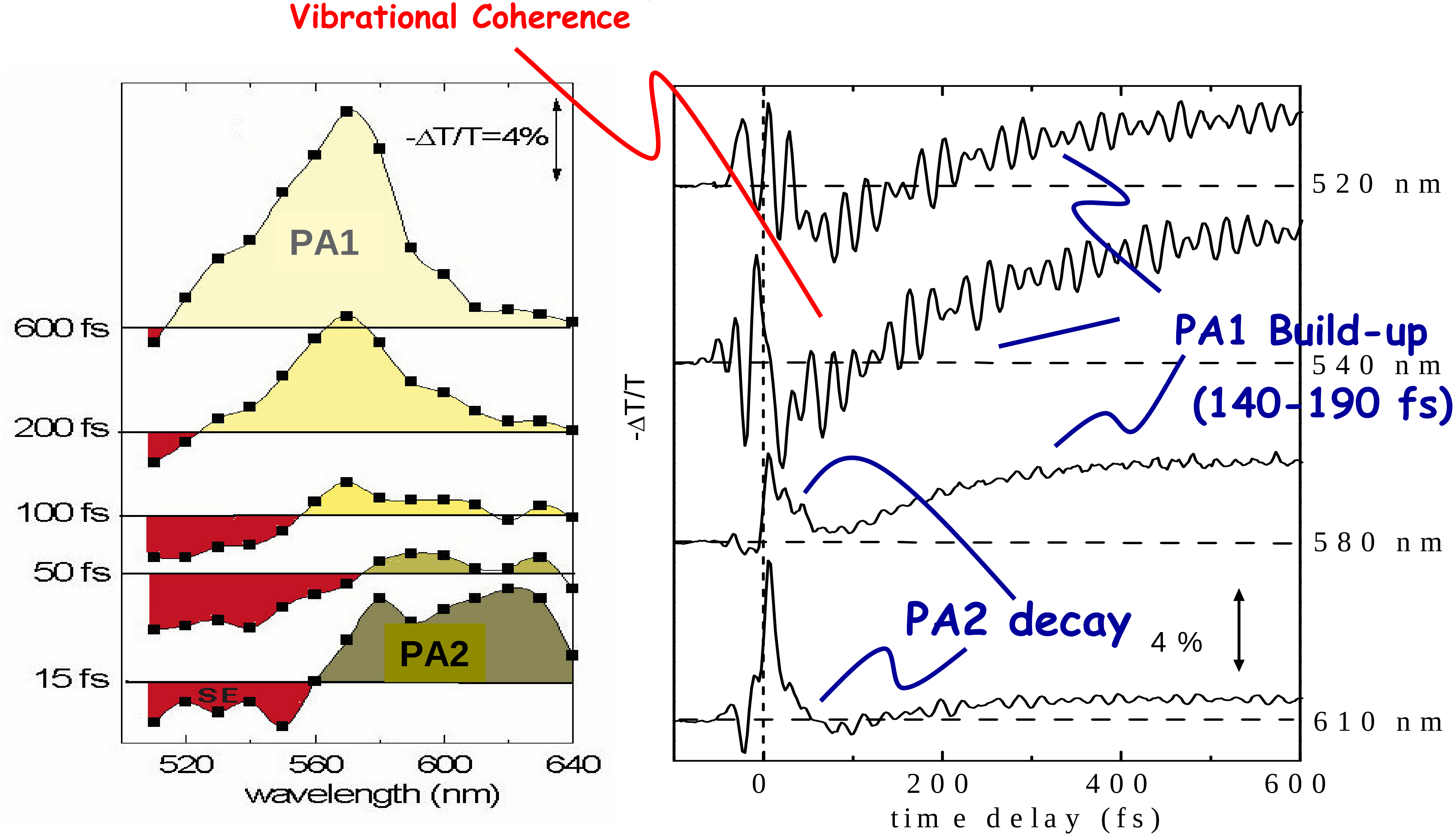


S_2-S_1 is fast ~ 10^2 fs

$S_1 \rightarrow S_2$ lies in the infrared (~ 1 eV for long chains)

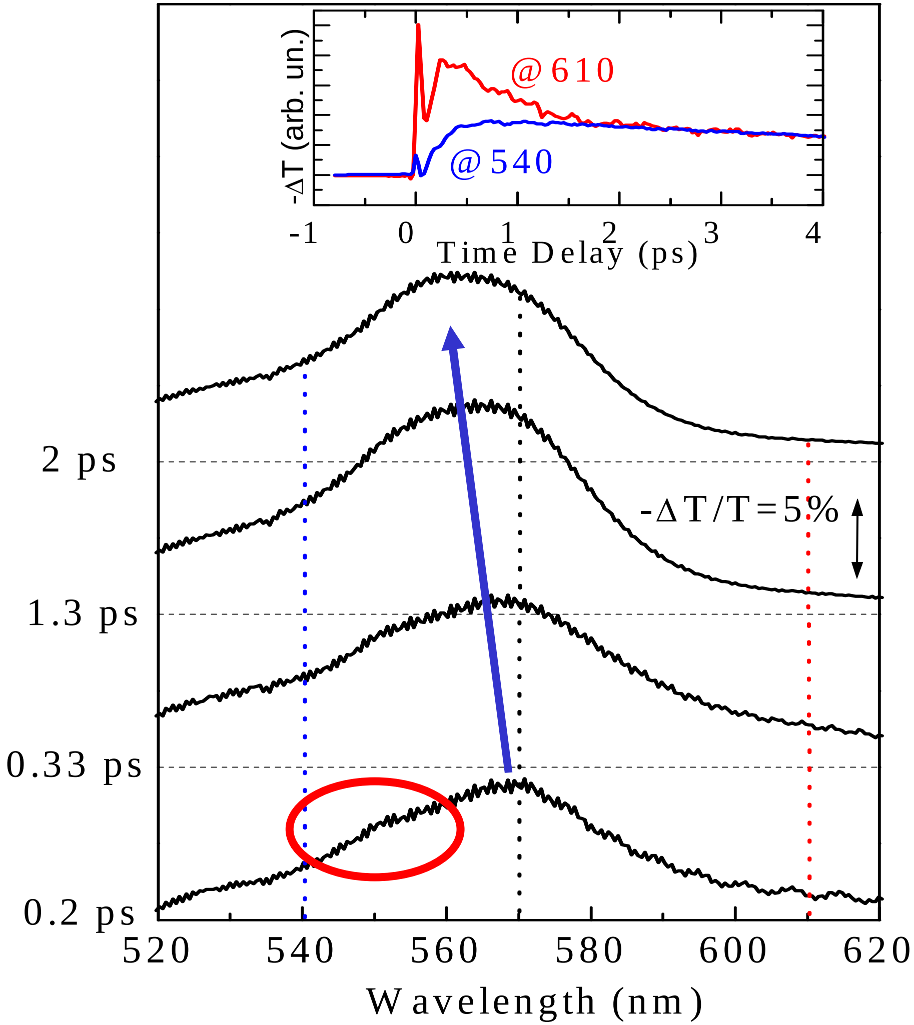
$S_1 \rightarrow S_n$ lies in the visible

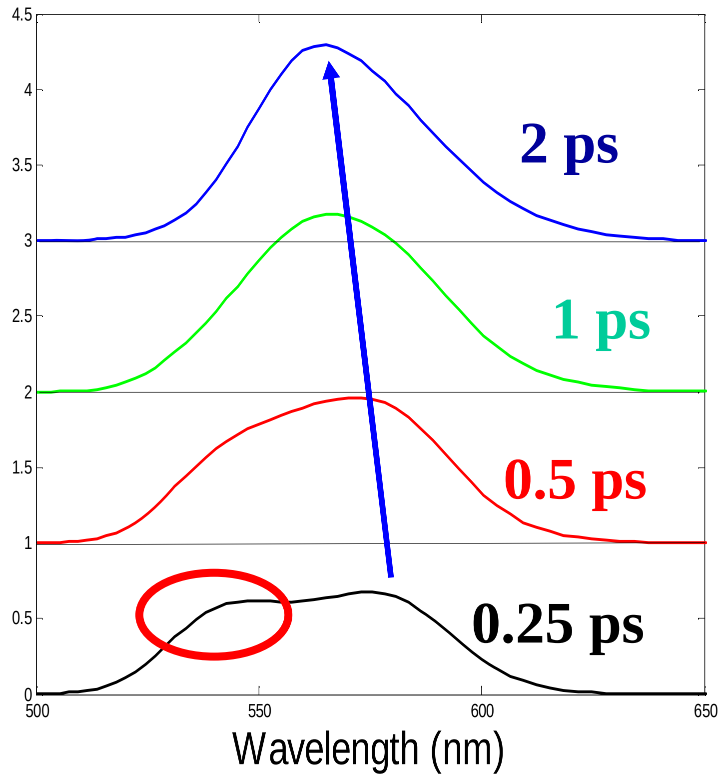
Early events of energy relaxation: Transient Spectra of β-car



Phys. Rev. B **63**, 241104 (2001)

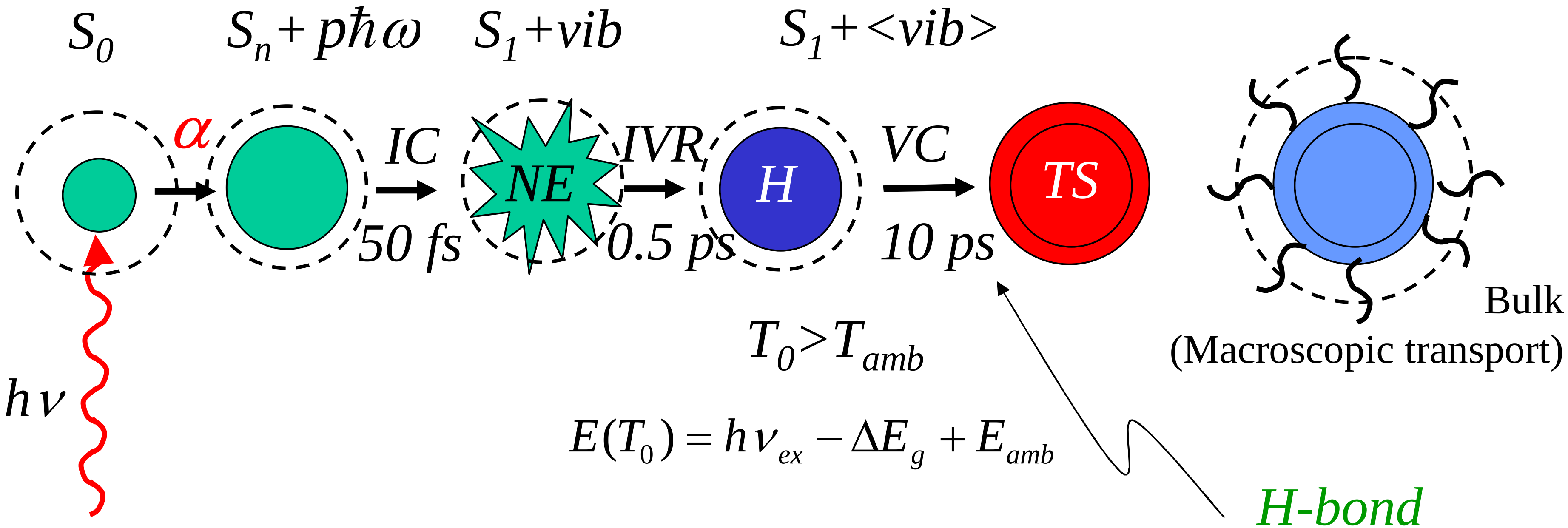
IVR in β-Carotene





Spectral Blue shift

Molecule in solution under optical excitation

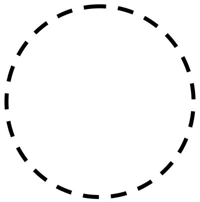


H-bond plays a role

NE= Non Equilibrium

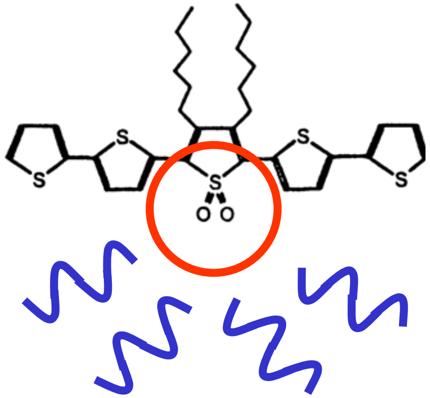
H= Hot State

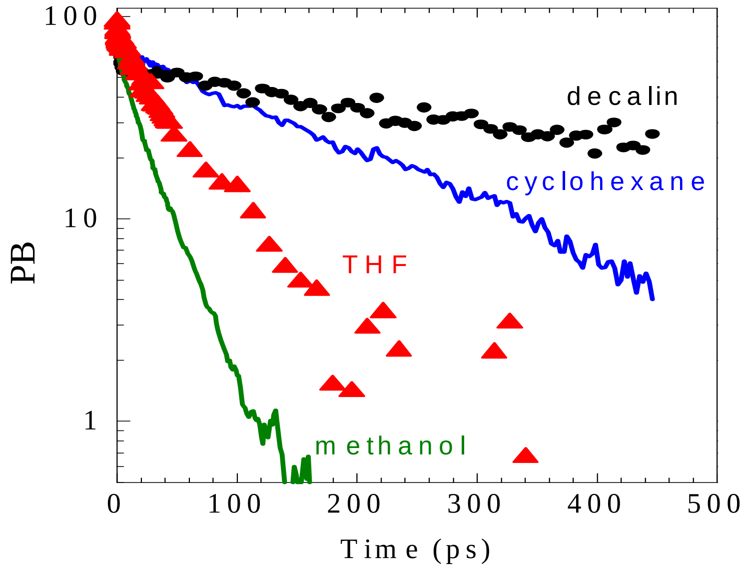
TS=Thermal State



= Solvent Shell

T_5AO_2 : The effect of the environment





	Abs.	*PL*	η	τ_R	τ
Methanol	468	600	0.5	4	**20**
THF	476	580	1.4	3.6	**50**
Cyclohexane	480	600	5	3.45	**180**
Decalin	482	580	7	3.4	**250**