Lecture 7:

Ch. 5 Ultrafast photophysics in conjugated polymers

Ref. G. Lanzani, G. Cerullo, D. Polli, A. Gambetta, M. Zavelani-Rossi, and C. Gadermaier, phys. stat. sol. (a) 201, 116, 1131 (2004).
M. Pope and C. E. Swenberg. Electronic Processes in Organic Crystals and Polymers, 2nd Ed. (Oxford, NY, 1999).
A. J. Heeger, S. Kivelson, J. R. Schrieffer, and W.-P. Su, Solitons in conducting polymers, Rev. Mod. Phys. 60, 781 (1988).

2009. 4. 2 & 7.

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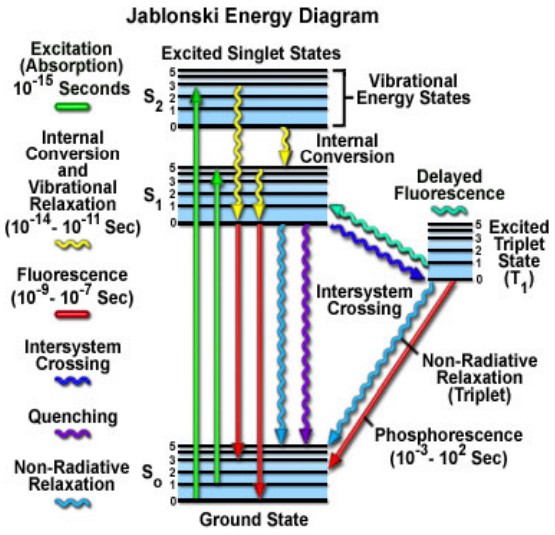
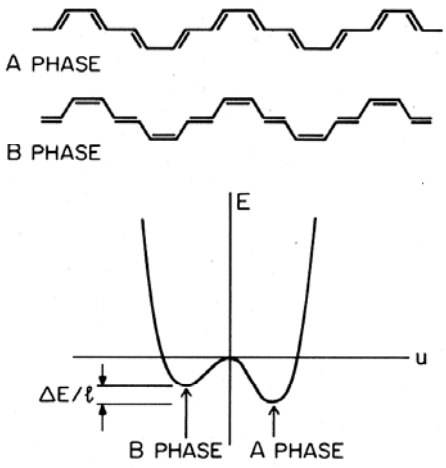
Jablonski Energy Diagram



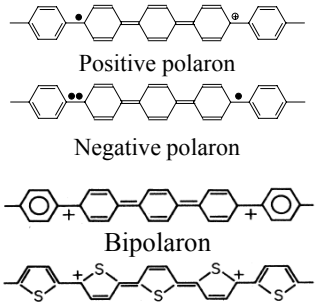
http://microscopy.fsu.edu/primer/java/jablonski/jabintro/

- Absorption occurs in the fs time regime ($\sim 10^{-15}$ s)
- Excess energy can be transferred to the lattice (multi-phonon emission) in the ps time regime ($10^{-14} \sim 10^{-11}$ s)
  → internal conversion and vibrational relaxation
- Transition from the singlet states to the ground state is allowed.
  → Fluorescence occurs in $10^{-9} \sim 10^{-7}$ s
- Transition from the triplet states to the ground state is forbidden.
  → Phosphorescence occurs in $10^{-6} \sim 1$ s
- Intersystem crossing ($S_1 \rightarrow T_1$, $T_1 \rightarrow S_o$,) is possible when spin-orbit coupling is strong.

Quasiparticles in Conjugated Polymers: Polarons



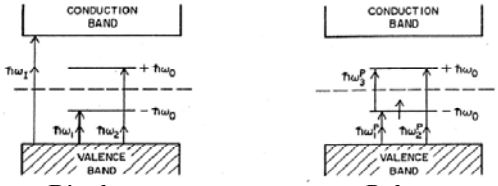
Potential Energy of conjugated polymers with non-degenerate ground-state



Positive polaron

Negative polaron

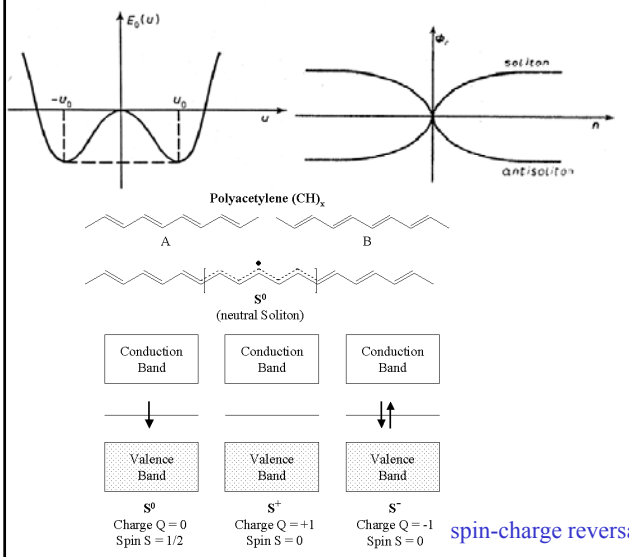
Bipolaron



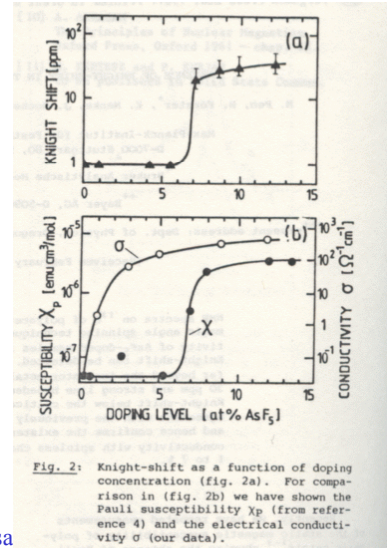
Bipolaron Polaron

A. J. Heeger et al., Solitons in conducting polymers, Rev. Mod. Phys. **60**, 781 (1988)

Quasiparticles in Conjugated Polymers: Solitons



spin-charge reversa



A. J. Heeger, et al., Rev. Mod. Phys. **60**, 781 (1988)

M. Peo et al., Solid State Comm. **38**, 467 (1981)

Quasiparticles in Conjugated Polymers: Solitons

IR active vibrational mode (IRAV mode)

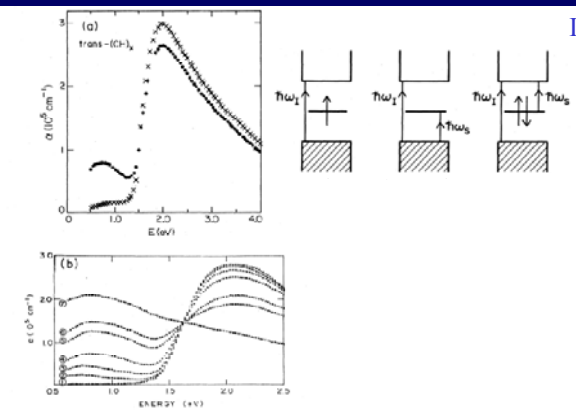
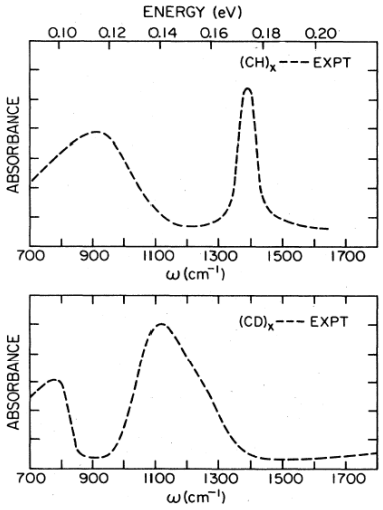
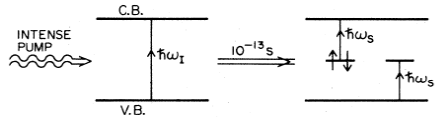


FIG. 34. Absorption spectra for neutral and doped *trans*-$(CH)_x$. (a) Absorption coefficient of *trans*-$(CH)_x$, γ, before doping; ●, after doping with a fraction of a percent by exposure to AsF_5 vapor (from Suzuki *et al.*, 1980). (b) *In situ* absorption curves for *trans*-$(CH)_x$ during electrochemical doping with $(ClO_4)^-$. The applied cell voltages (relative to Li) and corresponding concentrations are as follows: curve 1, 2.2 V ($y=0$); curve 2, 3.28 V ($y\sim0.003$); curve 3, 3.37 V ($y\sim0.0065$); curve 4, 3.46 V ($y\sim0.012$); curve 5, 3.57 V ($y\sim0.027$); curve 6, 3.64 V ($y\sim0.047$); curve 7, 3.73 V ($y\sim0.078$). From Feldblum *et al.*, 1982.



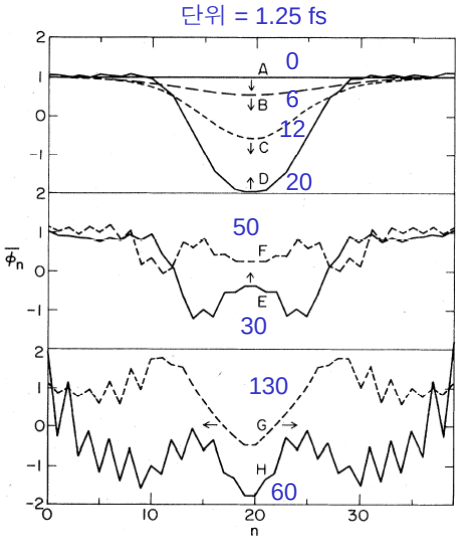
A. J. Heeger et al., Solitons in conducting polymers, Rev. Mod. Phys. **60**, 781 (1988)

Soliton dynamics



Energy to form a soliton at rest : $E_s = \frac{2}{\pi}\Delta \approx 0.63\Delta$

단위 = 1.25 fs



W.-P. Su and J. R. Schrieffer, Proc. Natl. Acad. Sci. U.S.A. **77**, 5626 (1980)

Polarons in Conjugated Polymers

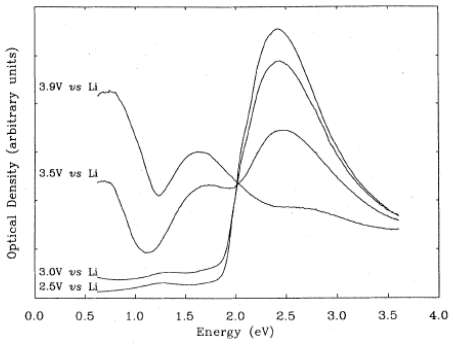


FIG. 48. Absorption spectra of poly(3-methylthiophene), taken *in situ* during electrochemical doping (from Harbeke *et al.*, 1985).

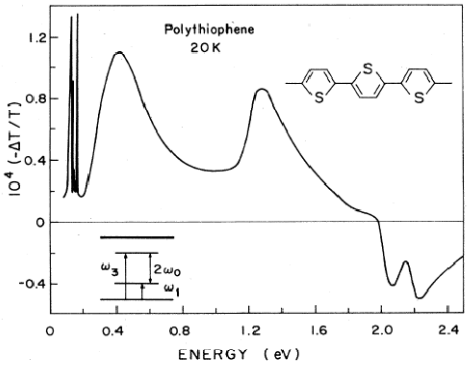
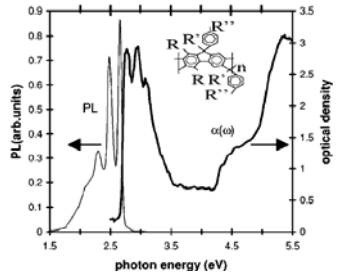
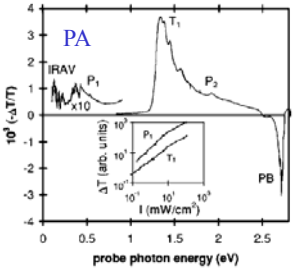


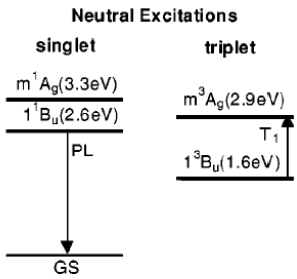
FIG. 51. Photoinduced absorption of polythiophene at 20 K (from Vardeny, Ehrenfreund, Brafman, Nowak, *et al.*, 1986).

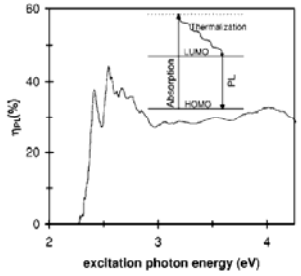
A. J. Heeger et al., Solitons in conducting polymers, Rev. Mod. Phys. **60**, 781 (1988)

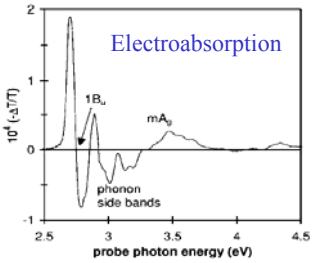
Excitons and polarons in Conjugated Polymers

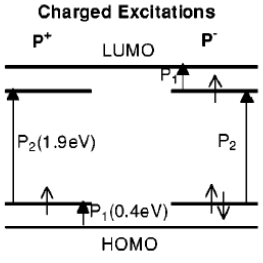












M. Wohlgenannt, et al., , Photogeneration and recombination processes of neutral and charged excitations in films of a ladder-type poly(para-phenylene), Phys. Rev. B **60**, 5321 (1999)

Transient absorption spectroscopy

Transient absorption spectroscopy: Information about the time-evolution of excited species created in a sample by photo-excitation.

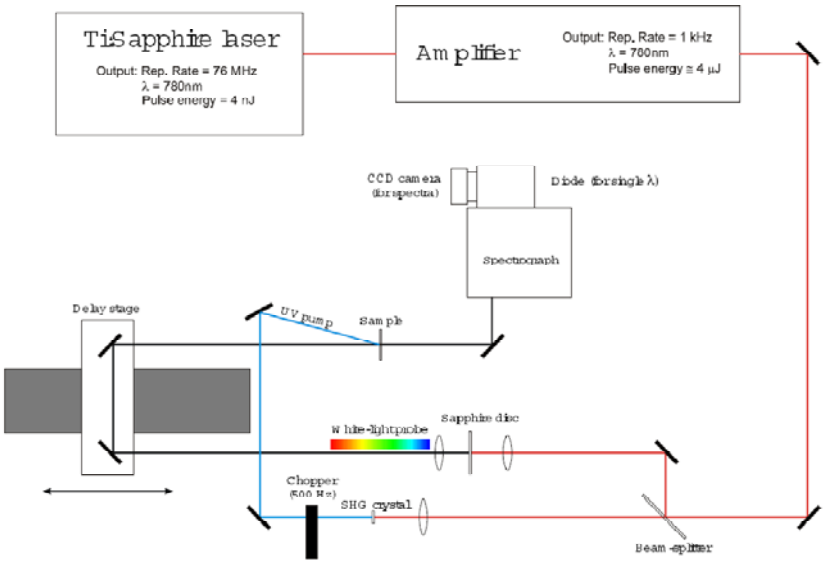
• pumping the sample with a very short pulse of laser light
• probing the excited states using a short pulse at some known time afterwards.
- Probe pulses can interact with the excited states and may be either partially absorbed or amplified.
- The amount by which the probe beam is modulated as it passes through the pumped sample is proportional to the number of excited states.
- This number changes with time as the excited species decay to lower energy states. By measuring the intensity of the transmitted probe at known times after pumping, the population at these times can be deduced.

• Excited-state species present in the photoexcited sample.
- Singlet excitons
- triplet excitons
- solitons
- polarons
- bipolarons, etc.

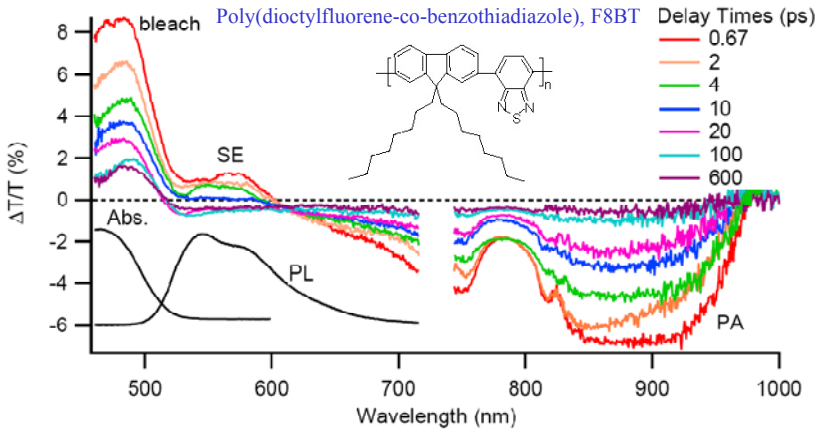
Each one of these has its own absorption spectrum. Thus, probe photons of different energies will be absorbed by the different species present.

•Transient dynamics at a given wavelength: Transmitted probe at that wavelength is monitored as a function of delay.
• Transient absorption spectrum: the entire transmitted spectrum over a range of wavelengths is monitored at a fixed delay to yield absorption features from different excited states.

Schematic diagram of transient absorption spectroscopy exp.

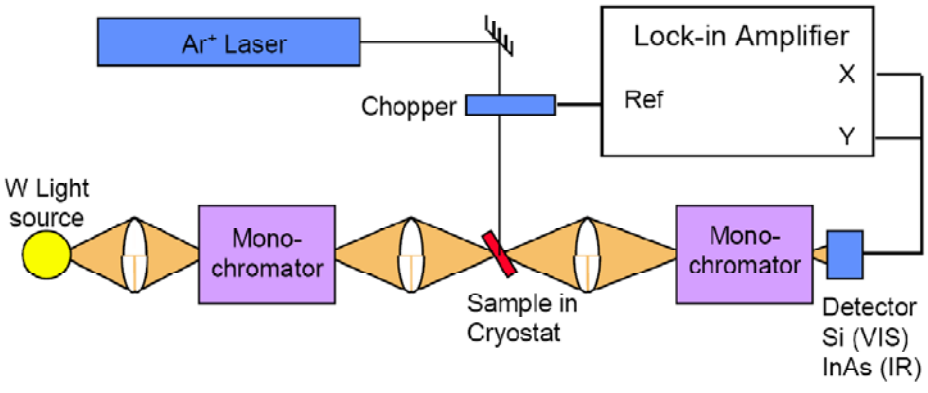


Transient photoinduced absorption spectrum



- Bleach: positive signal due to a bleaching of the $S_0 \rightarrow S_1$ transition.
- Stimulated emission: positive signal is seen at the same position as the PL.
- Photoinduced absorption: very broad and long-lived.

Steady-State PA measurement



- Spectral information to identify species
- Frequency, intensity, and temperature dependence used to assign absorptions and characterize states

PA signal: monomolecular decay

- Assume signal is proportional to number of excitations present at time t: n(t)
- I intensity, g generation efficiency, ω chop frequency

$$\frac{dn(t)}{dt} = gI[1+\cos(\omega t)] - \frac{n(t)}{\tau}$$

$$n(t) = gI\tau[1+\frac{1}{\sqrt{1+\omega^2\tau^2}}\cos(\omega t-\phi)],$$

$$\phi = \tan^{-1}(\omega\tau): \quad \phi \to 0 \text{ for } \tau << \omega^{-1}, \quad \phi \to \frac{\pi}{2} \text{ for } \tau >> \omega^{-1}$$

$$\Delta T \propto n_s = \frac{gI\tau}{\sqrt{1+\omega^2\tau^2}}.$$

- PA signal is linear with intensity at all frequencies
- Behaves as ω^{-1} for $\omega\tau >> 1$
- Independent of ω for $\omega\tau << 1$
- The crossover of the two regions ($\omega\tau \sim 1$) is used often to obtain the lifetime τ.
- The in-phase ($\phi=0$) and out-of-phase ($\phi=\pi/2$) spectra can be used to detect states with different lifetimes: in-phase ($\phi=0$) for a short lifetime state and out-of-phase ($\phi=\pi/2$) for a long lifetime states.

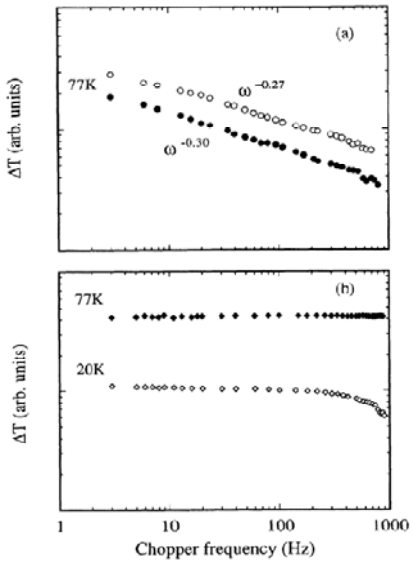
Ref. G. Delleiane, C. Cuniberti, D. Comoretto, G. F. Musso, G. Figari, A. Piaggi, A. Borghesi, Phys. rev. B 48, 7850 (1993)

PA signal: bimolecular decay

$$\frac{dn(t)}{dt} = gI[1+\cos(\omega t)] - \beta n(t)^2$$

Approximate solution :

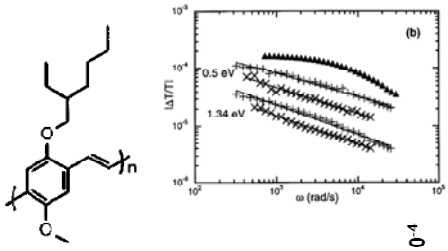
$$S(\omega,\tau) = \frac{\sqrt{\frac{gI}{\beta}}\alpha\tanh\alpha}{\alpha+\tanh\alpha}, \quad \alpha = \frac{\pi}{\omega\tau_s}: \quad \tau_s = \sqrt{\frac{1}{gI\beta}}$$



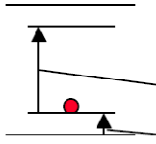
- For $\omega\tau_s << 1$ signal is indep. of ω and is dep. on $I^{-1/2}$
- For $\omega\tau_s >> 1$ signal is ω^{-1} and linearly dep. on I
- So intensity dependence can separate monomolecular and bimolecular decays,
but only for $\omega\tau_s << 1$ (low chop freq)

G. Delleiane, C. Cuniberti, D. Comoretto, G. F. Musso, G. Figari, A. Piaggi, A. Borghesi, Phys. rev. B 48, 7850 (1993)

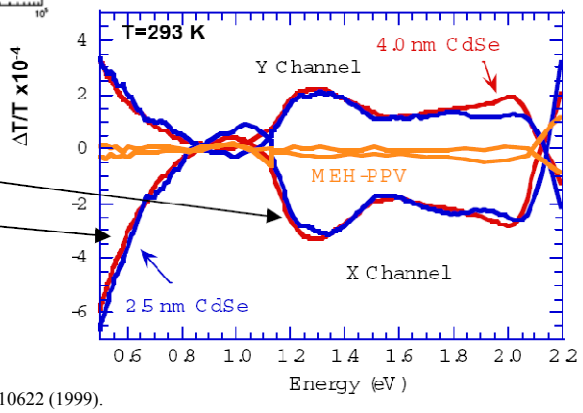
PIA Signal



MEH-PPV



two induced absorptions
due to polaron on polymer

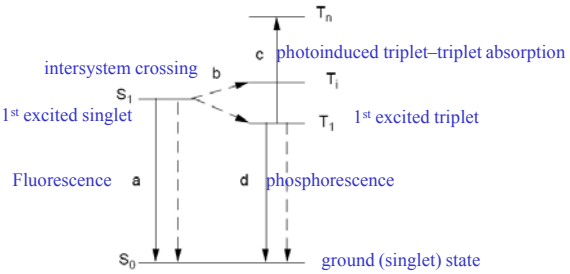


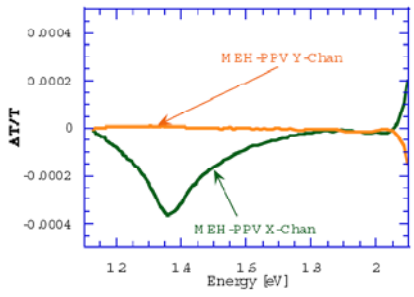
D. S. Ginger and N. C. Greenham, Phys. Rev. B 59, 10622 (1999).

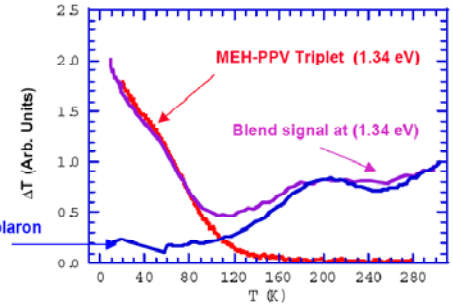
$T_1 \rightarrow T_n$ transition

Formation of triplets leads to new triplet - triplet ($T_1 \rightarrow T_n$)- absorptions

- Lifetime often increases at low T: larger signal
- T-dep can be used to correlate two different peaks

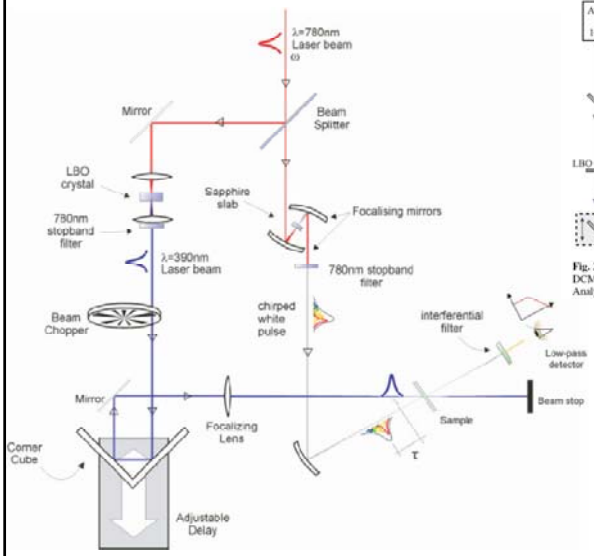






D. S. Ginger and N. C. Greenham, Phys. Rev. B 59, 10622 (1999).

Experimental set-up for pump-probe spectroscopy



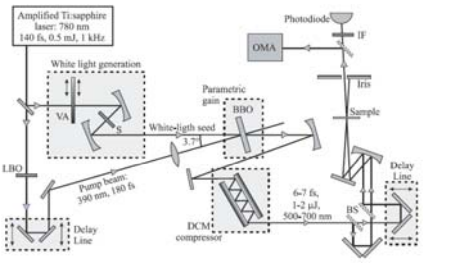


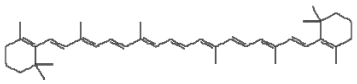
Fig. 2 Non-collinear Optical Parametric amplifier, compression stage and pump-probe set-up. DCM = Double Chirp Mirrors, BS = Beam Splitters; S = Sapphire plate; OMA = Optical Multichannel Analyzer; IF = Interference Filters.

$$\frac{\Delta T}{T} = -\sum_{i,j} \sigma_{ij}(\omega)\Delta N_j d$$

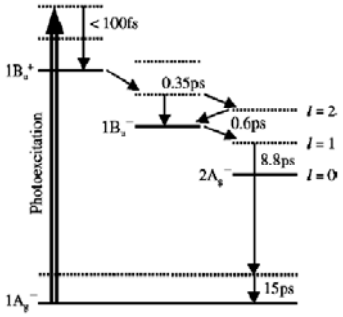
where σ_{ij} (ω) is the cross-section (in cm^2), and N_j is the population of the final states. σ is positive for upwards transitions and negative for downwards ones.

G. Lanzani, G. Cerullo, D. Polli, A. Gambetta, M. Zavelani-Rossi, and C. Gadermaier, phys. stat. sol. (a) 201, (6), 1116 (2004)

Example of fs-pump-probe experiment: β-carotene

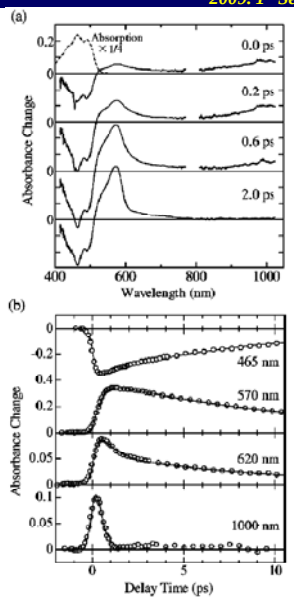


β-Carotene: can be found in yellow, orange, and green leafy fruits and vegetables such as carrots, tomatoes, sweet potatoes, oranges, etc..

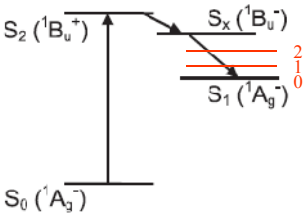


Schematic energy diagram of all-*trans*-b-carotene and relaxation kinetics after photoexcitation.

M. Yoshizawa, H. Aoki, and H. Hashimoto, Phys. Rev. B 63, 180301 (2001)



Coherent vibrational spectroscopy

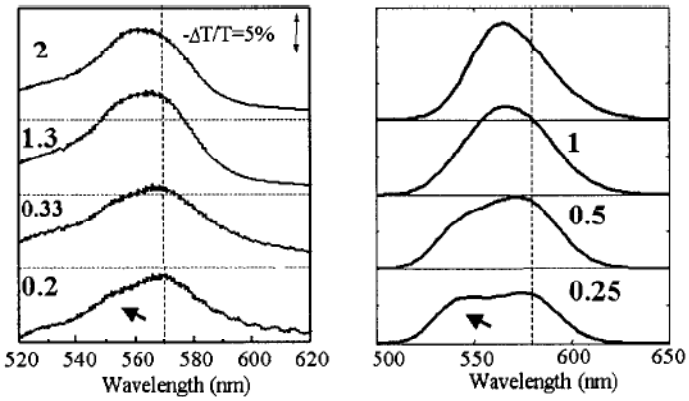


$$\frac{dN_{S_{1,2}}}{dt} = G_{IC} - k_{2,1}N_{S_{1,2}}$$

$$\frac{dN_{S_{1,1}}}{dt} = k_{2,1}N_{S_{1,2}} - k_{1,0}N_{S_{1,1}}$$

$$\frac{dN_{S_{1,0}}}{dt} = k_{1,0}N_{S_{1,1}} - R_{S_{1-0}}$$

In β-carotene in solution, the "hot" S_1 state thermalizes in about 2 ps upon internal conversion



$k_{21}/k_{10} = 20$: Vibrational relaxation slows down approaching the bottom of the potential well.

Left panel: transient spectra measured in β-carotene in solution at different pump-probe delays (labels) in ps
Right Panel: Numerical simulation. The arrows points out a feature of the lineshape.

G. Lanzani, G. Cerullo, D. Polli, A. Gambetta, M. Zavelani-Rossi, and C. Gadermaier, phys. stat. sol. (a) 201, 116, 1131 (2004).

Coherent vibrational spectroscopy

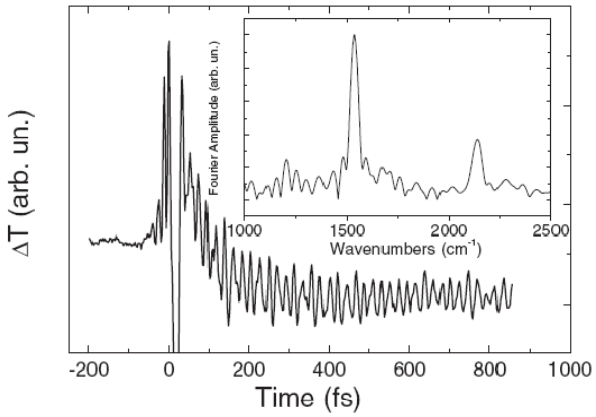


Fig. 5 Ultrafast dynamics in PDA following excitation with sub-10 fs pulses as measured monitoring the 620 nm spectral component of the probe pulse band. Structures at negative delay are due to coherent arteifacts, oscillations at positive delay reflect coherent nuclear motion. The inset shows Fourier transform of the oscillating signal at positive delays.

From the data the time scale for dephasing of the double stretching mode is extracted as $T_2 \approx 600$ fs, consistent with Raman linewidth and typical value for CPs, indicating that the vibrational lifetime is $T_1 \geq 300$ fs in the ground state.

G. Lanzani, G. Cerullo, D. Polli, A. Gambetta, M. Zavelani-Rossi, and C. Gadermaier, phys. stat. sol. (a) 201, 116, 1131 (2004).

Field-assisted pump-probe spectroscopy

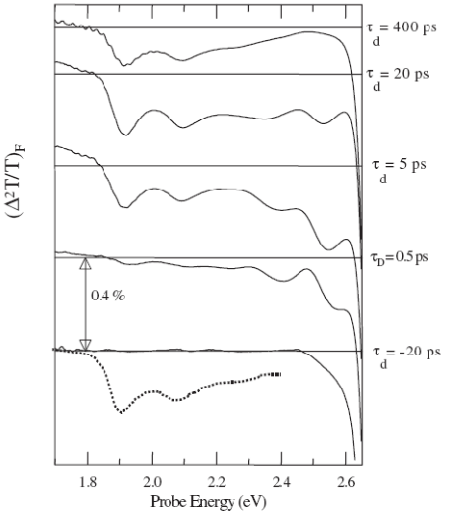


Fig. 8 Electric Field assisted Pump-probe spectra for m-LPPP films. The dashed line shows the absorption spectrum of charged states in m-LPPP measured by chemical doping.

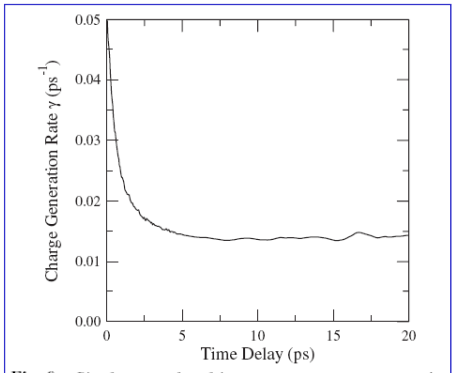
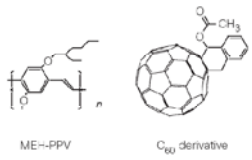
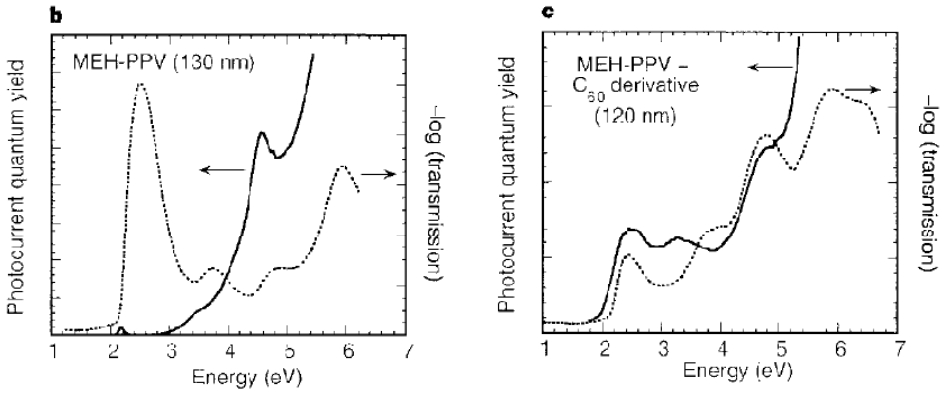


Fig. 9 Singlet-state breaking rate γ versus pump-probe delay in presence of an external electric field in m-LPPP.

G. Lanzani, G. Cerullo, D. Polli, A. Gambetta, M. Zavelani-Rossi, and C. Gadermaier, phys. stat. sol. (a) 201, 116, 1131 (2004).

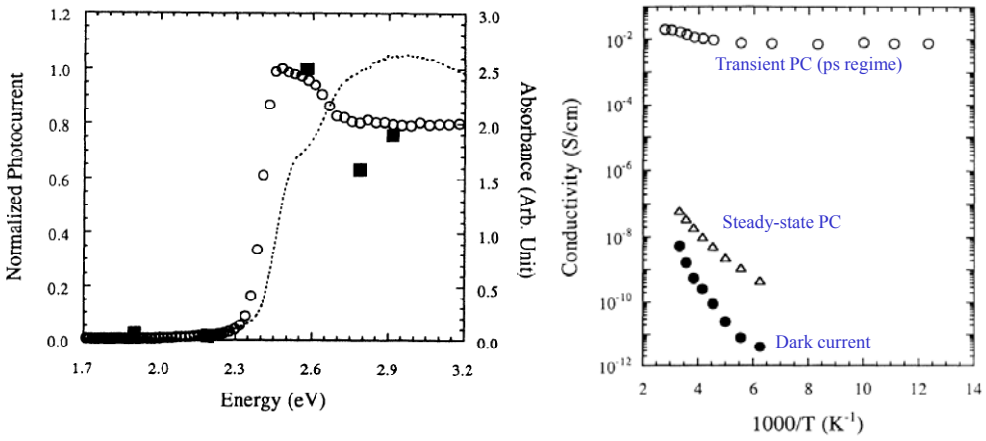
Photo-generation of charge carriers





A. Kohler et al., Nature 392, 903 (1998).

Photo-generation of charge carriers in PPV



C. H. Lee et al., Phys. Rev. B 49, 2396 (1994).

The role of higher-lying states

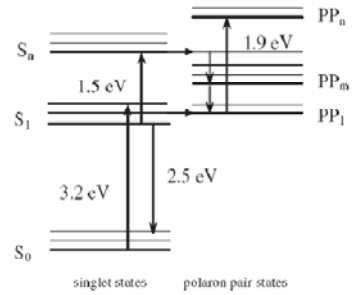
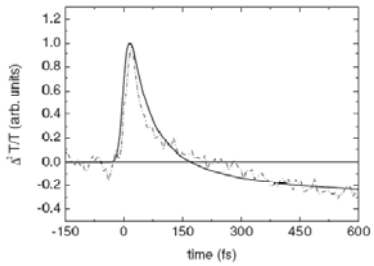
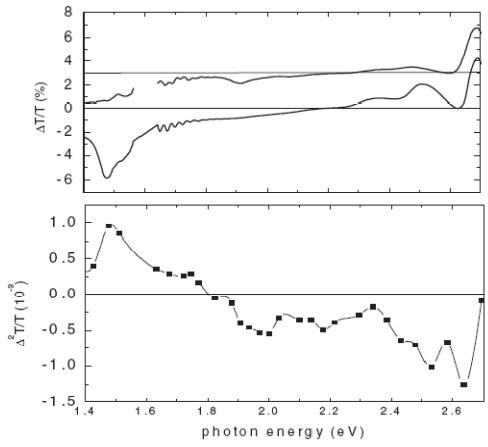


Fig. 10 Electronic states involved in double excitation techniques. Thick arrows: first and second excitation pulses (photon energy to their left side), thin vertical arrows: detection via probe pulse (photon energy to their right side), other arrows: spontaneous transitions.





G. Lanzani, G. Cerullo, D. Polli, A. Gambetta, M. Zavelani-Rossi, and C. Gadermaier, phys. stat. sol. (a) 201, 116, 1131 (2004).