Femtosecond transient absorption spectroscopy of photo- and thermo-switchable organic crystals

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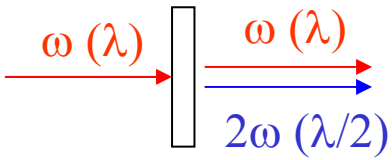
Outline

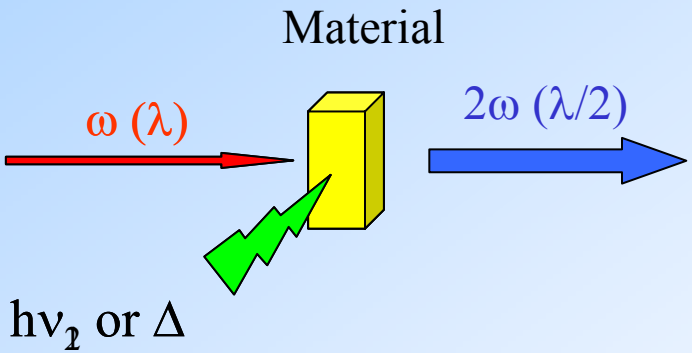
1. Photo/Thermo-chromism and Non Linear Optics (NLO): introduction of our goal, SHG switchable organic compounds
2. Dynamics of the photochromic reaction in solid state for salicylidene anilines
3. Understanding the origin of the modulation in the solid state: structure-properties relation

Non Linear Optical Properties

Second Harmonic Generation (SHG)



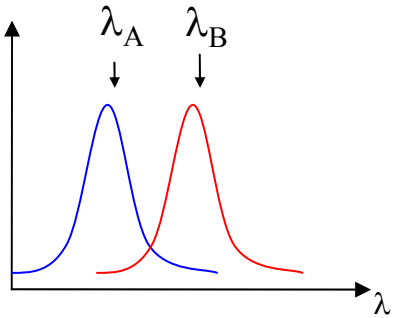
- frequency doubler
- electro-optic modulator



Photo/Thermo-chromism

$$A \underset{h\nu_B(\lambda_B)\text{ and/or }\Delta}{\overset{h\nu_A(\lambda_A)\text{ and/or }\Delta}{\rightleftharpoons}} B$$ Reversible

Absorption



Photo/Thermo-switching of SHG properties Data Storage

Molecular Crystals

- Photo/Thermo-chromism in solid state
- Fast reaction
- Non Centrosymmetric Material

Non Linear Optics (NLO)

Molecules

$\mu = \mu_0 + \alpha \mathbf{E}_l + \beta \mathbf{E}_l \mathbf{E}_l + \ldots$

E_l : local electric field
α : polarizability
β : quadratic hyperpolarizability

Material

$P = \frac{\sum \mu_i}{V}$ and $\mathbf{P} = P_0 + \chi^{(1)} \mathbf{E}_a + \chi^{(2)} \mathbf{E}_a \mathbf{E}_a + \ldots$

E_a : applied electric field
$\chi^{(1)}$: susceptibility
$\chi^{(2)}$: second order susceptibility

Second Order NLO

$E = E_0 \cos(\omega t)$

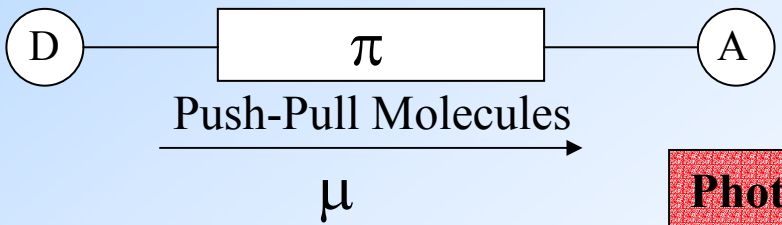
$P^{(2)}_{NL} = \chi^{(2)} E^2 = \chi^{(2)} /2 \{E_0^2 \cos(2\omega t) + E_0^2\}$

Second Harmonic Generation SHG

SHG-Active Organic Materials

1) Microscopic $\beta \neq 0$

→ Noncentrosymmetric molecules



2) Macroscopic $\chi^{(2)} \neq 0$

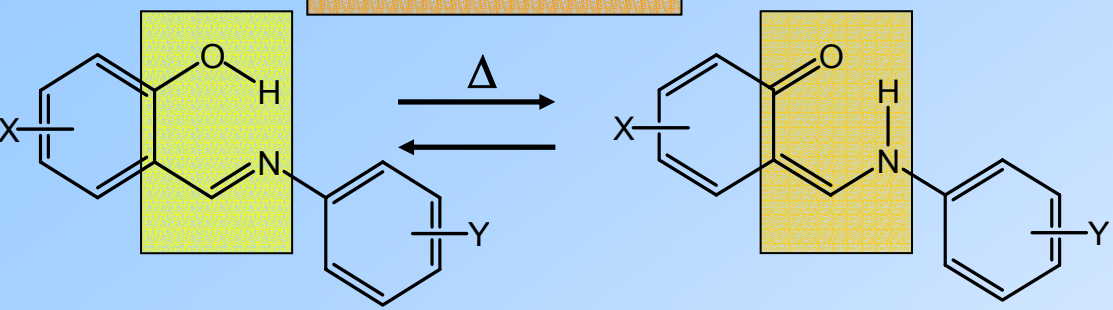
Noncentrosymmetric materials

$$\chi^{(2)} \propto \sum_{Molecules} \beta$$

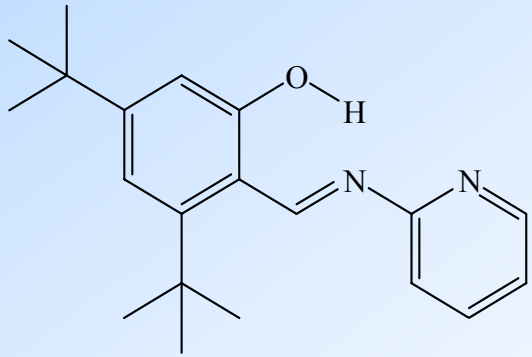
Photo/Thermo-chromic reaction:
Large spectral change rearrangement of the π electron
Fast reaction

Photo/Thermo-chromic system in the crystalline state
Proton transfer of Salicylidene anilines (anils)

Enol **Thermochromic** Cis-keto



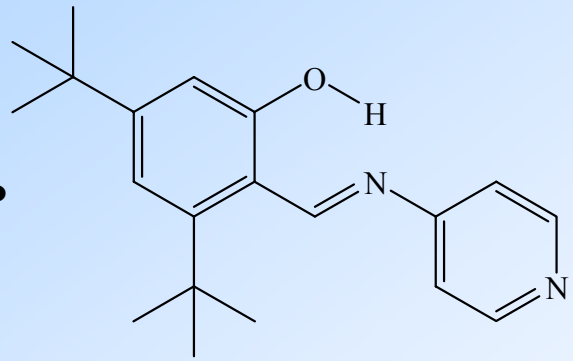
2-P

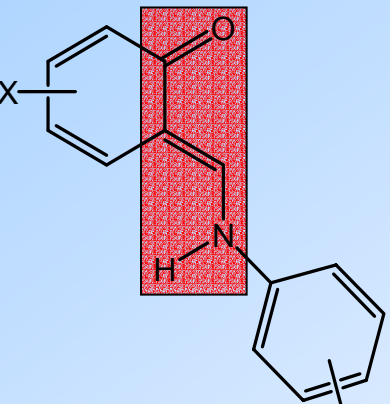


U.V.

1) λ≈480 nm
2) Δ , τ

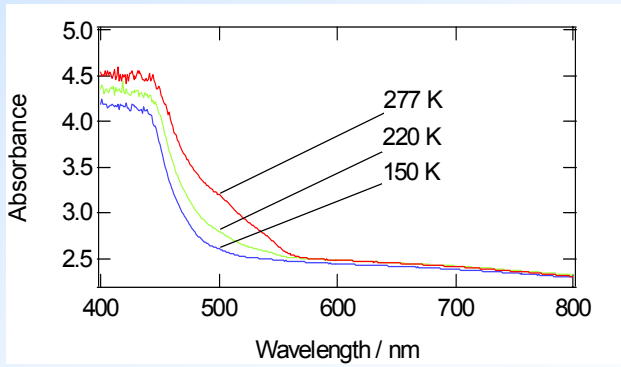
4-P

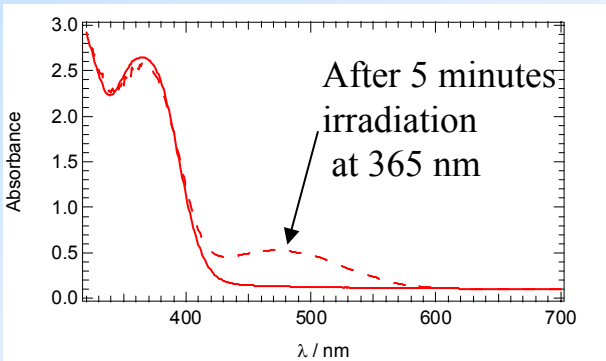




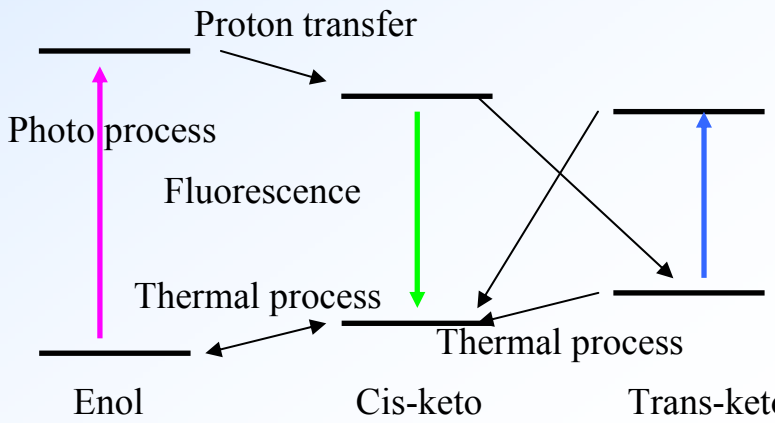
Trans-keto

Photochromic





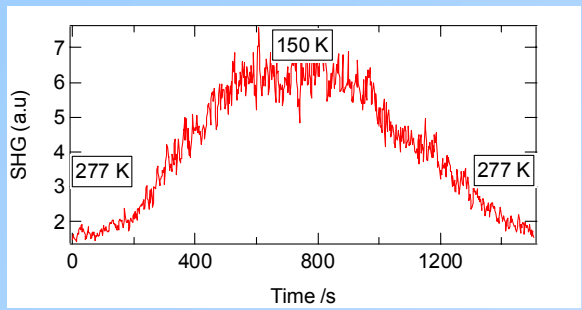
Absorption spectra of a polycrystalline film few μm



SHG switching at 1907 nm

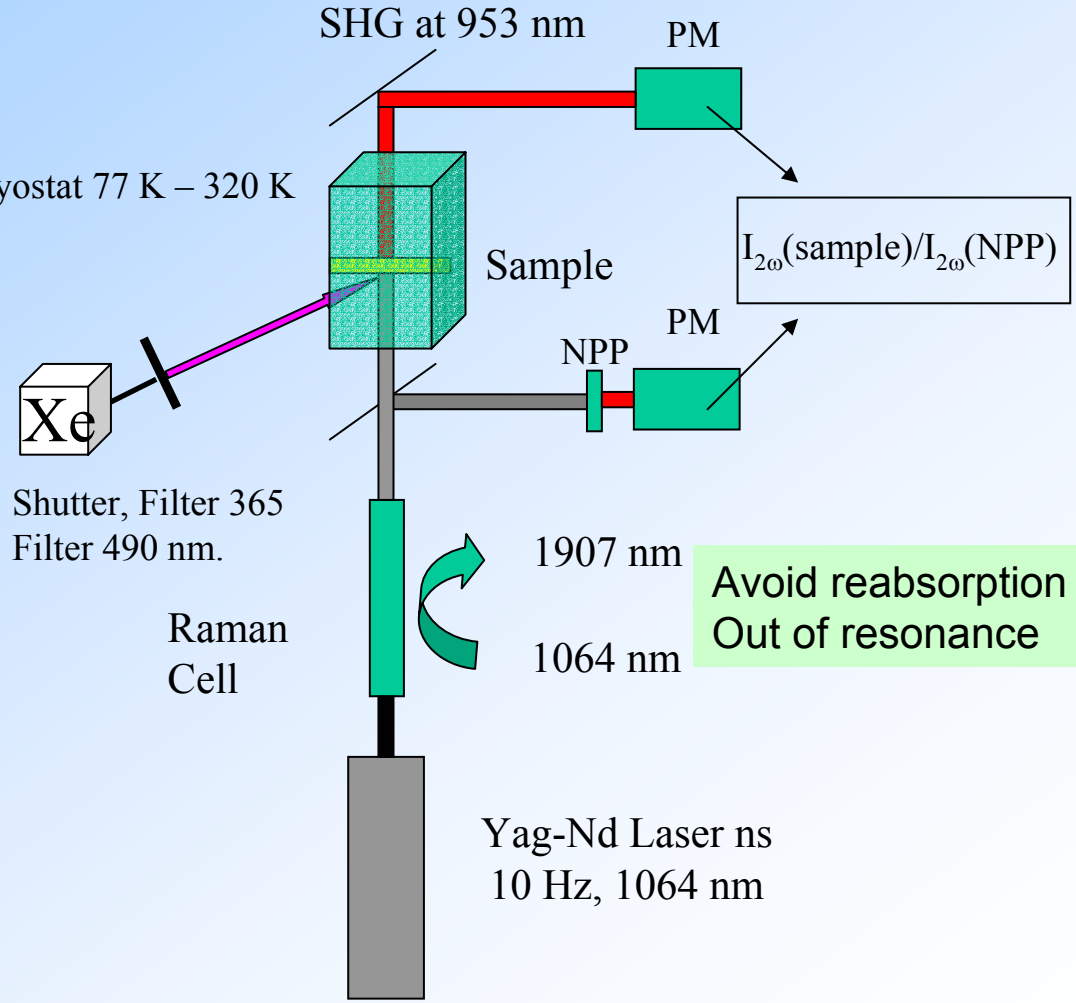
Thermochromic compound 2-P

Sample : polycrystalline film, few μm

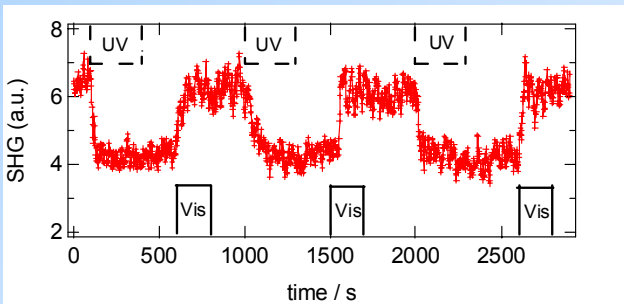


SHG (2-P) vs SHG (Urea) at RT: 100

Switching response speed: 500 s



Photochromic compound 4-P



SHG (4-P) vs SHG (Urea): 3

Switching response speed < 2s

Photoproduct half life: 460 days

Slowest back reaction for anil photochromes:

Quasi bistable system

Photoswitching: Fast switching ?

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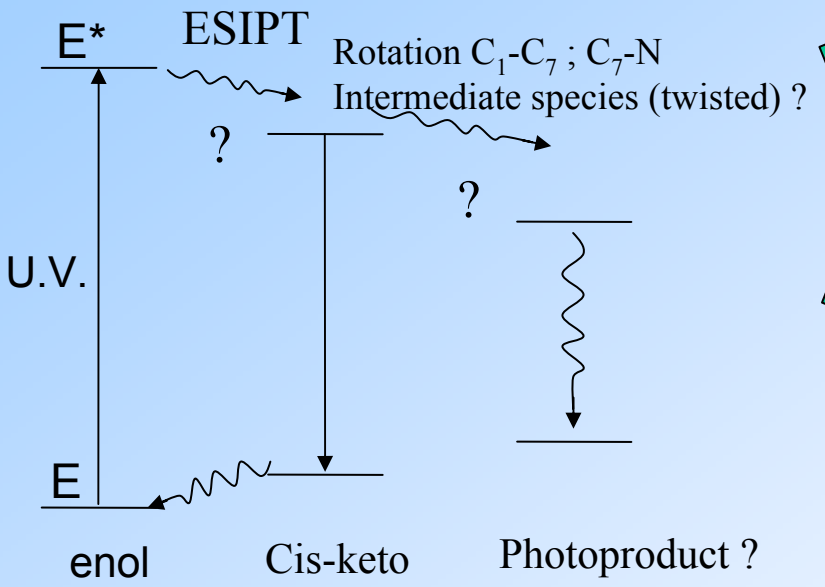
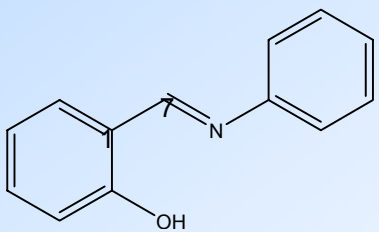
Dynamics of the photochromic reaction





Mitra & Tamai, PCCP 2003
Ziolek et al, PCCP 2004

Solution

Solution :

1. ESIPT : 100 fs
2. Photoproduct : $\tau = 10$ ps

Intermediate species ?

Solid State

?

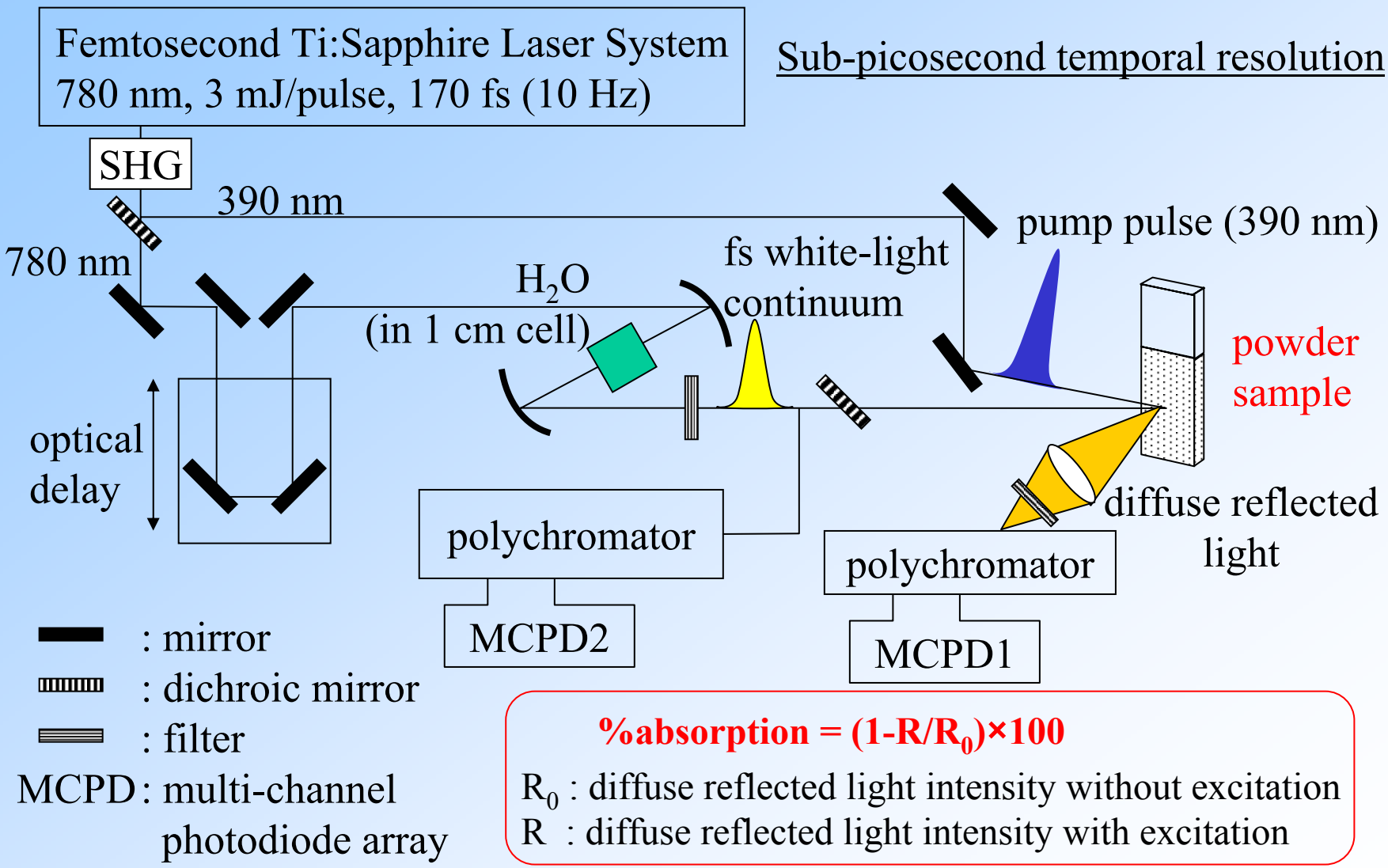
Compare photochromic dynamics reaction of 4-P in solution and in solid state

Solid state :

1. ESIPT : ?
2. Photoproduct : ?
3. Intermediate species ?

Limit of the SHG Switching response speed

Femtosecond Diffuse Reflectance Spectroscopy



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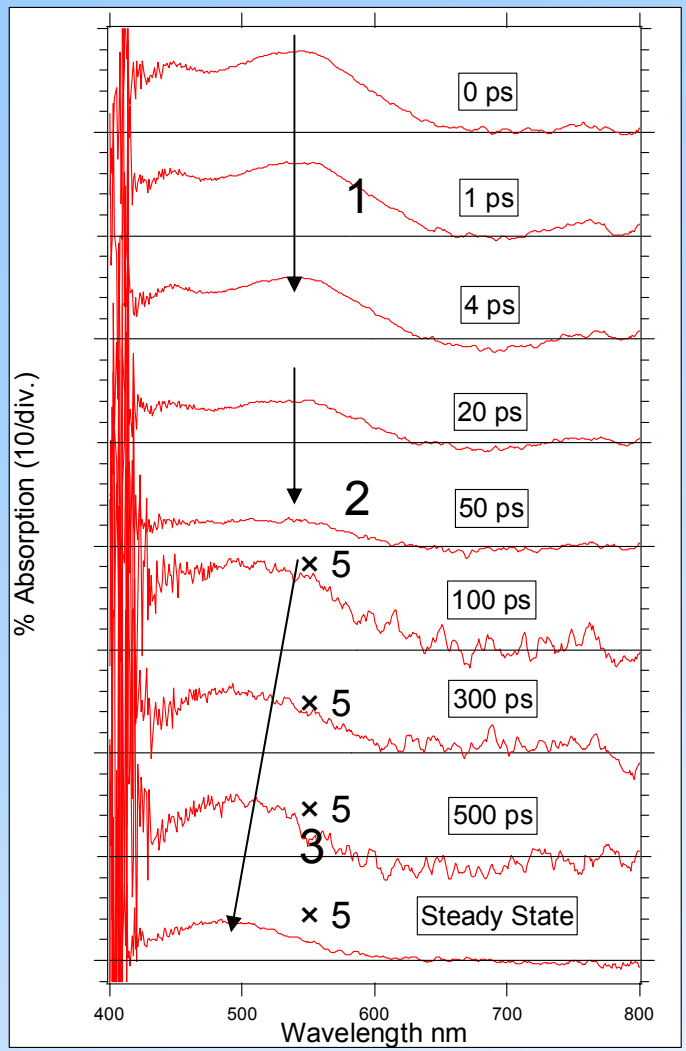
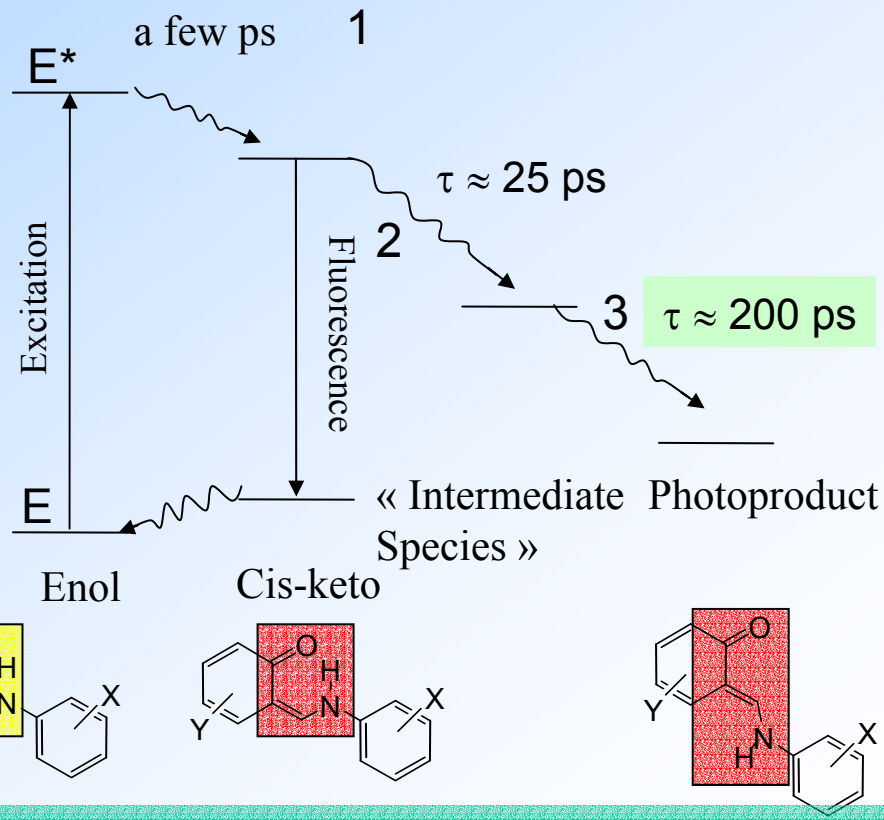
Dept. of Applied Physics, Osaka University

4-P powder sample



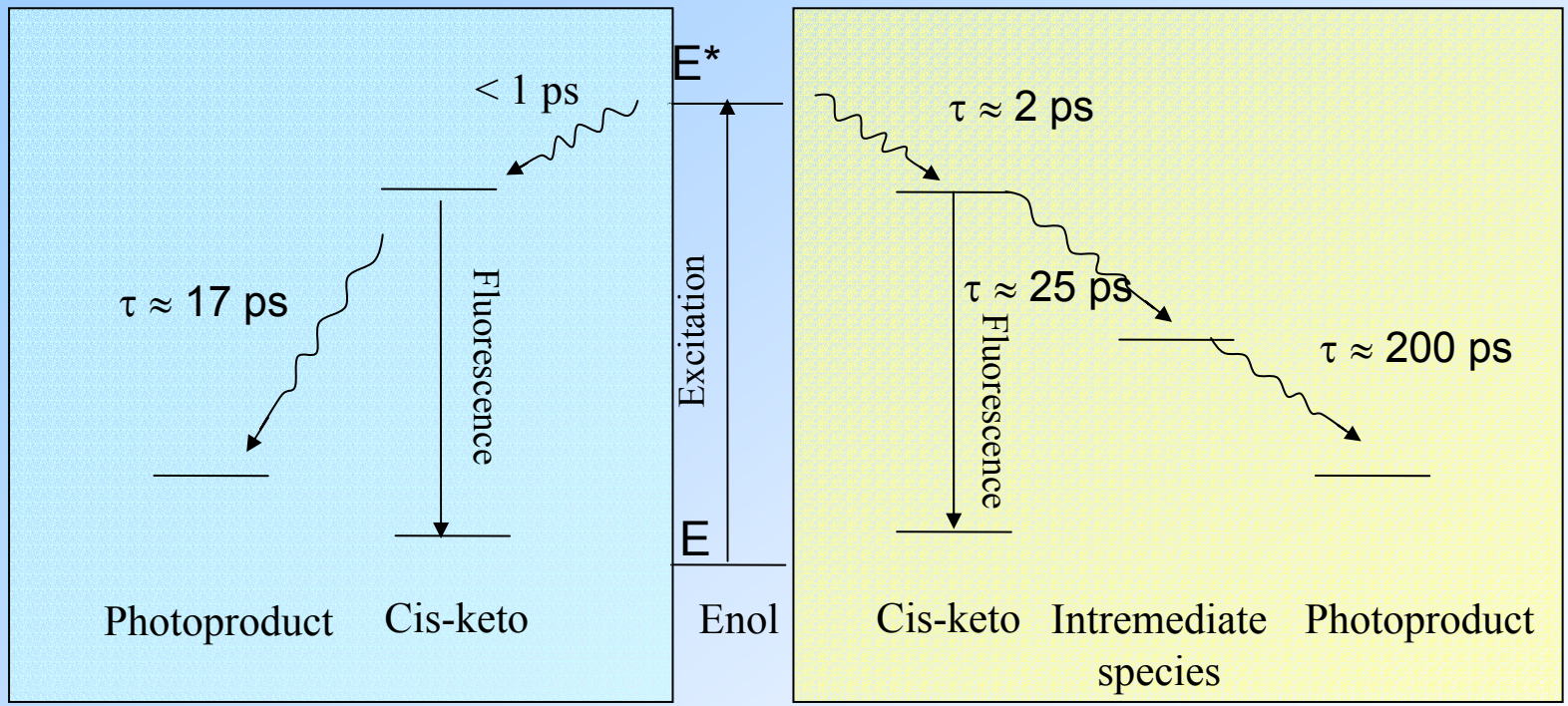
Transient absorption : single shot, Fluence 3 mJ/cm^2

Photochromic dynamics reaction of 4-P in solution and in solid state are compared to attribute each band



1. Two absorption bands: three-exponential decay with lifetimes of 2, 25 and 200 ps
2. Stimulated emission: Increasing in a few ps and single-exponential decay of a 25 ps lifetime
3. After 100 ps, broad absorption around 500 nm; temporal peak shifts to the absorption peak of the photoproduct (480 nm)

Photoreaction dynamics of 4-P



- **Similar photochromic reaction occurs in solid state and in solution**
- **Some intermediate species were observed before the long-lived photoproduct in solid state**
- **Maximum response speed is in an order of 10^{10} s^{-1}**

Outline

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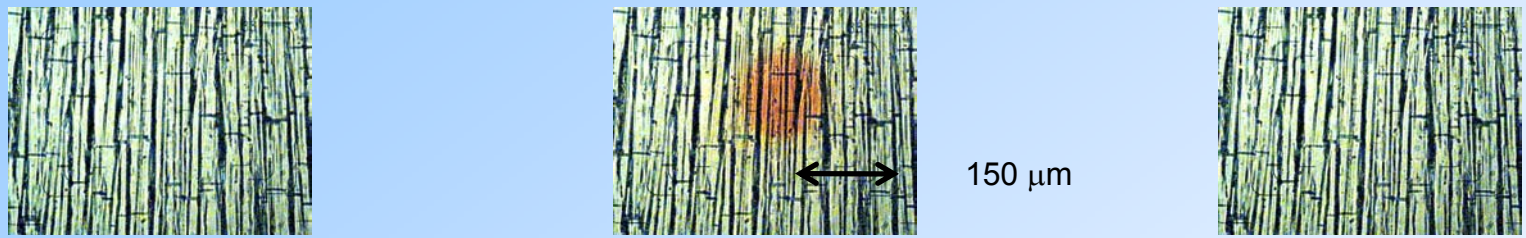
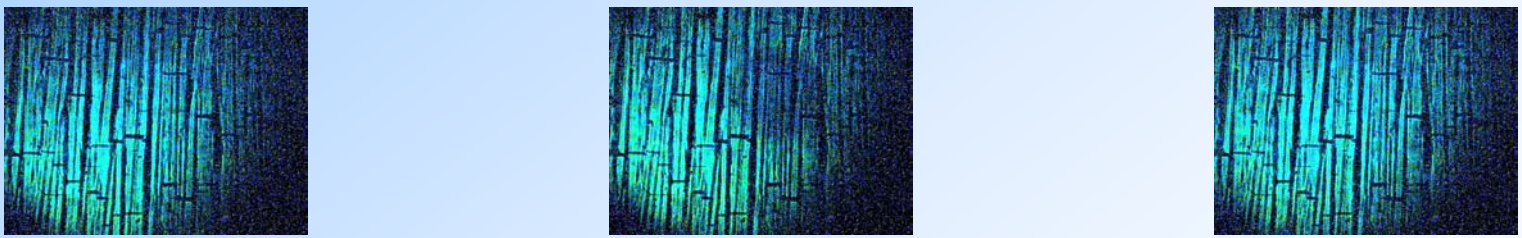
UNDERSTANDING THE MODULATION

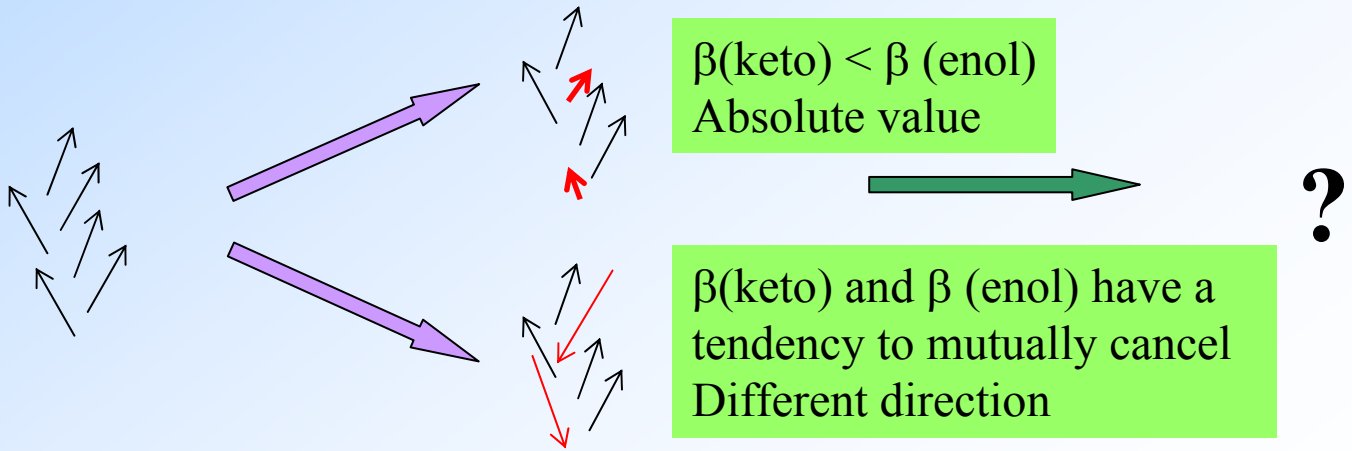
Visible light images using white-light continuum



Enol form → 405 nm (2 min, 75 mW/cm²) → **Photoproduct** → 520 nm (2 min, 270 mW/cm²) → **Enol form**

SHG images using IR continuum





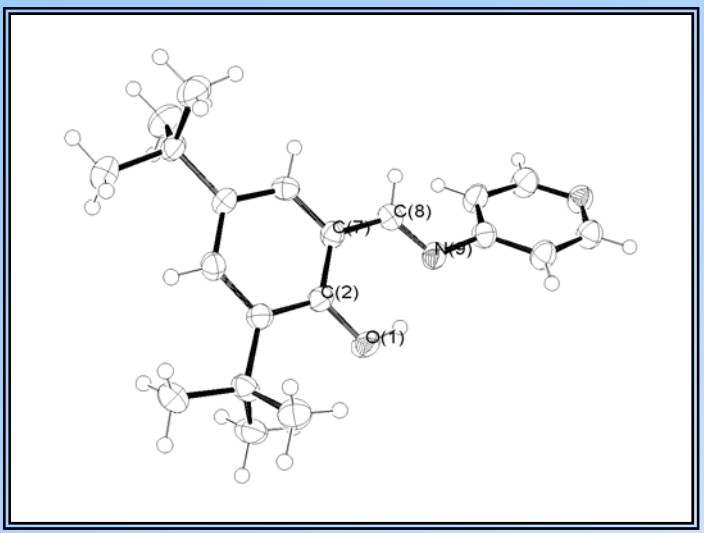
β(keto) < β (enol)
Absolute value

β(keto) and β (enol) have a tendency to mutually cancel
Different direction

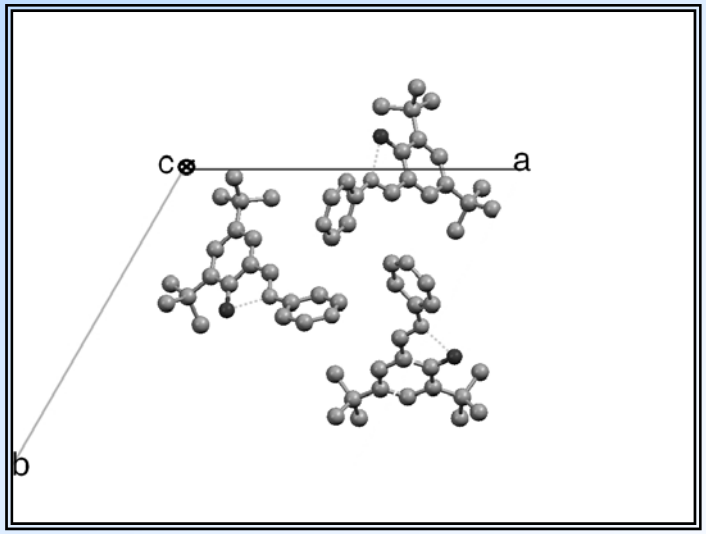
?

X-ray study on single crystal

4-P



Structure: $P3_2$
Needle, helicoidal arrangement around the c axis



	(a) before irradiation	(b) after UV irradiation	(c) after visible irradiation
a /Å	**15.976(2)**	**15.963(4)**	**15.977(2)**
b /Å	**15.977(2)**	**15.966(3)**	**15.977(2)**
c /Å	**6.027(1)**	**6.020(1)**	**6.027(1)**

- Reversible structure change
- Keto structure not resolved Because low yield of enol to keto conversion

CONCLUSION

1 Crystalline salicylidene aniline can be used as a SHG photo/thermo-commutator

2 Photochromic dynamics for anils (4-P) in crystalline state :
- Similar photochromic reaction occurs in solid state and in solution
- Some intermediate species were observed before the long-lived photoproduct in solid state

3 Obtention of a bi-stable SHG photocommutator which has a maximum response speed in an order of 10^{10} s^{-1}

4 Reversible structure change demonstrated by X-ray

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