

シアニン色素の 多光子退色反応機構の解明



神戸大学

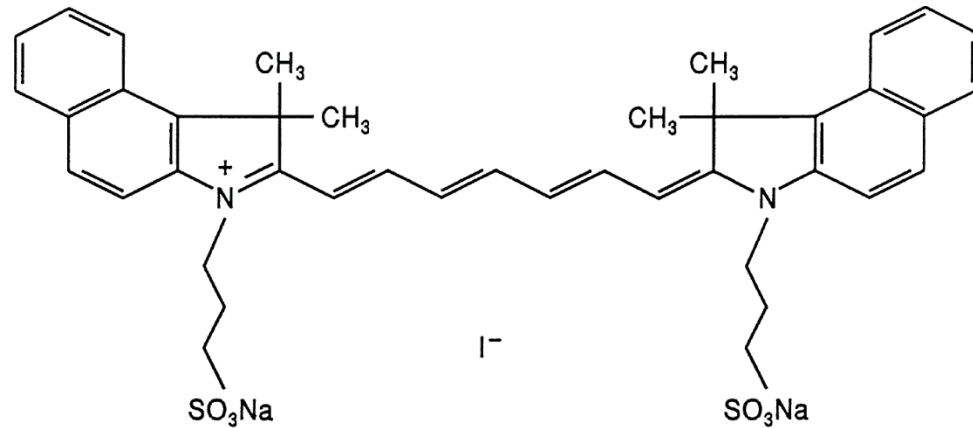
冬木正紀、和田昭英

Cyanine dye

Photosensitive pigment

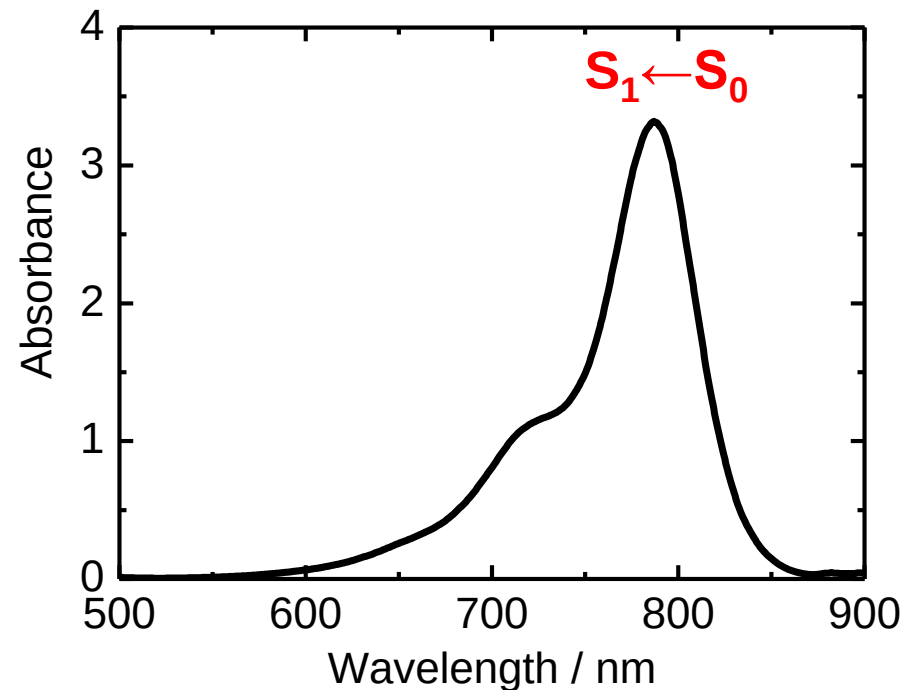
Intensive studies for a century

! **Geometric structure**



ICG (indocyanine green)

! **Electronic structure**



Low quantum yield of photoreaction from S₁: $\sim 10^{-5}$ [Gratz et al. (1999)]

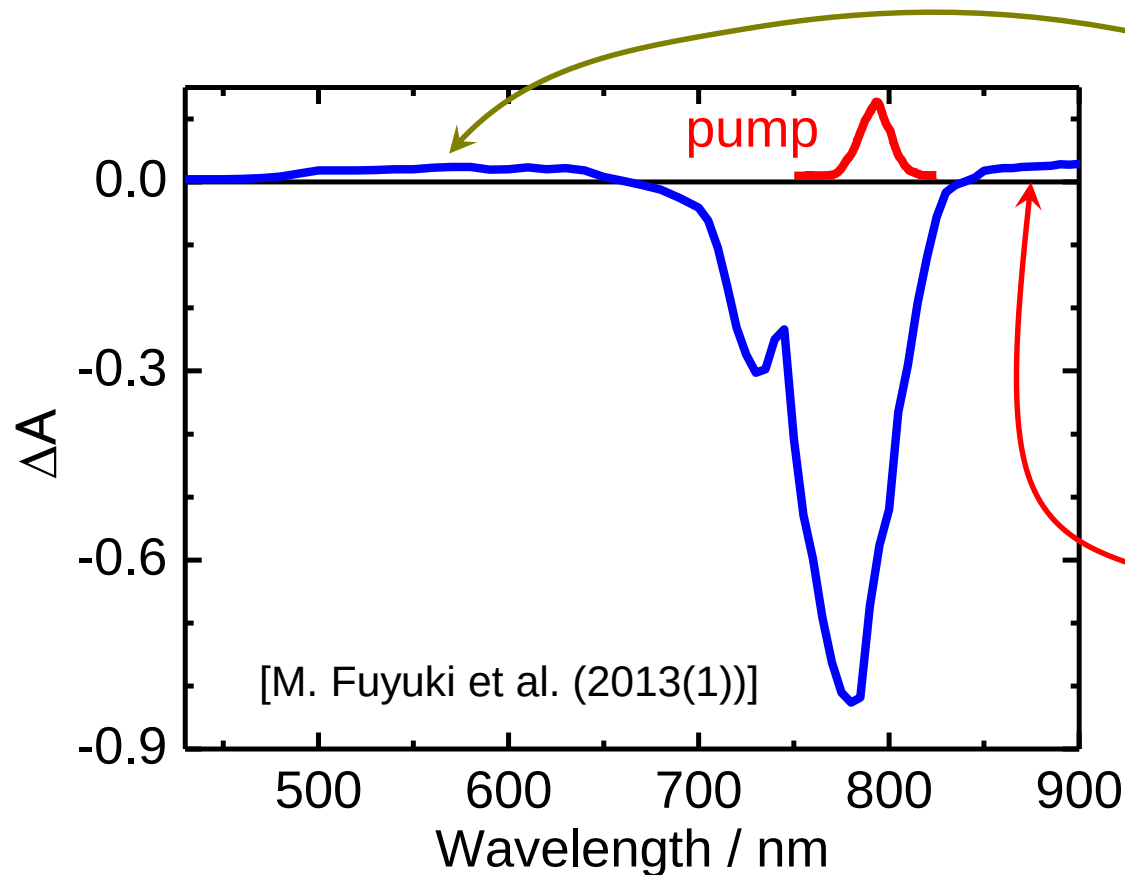
➡ photodetector for specific cancers [Sugie et al. (2010)]

Multiphoton reactions under fs irradiation

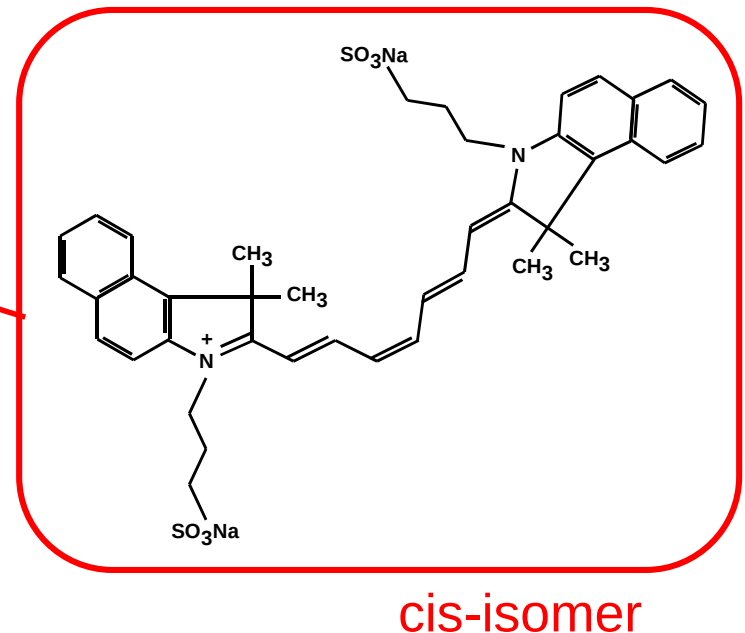
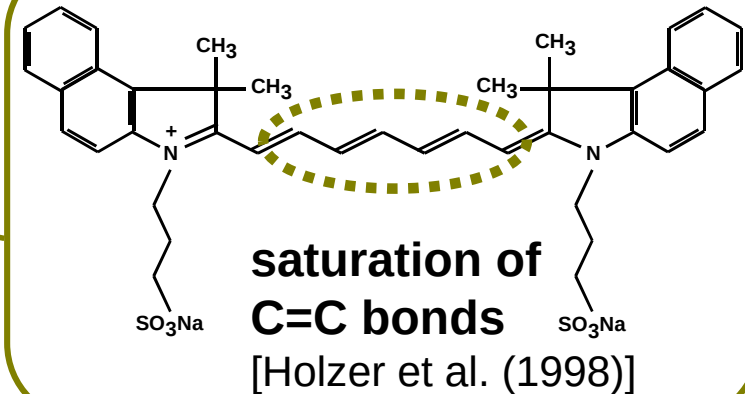
Transient absorption

Pump pulse: 800 nm, 70 fs, 40 mJ/cm²

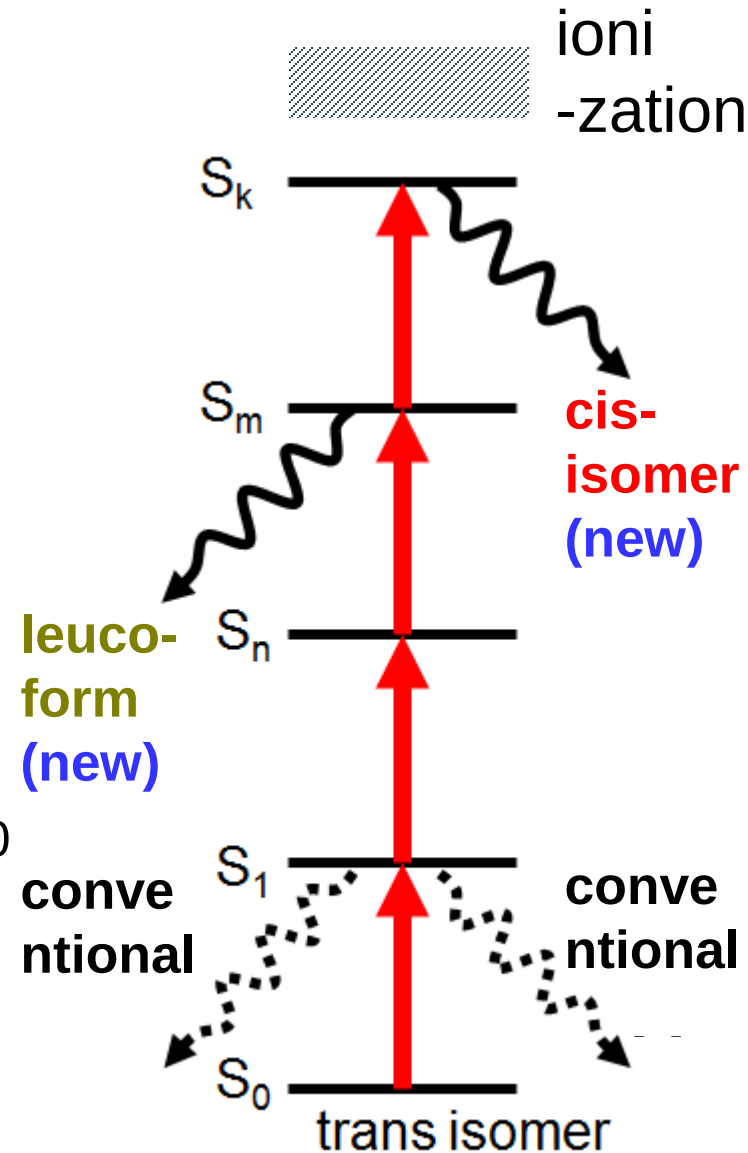
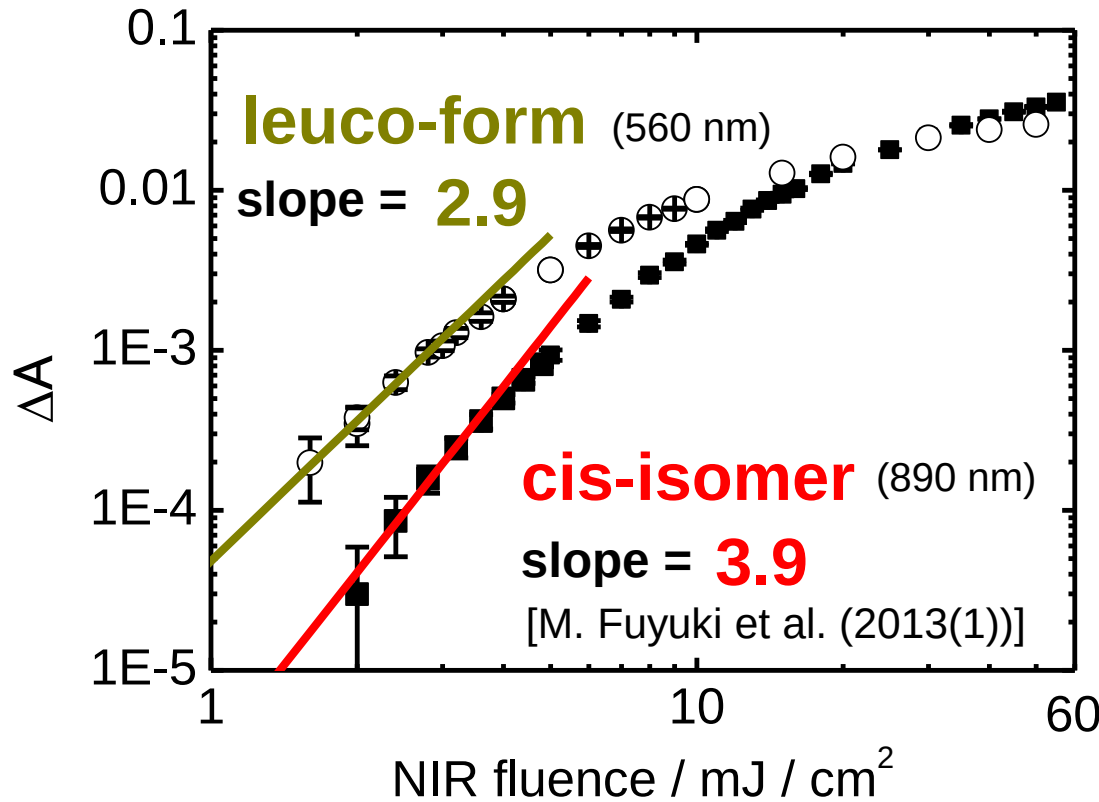
Pump-probe delay: 2.5 ns



leuco-form



NIR pump fluence dependence

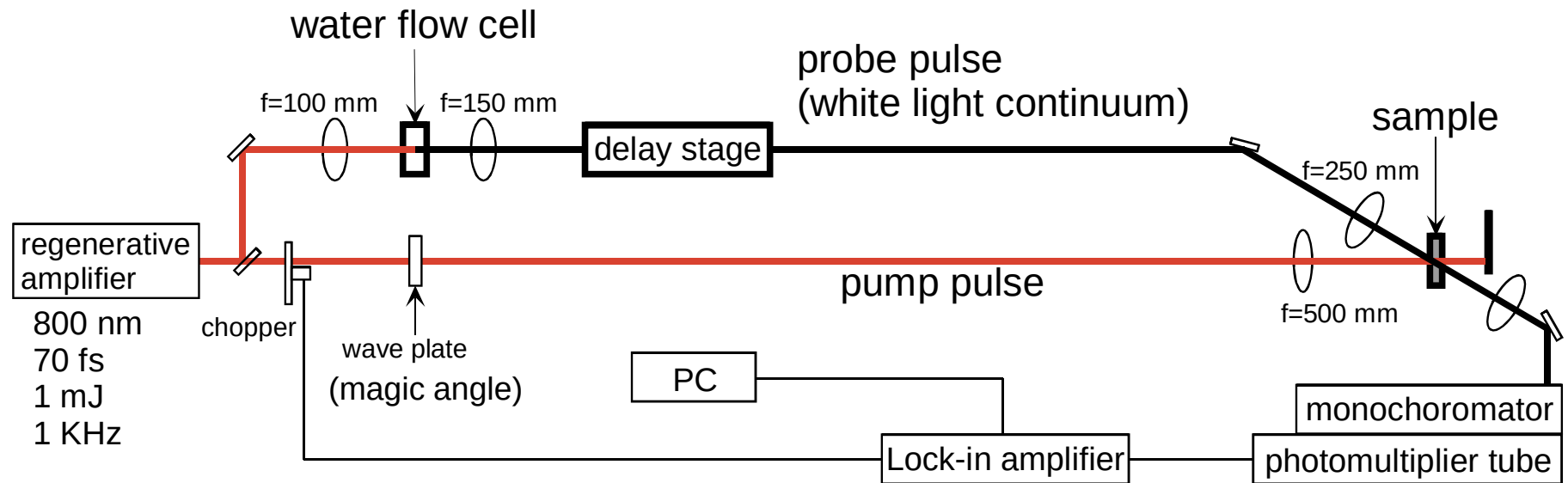


one-photon process:
buried in **multiphoton** process

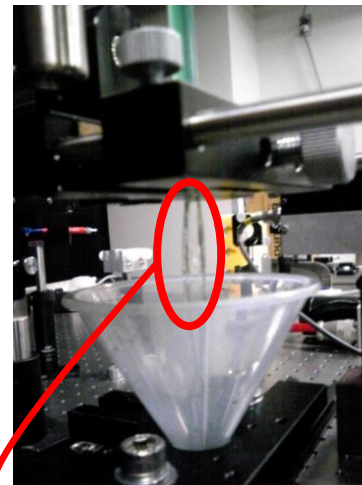
➡ Quantum yield: higher electronic state $\gg S_1$

Today's topic: Reaction dynamics of photodegradation

Experimental setup (transient absorption)



Probe pulse



Sample jet

Cyanine dye in ethanol:
0.6 mM

Thickness of jet:
0.2 mm

Spot size:
pump 0.2 mm
probe 0.1 mm

[Fuyuki et al. 2010, 2011, 2013]

Transient absorption spectra

1 pump – 1 probe measurement

NIR pump fluence = 50 mJ/cm²

Excited state absorption (ESA) [Meyer et al. (1998)]

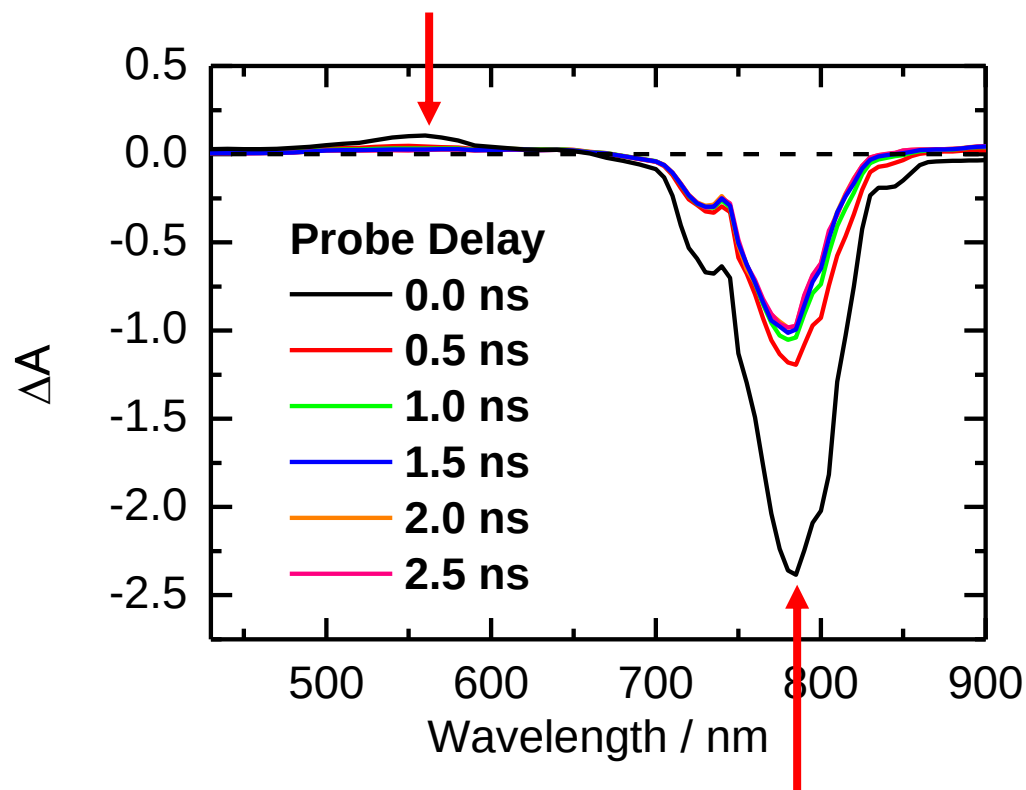
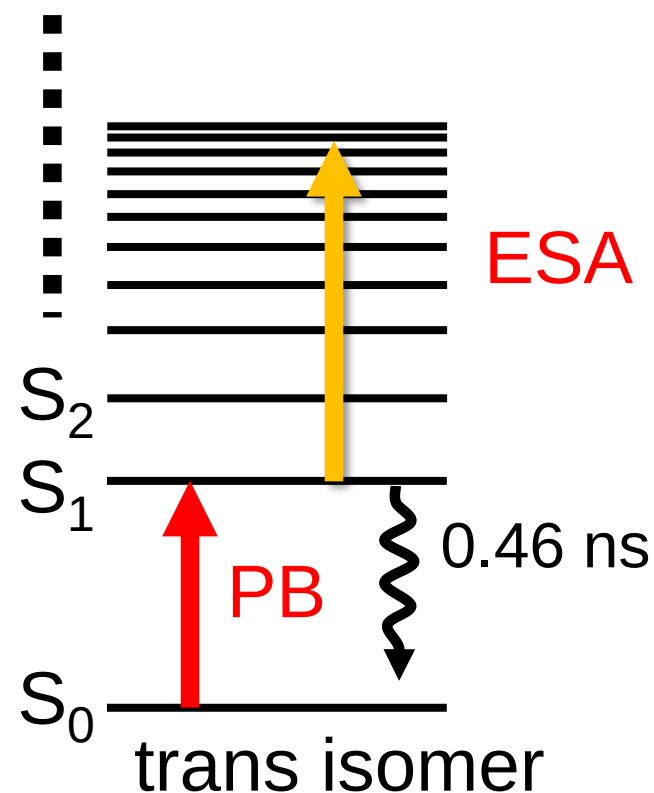
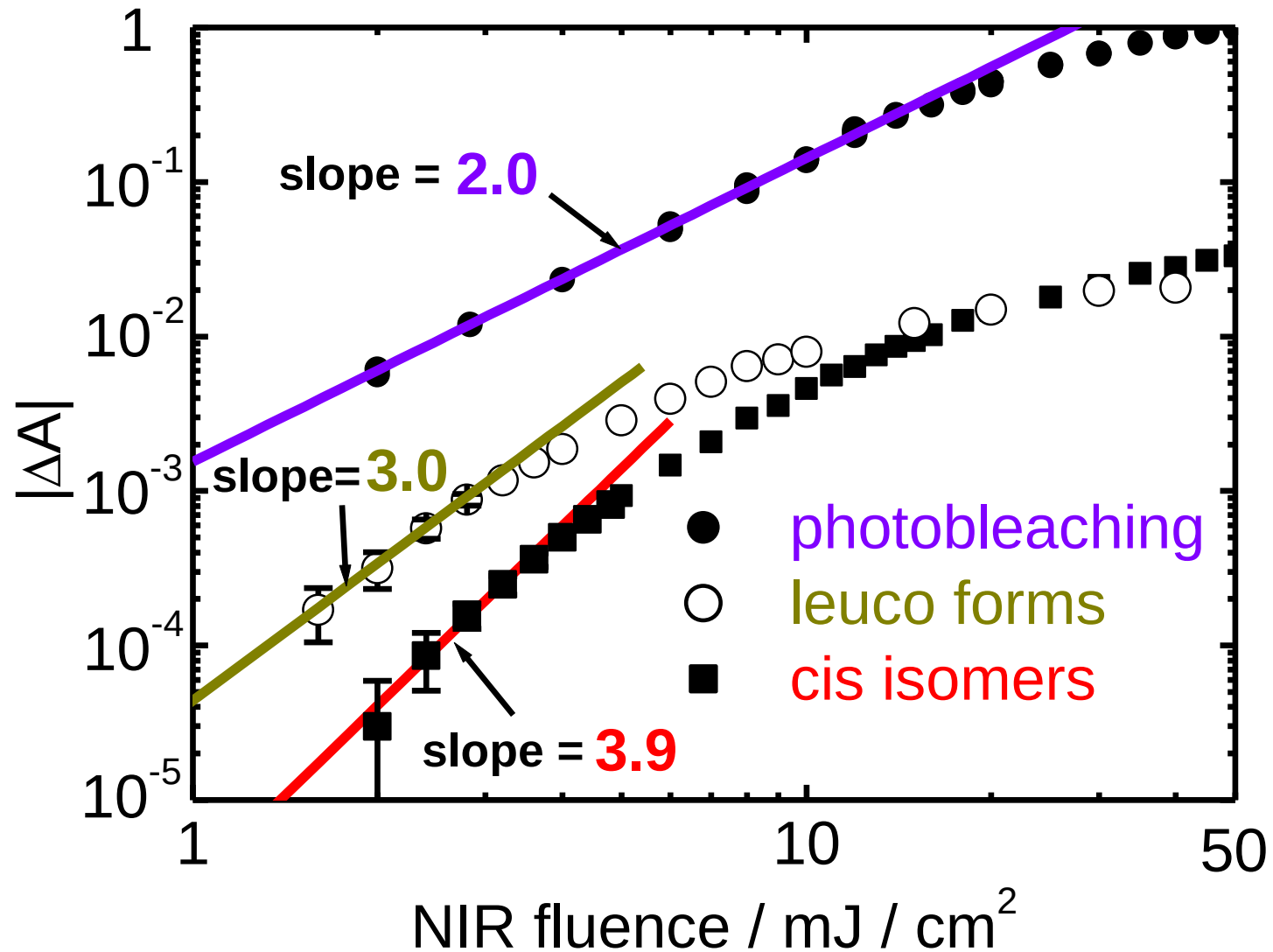


Photo-bleaching (PB) of trans-isomer
[Philip et al. (1996)]



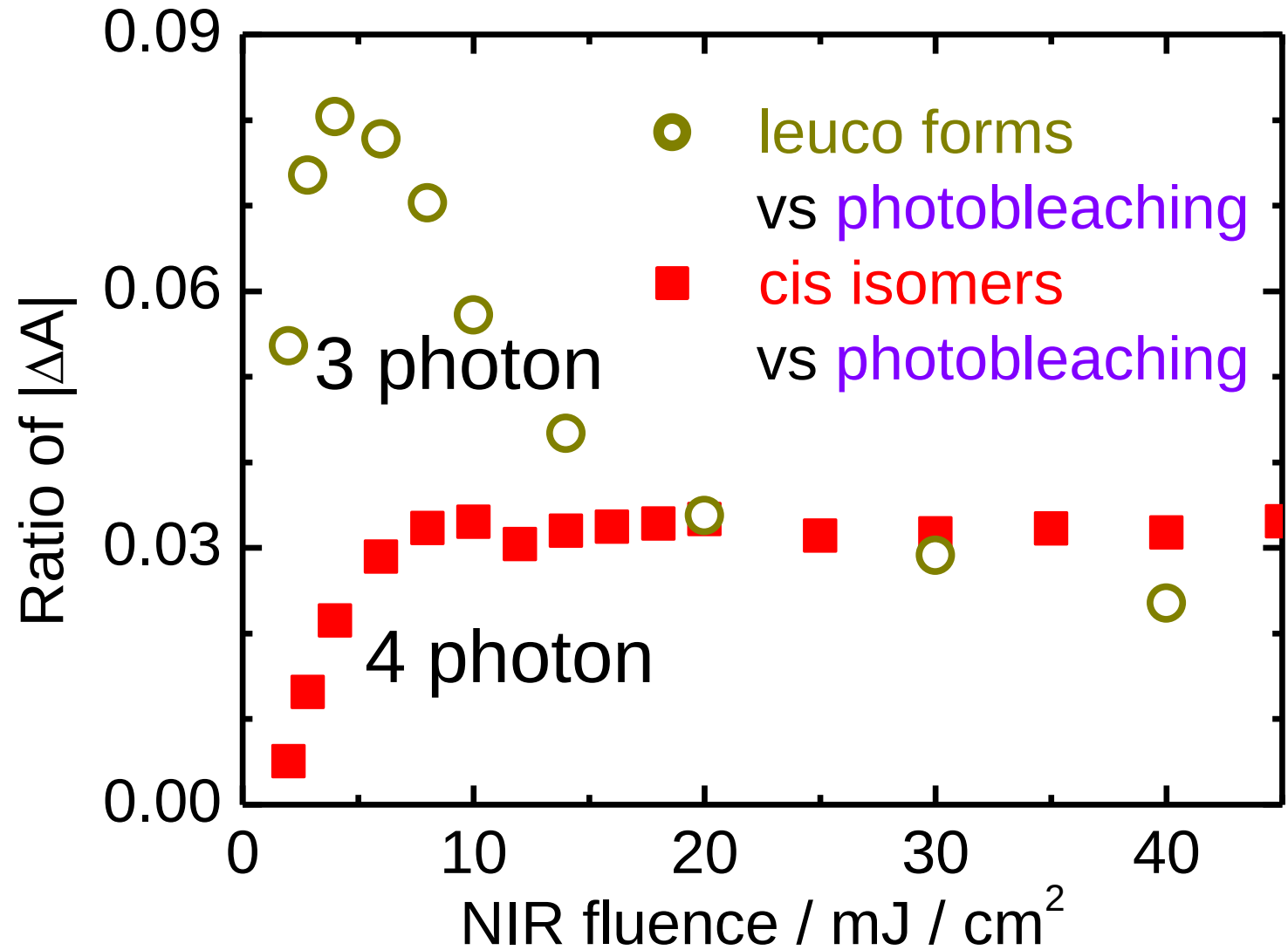
[Ashworth et al. (1996)]

NIR pump fluence dependence



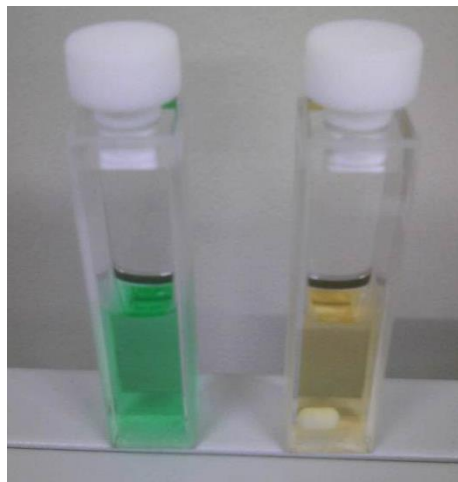
Main photodegraded species were ICG fragments.

Photoproducts vs photobleaching

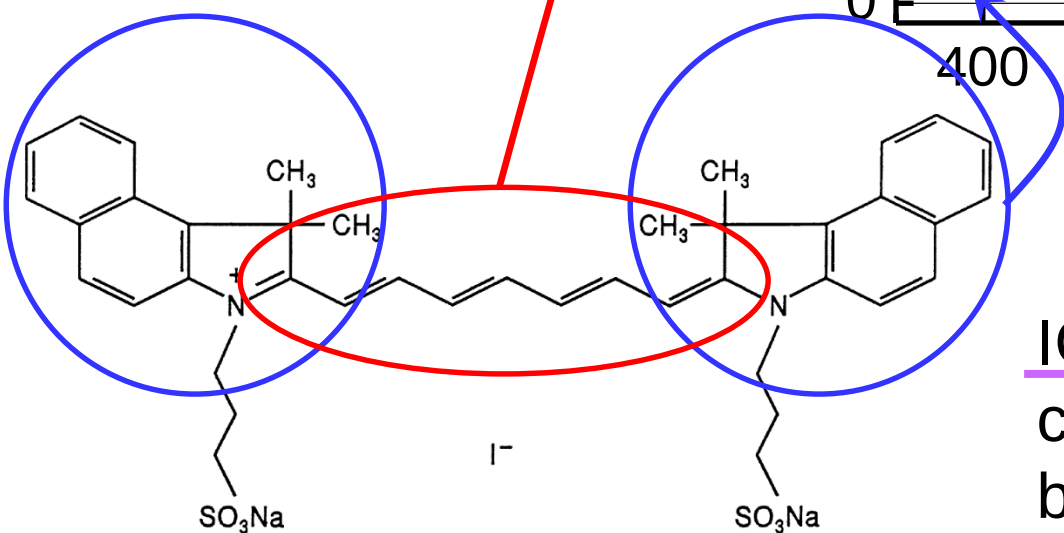
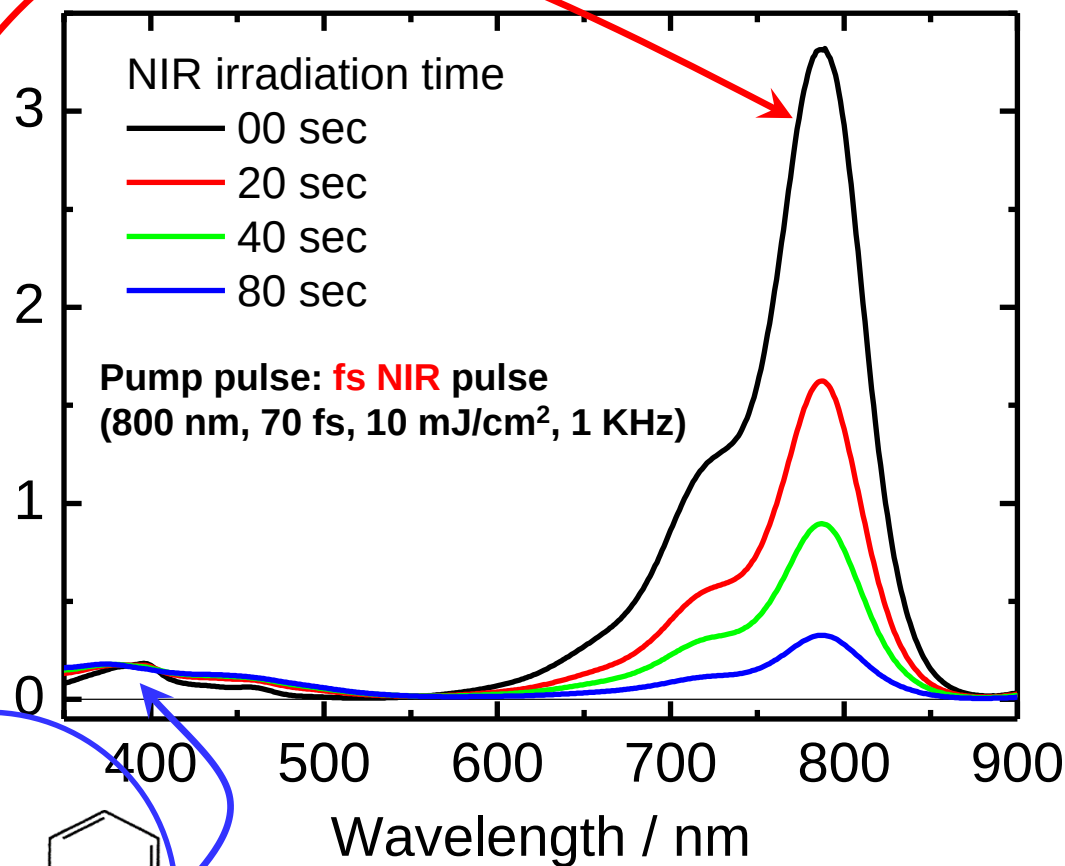


Optical order of photodegradation changed from 2 to 4.

Steady state spectra

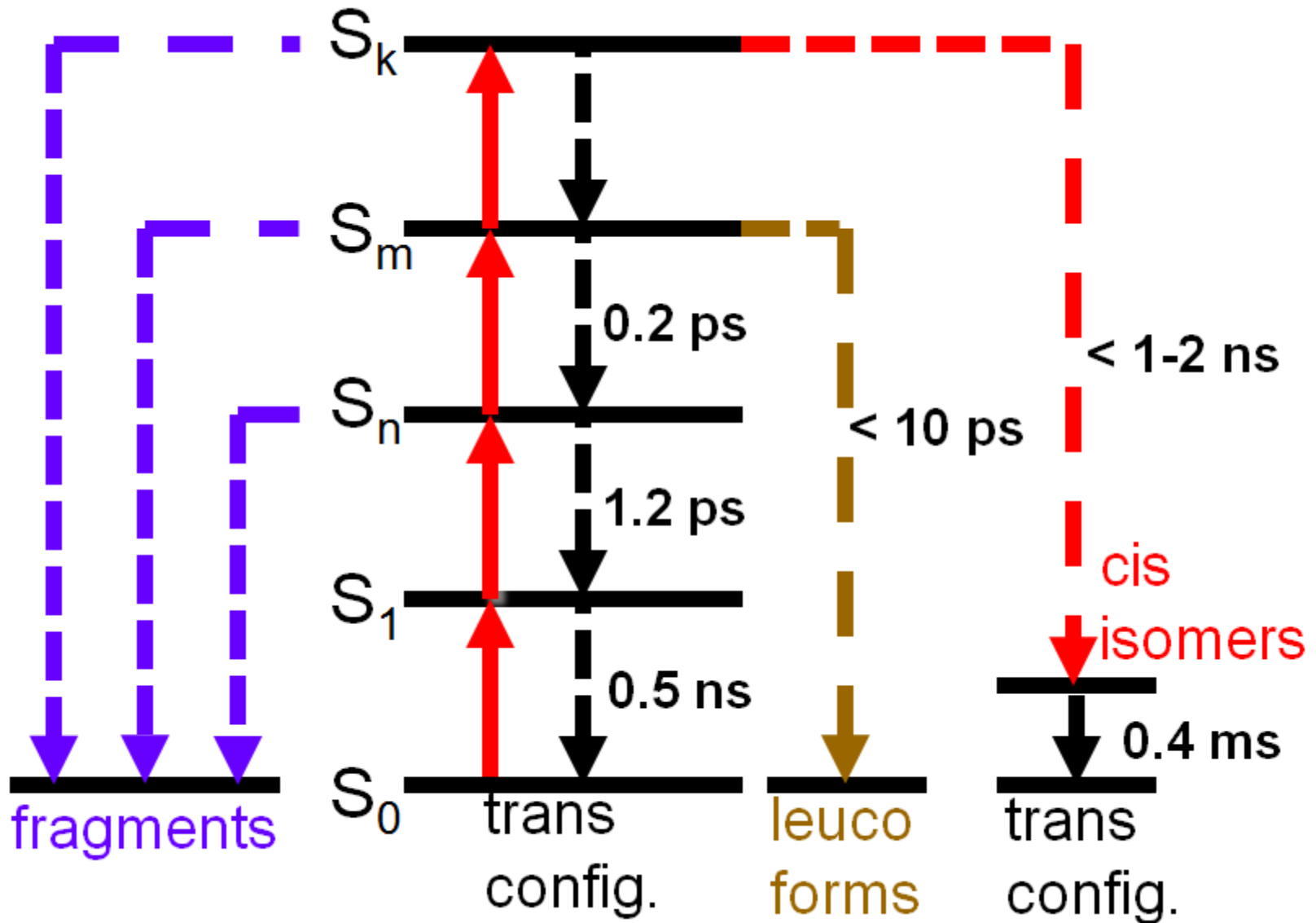


Absorbance



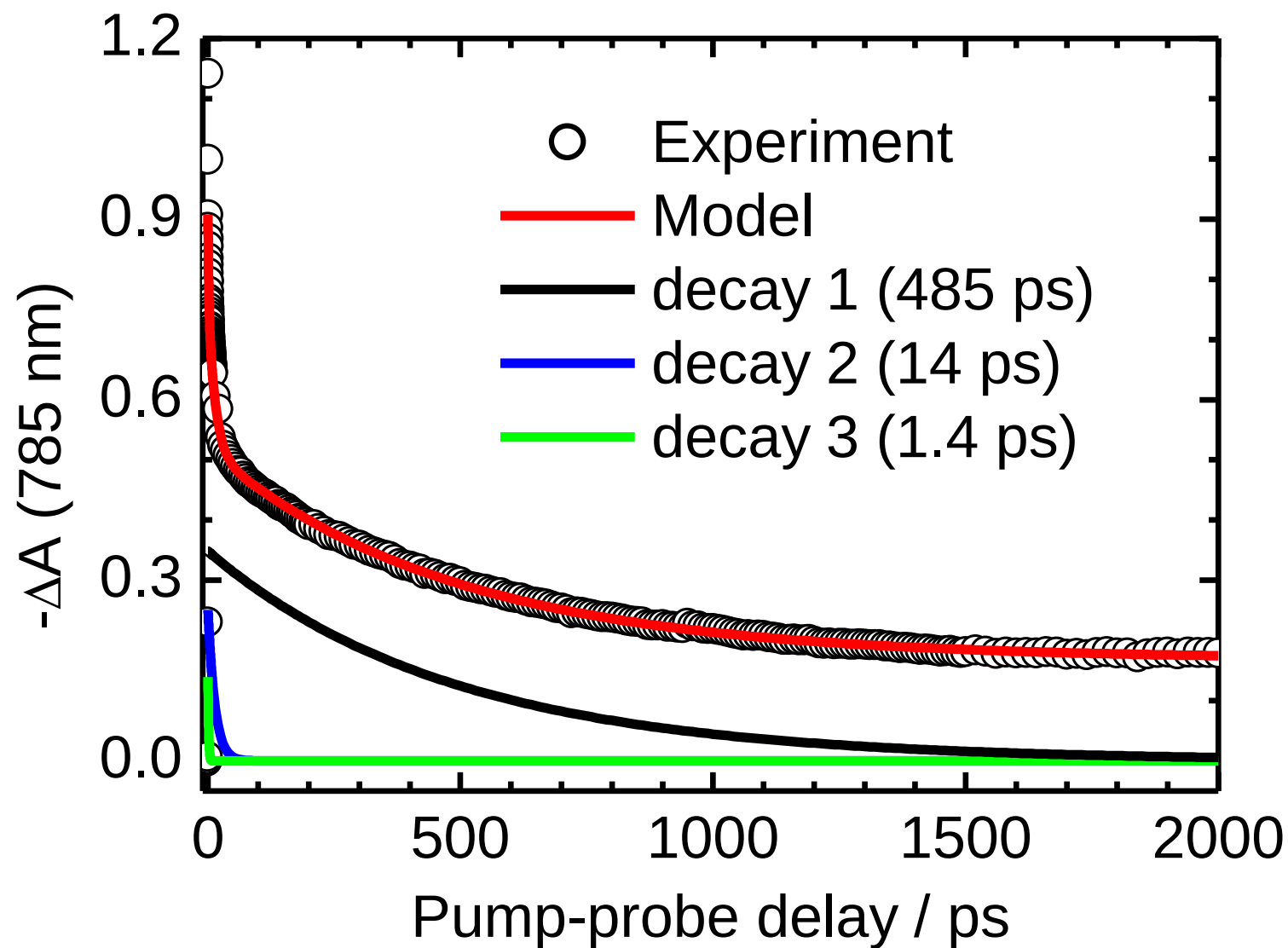
ICG fragment
cleavage of carbon double
bonding chain

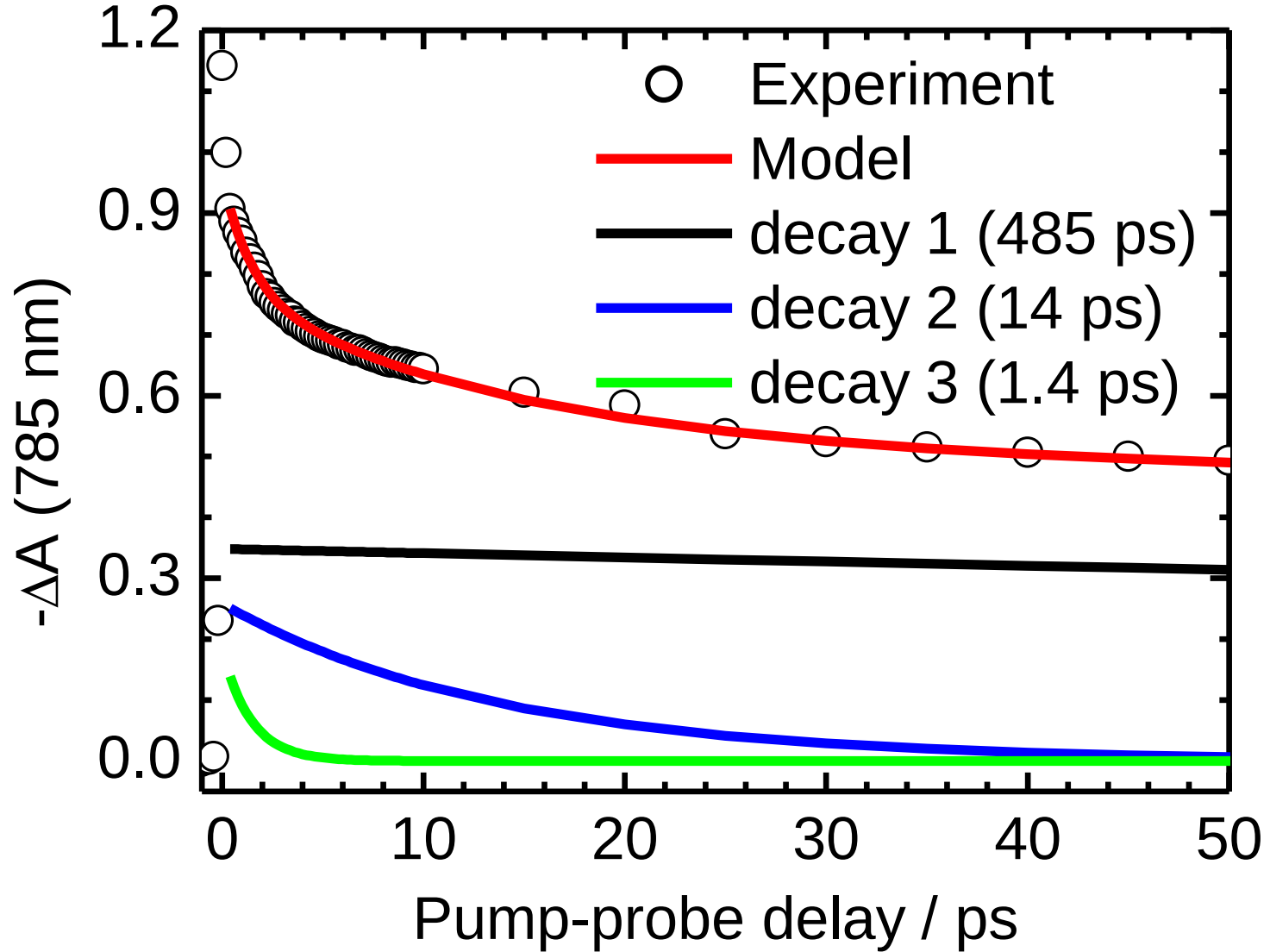
Multiphoton reaction paths of ICG/ethanol



[Fuyuki et al. (2010-2013), Ashworth et al. (1996), Gratz et al. (1999)]

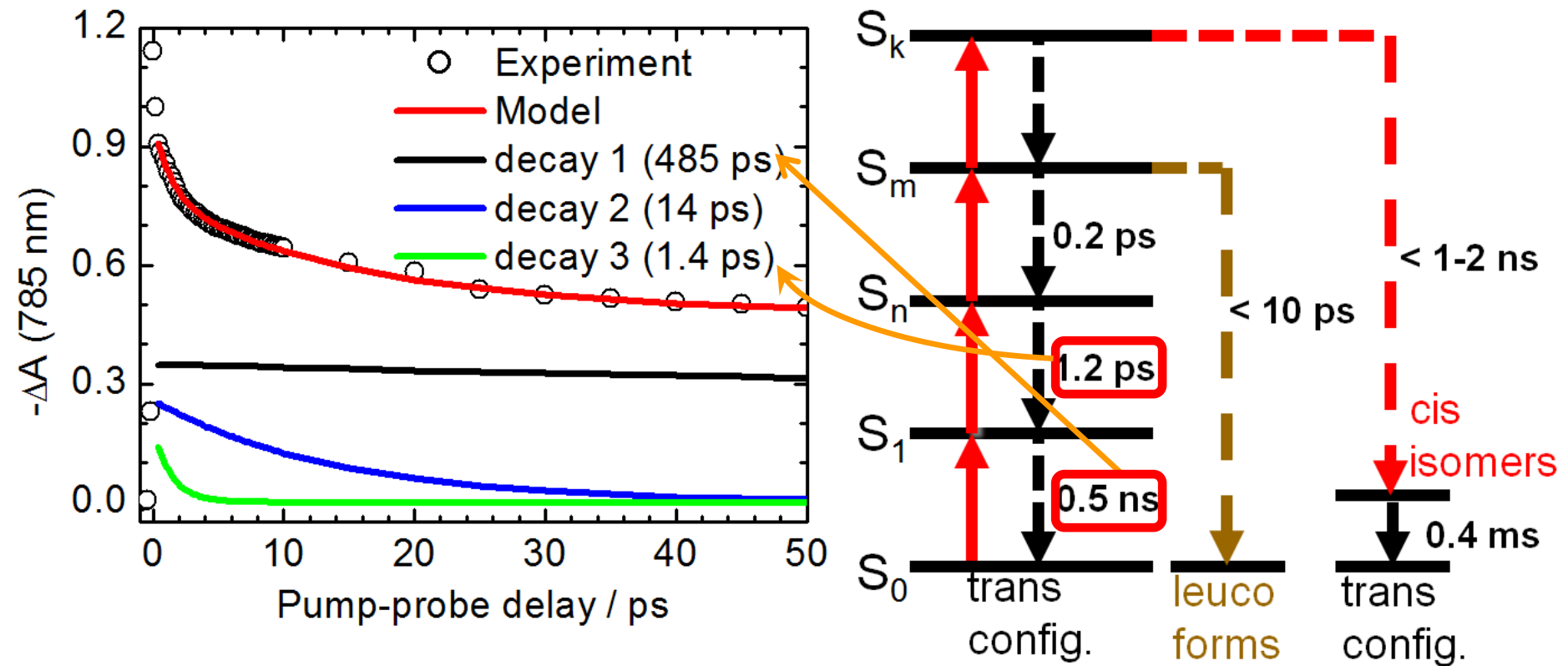
Temporal profile of photobleaching





The profile includes 3 exponential decay components.

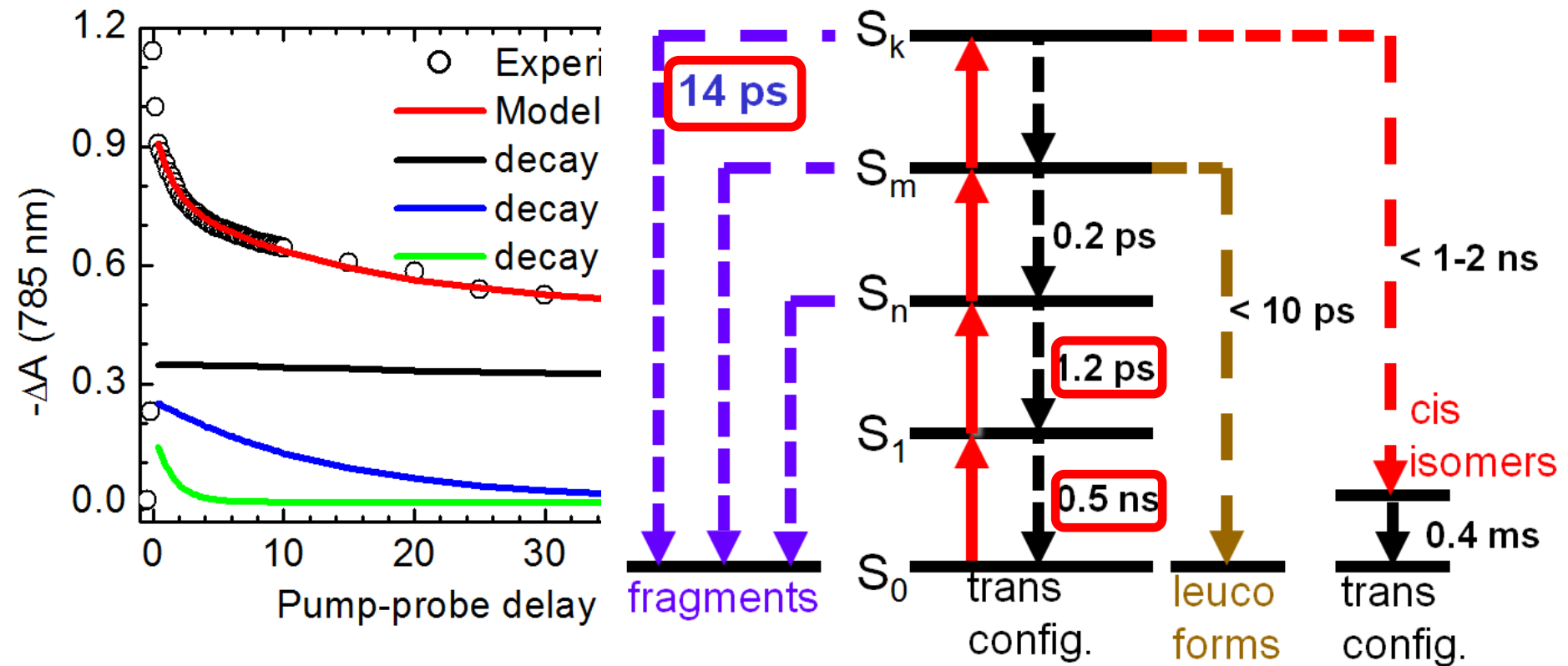
Assignment



Decay components 1 and 3 correspond to relaxations in trans singlet system.

14ps time constant corresponds to photofragmentation.

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Conclusions

fs超短パルス照射下におけるICGの退色反応ダイナミクスを時間分解過渡吸収測定により研究した。

- (1) 10 mJ/cm²以下のNIRパルス照射下では、光退色物質の量はパルス強度の2乗に比例した。
- (2) 10 mJ/cm²以上の強度領域では、強度の増加に伴い、光退色物質に対するロイコ体の量比は減少したが、シス体の生成量比はほぼ一定であった。
- (3) パルス強度の増加に伴い、光分解を引き起こすNIR多光子励起の光子数が、2から4へと増加したことを示唆している。
- (4) 主な光退色物質は炭素共役鎖が切断されたフラグメントである。
- (5) 光ブリーチングの時間プロファイルは3つの指数減衰成分の和により再現された。
- (6) 14 psの成分が多光子励起光分解反応ダイナミクスを反映していると同定した。

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