

# Femtosecond Laser Spectroscopy and Singlet Fission

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## Introduction

Singlet exciton fission or singlet fission (SF) is a process in which a singlet excited molecule, usually in a densely packed organic solid or in a polymer, shares its energy with a neighboring molecule in its electronic ground state, both molecules forming a pair of triplet states in a spin allowed process. SF was first proposed in 1965 to explain the delayed fluorescence in anthracene crystal [1]. It was further proven by the magnetic field effect on tetracene crystal [2,3]. Interest towards SF rises in recent years due to its potential applications in photovoltaics. SF may dramatically increase efficiency of the solar cells.

SF is an analogue of the Multiple-Exciton Generation (MEG) in the organic materials. A comprehensive review on SF is given by Smith and Michl [4,5].

Femtosecond laser spectroscopy is a powerful method for studying the kinetics of SF. Transient absorption allows monitoring with femtosecond time resolution decay of the excited singlet state and corresponding rise of the triplet state, as well as existence of intermediate states. Thus the rate constant of the singlet fission can be determined and the mechanism of SF can be resolved.

## Singlet fission: rate constant

Transient absorption spectra in rubrene single crystal were measured under 500 nm excitation. Two positive transient bands with maxima at 444 and 510 nm were attributed to singlet-singlet and triplet-triplet absorption, respectively [6]. Transient band at 444 nm decays and at 510 nm develops biexponentially:  $\tau_1=2.3$  ps,  $\tau_2=23$  ps. An isosbestic point at 455 nm is an indication of a single transformation process, in which singlet states are converted into triplet states ( $S_1 \rightarrow TT$ ). The triplet states form with two rate constants,  $k_1=4.3 \times 10^{11} \text{ s}^{-1}$  and  $k_2=4.3 \times 10^{10} \text{ s}^{-1}$ , which correspond to the direct fission from the upper vibrational states of  $S_1$  and thermally activated fission from the relaxed  $S_1$ , respectively.

## Efficiency of singlet fission

SF is a spin allowed highly efficient process; it can reach 200% [7,8]. Efficiency can be determined from the quenching of the excited state lifetime in crystals compared with the solution; in rubrene single crystal was obtained 99.99% efficiency of SF, which corresponds to triplet formation with 199.98% [6,9]. Moreover, SF is a linear optical process, i.e. low intensity sunlight may be used for this purpose.

## Singlet fission: temperature dependence

Apart from the transient absorption spectroscopy, time resolved fluorescence (up-conversion and time-correlated single photon counting) also provides a direct way for studying SF. For example, in

rubrene single crystal SF is a thermally activated reaction, therefore it is temperature dependent. The quenching of fluorescence is mainly due to SF, and the fluorescence lifetime reflects the rate of SF.

It was demonstrated that at low temperatures 80K, SF in rubrene can be fully suppressed [9]. This was however not observed in tetracene [10].

## Singlet fission from upper vibrational states of $S_1$

Excitation wavelengths of 400, 500 and 550 nm were used in order to excite different vibrational states of the first excited singlet state  $S_1$  in rubrene crystal. SF rate was found to be pump wavelength dependent [11]. The triplet states form faster with decreasing pump wavelength (i.e., increasing pump photon energy). It points out that singlet fission can proceed directly from the upper vibrational states of  $S_1$ . Singlet fission is faster from the upper excited states (2.3 ps) since it is exoergic.

## Singlet fission from upper excited singlet states $S_N$

Singlet fission was observed to proceed directly from upper excited singlet states  $S_N$ , after excitation with 250 nm [11]. It can be considered as violation of Kasha rule (and corresponding analogue in spectroscopy: Vavilov law), which states that all photophysical and photochemical processes necessarily proceed from the lowest excited electronic states  $S_1$  or  $T_1$ . The relation between the direct singlet fission rate  $\ln k_{\text{fiss}}$  versus the pump photon energy undergoes a linear increase, i.e. follows the Arrhenius law.

## Singlet fission: two-photon excitation

Two-photon excited state relaxation processes in rubrene single crystal were studied under excitation with  $\approx 750$  nm, i.e. no linear absorption [11]. Although the two-photon excited states have different symmetries relative to the one-photon excited states, SF was still observed. The rate of SF was  $k=6 \times 10^{11} \text{ s}^{-1}$ .

Thus with two photons of 1.6 eV two triplet states with energies of 1.14 eV can be populated. Hence via SF triplet states can be formed not only with high quantum, but also high energy conversion efficiency. Note that the quantum yield of two-photon process is constant and does not depend on the intensity of exciting light.

## Singlet fission: consecutive two-quantum (two-step) excitation

SF can proceed also after excitation of the high-lying excited electronic states via consecutive singlet-singlet absorption:  $S_0 \rightarrow S_1 \rightarrow S_N$ . In this case much lower radiation intensities are required compared

with the above described two-photon excitation. This was demonstrated for the organic single crystal  $\alpha$ -perylene [12].

In  $\alpha$ -perylene SF has a threshold: 3.51 eV (353 nm) [13]. The competing reaction is a fast excimer formation. In [12] efficient SF was observed under high intensity femtosecond laser excitation both below and above this threshold. Below the threshold, it is explained in terms of both two-photon absorption (simultaneous absorption of two photons) and consecutive two-quantum absorption. Due to the dimeric structure of  $\alpha$ -perylene the observed fission occur ultrafast:  $\ll 50$  fs.

## 2D coherent laser spectroscopy

Series of pentacene derivatives were studied by using ultrafast two-dimensional electronic spectroscopy in order to unravel the origin of the states involved in fission [14]. Obtained data indicate the crucial role of vibrational degrees of freedom coupled to electronic excitations that facilitate the mixing of multiexcitonic states with singlet excitons. The resulting manifold of vibronic states drives sub-100 fs fission with unity efficiency.

## Ultrafast microscopy

Direct visualization of exciton transport in single tetracene crystals using transient absorption microscopy with 200 fs time resolution and 50 nm spatial precision was reported [15]. These measurements reveal a new singlet-mediated transport mechanism for triplets, which leads to a factor of 10 enhancement in effective triplet exciton diffusion.

## Singlet fission in solution

SF was reported to yield triplet formation with 200% efficiency in solutions of bis(triisopropylsilylethynyl (TIPS)) pentacene. This is a relatively slow process (ns scale) since triplet formation rates are controlled by the diffusion limit [16]. One main direction of singlet fission material design is to synthesise a properly coupled dimer structure, aiming to achieve high efficient intramolecular SF in dilute solution or low crystallinity films from simple solution deposition method [17]. By use of transient absorption spectroscopy SF was observed in perylene-3,4,9:10-bis(dicarboximide) (PDI) covalently linked with  $\beta$ -apocarotene (Car) in two-step process: fast triplet formation in the PDI-Car dyad with subsequent triplet-triplet energy transfer to the Car triplet state [18].

## Singlet fission versus triplet fusion

Triplet fusion or triplet-triplet annihilation is a process reversed to SF, when two neighboring molecules in their triplet states interact with formation of one singlet exciton and the other one in the ground state. Triplet fusion leads to delayed fluorescence [19,20] and may lead to a delayed SF.

## On the mechanism of SF

Detailed mechanism of SF is not yet resolved. Direct SF has been implicated, whereby the Coulomb potential yields a direct interaction between  $S_1$  and correlated triplet pair TT, avoiding any intermediates [20,21].

Indirect SF assumes existence of an intermediate state. This intermediate state was considered (i) to have multiexcitonic character, (ii) to be energetically accessible from the optically allowed excited

state, and (iii) able to efficiently dissociate into multiple electron-hole pairs [22,23].

Intermediate states such as charge-transfer state [24], "multiexcitonic state" [22,25], "dark state" [26], "doubly excited state" [27] or excimer state [16] have been reported.

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