Anomalous emisson in photosynthetic systems

Sun Binrong *Zhao Shenduan*

(Shanghai Institute of Plant Physiology, Academia Sinica)

Liu Yixian *Li Fuming* *Zhao Yancheng*

(Department of Physics, Fudan University)

We have observed fluorescence at visible wavelengths from spinach chloroplasts suspension (20μg. chl/ml) excited with chl d Q-switched ruby laser pulses (10ns full at half maximum) of a wavelength of 694. 3nm and power flux densities in the range $\sim 10^6$–3×10^8 w/cm^2. In observation of emisson of ligth in the visible region (360–580nm), we used a monochromator, a EMI 9558B photomultiplier (rise time 10ns), and a 300MHz oscilloscope.

The fluorescence spectrum shows peaks at 410, 490 (the broadest) and 500 nm (See. Fig. 1). The fluorescence intensity increases exponentially with the excitation intensity. The fluorescence integrated intensity decreases (about 5–15%) in the presence of FeCY ... (25μ moles). The fluorescence lifetime was not longer than the response-time of the detection system and the duration of the excited pulse.

These results can be explained as follows: (1) The observed photons (410 nm) have up to twice the energy of the absorbed photons, and the emitted light intensity increases exponentially with the excitation intensity in the range of interest. It is clear that two or more absorbed photons must have contributed to the energy of the emitted photons, that is (a) $s_o+h\nu \longrightarrow s_1$, $s_1+h\nu \longrightarrow s_n$, $s_n \longrightarrow s_o+h\nu$, or (b) $s_o+Nh\nu \longrightarrow s_n$, $s_n \longrightarrow s_o+h\nu'$ (s_o, s_1, s_n are respectively the ground, the first excited and a higher excited singlet states of Chl, N is the number of photons) (2) The lifetime of emission light was estimated not longer than the response-time of the detection system and the duration of the excited pulse. This means that the phenomenon is dependent on singlet excited states and not on triplet states and that "fluorescence" rather than" phosphorescence" is the correct description. (3) the possible source of fluorescence quenching by FeCY is FeCY-Chl singlet-reaction center charge transfer state interaction, that is $A_o+D \xrightarrow{Nh\nu} A_n^*+D \rightleftarrows (A^-D^+)^* \xrightarrow{h\nu'} (A_o^-D^+)$ (A_o, A_n^* are chl singlet-reaction center charge transfer state ground and a higher excited singlet states, respectively, D-FeCY; if the excited complex (AD) is non-fluorescing, the addition of D to A result merely in quenching of the fluoroscence of A, which is generally believed to be a possible mechanism of the so-called dynamic quenching of fluorescence; on the other hand, if the excited complex is fluorescing, a new fluorescence band appears, while the original fluorescence dissappears with the addition of D.

In summary the observation of a fluorescence from excited state higher than the first singlet excited state provides further evidence for the non-linear effects at high intensities, and high light intensity effects are beginning to provide information on topology of photosynthetic pigment systems. Under high intensities, the emission of fluorescence can be explained as arising from higher excited states of a pigments system populated through exciton-exciton annihilation, or through second photon absorption, or through multiplier photon absorption.

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光合作用系统的异常发光

孙炳荣 赵贤端　　　　刘一先 李富铭 赵衍盛

(中国科学院上海植生所)　　　　(复旦大学物理系)

用694.3nm的叶绿素 d Q-开关红宝石激光器(半宽～10ns),在能流密度～$10^6-3\times10$ W/cm^{2}范围内,激励菠菜叶绿体悬浮液(20μg·chl/ml),在可见光范围内,我们观察由菠菜叶绿体悬浮液产生的荧光。在可见范围内(360～580nm),观察光发射,我们使用一台单色器,EMI 9558 B光电倍增管(上升时间10ns),以及300MHz示波器。

荧光光谱带的峰在410、490(宽)和550nm处,荧光强度随着激励光强指数地增加。在FeCY (25μmoles)存在时,荧光积分强度减小(大至5～15%),荧光寿命不大于检测系统的响应时间和激励脉冲期间。

这些结果可以解释如下:(1)观察到光子发射(410nm)二倍于吸收光子的能量,并且发射光强度随激励光强度指数地增加,这清楚地表明,二个或更多光子吸收贡献给发射光子的能量,也就是:(a) $So+h\nu\longrightarrow S_1$, $S_1+h\nu\longrightarrow Sn$, $Sn\longrightarrow So+h\nu$, 或 (b) $So+Nh\nu\longrightarrow Sn$, $Sn\longrightarrow So+h\nu$ (So、S_1、Sn分别为叶绿素的基态、第一单线激发态及更高单线激发态,N为量子数)。(2)荧光寿命估计不大于检测系统的响应时间和激励脉冲期间,这意味着,此现象依赖于单线激发态,而不依赖于三线态。并且是"荧光"而不是"磷光"。(3)由FeCY猝灭荧光的可能原因是FeCY—叶绿素单线态—反应中心电荷转移态相互作用。即 $Ao+D\xrightarrow{Nh\nu}An^*+D\rightleftarrows(An^-D^+)^*\xrightarrow{h\nu'}(Ao^-D^+)$ (Ao、An* 分别是叶绿素单线态—反应中心电荷转移态的基态和激发态,D为FeCY),如果激励复合物$(Ao^-D^+)^*$是不发荧光的,那末D加到A仅猝灭A的荧光,一般称之为动力学荧光猝灭,另一方面,如果激励复合物是发荧光的,那末一个新的荧光带出现,而原来的荧光随着加入的D而消失(或降低)。

总之,高于第一单线激发态的激发态发射的荧光观察,进一步为高光强下的非线性效应提供证据,同时,高光强效应也开始为光合作用色素系统提供关于拓扑学方面的信息,在高光强下,荧光发射可以解释为通过激励态-激励态湮没,或者通过第二个光子吸收,或者通个多光子吸收而产生粒子数增加的色素系统的更高激励态引起。

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