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Minireview

Thermoluminescence from the photosynthetic apparatus

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Abstract

One of the fundamental discoveries of W. Arnold was the detection of thermally stimulated light emission from preilluminated photosynthetic material (Arnold and Sherwood (1957) Proc Natl Acad Sci USA 43: 105–114). This phenomenon, called thermoluminescence (TL), is characteristic of a wide range of materials (semiconductors, minerals, inorganic and organic crystals, and complex biological systems such as the photosynthetic apparatus) which share the common ability of storing radiant energy in thermally stabilized trap states.

The original discovery of TL in dried chloroplasts later proved to be a phenomenon common to all photosynthetic organisms: photosynthetic bacteria, cyanobacteria, algae and higher plants. Following the pioneering work of Arnold, considerable effort has been devoted to identification and characterization of photosynthetic TL components. This work has firmly established the participation of various redox states of the water-oxidizing complex and the quinone electron acceptors of Photosystem II in the generation of photosynthetic glow curves. Since TL characteristics are very sensitive to subtle changes in redox properties of the involved electron transport components, the TL method has become a powerful tool in probing a wide range of PS II redox reactions. In this paper, we will review the impact of Arnold's work in initiating and promoting TL studies in photosynthesis and will cover the most important developments of this field of research until the present day.

Abbreviations: Chl – chlorophyll; DL – delayed luminescence; PS – photosystem; TL – thermoluminescence

Introduction

TL is a well known phenomenon in solid states, which can be described as emission of light at characteristic temperatures from samples which had been exposed to electromagnetic or particle radiation prior to their warming up in the dark (Chen and Kirsh 1981). A common feature of all TL phenomena is the storage of radiant energy in metastable trap states which can be released via thermally stimulated radiative detrapping. The energetic depth of the traps determines the characteristic temperatures where the peak of TL emission is observed. As a rule of thumb, the higher the peak temperature of a TL band the deeper the energetic stability of the related trap (provided that the experimental conditions, especially the heating rate, are the same). The temperature domain where TL can be observed is rather wide, starting from –250 °C in photosynthetic pigment assemblies and solutions, through the –50 to +50 °C region where the most important photosynthetic TL components appear, up to several hundred °C in minerals and other solid states.

The basic idea that part of the absorbed light energy is stored in the photosynthetic apparatus in long lived and remarkably stable trap states has already been derived from the earlier observation of delayed luminescence from chloroplasts by Strehler and Arnold (1951). 'So to try to make glow curves from chloroplasts was obvious' (Arnold 1991). The idea was not only obvious, but also successful, which led to the discovery of photosynthetic TL (Arnold and Sherwood 1957). In the same year, Tollin and Calvin (1957) also reported TL from dried chloroplasts. Later, Arnold (1966) showed the presence of TL in intact cells of the green alga *Chlorella.* These early observations were followed by a large number of studies which have been covered by extensive reviews (Inoue and Shibata 1982; Inoue 1983; Sane and Rutherford 1986; Horváth 1986; Demeter and Govindjee 1989; Vass and Inoue 1992; Inoue 1996).

The main characteristics and origin of photosynthetic TL bands

Photosynthetic glow curves contain several components

In their early DL experiments, Arnold's group observed that the decay of DL intensity, when depicted in a double logarithm plot versus time, shows small waves which indicated that there are more than one energy storage states in the photosynthetic apparatus (Arnold and Azzi 1971; Arnold 1991). This idea was evident from the glow curve measurements showing several peaks (Arnold and Sherwood 1957, 1959; Arnold 1966). Later studies have fully confirmed the existence of multiple energy storage states, and identified at least 10 different TL components from photosynthetic material (see below, Table 1).

The main mechanism of photosynthetic TL is thermally stimulated radiative charge recombination

The initial idea emerging from the discovery of TL and DL was that the photosynthetic apparatus behaves like semiconductors (Arnold and Sherwood 1957, 1959; Tollin and Calvin 1957). This idea was developed into an electron-hole picture of photosynthesis (Arnold 1965). In this picture a bound electron (to be used in the Calvin cycle) and a free hole is formed in reaction center A (PS I) as well as a bound hole (to be used in water oxidation) and a free electron is formed in reaction center B (PS II). According to this hypothesis of Arnold the recombination of the free hole (from PS I) and of the free electron (from PS II) would have been the mechanism for the production of delayed light and TL (Arnold 1966). The idea of free moving electrons and holes in a solid-state like photosynthetic apparatus has not been fully supported by later experiments. Arnold and Azzi (1968) modified this model by postulating that the positive and negative charge traps reside within PS II. The main mechanism of TL emission has indeed been proven to be thermally induced radiative charge recombination from similar charge traps of PS II.

TL and DL are closely related phenomena

The close relationship of photosynthetic DL (see Lavorel 1975) and TL emission was recognized in the early experiments based on the analogy with semiconductors that had actually led to the discovery of TL (Arnold and Sherwood 1957; Tollin and Calvin 1957). Following the initial work of Arnold, the relationship of TL and DL received general support (Shuvalov and Litvin 1969; Malkin 1977; Rutherford et al. 1984; Hideg and Demeter 1985). This correlation was also utilized in the so called temperature jump experiments where the temperature of the preilluminated samples was suddenly raised thereby inducing delayed light emission (Mar and Govindjee 1971; Jursinic and Govindjee 1972; Malkin and Hardt 1973).

It is also of note that the correspondence of DL and TL is not one-to-one. Each TL component which arises from thermally stimulated energy release has a related DL component. However, DL emission may arise from temperature independent processes, e.g. recombination via electron tunnelling, which have no TL counterpart. Such DL components have also been observed by Arnold (1977). Further details on photosynthetic DL can be found in comprehensive reviews (Lavorel 1968, 1975; Fleishman and Mayne 1973; Malkin 1977; Amesz and van Gorkom 1978; Govindjee and Jursinic 1979; Jursinic 1986).

The simulation and analysis of photosynthetic glow curves can be based on the generalization of simple TL models of solid states

Despite the non complete correspondence of the photosynthetic apparatus to solid states in terms of the electronic band structure of semiconductors, the basic features of photosynthetic TL can be described in the framework of the simple model that has been developed by Randall and Wilkins (1945) to explain TL from solid states. The Randall – Wilkins model was used to calculate activation energies without modification (Arnold and Sherwood 1959; Arnold and Azzi 1968; Lurie and Bertsch 1974b; Tatake et al. 1981) and was later generalized for biological systems (Vass et al. 1981; deVault et al. 1983).

Table 1. The peak temperature and origin of photosynthetic TL bands

TL component	Peak temperature (°C)	Origin/charge pair
Low temperature bands[1]	–250, –220, –200	Energy storage in aggregated Chls[1]
Z-band[2]	∼–160	$Chl^{+}(?)Chl^{-}(?)$[3]
Zv-band[4]	Variable (–80 to –30)	$P_{680}{}^{+}(Chl^{+}?)Q_A{}^{-}$[5]
A-band[6]	∼–15	$S_3Q_A{}^{-}$[7]
A_T-band[8]	∼–15	$His^{+}Q_A{}^{-}$[9]
Q-band[10]	∼+5	$S_2Q_A{}^{-}$[11]
B_1-band[12]	∼+30 to +40	$S_2Q_B{}^{-}$[13]
B_2-band[12]	∼+30	$S_3Q_B{}^{-}$[13]
C-band[14]	∼+50	$TyrD^{+}Q_A{}^{-}$[15]
High temperature bands[16]	∼+50 to +70	Oxidative chemiluminescence[17]

The references given as superscripts in the first column refer to the observation of the components, whereas the references indicated as superscripts in the third column refer to the interpretation of their origin. [1] (Noguchi et al. 1992), [2] (Arnold and Azzi 1968; Shuvalov and Litvin 1969), [3] (Sonoike et al. 1991), [4] (Ichikawa et al. 1975; Desai et al. 1977), [5] (Vass et al. 1989; Chapman et al. 1991), [6] (Rubin and Venediktov 1969; Desai et al. 1975; Inoue 1981), [7] (Demeter et al. 1985a; Koike et al. 1986), [8] (Inoue et al. 1977; Rózsa and Demeter 1982), [9] (Ono and Inoue 1991; Kramer et al. 1994), [10] (Rubin and Venediktov 1969; Lurie and Bertsch 1974a), [11] (Rutherford et al. 1982. If DCMU is added after the flash excitation, the $S_3Q_A^-$ recombination also results in the Q band, Demeter et al. 1982), [12] (Arnold and Azzi 1968; Rubin and Venediktov 1969; Lurie and Bertsch 1974a; Inoue 1981), [13] (Rutherford et al. 1982; Inoue 1983; Demeter and Vass 1984), [14] (Rubin and Venediktov 1969; Desai et al. 1975), [15] (Demeter et al. 1993; Johnson et al. 1994), [16] (Sane et al. 1977; Rózsa et al. 1989; Hideg and Vass 1992), [17] (Vass et al. 1989; Hideg and Vass 1993).

The present view of photosynthetic TL from charge recombination in PS II is summarized in Figure 1. Light-induced charge separation in the PS II reaction center produces the singlet radical pair of $^{1}[P_{680}{}^{+}Pheo^{-}]$. (Details of electron transport in PS II are reviewed by Andersson and Styring 1991 and Debus 1992.) This step is followed by sequential stabilization of the separated charges forming a pair of oxidized donor (D^{+}) and reduced acceptor (A^{-}). During this process part of the free energy increase, induced by light absorption, is lost and stabilizes the separated charge pair against recombination.

The recombination of the $D^{+}A^{-}$ pair proceeds through intermediate charge stabilization states via a series of equilibrium reactions (deVault et al. 1983; deVault and Govindjee 1990) until the $P_{680}{}^{+}Ph^{-}$ radical pair is formed. The recombination of the radical pair results in the formation of singlet excited $P_{680}{}^{*}$. Light emission from $P_{680}{}^{*}$ or from the coupled antenna system leads to the appearance of delayed light. As a simple approximation, the multistep recombination can be treated as a single step process using the first order kinetic equation of the Randall–Wilkins model. For the intensity of thermoluminescence,

$$I_{TL}(T) = -c\frac{dn}{dT} = \frac{cnk(T)}{\beta}$$

(T: temperature, c: proportionality factor, n: concentration of trapped charges, β: heating rate). $k(T)$ is the overall rate constant of detrapping which is given by $k(T) = A\exp(-E_a/k_BT)$ (E_a: activation energy, k_B: Boltzmann's constant, A: preexponential or frequency factor). The frequency factor can be described for a thermally activated biological electron transport reaction by the $A = (Kk_BT/h)\exp(\Delta S^{*}/k_B)$ expression (see Marcus and Sutin 1985) (h: Planck's constant, K: transmission coefficient, whose value is 1 if the process is adiabatic, but falls between 0 and 1 if the process is nonadiabatic, ΔS^{*}: entropy of activation). By using this expression for $k(T)$, an explicit expression was derived for the intensity of TL as a function of temperature (Vass et al. 1981). The combination of this formalism with multicomponent curve fitting enabled the resolution of overlapping TL bands yield-

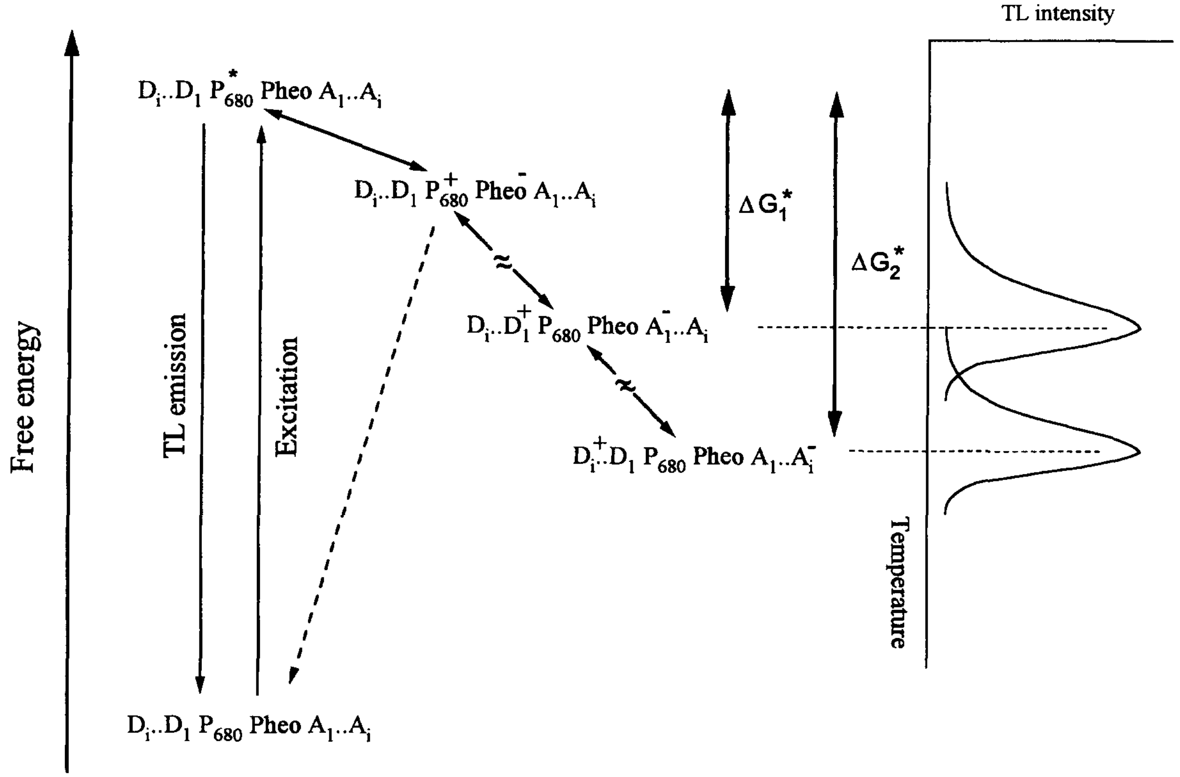

Figure 1. The scheme of TL emission arising from charge recombination in PS II. $D_1,...,D_i$ and $A_1,...,A_i$ represent various donor and acceptor components of PS II, respectively. For the Q band A_i is Q_A^- and D_i is S_2, whereas for the B band A_i is Q_B^- and D_i is $S_2(S_3)$. ΔG^* is the free energy of activation for the radiative charge recombination of the particular charge pair, which approximately equals the free energy loss during charge separation and stabilization. The dashed arrow indicates non-radiative charge recombination. The shape and peak position of a TL band is determined by the ΔG^* value. A higher peak position indicates a higher ΔG^*, i.e. a deeper stabilization of the charge pair.

ing the activation parameters E_a; ΔS^* and $\Delta G^* = (E_a - T\Delta S^*)$ of the various trap states (assuming an adiabatic recombination process). More recently a graphical and numerical analysis method of glow curves was developed by Ducruet and Miranda (1992), which is based on the numerical solution of the Randall–Wilkins-type differential equation.

It is important to note that the shape and peak temperature of a TL band is not determined by the activation energy (more precisely activation enthalpy) alone. Full description of the energetics of charge recombination and the related TL component requires the free energy of activation (ΔG^*), which reflects the redox potential difference of the stabilized charge pair. The work of deVault and his coworkers, including contribution of Arnold (deVault et al. 1983; deVault and Govindjee 1990) provided a theoretical background for the approximation of the multistep recombination with a hypothetical single step. They have shown that the free energy of activation, that can be calculated from a TL band assuming a single step recombination, approximately equals the sum of the free energies of the involved equilibrium reactions plus the free energy of activation for the final $P_{680}^{+}Ph^{-}$ recombination. However, the correct calculation of the entropy contribution is hampered not only by the multistep recombination process, but also by the extent of adiabacity of the final recombination step. In case of a non-adiabatic electron transfer the calculated entropy may be underestimated. Despite its simplicity and limitations, this approach resulted in good predictions for the stabilization free energies and room temperature halftimes of different charge pairs of PS II (see Vass et al. 1981; Vass and Inoue 1992).

A further development in the description of photosynthetic TL curves was the application of so called general order kinetics models, instead of the first order kinetics Randall–Wilkins model, by Vidyasagar et al. (1993). However, the kinetic orders obtained from this approach were in the range of 1.1, which are prac-

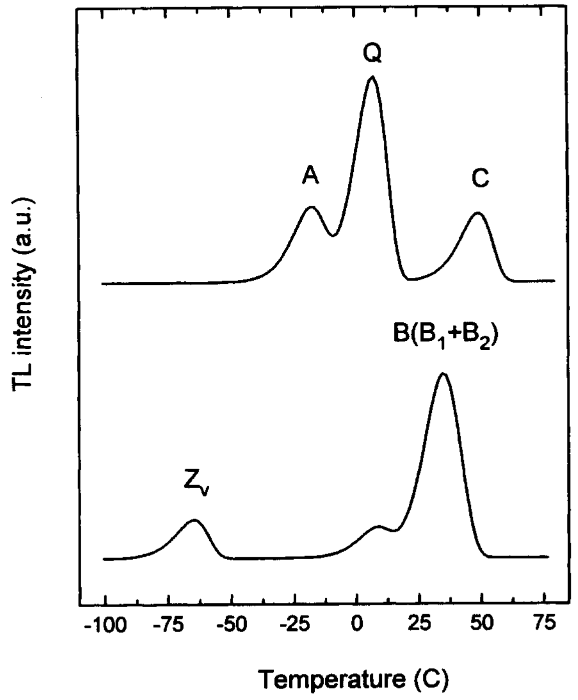

Figure 2. The main photosynthetic thermoluminescence (TL) bands. Top graph: A (−15 °C); Q (+5 °C); and C (+50 °C) bands. Bottom graph: Z_v (−60 °C); and $B(B_1 + B_2)$ (+30 °C) bands. The curves do not represent actual measurements; instead, they show the approximate shape and peak temperature of the most important TL bands related to the back reaction of photosynthetic electron transport. See Table 1 for the charge storage states involved in the origin of these TL bands.

tically the same as in the first order kinetics of the Randall–Wilkins approximation.

Assignment of thermoluminescence bands to known reactions of the photosynthetic apparatus

The early experiments of Arnold, which were performed using various combinations of filters and photomultipliers with different spectral sensitivity, indicated that chlorophyll is involved in absorption and emission of the light in the glow curves (Arnold and Sherwood 1956) and in delayed luminescence (Arnold and Davidson 1954; Arnold and Thompson 1956). These findings provided strong support for the origin of TL and DL from the light energy converting photosystems. Identification of PS II as the main source of photosynthetic TL was based on experiments with purified preparations and mutants which contained either PS I or PS II (Arnold and Azzi 1968; Lurie and Bertsch 1974a; Ichikawa et al. 1975; Sane et al. 1977). These experiments verified that the TL components which are related to photosynthetic electron transport arise from PS II. (The approximate shape and peak temperature of these bands is shown in Figure 2.) In contrast, no TL component has been confirmed to originate from electron transport processes in PS I. Although TL is emitted from PS I, these components seem to originate from energy storage in the antenna pigment system (Sonoike et al. 1991; Noguchi et al. 1992) or light emission by oxidative chemiluminescence (Hideg and Vass 1993). Origin of the main TL bands from PS II is further supported by high resolution measurements of spectral distribution of the emitted light (Sonoike et al. 1991). This is also in agreement with the spectral distribution of the related DL components (Hideg et al. 1991).

Identification of the source of positive charges which participate in the TL yielding recombination was initiated by the observations that the major TL bands were missing in dark-grown gymnosperm leaves, angiosperm leaves greened under widely spaced intermittent illumination or in algae cells grown in Mn-deficient medium. When the latent water-oxidizing complex in the above systems was photoactivated by continuous light or closely-spaced flashes, the TL bands were also induced, which indicated that the oxidation states of the water-oxidizing complex are involved in the generation of TL as positive charge reservoirs (Ichikawa et al. 1975; Inoue 1976; Inoue et al. 1976). This idea was confirmed by the finding of a period-four oscillation in the intensity of the main TL component when excited by single turnover flashes (Inoue and Shibata 1977) that could be simulated by assuming that charge recombination involved the S_2 and S_3 oxidation states of the water-oxidizing complex (Rutherford et al. 1982; Inoue 1983; Demeter and Vass 1984).

The first indication for the identity of the negative charge reservoir came from the observations of Rubin and Venediktov (1969), who found the interconversion of two TL components by DCMU, an electron transport inhibitor that interrupts electron transport between the first, Q_A, and the second, Q_B, quinone electron acceptor of PS II. This observation was extended by a number of studies on the effect of various electron transport inhibitors acting between Q_A and Q_B (Lurie and Bertsch 1974a; Ichikawa et al. 1975; Demeter et al. 1979), which led to identification of the semiquinone states of these two quinone electron acceptors (Q_A^- and Q_B^-) as the main, negatively charged participants of TL yielding recombinations (Rutherford et al. 1982; Demeter et al. 1982; deVault et al. 1983).

Besides the TL components which originate from charge recombination in PS II, there are further bands at low temperatures, between –250 and –160 °C (Noguchi et al. 1992); at –160 °C (Arnold and Azzi 1968; Shuvalov and Litvin 1969), which are related to energy storage in the pigment assemblies of PS II and PS I (Sonoike et al. 1991; Noguchi et al. 1992). Other components which appear at high temperatures (in the +50 to + 80 °C range) most likely arise from oxidative chemiluminescence of protein bound pigments (Hideg and Vass 1993).

It has to be noted that some of the originally observed TL bands from dried chloroplasts, which appear above +90 °C (Arnold and Sherwood 1957, Tollin and Calvin 1957), have no clear counterparts in intact systems. Even though these high temperature components are undoubtedly related to photosynthetic electron transport their origin is not clear. They are probably characteristic only for the dried state of chloroplasts.

TL emission can also be observed from photosynthetic bacteria (see Arnold and Thompson 1956). Fleishman (1971) found two TL peaks under aerobic conditions, and one peak under anaerobic conditions in *Rhodopseudomonas viridis.* The band was suggested to arise from the recombination of $P_{960}{}^{+}$, the oxidized primary donor, with a reduced secondary acceptor, probably Q_B^- (see Sane and Rutherford 1986). Govindjee et al. (1977) also reported TL from photosynthetic bacteria, which was shown to arise from magnesium protoporphyrin IX, a precursor of bacteriochlorophyll.

The peak temperature and origin of the main photosynthetic TL bands are listed in Table 1. Among the components, the assignments of the B and Q bands are the most solid, and these bands are used most frequently in probing PS II photochemistry. The assigments of the other bands are sometimes less clear as indicated by question marks in the third column of Table 1.

Probing the redox reactions of Photosystem II by thermoluminescence

The main redox components that participate in TL emission are the reduced forms of the Q_A and Q_B quinone electron acceptors, the S_2 and S_3 redox states of the water- oxidizing complex and Tyr-D^+ (Table 1). Consequently, TL provides a powerful tool to monitor the function and activity of the above redox components in various plant materials, which range from isolated PS II reaction center complexes through PS II enriched membranes and thylakoids to intact leaves and whole cells of cyanobacteria or algae.

One field of application covers the energetic stability of the reduced quinone electron acceptors. Since various electron transport inhibitors, including agriculturally important herbicides like atrazine and diuron, block the Q_A^- to Q_B electron transfer, which result in the conversion of the so-called B band into the Q band, the TL method can be utilized in studying the mode of action of different inhibitors (Demeter et al. 1982; Vass and Demeter 1982), testing and identifying new chemicals and potential herbicides (Asami et al. 1988; Koike et al. 1989). A related area of research is the study of resistance against photosynthetic herbicides. A number of naturally selected or genetically created mutants are known, which exhibit increased resistance against various herbicides acting at the Q_B site. These mutants have one or more amino acid changes in the Q_B binding region, which decreases not only herbicide binding but in many cases also the binding affinity of Q_B and the energetic stability of Q_B^-. This latter effect results in the shift of the B band to lower temperatures that can be conveniently studied by TL and can be used to identify and characterize herbicide resistant biotypes (Demeter et al. 1985b; Etienne et al. 1990; Gleiter et al. 1990). The sensitivity of the TL method is well demonstrated by the fact that a 50–70 mV redox potential difference between the Q_B/Q_B^- and Q_A/Q_A^- couples results in about 25–30 °C difference in the peak temperature of the corresponding B and Q bands (Demeter et al. 1985b).

The TL method has also been useful in studying removal and reconstitution of the Q_A and Q_B quinone electron acceptors from PS II (Wydrzynski and Inoue 1987; Chapman et al. 1991). A further application of TL concerning acceptor side characteristics is the study of protonation events at or around the Q_B site. The upshift of the B_1 band, arising from the $S_2Q_B^-$ recombination, at low pH is assigned to protonation induced stabilization of Q_B^-, providing an approach to study protonation effects (Rutherford et al. 1985; Vass and Inoue 1986). This topic is also related to the effect of bicarbonate in modifying electron transport between Q_A and Q_B as well as the protonation of Q_B^- (Govindjee et al. 1984; Sane et al. 1984; Garab et al. 1988; Demeter et al. 1995).

The participation of the S_2 and S_3 states of the water-oxidizing complex in the B band provides an easy tool to study S-state turnovers, in particular the formation and interconversion of these redox states under various conditions which affect the redox cycling of the S states. This approach has been applied to study the temperature dependence of the particular S-state transitions (Inoue and Shibata 1977; Koike and Inoue 1987); the effect of the so called ADRY agents in destabilizing the higher S states (Renger and Inoue 1983); the effects of water analogs on the S-state turnovers (Ono and Inoue 1988; Vass et al. 1990); the role of the inorganic cofactors, Mn^{2+} (Inoue et al. 1977; Ono and Inoue 1985), Cl^{-} (Homann et al. 1986; Vass et al. 1987; Homann 1993) and Ca^{2+} (Ono and Inoue 1989), in the S-state cycling; the function of the extrinsic polypeptides, especially of the 33 kDa protein, associated with the water-oxidizing complex (Ono and Inoue 1985; Vass et al. 1987).

Due to its applicability to intact systems, TL has proven a useful method of probing PS II activity in intact leaves (Rutherford et al. 1984; Krieger et al. 1993; Johnson and Krieger 1994) or even in lichen thalli (Sass et al. 1996).

With the recent development of genetic engineering techniques in studying structure-function relationships of PS II electron transport, various algal and cyanobacterial mutants are being constructed in a steadily increasing number. TL is especially suitable to characterize the function of PS II in such mutants since it can be applied in intact cells without the need of time consuming and costly isolation procedures (for examples see Vass et al. 1992; Burnap et al. 1992; Mayes et al. 1993; Gleiter et al. 1994, Mäenpää at al. 1995; Nixon et al. 1995).

Since PS II is a sensitive site of the photosynthetic apparatus which is easily affected by various environmental factors, TL has proven a very useful method in studying the damaging mechanisms of a number of environmental effects. These include the mechanism of photoinhibition by visible light (Ohad et al. 1988, 1990; Vass et al. 1988) and ultraviolet radiation (Desai 1990; Hideg et al. 1993), the mode and site of action of heavy metals, like Cu^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+} (Mohanty et al. 1989) and acclimation to elevated temperatures (Govindjee et al. 1985).

Concluding remarks

Studies on the phenomenon of photosynthetic TL during the almost 40 years since its discovery have clarified the origin of many TL components, and proved the usefulness of TL method in the studies of many of the redox reactions in PS II. This method has the advantage of a relatively simple instrumentation and easy applicability to study almost all redox components of PS II in intact and isolated systems. Since the most important TL components appear between 0 and +40 °C, harmful effects of nonphysiological temperatures can be avoided. However, as other methods (see Govindjee 1995 for fluorescence), TL also has limitations and disadvantages. Due to its origin from charge recombination, only pairs of donor-acceptor components can be studied with a single TL band. Thus, characterization of changes in a particular donor or acceptor can be achieved only by comparing two different TL bands, which have a common acceptor or donor component, respectively. Because of the complexity of the underlying processes it is not always straightforward to utilize the full potential of energetic information from the measurements. Taking together its benefits and limitations, TL is a useful and informative method which will keep helping us in exploring a number of current and future problems of photosynthesis research. It is expected that the application of TL will extend not only in stress physiology, but also in studies on the impact of global climate changes (UV, CO_2, temperature increase, etc.) on ecosystems.

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