**Temporal correlations of sunlight may assist photoprotection in Photosynthesis**

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Photon-excitation and exciton migration in photosynthetic light harvesting membranes is followed by a charge separation which initiates the reduction of several cofactors and eventually, sustains the charge gradient that drives the synthesis of Adenosine Triphosphate. Earlier, the interplay between charge dynamics and light intensity has been proven essential to understand adaptation of bacterial photosynthesis, while the statistics of thermal light proper of physiological environments was not considered to be important for the performance of these membranes. Here, we show that a more specific analysis of the dynamics occurring in the reaction centres, in particular the dissipative process of charge recombination, introduces metastable states which make the performance of the photosynthetic apparatus sensitive to the spatio-temporal correlations of sun light. The dynamics of these metastable states elucidates a photo-protective mechanism based on thermal light correlations, suggesting that the operating rates within the reaction centres are adapted to dissipate photo-excitations in the high intensity regime, when it is required to support bacterial survival.

Keywords: Bacterial photosynthesis, charge transfer, thermal light.

**Introduction.** Natural photosynthesis can function under constantly changing environmental conditions, thanks to regulatory mechanisms which enable either highly efficient excitonic energy transfer to drive light-chemical energy conversion, or by the quenching of surplus excitations to avoid photo-damage. The balance of these two processes emerges from adaptations through structural and conformational changes [16]. Along these lines, the adaptability of bacterial photosynthesis to varying environmental conditions raises relevant questions about further mechanisms which may allow robustness, flexibility and efficiency of photoprotection [7–14].

The theoretical description of the coherence properties of thermal light was formulated by Kano and Wolf more than fifty years ago [17]. More recently, R. Silbey refined the theoretical analysis of excitonic energy transfer in photosynthetic structures [18]. In parallel, the increasing accuracy on linear and multidimensional spectroscopic techniques allowed for the experimental investigation of transport paths [19–21] which feed forward the formulation of more accurate models of a process where a detailed microscopic modelling is currently unavailable. Excitonic dynamics provides the initial input for the description of the dynamics of charge separation, a process that is also amenable to experimental probing using multilinear techniques [22]. The sheer complexity of the individual processes of absorption, excitation energy and charge transfer has made their combined description a challenging problem. However, in biological niches of photosynthesis these scenarios do come together, since the absorption of thermal light precedes excitonic energy transfer which ends up either being dissipated into the environment or triggering the successful generation of a free charge. Heuristically, it is expected that the characteristics of each process may affect the next, which in the particular case of photosynthesis, suggests the possibility that the statistics of thermal light could affect the nature of charge separation, and therefore the metabolism of the organism. How and to what extent, is the puzzle we want to start putting together in this manuscript.

In more detail, the principle that motivates this work is illustrated in Fig.1(a)-(c). The coherence area of sunlight at the earth’s surface is estimate to be of the order of 50 µm [23–24], which greatly exceeds the size of any unicellular photosyn-

![FIG. 1. Thermal light and Photosynthetic complexes.- The parameters describing the incoherent light source provided by sunlight are shown in (a), where a denotes the source diameter, D the distance to the light reception system and \( \lambda \) the mean wavelength of the incident light. In (b) the large orange circle with diameter \( l' \approx 50 \mu m \) represents the coherence area of sunlight, encircling a complete photosynthetic bacterium of length \( \approx 40 \mu m \) [16]. The photosynthetic apparatus of the bacterium is embedded in characteristic vesicles as sketched in (c), which contain the light harvesting complexes LH1 and LH2 and the reaction centres, with typical inter-complex distance \( r_{ij} \ll l' \).](attachment:fig1.png)
Preliminaries: Statistical model of thermal light detection.

Based upon the seminal works of Glauber and others [30–34], a fully comprehensive theory of the statistics of finite bandwidth photon absorption, characteristic of chromophores, is yet to be developed. In the following, we will use a stochastic framework [23, 35], which is already able to accommodate the spatio-temporal correlations of the incident light to account for the statistics of the subsequent photodetection events recorded by a set of $N$ detectors, each of which we identify as individual LH units. The central quantity in the formalism is the probability $P(n, t)$ to have $n$ absorption events within a time interval $t$. In this framework, the cumulative distribution function $F(t) = 1 - P(n = 0, t)$ of having no photon absorption events for a waiting time $t$ depends on the aperture time $T$ (time window for photo-detection), on the effective absorbed intensity, and on the temporal and spatial normalised correlation functions $\gamma(t_1 - t_2) = \sin(\tau_{1,2})/\tau_{1,2}$ and $\gamma(r_{k,l}) = 2J_{\nu_{k,l}}/\nu_{k,l}$, respectively [28]. Here, $J_{\nu_{k,l}}$ is the first order Bessel function, and its argument $\nu_{k,l} = 2\pi|\vec{r}_{k,l}|/l_\text{c}$ is the inter-detector distance $|\vec{r}_{k,l}|$ normalised by the coherence length of the incoming light, $l_\text{c}$. This length $l_\text{c} = \lambda_0^2$, relates the average wavelength $\lambda$ of the field, the distance to the light source $D$, and its diameter $a$, as depicted in Fig. 1(a)-(b) [29]. The spatial correlation function quantifies the decay of spatial correlations, which are relevant for $|\vec{r}_{k,l}| \lesssim l_\text{c}$. As noticed earlier [23, 28] and illustrated in Fig. 1(b)-(c), the transverse coherence length $l_\text{c} \approx 50\mu$m of sunlight measured at earth’s surface [24] is about 100 times the diameter $\approx 500\text{nm}$ of a typical vesicle. This scale mismatch suggests that the excitation of LH complexes stored within photosynthetic vesicles will be subject to the (classical) correlations exhibited by thermal light.

Within the coherence area, spatial correlations of thermal light are accounted for by a temporal correlation function, whose argument $\tau_{1,2} = \frac{2\pi|\vec{r}_{k,l}|}{\nu_{k,l}}$ depends on the ratio between the inter-detections time $(t_1 - t_2)$ and the coherence time of the light $\tau_\text{c}$. The ratio $T/\tau_\text{c} \ll 1$ or $T/\tau_\text{c} \gg 1$, sets the limits of Bose-Einstein (maximum correlations) or Poissonian (no correlations) statistics for light absorption, respectively. Within this formalism, the absorption of thermal fields have similar statistics to bosonic fields, if the aperture time $T$ is smaller or commensurate to the coherence time $\tau_\text{c}$ [29]. In principle, the waiting time cumulative distribution depends on all order of $P(n, t)$. However, only a few photo-counting probabilities, namely $P(n = 1, t)$ and $P(n = 2, t)$ have been obtained for finite spectral width absorption [34] and a direct analogy between the aperture time and the absorption linewidth of chromophores is not currently available. Thereby, we will use instead the ratio $T/\tau_\text{c}$ as a parameter that allows continuous statistical tuning of the absorbed excitations from a thermal to a Poissonian field.

In the limit $T/\tau_\text{c} \leq 1$, this framework results in a waiting time distribution $f(t)$ for the associated waiting time probability $F(t) = \int_0^t f(t')dt'$ that exhibits longer tails than the exponential distribution expected from independent events.

![Image of Burstiness as a function of the temporal correlations (T/τc).](image)

**FIG. 2.** Burstiness of the reception signal as a function of the temporal correlations $(T/\tau_\text{c})$. In the inset, we show the characterisation of these signals using as figure of merit the quantities $\langle \tau \rangle$, $\sigma_\tau$, $\langle \tau_{\text{intra}} \rangle$, and $\langle \tau_{\text{inter}} \rangle$ (descriptions in the text). All quantities are displayed in milliseconds on a semi-logarithmic scale. We considered $\langle \tau \rangle = 10^6$ photons/(LH-ms), $\tau_{\text{intra}} = 2000\text{ms}$ and $10^6$ light absorption events.
The consequence of these slow-decaying tails is a bursted structure, with photo-excitation traces that have very long waiting times scattered between bursts of clustered events. The statistics of bursts in a sequence of absorption events can be quantified by the so-called burstiness, $B = (\langle \sigma \rangle - \langle t \rangle) / (\langle \sigma \rangle + \langle t \rangle)$. This quantity vanishes in a fully Poissonian process where the mean inter-event time $\langle t \rangle$ equals the standard deviation of waiting times $\sigma_t$, but has a positive value whenever times series exhibits bursts of events. As shown in Fig. 2, the ratio $T / \tau_c$ and $B$ are related monotonically. Hence, either of them can be used to quantify the bunching of the light absorption, but only $B$ can be used to compare these results on equal footing with the statistics of excitations reaching the RCs after traveling across the harvesting membrane.

We characterise the statistical properties of the waiting times $t$, in terms of the average $\langle t \rangle$, the variance $\sigma_t$, and average waiting time between and within bursts, namely $\langle t_{\text{inter}} \rangle$ and $\langle t_{\text{intra}} \rangle$, respectively. As it can be confirmed in the inset of Fig. 2, for the simulated events, all the four quantities increase when the burstiness increases – for the same intensity value – as a consequence of correlations, preserving the average rate of photon arrivals, as required for energy conservation and verified in our calculations. Notice that $\sigma_t$ grows faster than $\langle t \rangle$, which results in $\langle t_{\text{inter}} \rangle$ having a faster growth than $\langle t_{\text{intra}} \rangle$ for greater values of $B$. The results show that $\langle t \rangle$ and $\sigma_t$ quickly converge to equal values for $T / \tau_c \lesssim 1$, as expected from the trend towards independent random events following a Poissonian distribution.

![Diagram](image.png)

**FIG. 3.** (a) Scheme for photo-excitation of the special pair $P$ and subsequent charge transfer to the accessory pigment $BChl_a$, the bacterio-pherophytin ($Bphe_a$) and the quinone $Q_b$, which take place in the active branch $BChl_a \rightarrow Bphe_a$. If available and neutral, $Q_b$ is reduced, but if it was already reduced, the anionic species $Q_b^-$ becomes a two-proton acceptor that results in a Quinol $Q_bHz$. The Quinol dissociates from the RC in order to deliver protons to the intracytoplasm and increase the voltage that drives the ATP synthesis, driven concomitantly by the oxidation of the cytochrome $cyt^+$ to $cyt^−$. As a consequence of correlations, preserving the average rate $T / \tau_c$, the variance of photon arrivals, as required for energy conservation and verified in our calculations. Notice that the standard deviation of waiting times $\sigma_t$ grows faster than $\langle t \rangle$, which results in $\langle t_{\text{inter}} \rangle$ having a faster growth than $\langle t_{\text{intra}} \rangle$ for greater values of $B$. The results show that $\langle t \rangle$ and $\sigma_t$ quickly converge to equal values for $T / \tau_c \lesssim 1$, as expected from the trend towards independent random events following a Poissonian distribution.

![Graph](image.png)

**FIG. 4.** Effect of thermal light correlations in quinol production. (a) Shows the burstiness of the absorption traces and that of the excitations reaching each RC, these latter calculated from typical traces as those presented in the inset. In (b) Quinol yield for different degree of burstiness of the absorbed excitations. (c) Quinol production rate, relative to the maximum capacity of the ATPase (set in 100 Quinols/s) as a function of the temporal correlation $T / \tau_c$. Inset: ratio of annihilation events as a function of the temporal correlations $(T / \tau_c)$. $t_{\text{low}} = 3000$ ms and $10^6$ absorption events. In (a) and (b) we use high intensity $\langle I \rangle = 10^3$ photons/(LH·ms), while in (c), additionally, we show the results for low intensity $\langle I \rangle = 10^4$ photons/(LH·ms).
Thermal light excitation and Charge separation. Photosynthesis captures and processes thermal light in order to produce ATP. Initial light harvesting is followed by subsequent excitonic transfer to RCs, where the electronic excitation of the special pair (P) chromophores within the RC, \(P \rightarrow P^*\), induces a charge separation of the special pair \(P^* \rightarrow P^+ + e^-\). This electron \(e^-\) is transferred along an active branch of the RC as shown in Fig.3(a), reducing several cofactors until it reduces a quinone molecule \(Q_A \rightarrow Q_A^*\). If an auxiliary quinone \(Q_B\) is available, the reduction \(Q_A^*Q_B \rightarrow Q_AQ_B\) takes place. The oxidised \(P^+\), after becoming neutral, can reduce the quinone \(Q_A\) again, \(P^*Q_AQ_B \rightarrow P^*Q_AQ_B^*\), in order to proceed with the uptake of two intracytoplasmic protons \(Q_A^*Q_B^* + 2H^+ \rightarrow Q_A(Q_BH_2)\), i.e., two \(Q_A\) reductions take place before a quinone molecule is synthesized. Each reduction has two possible pathways I and II depending on the availability of quinones and cytochromes, as displayed in Fig3(b)-(c). In a later stage (see Fig3(c)) Quinol \(Q_BH_2\) releases these protons in order to develop the electrochemical gradient that drives bacterial metabolism. Intermediate metastable states occur between the first \(Q_A^*Q_B \rightarrow Q_AQ_B^*\) and second \(Q_A^*Q_B^*\) reduction of the quinone pair. In particular, the metastable states \(P^*Q_A^*\) or \(P^*Q_B^*\) will degrade to \(PQ_A^{\cdot}\) or \(PQ_B^{\cdot}\) due to charge recombination in about 100 ms or 1000 ms, respectively [36, 39, 40]. The \(P^*Q_B^*\) recombination is of special relevance, since the dynamics within the RCs will more often populate this state between consecutive \(P\) photo-excitations [39]. While the absorption of photon pairs may help to avoid the decay of the metastable state, quinol production may be inhibited whenever excitations that reach a given RC are delayed longer than charge recombination.

In order to determine which situation describes the physiological function, the interplay between quinol production, ATP synthesis and light illumination must be considered. The ATPase is the molecular motor that synthesises ATP, with an estimated maximum turnover rate of 100 ATPs/s [8] (about 200 excitations/s given that one ATP is produced from a quinol molecule as a result of two events of charge separation at \(P\)). For a normal size membrane vesicle with \(\approx 400 - 600\) light harvesting complexes (LHs) [22] and 100% excitonic transfer efficiency towards RCs, this turnover rate translates into an absorption of about \(0.5 \times 10^{-3}\) photons/(LH-ms). Higher rates of quinol production will lead to a harmful excess of acidity in the vesicle’s periplasm [8]. Light intensities from 10 to 100 W/m² were observed to induce harvest membranes’ adaptation in Rps. Photometricum and Rp. Sphaeroides purple bacteria [17, 22], which result in absorption rates ranging between 0.05-0.5 photons/(LH-ms) [8, 14]. Hence, we notice that light intensities that induce adaptation in purple bacteria are at least one order of magnitude higher than the intensity required to reach the maximum turnover of ATPase. Photo-protection mechanisms can help to explain this discrepancy. We will show that the statistics present in thermal light may assist photo-protection via long interphoton delay times that result in dissipation upon charge recombination in the RCs.

Performance of vesicles under thermal light excitation. We now couple the photo-excitation traces to a dynamical model of the photosynthetic vesicle, based upon experimental estimations of excitonic transfer rates and charge transfer dynamics, as discussed in [14]. In summary, we simulate the photon absorptions, a discrete-time random walk for the excitations hopping among neighbouring LHs, and the processes taking place inside the RCs (quinol separation and quinone binding to RCs); and integrate them using a Monte Carlo method. Additional to the previous work [14], we also include the recombination of the intermediate metastable state \(P^*Q_B^*\), which is described by a stochastic process with associated lifetime \(t_{\text{crit}}\) after charge separation \(P^* \rightarrow P^+\) occurred.

A key observation of this work is that the bursted structure of thermal fields is preserved for excitations reaching the RCs. In detail, the calculation of \(B\) for the waiting times between absorbed excitations and for the waiting times between excitations reaching each of the RCs, shows that the bursts from the thermal light, conspicuous in the inset time traces of events, drive a bursted arrival of excitations to individual RCs, as shown in Fig4(a). As a consequence, the charge recombination, which depends on a pairwise photon arrival to RCs, might be sensitive to the burstiness of the initial absorption and therefore, quinol production may also be influenced by the arrival statistics. In Fig4(b) we show that temporal correlations of thermal light are able to tune the quinol production, as quantified by the quinol yield \(\eta = 2\hat{N}_{\text{QH2}}/I_{\text{tot}}\), where \(\hat{N}_{\text{QH2}}\) represents the rate of quinol production in the stationary state and \(I_{\text{tot}}\) is the photon absorption rate of the vesicle. Notice that the quinol yield decreases for higher temporal correlation of the absorbed photons. Thermal light exhibits long time intervals \(\langle I_{\text{inter}} \rangle\) which allow the relaxation of the mentioned RC metastable state, such that higher correlations in the absorption events, result in lower efficiency of quinol production. Temporal correlations arise whenever spatial correlations of thermal light are appreciable. Although spatial correlations are high on the length-scale of bacterial vesicles (cf. Fig4), their almost constant spatial profile across a full vesicle, explains the robust performance of vesicles to the geometrical arrangements of LH1 and LH2s (see SI section I for details).

Under a physiological average light intensity \(\langle I\rangle = 10^{-3}\) photons/(LH-ms) and and lifetime \(t_{\text{crit}}\) of \(P^*Q_B^*\) recombination between 100 and 1000 ms as observed [36, 39, 40], the quinol efficiency of the membrane varies across the full range \(\approx 0 - 90\%\), depending on \(T/\tau_c\). For this light intensity, the range of efficiency is thereby strongly dependent on the degree of temporal correlation from absorbed photons. Figure4(c) depicts the quinol production rate relative to the ATPase maximum capacity. For physiological light intensity, this figure shows an interesting crossover for \(T \leq 0.7\tau_c\), where the maximum ATP turnover is achieved (the exact crossover depends on the particular value of \(t_{\text{crit}}\)). For the same membrane vesicle under much lower light intensity \(\langle I\rangle = 10^{-4}\) photons/LH-ms, this maximum turnover is never reached. In this situation a very low \(\approx 0\%\) quinol yield results, independent on the degree of temporal correlations in the absorbed light. This last
observation pinpoints a possible photoprotection mechanism. The lifetime of charge recombination within the RCs seems to place an important constraint on the physiological light intensity for survival of photosynthetic bacteria. The sensitivity of a metastable pairwise charge separation to thermal light correlations can therefore help tune quinol production to the ATPase turnover capacity in order to avoid acidity excess and cell damage.

The strong photo-protection mechanism is a consequence of the metastable state lifetime and delayed arrival of bursts, and does not result from additional dissipative processes. For instance, when a burst of photons arrives to the membrane, two photo-excitations have a higher probability to coincide in the same LH structure and annihilate \[ \text{[43]} \]. The dissipation by annihilation, shown in the inset of Fig. 4 (c) increases with temporal correlations for the physiological intensity, but its effect remains minimal (a decrease in quinol yield of 0.1–1%) in contrast to the decrease in performance due to the temporal correlations of photo-excitation events shown in Fig. 4 (b).

Concluding remarks. We have demonstrated that the performance of photosynthesis is likely to be affected by the spatio-temporal correlations present in thermal sunlight. The interplay between these correlations and the dynamics within RCs, sets constraints to the light intensities appropriate for bacterial survival, while it provides insight into a pathway for photoprotection, which balances the long intervals between thermal light bursts, and charge recombination taking place in the RCs. This work underlines that not only the average light intensity and the exciton dynamics, but also the statistics of the absorption events and the RC charge dynamics, are relevant aspects for the performance of photosynthetic membranes.

It should be noticed that this photo-protective mechanism might operate in different ecological niches, since it encompasses the properties of the exciting field common to all forms of photosynthesis (thermal light), and the dynamics on the RCs which is, except for minor changes, conserved across species. This may suggest a concept of evolutionary fitness of pairwise charge separation for quinol production and synthesis of ATP, which has endured due to the spatio-temporal correlation present in thermal light. Arguably, the actual quantification of the statistics of absorption by a finite absorption linewidth requires further development and provides an interesting perspective for future work, but we should stress that beyond this specific quantification, the presented unified analysis of absorption, excitonic transfer and charge dynamics already provides a glimpse on an adaptation mechanism of biological photosynthesis that is driven by the coherence of thermal sunlight.

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