Temporal correlations of sunlight may assist photoprotection in bacterial photosynthesis

To cite this article: Adriana M De Mendoza et al 2020 New J. Phys. 22 073042

View the article online for updates and enhancements.
Temporal correlations of sunlight may assist photoprotection in bacterial photosynthesis

Adriana M De Mendoza 1,4, Felipe Caycedo-Soler 1, Susana F Huelga 3 and Martin B Plenio 3

1 Physics Department, Universidad de Los Andes, A.A. 4976 Bogotá, Colombia
2 OncoRay—National Center for Radiation Research in Oncology, Faculty of Medicine and University Hospital C. G. Carus, TU Dresden, HZDR, Dresden, Germany
3 Institut für Theoretische Physik and IQST, Universität Ulm, Albert-Einstein-Allee 11, 89081 Ulm, Germany
4 Author to whom any correspondence should be addressed.
E-mail: am.de259@uniandes.edu.co

Keywords: bacterial photosynthesis, charge transfer, thermal light, photoprotection

Abstract
Photosynthetic systems utilize adaptability to respond efficiently to fluctuations in their light environment. As a result, large photosynthetic yields can be achieved in conditions of low light intensity, while photoprotection mechanisms are activated in conditions of elevated light intensity. In sharp contrast with these observations, current theoretical models predict bacterial cell death for physiologically high light intensities. To resolve this discrepancy, we consider a unified framework to describe three stages of photosynthesis in natural conditions, namely light absorption, exciton transfer and charge separation dynamics, to investigate the relationship between the statistical features of thermal light and the Quinol production in bacterial photosynthesis. This approach allows us to identify a mechanism of photoprotection that relies on charge recombination facilitated by the photon bunching statistics characteristic of thermal sunlight. Our results suggest that the flexible design underpinning natural photosynthesis may therefore rely on exploiting the temporal correlations of thermal light, manifested in photo-bunching patterns, which are preserved for excitations reaching the reaction center.

Natural photosynthesis thrives under constantly changing environmental conditions thanks to active regulatory mechanisms. These mechanisms must balance the interplay between thermal light absorption, transport of the resulting electronic excitations (excitons) to a reaction center (RC), charge separation and metabolic output.

However, the sheer complexity of these four individual processes makes their combined description challenging and fundamental questions remain open. In particular, photosynthetic bacteria can survive in light intensities that exceed predictions from current theoretical models [1–7]. To resolve this discrepancy, we propose a novel approach to describe the coupled dynamics resulting from those fundamental processes in real photosynthetic vesicles, as depicted in figure 1.

Several works have focused on the interplay between light absorption and excitons transfer. There is a vast literature debating the existence and duration of coherent transport when triggered by incoherent light absorption at the light harvesting complexes (LHs) [8–18], some of them propose to treat thermal light as a series of random ultrashort femtosecond pulses [13, 14, 19]. Here, we do not wish to engage in this stimulating debate, but in a simplified version of the light absorption process, we assume that photons are absorbed by the antenna pigments [20–22] and study the effects of the thermal light photon-statistics on the subsequent steps of the photosynthetic process. After a photon-absorption takes place, the created excitation travels through the network of LHs by random hopping until reaching a reaction center (RC), where it triggers a photoinduced charge separation required to synthesize Quinol molecules.
Figure 1. (a) Relevant length scales in typical bacterial photosynthetic apparatus. On the left side, we illustrate the parameters describing the incoherent light source provided by sunlight. Here $a$ denotes the source diameter, $D$ the distance to the light reception system and $\lambda$ the mean wavelength of the incident light. The large orange circle with diameter $l_c \approx 50 \mu m$, [24] represents the coherence area of sunlight, encircling a complete photosynthetic bacterium of length $\approx 40 \mu m$[45]. It is within this coherence region defined by $l_c$ where thermal temporal correlations will become manifest. On the right side of panel (a) we depict the photosynthetic apparatus of the bacterium, embedded in characteristic vesicles. They contain the light harvesting complexes LH2 and LH1 and the encircled reaction centers (RCs), with typical inter-complex distance $r_{ij} \ll l_c$. (b)–(d) Flow diagram illustrating the elementary processes in bacterial photosynthesis. Photons (depicted as orange bolts) are detected by the light harvesting complexes (LH1 and LH2) and converted into photo-excitations totally or partially delocalized along individual harvesting complexes (excitons), which travel through the network of LHs until reaching an open RC as depicted in (b). Once in the RC, the exciton induces charge separation and a chain of electron transport steps that end up in quinol ($Q_BH_2$) production. Charge can be recombined, as represented by the red arrow, with recombination lifetime $t_{crit}$ in (c). In (d) quinol oxidizes and the liberated hydrogen (together with two additional hydrogens pumped from the cytoplasm) produce the electrochemical gradient required to make the ATPase macromolecule rotate and produce ATP. The ATPase molecule catalyzes the reaction between adenosine diphosphate (ADP) and inorganic phosphate ($P_i$).

Illumination. The coherence length of sunlight at the earth’s surface is approximately $50 \mu m$ [23, 24]. This value exceeds the size of any unicellular photosynthetic organism, e.g. a purple bacterium, as illustrated in figure 1(a). Hence, the optically active molecules of photosynthesis, which arrange in light harvesting complexes (LH1 and LH2 in purple bacteria) within photosynthetic vesicles, will absorb thermal photons with significant temporal correlations leading to interspersed bursts of photons, as noted decades ago [25–27].

Exciton transfer. After photon absorptions, the resulting excitons diffuse across the network of LHs until reaching an available RC within an LH1 (see figure 1(b). The transfer rates $t_{ij}$ between complexes $i \rightarrow j$ are adequately described via generalized Förster theory [28] and accurately tested by linear and multidimensional spectroscopic techniques [29–36].

Charge separation dynamics. Once an exciton arrives at an RC it triggers an electron transport chain, whose outcome is the production of quinol molecules ($Q_BH_2$). This transport goes through intermediate metastable states of charge separation with relevant recombination times ($t_{crit}$ in figure 1(c)) [37–39], which in combination with the bursted structure of the incoming excitons may effectively reduce the conversion efficiency of the photosynthetic machinery. These processes are described in detail in the next section.

Metabolism. Quinol reduction facilitates the formation of an electrochemical gradient that drives the rotation of a transmembrane macromolecule ATP-synthase (ATPase) to synthesize adenosine triphosphate (ATP) (figure 1(d)). The number of ATPases present per photosynthetic vesicle in the purple bacteria is still controversial, particularly because their visualization on the AFM experiments remain elusive [40, 41]. Kinetic analysis from bacteria grown under light intensity $\langle I \rangle = 18 \text{ W m}^{-2}$ estimates at most one ATPase...
per vesicle [42], while kinetics measured from cells grown at \( \langle I \rangle = 500 \text{ W m}^{-2} \) suggest between 9–13 ATPases per vesicle [43]. Assuming the accuracy and validity of both experimental techniques/results, we infer that the discrepancy between the number of ATPases per vesicle is explained by the intensity conditions of the experiments. On this basis we use in our analysis the value of one ATPase per photosynthetic vesicle, since low-light illumination is characteristic for the habitat of purple bacteria [44].

This single ATPase present per vesicle may synthesise at most 100 molecules (about 200 excitations/s) of ATP for bacterial photosynthesis [2, 46, 47]. Based on this analysis, typical membranes with \( \sim 400–600 \) LHs [1, 48] and 90% transport efficiency [44, 49], will accumulate hydrogen, increasing dangerously the cytoplasmic acidity for intensities as low as \( \langle I \rangle = 0.1–0.2 \text{ W m}^{-2} \). This estimate is in stark contrast with the proven survival of purple bacteria for light intensities as high as 100 W m\(^{-2} \) [1, 44]. In principle, charge recombination could provide the means to avoid the formation of excess quinol, but it has not been considered in previous attempts to provide a global description of the primary steps in bacterial photosynthesis [44, 49–52].

In this article, we show that a detailed but comprehensive model of the elementary processes in the photosynthesis of purple bacteria unveils a dynamical interplay between the bunched statistics of thermal light, the process of charge recombination and quinol production. In particular, the long time-intervals between photon bursts resulting from thermal light absorption provide an essential element to determine the photoprotective role of metastable states in RCs.

1. Results

1.1. Thermal light illumination and excitons statistics

The photon-statistics of thermal light absorption shows typical intensity fluctuations that lead to patterns of bunched photo-detections separated by waiting times (where no detection happens), when the detection takes place within the coherence length and coherence time of the light [53–55]. This pattern—also called bunching of the light—arises as a consequence of the light–matter interactions and hence depends on the joint properties of the light field (frequency spectrum, intensity and correlations) and the detection system provided by the LH1–2 complexes (absorption efficiency, absorption bandwidth, spatial configuration and detection time window). We have implemented a statistical model of thermal light detection where the probability distribution of absorption events is characterized by its factorial moments generating function [56]. This framework, whose main features are revised in the methods, allows for the inclusion of light correlations in a natural manner, showing that the degree of burstiness can be tuned by the ratio between the detection time window and the coherence time of the detected light \( T/\tau_c \). This parameter allows the continuous statistical tuning of the absorbed excitations from a thermal (\( T/\tau_c \ll 1 \)) field with maximal burstiness, to a Poissonian field (\( T/\tau_c \gtrsim 1 \)) without burstiness, as shown in figure 2(a).

The statistics of bursts in a sequence of absorption events can be characterized by the so-called burstiness parameter, \( B = (\langle \sigma_t \rangle - \langle t \rangle)/\langle \sigma_t + \langle t \rangle \rangle \). 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 the times series exhibit bursts of events [57]. Unsurprisingly, in figure 2(b) we show that the ratio \( T/\tau_c \) and \( B \) are related monotonically. This implies that either of them can be used to quantify the bunching of the light absorption, and supports our use of \( B \) in what follows as a measure of the burstiness in traces of events, in particular, on the arrival of excitations to the RCs.

To characterise the statistical properties of the waiting times \( t \) between consecutive absorption events beyond the average \( \langle t \rangle \) and variance \( \sigma_t \), we consider the average waiting times between and within bursts, namely \( \langle t_{\text{inter}} \rangle \) and \( \langle t_{\text{intra}} \rangle \), respectively. For the simulated events, all four statistical quantities increase as \( B \) increases and approaches 1 for a thermal distribution (see inset in figure 2(b)), while preserving the average intensity of the source (which is obtained by energy conservation and not by the reciprocal of \( \langle t \rangle \) for thermal fields [58]). It is worth stressing from the inset in figure 2(b) that \( \sigma_t \) grows faster than \( \langle t \rangle \). This reflects the faster growth of \( \langle t_{\text{inter}} \rangle \) compared with \( \langle t_{\text{intra}} \rangle \) for larger burstiness \( B \). It can also be observed in the same figure the quick convergence among \( \langle t \rangle \) and \( \sigma_t \) for \( T/\tau_c \gtrsim 1 \), as expected from the trend towards independent random events following a Poissonian distribution.

Chan and collaborators recently showed that for the conditions of sunlight absorption, namely ultraweak chromophore–light coupling and intensity, the key parameter determining the quantum dynamics of absorption in photosynthetic systems is the ratio between the chromophores absorption spectral bandwidth \( \Delta \omega \), and their concomitant emission rate \( \Gamma \) [14], which characterizes the recovery time of the pigments.
Figure 2. Thermal versus Poissonian light. (a) Typical time traces of absorption events for different values of the ratio $T/\tau_c$. (b) Burstiness $B$ of the reception signal as a function of the temporal correlations ($T/\tau_c$). In the inset, we show the characterisation of low-$B$ signals using as figure of merit the quantities $\langle t \rangle, \sigma_t, \langle t \rangle_{\text{intra}}, \text{and} \langle t \rangle_{\text{inter}}$ (descriptions in the text). All quantities are displayed in milliseconds on a semi-logarithmic scale. We considered $10^6$ light absorption events.

Since the coherence time of absorption events is approximated as the inverse of the spectral bandwidth of the absorption ($\tau_c \approx 2\pi/\Delta \omega$), and the recovery time of the chromophores sets the maximum of the detection time ($T_{\text{max}} \approx 1/\Gamma$); the ratio is analogous to the maximum of $T/\tau_c$, i.e., $\Delta \omega/\Gamma \approx 2\pi T_{\text{max}}/\tau_c$ (see SI-section IB for further discussion) (stacks.iop.org/NJP/22/073042/mmedia). Regarding the recovery time, experiments have shown that excited state absorption occurs in LH complexes with about 90% of the intensity of ground state absorption after $\sim 0.1 \text{ ps}$ [59]. Therefore, at the chromophores absorption spectra ($\lambda_{\text{LH1}} = 875 \pm 20 \text{ nm and } \lambda_{\text{LH1}} = 850 \pm 20 \text{ nm}$) the coherence time ($\tau_c \sim 0.1 \text{ ps}$) is comparable to their recovery time ($1/\Gamma$), reflecting the similar energetic scales of exciton-exciton, exciton-phonon, phonon-phonon couplings and energetic disorder of this system [14]. In practice, due to the rather low physiological light intensity, doubly excited states will seldom arise in LHs and hence, the photosynthetic absorption set –composed of hundreds of available LHs– should be capable to discriminate individual photons within the coherence time. These results indicate that thermal light detection in photosynthetic systems might operate in a regime where the detection time is smaller or comparable to the coherence time, which makes it at least plausible that the temporal correlations present in thermal light may affect absorption statistics.

1.2. Coupling thermal light absorption with exciton dynamics and charge separation on bacterial vesicles

After photon absorption, the exciton dynamics across the membrane vesicle can be modeled based on the transfer rates between nearest neighbor complexes. Figure 3 summarizes the excitation kinetics and spatial arrangements of the biomolecular complexes LH1, LH2 and RC in purple bacteria. In typical vesicles, the LH2 antenna outnumbers the LH1 complexes, which form an ellipse that encircle the RC protein. Excitation transfer between RCs, LH1s and LH2s occurs from induced dipole transfer on a picosecond time-scale [52], while vibrational dephasing destroys coherences in hundreds of femtoseconds at most [33–36], resulting in incoherent energy transfer between the RC $\leftrightarrow$ LH1 $\leftrightarrow$ LH2 sustained, however, by delocalized excitons over single complexes [28–36, 56, 60, 61]. Transfer rate measures from pump-probe experiments are available for LH2 $\leftrightarrow$ LH1 and LH1 $\leftrightarrow$ RC transfer steps [29–32, 52], whereas transfers LH2 $\leftrightarrow$ LH2 and LH1 $\leftrightarrow$ LH1, i.e. between the same type of complexes, have been estimated via generalized Förster rates [52, 62]. Fluorescence, inter-system crossing, internal conversion and further dissipation mechanisms, have been included with a single conservative lifetime $1/\gamma_D$ of 1 ns [62]. All transfer rates are depicted in figure 3(a) and their values are given in table 1.
Even though consecutive photo-excitations are typically absorbed after millisecond (cf figure 2(a)), the bunched structure of thermal light requests to consider the relevant effects from two excitation dynamics. In our model, whenever two excitations meet in an LH1 or LH2 complex, they always annihilate, in order to consider singlet-singlet annihilation [59, 65]. In this process, when two excitations meet in close proximity (typically within a single LH1), one of the excitations is promoted to a doubly excited state of a pigment while the other is de-excited to the ground state of a neighboring pigment. Then, the doubly excited state relaxes to the single excitation state via intra-pigment relaxation (through the so-called internal conversion process), resulting in a single singlet excitation, as our model effectively describes.

The formation of a ‘special pair’($P^*$) in the RC initiates the first electron transfer step $P^* \rightarrow P^+$, followed by several reactions ending up with the reduction of the quinone $Q_A$ or auxiliary quinone $Q_B$. After $P$ becomes neutral following a rather fast cycle of 1 μs, (See SI section II for details on other photo-chemical transfer times scales involved) [37, 63], it can initiate a second electron transfer that results in the reduction of both quinones $Q_A, Q_B$, which triggers the uptake of two intracytoplasmic protons to produce quinol $PQH_2$. The cycle starts over when $P$ is neutral again, and quinol is exchanged by $Q_B$ via affinity reactions [37] (see SI section II for a more detailed explanation). Previous work showed that the interplay between exciton dynamics and the cycling of quinol and the auxiliary quinone affects the quinol output in vesicles [49, 50], which were observed to adapt to low and high light intensities [1]. However, the actual output of quinol production in such a model is larger than the turnover of the ATPase molecular rotor as discussed in the introduction, and would lead to bacterial death. The subsequent consideration of burst statistics in thermal light did not result in a notable reduction of the quinol output [31], which is the achievement of the present work. Using the photon absorption time-traces exemplified in figure 2, we initiate the excitonic dynamics with the rates ($\gamma_{ij}, t_{ij}$ for $i,j \equiv \text{LH1, LH2, RC}$) depicted in figure 3(a), over a typical photosynthetic vesicle composed of a few hundreds of LHS, illustrated in figure 3(b). In our simulation we include the charge dynamics occurring within the RCs, therefore, excitations reaching RCs initiate charge separation $P^* \rightarrow P^+ \rightarrow \gamma^-$ and, crucially, going beyond previous considerations made in references [49–51], we also include the recombination of the intermediate metastable state $P^+ \rightarrow \gamma^-$. This recombination takes place in about 100 ms to 1 s, a time-scale commensurable with photon absorption waiting times in physiological conditions.

A crucial observation of this work is that the bursted structure of thermal field’s statistics is preserved for excitations reaching the RCs. Because the inter-photoexcitation waiting times lie within ms range, whereas the dynamics from absorption until arrival to the RCs occurs within a few hundred of picoseconds. 

### Table 1. Considered excitonic transfer rates $t_{ij}$ ($i,j = 1,2,RC$) for the simulation of the primary steps of photosynthesis in purple bacteria.

| Process | Value | Data source [reference] |
|---------|-------|------------------------|
| LH2 → LH2 | $t_{22} = 10$ ps | Calculated [52] |
| LH2 → LH1 | $t_{21} = 3.3$ ps | Measured for $R$. Sphaeroides [60] |
| LH1 → LH2 | $t_{12} = 15.5$ ps | Measured for $R$. Sphaeroides [60] |
| LH1 → LH1 | $t_{11} = 20.0$ ps | Calculated by Förster interaction [62] |
| LH1 → RC | $t_{1,RC} = 25$ ps | Calculated at 300 K [31] |
| RC → LH1 | $t_{RC,1} = 8.0$ ps | Calculated [85] and measured [30] |
| Dissipation | $\gamma_D = 1$ $\text{ns}^{-1}$ | Estimated from fluorescence [62] |
Figure 4. Effect of thermal light correlations on quinol production. (a) Burstiness $B$ of the absorption traces and of the average burstiness of excitations reaching each RC. In (b) Quinol yield $\eta$, for different temporal correlation $T/\tau_c$ of the absorbed excitations. (c) Quinol production rate, relative to the maximum capacity of one ATPase (horizontal continuous line) as a function of the temporal correlation $T/\tau_c$. Inset: ratio of annihilation events as a function of the temporal correlations ($T/\tau_c$).

In figure 4(a) we show how temporal correlations of thermal light can tune the quinol production, as quantified by the quinol yield $\eta = 2\dot{N}_{QH_2}/I_{tot}$, where $\dot{N}_{QH_2}$ represents the rate of quinol production in the stationary state and $I_{tot}$ is the photon absorption rate of the simulated photosynthetic vesicle. Notice that the quinol yield decreases for higher temporal correlations of the absorbed photons. Thermal light exhibits long waiting time intervals $\langle t_{inter} \rangle$ which allow the relaxation of $P^+Q^-B$. In this way, 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. figure 1), their almost constant spatial profile across a full vesicle explains the robust performance of vesicles to changes in the specific geometrical arrangements of LH1 and LH2s (see SI section III for details).

Under average physiological light intensity $\langle I \rangle = 10^{-3}$ photons/(LH·ms), which is near to the maximum ATPase capacity, and recombination lifetime $t_{crit}$ between 100 and 1000 ms, the quinol efficiency of the membrane varies across the full range $\approx 0\% - 90\%$, depending on the ratio $T/\tau_c$ (see figure 4(b)). For this light intensity, we obtain that the efficiency is strongly dependent on the degree of temporal correlation from absorbed photons. The quinol yield is kept on very small levels for increasing values of $t_{crit}$ the lower the burstiness, as shown in figure 4(a). Moreover, figure 4(c) depicts the quinol production rate relative to one ATPase maximum capacity. For physiological light intensity, this figure shows an interesting crossover for $T \lesssim 0.7\tau_c$ where the maximum ATP turnover is achieved (the exact crossover depends on the particular value of $t_{crit}$). This last observation identifies a possible photoprotection mechanism. 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 is due to the recombination mechanism, independent on the degree of temporal correlations in the absorbed light. The lifetime of charge recombination within the RCs seems to place an important constraint on the physiological light intensity for the 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 excess acidity and cell damage.

To confirm that the found photo-protection mechanism relies mainly on the metastable state of the RC, we also quantified the effect of excitations annihilation during the transport through the network of LHs. Because of the low physiological light intensities studied, our treatment does not consider triplet accumulation leading to triplet-singlet annihilation [65]. We nevertheless consider singlet-singlet annihilation [59, 64]. In our model, whenever two singlet photo-excitations coincide at the same LH during their dynamics across the vesicle, the annihilation of one of these singlet excitation occurs. This model represents a more extreme scenario as the observations in [59], which address a finite probability of annihilation (less than 100%) whenever two singlet excitations reside in the same LH complex. We observed a marginal dissipative contribution of the annihilation process to photo-protection. This dissipation is also enhanced by the spatiotemporal correlations of the light absorptions. When a burst of photons arrives to the membrane, two photo-excitations have a higher probability to coincide in the same LH structure, and one of them annihilates. Correspondingly, the percentage of excitons dissipated by annihilation, shown in the inset of figure 4(c), increases with temporal correlations for the physiological intensity. As can be also observed in this figure, the annihilations percentage is larger for a lower intensity, which is consistent with the experiments of Pflock et al [65]. Nevertheless, the dissipative effect of annihilations remains minimal (a decrease in quinol yield of \( \approx 0.1\% \)–1%) in contrast to the decrease in performance due to the temporal correlations of photo-excitation events shown in figure 4(b). In conclusion, we suggest that the strong photo-protection mechanism is predominantly a consequence of the metastable state lifetime and delayed arrival of bursts.

2. Discussion

This work studies the role of the statistics of absorption events in the performance of photosynthesis. In our model we have shown that the performance of photosynthesis is 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 photo-protection, which balances the long intervals between thermal light bursts, and charge recombination taking place in the RCs. Our work underline 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 versatile performance of photosynthetic membranes.

We chose a relatively low physiological intensity \((I) = 10^{-3}\text{photons/LH} \cdot \text{ms} \sim 1\text{ W m}^{-2}\) which exceeds the capacity of one ATP synthase by about three times as shown in figure 4(c). Although the exact number of ATPases per vesicle is still not clear, here we propose a mechanism in which the quinol yield in the photosynthetic process of purple bacteria is reduced because of the interplay between the correlations present in the thermal light and the recombination process inside de RCs. Therefore, with a larger amount of ATPases per vesicle the mechanism for energy dissipation would be still valid, but its importance for survivability would depend on the incoming light intensity. For instance, in the experiment of Feniouk et al. [42] this mechanisms would be dearly needed for the cell cultures grown under \((I) = 18\text{ W m}^{-2}\) with just one ATPase per vesicle. In the same way, in experiments of Gubellini et al. [43], the proposed photoprotective mechanism would be important with \(\sim 10\) ATPases per vesicle, for bacteria grown under \((I) = 500\text{ W m}^{-2}\). Although some parameters of the real photosynthetic system are unknown, depend on the precision of the experimental technique, or are on debate, our work proposes foundational aspects that relate the photon absorption statistics to the properties of the photosynthetic machinery, setting the ground for future ideas and experiments.

We note 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 a regulation mechanism of biological photosynthesis that is driven by the coherence of thermal sunlight.

Besides opening new avenues for further theoretical studies, we stress that our findings lead to predictions that can be experimentally tested with present resources to measure cellular fitness and regulation, e.g., bacterial growth rate, metabolic activity, or gene expression among others. Comparison of
fitness indicators for bacteria grown under illumination with attenuated laser and pseudo-thermal sources [66, 67] will shed light on the response of these organisms to the spatio-temporal correlations of the incident light. Better fitness indicators for pseudo-thermal light will confirm the significance of the interplay of light absorption statistics and charge recombination, in agreement with our predictions.

Moreover, the statistics of illumination have been shown to improve the rectification stage, i.e. Alternating-to-Direct current conversion in solar antennas [68–70]. Rectification nowadays drops the solar antennae collection efficiency (> 80%) to about 0.01% [71, 72], but might be improved by the coherent combination of the light detected by different antennas, i.e., the spatio-temporal correlations [68–70]. In view of our results, it is an interesting perspective to understand to what extent the spatio-temporal correlations of thermal light could also assist the rectification process in artificial light-harvesting technologies.

3. Methods

3.1. Statistical model of thermal light detection

The absorption of light by a set of receptors is a stochastic process, in which the absorption events are not independent of each other. The quantum photon-interference leads to spatial and temporal correlation between absorption events, affecting the respective photon-counting statistics [73]. Our aim is to introduce the spatio-temporal correlations into the calculation of the probability f(t) for the time elapsed between consecutive detections t. This is used to generate the photon-absorption events required at the beginning of our photosynthesis simulations. That is, our algorithm generates a random number between 0 and 1 for $F(t) = \int_0^t f(t') \, dt'$ and resolves the corresponding $t$ value, which is the elapsed time since the last detection event until the current one.

In summary the calculation workflow reads as follow: the spatial $\gamma_{kl}$ and temporal $\gamma(t_1, t_2)$ normalized correlation functions are plugged into the generating functional $G(s, T)$, which in turn allows the calculation of the cumulative probability distribution for inter-event time $F(t)$. Finally $F(t)$ is used to generate the photon-absorption events that will be subsequently converted into photo-excitations in the Montecarlo simulations. Schematically, this is:

$$\gamma_{kl} \gamma(t_1, t_2) \rightarrow G(s, T) \rightarrow F(t) \rightarrow \text{simulations.}$$

For the convenience of the reader, we describe below all the quantities involved, while we refer to the SI for a review of their derivation for the relevant field; namely a Gaussian light field in the far-field approximation, assuming a low absorption bandwidth.

The calculation starts with the spatio-temporal normalized correlation functions (also called coherence functions) $\gamma_{kl}(t_1, t_2) = \langle \hat{E}^+(\vec{r}_k, t_1) \hat{E}^-(\vec{r}_l, t_2) \rangle / \sqrt{\langle n_k \rangle} \sqrt{\langle n_l \rangle}$. Here $\hat{E}^+$ is the electric field operator, $k, l$ refer to a couple of absorbers, $r_{kl}$ is the position of the detector labelled $k(l)$, which receive photons at time $t_{kl}$; and $\langle n_{ij} \rangle$ is the average number of photon-absorptions at each detector. Assuming that the superposition of the light field coming from different points at the source, does not affect its spectral properties at the reception positions—a feature called cross-spectral purity—the spatial and temporal contributions can be separated $\Gamma_{kl}(t_1, t_2) = \sqrt{\langle n_k \rangle} \sqrt{\langle n_l \rangle} \gamma_{kl} \gamma(t_1, t_2)$ [74]. These coherence functions are obtained for quasi-monochromatic light in the far field approximation [75, 76] (see SI-section IA for derivation):

$$\gamma_{kl} = \frac{I(v_{kl})}{v_{kl}},$$

$$\gamma(t_1, t_2) = \frac{\sin(\tau_{1,2})}{(\tau_{1,2}).}$$

The spatial correlations are described by equation (1), where $I(v_{kl})$ is the first order Bessel function, and the argument $v_{kl} = 2\pi |\vec{r}_{kl}| / \lambda$ compares the inter-detectors distance with the transverse coherence length $l_c$. The spatial correlation function $\gamma_{kl}$ quantifies the decay of the spatial correlations as a function of the distance between the detectors $k$ and $l$. Spatial coherence is relevant for distances inside the transverse coherence length $|\vec{r}_{kl}| \lesssim l_c$. In turn, the transverse coherence length $l_c = \lambda a / 2\pi$, relates the average wavelength $\lambda$ of the field, the distance to the light source $D$, and its diameter $a$, as depicted in figure 1(a) [56]. Within the coherence area, temporal correlations of thermal light are accounted for by a temporal correlation function (equation (2)), whose argument for a stationary field is $\tau_{1,2} = (t_1 - t_2) / a$. Similarly to spatial case, $\gamma(t_1, t_2)$ describes the decay of the correlations as a function of the inter-detections time $(t_1 - t_2)$, normalized by the coherence time of the light $\tau_c$. The maximum possible value that $(t_1 - t_2)$ can get is the detection time $T$. Since the photo-detection probability depends on the convolution of the spectral density function of the field with the response function of matter [55, 75], only the effectively absorbed modes of...
light are relevant to the statistics of the photo-excitations [77]. Therefore, $\tau_c$ is approximated as $1/\Delta \omega$.

Both, temporal and spatial normalized correlation functions have been experimentally well tested, see references [78, 79].

Correlation functions (equations (1) and (2)) are introduced into the statistical description of the light-absorption process by means of the factorial moments generating function $G(\{s_i\}, T)$, which encodes all the statistical information of the process [23, 80–82]. This formalism accounts for the statistics of the photodetection events recorded by a set of $N$ detectors, each of which we identify as individual LH units in our case. Here we use the generating functional formalism to calculate the photocounting joint probability $P(n_1, n_2, \ldots, n_N, T)$, that $n_i$ absorption events occur at the $i$th LH ($i = 1, \ldots, N$) during the time window $T$ [23, 56, 80, 81, 83]:

$$P(n_1, n_2, \ldots, n_N; T) = \left\{ \prod_{i=1}^{N} \frac{(-1)^{n_i} \partial^{n_i} \phi_i}{n_i!} \right\} G(\{s_i\}, T)|_{\{s_i=1\}}.$$  

(3)

The probability to absorb $n$ photons in the total set of detectors, regardless of the specific counting record of any individual detector, is then

$$P(n, T) = \sum_{\{n_i\}} \delta \left(n - \sum_{i=1}^{N} n_i\right) P(n_1, n_2, \ldots, n_N, T).$$  

(4)

The calculation of the generating functional for Gaussian light leads to [80, 81]:

$$G(\{s_i\}, T) = \prod_{j=1}^{T} \prod_{k=1}^{N} (1 + s_j \bar{\varpi}_j b_k)^{-1},$$  

(5)

such that the spatial and temporal coherence functions enter into the model by means of the eigenvalues $\bar{\varpi}_j$ and $b_k$ of the spatial and temporal Fredholm equations (see SI-section IB for the derivation),

$$\int_0^T dt_2 \gamma(t_1 - t_2) \psi_j(t_2) = \bar{\varpi}_j \psi_j(t_1)$$

$$\sum_{i=1}^{N} \sqrt{\alpha_k(n_k)} \gamma(t) \sqrt{\alpha_i(n_i)} \phi_i(t) = b_k \phi_k(t).$$

Finally, it can be demonstrated [58] that the cumulative distribution function $F(t) = 1 - P(n = 0, t)$ (see SI section IC for calculation). Therefore, $F(t)$ just depends on the generating functional $G(s, T)|_{s=1}$, which in turn depends on the aperture time $T$ (time window for photo-detection), and on the temporal and spatial normalised correlation functions [56].

This photo-detection theory was developed for avalanche photo-diodes where the detection time is a controllable experimental parameter. Therefore the main limitation of this formalism to describe an actual LH complex is the definition of this time window $T$ for photon-arrivals counting. Despite the large amount of existent works regarding the theory of photon-statistics of finite band-width light absorption [26, 27, 53–55], a fully comprehensive theory applicable to chromophores is yet to be developed. Notwithstanding, the ratio $T/\tau_c \ll 1$ or $T/\tau_c \gg 1$, sets the limits of Bose–Einstein (maximum correlations) or Poissonian (no correlations) statistics for light absorption, respectively. For $T/\tau_c \lesssim 1$, this framework results in waiting time distributions $f(t)$ that exhibit longer tails than the exponential distribution expected from independent events [58]. The consequence of these slow-decaying tails is a bursted structure [57], with photo-excitation traces that have very long waiting times scattered between bursts of clustered events (typical traces shown in figure 2(a)).

Even though there are many possible arrangements of the LH complexes in the vesicles, depending on the species and the light conditions, previous work [49, 84] showed that the Quinol yield is not sensitive to actual architectures under Poissonian light. Hence, we simulate the full photosynthetic vesicle depicted in figure 3(b), consisting of 400 LHs (44 core complexes and 356 LH2 antenna complexes), in agreement with realistic stoichiometry for the simulated light intensity [1]. We leave the effect of the LHs arrangement under thermal illumination open for future studies. Simulations were performed for two fixed light intensities ($\langle I \rangle = 10^{-4}$ photons/(LH $\cdot$ ms) or $\langle I \rangle = 10^{-4}$ photons/(LH $\cdot$ ms)), scanning different values of $T/\tau_c$, always verifying that the average rate of photon arrivals is preserved and equals the light intensity.

Although equation (3) allows to obtain the probability of photon arrivals at each LH, the calculation of the photo-detection traces for the total set of 400 LH units is a very expensive computational task. Instead of that, we simulate the photo-detection traces for the full membrane (equation (4)) and in a next step we...
spatially distribute the detected photons in the membrane according to the second-order spatial coherence function of the intensity (see SI section III for details).

3.2. Photosynthesis simulations

The generated photo-excitation traces are coupled to a dynamical model of the photosynthetic vesicle, in which the excitons travel through the membrane by individual hopping processes between LH rings until reaching an available RC. This transport process is based upon experimental estimations of excitonic transfer rates and charge transfer dynamics [50]. Here 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.

After a detection event is simulated, the photo-excitation is located on the corresponding ring (LH1 or LH2), and travels to a reaction center with some probability of being dissipated during the transference. Once the excitation has arrived at the RC, the latter performs the reduction–oxidation cycle described before, and two of these photo-excitation events are necessary to form a quinol molecule ($Q_B^*H_2$). In the simulations, when an RC receives the first photo-excitation there is a check for the metastable condition; if the next one does not arrive during the life-time window $t_{\text{crit}}$, the charge is recombined and the excitation is wasted (in this case the next photo-excitation will occupy its place). Otherwise, the reaction center is closed and not available during some time $\tau_{RC} = 10$ ms while finishing the process and produces a quinol molecule [49]. Although the turnover of the RCs depends on the acidity, we did not include that dependence and only chose an intermediate rate of quinol production (100 per second at pH 5 [63]), in such a way that the closing time of the reaction centers obeys an exponential distribution with that average throughput. The transfer rates used in our simulations are summarized in table 1, with values taken from pump-probe experiments or Föster calculations assuming intra-complex delocalization, which is in good agreement with experiments [52, 86, 87].

In the photosynthetic membrane, after a quinol is produced, its two hydrogens are dissociated and used by the ATP-ase enzyme to produce ATP. Impulsed by the proton gradient, the ATPase goes through conformational changes that push its subunits to rotate, catalyzing the synthesis of ATP. Although the throughput of the ATPase depends on the proton gradient across the membrane, and the reverse process—called hydrolysis—can take place, its maximum turnover plateaus to an estimated value of 100 ATPs/s for bacterial photosynthesis [46, 47]. It is worth to mention that as little as 5 RCs already saturate the capacity of the ATP-ase, in the case of slowest RCs turnover equal to 50 quinols per second for a pH = 2 [63]. The mismatch between the overall quinol production and the ATPase turnover determines the bottleneck of the system, restricting the maximum quinol throughput that can be converted into ATP and the incoming-photons rate to 200 photons/s. In our simulations, we use the average intensity 0.4 photons/ms for the whole vesicle ($I = 10^{-3}$ photons/ms · LH), which is processed without limitations by the set of 44 RCs depicted in figure 3(b), whose minimum total capacity is 4.4 photons/ms at pH = 2 [63].

Authors contributions All authors contributed to the development of the underlying model and discussed the results; ADM performed all numerical calculations with support and guidance from FC-S; all authors designed, wrote and discussed the manuscript.

Acknowledgments

This work was supported by the ERC Synergy grant BioQ, and by COLCIENCIAS and Universidad de Los Andes. We thank Neil Johnson, Pedro Manrique, Dario Egloff and ADM’s thesis supervisors Luis Quiroga and Ferney Rodriguez for very interesting discussions and comments. This publication was made possible through the support of the John Templeton Foundation.

References

[1] Scheuring S and Sturgis J N 2005 Science 309 484
[2] Geyer T and Helms V 2006 Biophys. J. 91 921
[3] Cogdell R J, Howard T D, Britik R, Schlodder E, Geisenheimer I and Lubitz W 2000 Phil. Trans. R. Soc. B 355 1345
[4] Kim H, Li H, Maresca J A, Bryant D A and Savikhin S 2007 Biophys. J. 93 192
[5] Scholes G D, Harcourt R D and Fleming G R 1997 J. Phys. Chem. B 101 7302
[6] Kosumi D, Horibe T, Sugisaki M, Cogdell R J and Hashimoto H 2016 J. Phys. Chem. B 120 951
[7] Dong H, Li S-W, Yi Z, Agarwal G S and Scully M O 2017 arXiv:1608.04364v2 [physics.chem-ph]
[8] Brumer P and Shapiro M 2012 Proc. Natl Acad. Sci. 109 19575
[9] Han A C, Shapiro M and Brumer P 2013 J. Phys. Chem. A 117 8199
[10] Brumer P 2018 J. Phys. Chem. Lett. 9 2946
[80] Zardecki A 1971 *Can. J. Phys.* **49** 1724
[81] Bures J, Delisle C and Zardecki A 1972 *Can. J. Phys.* **50** 1307
[82] Van Kampen N G 1992 *Stochastic Processes in Physics and Chemistry* vol 1 (Amsterdam: Elsevier)
[83] Bédard G 1967 *Phys. Rev.* **161** 1304
[84] Caycedo-Soler F, Rodríguez F J, Quiroga L and Johnson N F 2010 *Phys. Rev. Lett.* **104** 158302
[85] Damjanović A, Ritz T and Schulten K 2000 *Int. J. Quantum Chem.* **77** 139
[86] Monshouwer R, Abrahamsson M, van Mourik F and van Grondelle R 1997 *J. Phys. Chem.* B **101** 7241
[87] Schroeder C A, Caycedo-Soler F, Huelga S F and Plenio M B 2015 *J. Phys. Chem.* A **119** 9043