



Excitation Properties of Photopigments and Their Possible Dependence on the Host Star

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Abstract

Photosynthesis is a plausible pathway for the sustenance of a substantial biosphere on an exoplanet. In fact, it is also anticipated to create distinctive biosignatures detectable by next-generation telescopes. In this work, we explore the excitation features of photopigments that harvest electromagnetic radiation by constructing a simple quantum-mechanical model. Our analysis suggests that the primary Earth-based photopigments for photosynthesis may not function efficiently at wavelengths $>1.1 \mu\text{m}$. In the context of (hypothetical) extrasolar photopigments, we calculate the potential number of conjugated π -electrons (N_*) in the relevant molecules, which can participate in the absorption of photons. By hypothesizing that the absorption maxima of photopigments are close to the peak spectral photon flux of the host star, we utilize the model to estimate N_* . As per our formalism, N_* is modulated by the stellar temperature, and is conceivably higher (lower) for planets orbiting stars cooler (hotter) than the Sun; exoplanets around late-type M-dwarfs might require an N_* twice that of the Earth. We conclude the analysis with a brief exposition of how our model could be empirically tested by future observations.

Unified Astronomy Thesaurus concepts: [Astrobiology \(74\)](#); [Biosignatures \(2018\)](#); [Low mass stars \(2050\)](#); [Stellar types \(1634\)](#)

1. Introduction

With the ongoing explosion in the number of exoplanets, there has been a commensurate rise in interest in ascertaining/establishing (1) the conditions that render a planet habitable, and (2) the traits of the putative biospheres (Lammer et al. 2009; Cockell et al. 2016; Cockell 2020). This endeavor, in addition to its theoretical import, will also have real consequences in shaping and prioritizing the selection of target planetary systems for in-depth characterization by forthcoming telescopes (Fujii et al. 2018; Schwieterman et al. 2018).

Although habitability and potential biospheres are clearly constrained by the properties of the world (e.g., planet or moon) in question, it is evident that these aspects are also conditioned by the host star(s). The inner and outer limits of the habitable zone (HZ)—namely, the region surrounding the star where surface temperatures on rocky planets could be conducive for liquid water—is manifestly regulated by the stellar spectral type (Dole 1964; Kasting et al. 1993; Kopparapu et al. 2013).⁵ Aside from the HZ, a multitude of vital processes on habitable planets such as abiogenesis and atmospheric retention (reviewed, for instance, in Lingam & Loeb 2019a) may be profoundly influenced by the star.

If we turn our attention to the attributes of the conjectured biospheres, photosynthesis immediately springs to mind. The vast majority of biomass on Earth is dependent, either directly or indirectly, on (oxygenic) photosynthesis (Bar-On et al. 2018); this is not surprising given the bountiful supply of

sunlight. Since the stellar temperature of different spectral types is subjected to considerable variation, and consequently so is the ensuing spectral energy distribution, it would appear reasonable to surmise that the modes of photosynthesis might diverge from those prevalent on Earth.

Unraveling the potential characteristics of extrasolar photosynthesis is especially valuable because it can engender distinctive gaseous (e.g., molecular oxygen) and surface (e.g., vegetation red edge) biosignatures (Schwieterman et al. 2018; Lingam & Loeb 2021a). Thus, acquiring a deeper knowledge about how photosynthesis may function elsewhere has direct ramifications in the quest for biosignatures. This topic has been extensively investigated in the twenty-first century (Wolstencroft & Raven 2002; Kiang et al. 2007a, 2007b; Gale & Wandel 2017; Takizawa et al. 2017; Lehmer et al. 2018; Ritchie et al. 2018; Lehmer et al. 2021; Lingam & Loeb 2019b, 2020, 2021b; Claudi et al. 2021; Covone et al. 2021), and even in earlier publications (Rueda 1973; Pollard 1979; Heath et al. 1999).

In this paper, we will focus on reexamining the oft-employed assumptions that the pigments facilitating the transduction of light energy (viz., photopigments) must necessarily belong to the family of chlorophylls and other such Earth-based molecules and that photosynthetically active radiation must, for the most part, coincide with visible light. By computing the possible number of conjugated electrons that are involved in photosynthesis, we suggest that this quantity might be modulated by the spectral type. We elucidate the theoretical model in Section 2 and analyze the attendant implications in Section 3.

2. Model Description

In this section, we describe the model used for estimating the traits of putative photopigments on temperate exoplanets around different stars.

⁵ The HZ has a labyrinthine history that stretches back to the nineteenth century and beyond (Lingam 2021).



2.1. Model for Electronic Excitation

It is a well-known fact that the excitation of electrons is a vital prerequisite for photosynthesis, as expounded in Lodish et al. (2000, Chapter 16), Falkowski & Raven (2007, Chapter 2), and Blankenship (2014, Chapter 1). A panoply of models have, therefore, sought to relate key characteristics of photopigments with their absorption spectra. A crucial parameter in the model is the number of conjugated π -electrons (N_*). Since these electrons can be delocalized and are liable to excitation in response to a flux of photons (Johnson 2016), their number is a determinant of the pigment characteristics.

Attempts to quantify the aforementioned relationship span a broad range of complexity: in this work, we will draw on the basic free-electron model propounded in the 1940s (Bayliss 1948; Kuhn 1948, 1949; Simpson 1949). Our rationale for doing so is twofold. First and foremost, as we shall explicate hereafter, it is endowed with a sufficient degree of accuracy and realism, while retaining simplicity and transparency. Second, as we are adopting an astrobiological perspective where we must deal with a lack of concrete data, it is desirable to keep the model generic and minimize the proliferation of free parameters that could take on arbitrary values. We will accordingly, for the most part, mirror the approach delineated in Phillips et al. (2012, Chapter 18).

We will model the conjugated π -electrons as though they are placed within a “well” of infinite depth, with the photopigment comprising the real-world counterpart of the latter. Although the derivation is fairly elementary and can be found in any standard book on quantum mechanics (e.g., Griffiths & Schroeter 2018, Section 2.2), we will recapitulate the salient steps below for the benefit of the general readership. The wave function $\psi(x)$ for an electron confined within an infinite well obeys the time-independent Schrödinger equation as follows:

$$-\frac{\hbar^2}{2m_e} \frac{d^2\psi}{dx^2} = \mathcal{E}\psi, \quad (1)$$

where m_e is the mass of the electron and \mathcal{E} signifies the energy. The two boundary conditions for the system are $\psi(0) = 0$ and $\psi(L) = 0$, where L is the width of the infinite well. It is straightforward to verify that the mathematical solution of the above ordinary differential equation (ODE) is given by

$$\psi(x) = C_1 \sin(kx) + C_2 \cos(kx), \quad (2)$$

where $k = \sqrt{2m_e\mathcal{E}/\hbar^2}$. The boundary condition at the origin demands $C_2 = 0$ implying $\psi(x) = C_1 \sin(kx)$, and the boundary condition at the edge of the box leads to the quantization condition

$$kL = n\pi, \quad (3)$$

where n is an integer. The resulting expression for the quantized energy of the n -th level (\mathcal{E}_n) is

$$\mathcal{E}_n = \frac{k^2\hbar^2}{2m_e} = \frac{n^2\hbar^2}{8m_eL^2}. \quad (4)$$

We will, now, suppose that the conjugated π -electrons are treated as effectively being situated on a chain or loop (Platt 1949; Taubmann 1992), with a mean spacing of ℓ_* . By drawing on this assumption, it becomes apparent that $L = (N_* - 1)\ell_*$ in (4).

We are interested in the minimal energy ($\Delta\mathcal{E}$) theoretically needed for electronic excitation and how that ties in with the longest viable photon wavelength λ_{\max} . With respect to the former, we are essentially attempting to gauge the theoretical limit of the HOMO-LUMO gap (Atkins & de Paula 2009), where these abbreviations stand for highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). The wavelength λ_{\max} in terms of $\Delta\mathcal{E}$ is calculated to be

$$\lambda_{\max} = \frac{hc}{\Delta\mathcal{E}}. \quad (5)$$

If we express $\Delta\mathcal{E}$ in terms of N_* and ℓ_* , our preceding objective is fulfilled. As indicated in the prior paragraph, we must investigate the highest occupied level. As electrons are fermions, each level contains only two of them as per the Pauli exclusion principle, with this duo differing in their spin quantum numbers. Hence, if there exists an even number of electrons in total, the highest occupied level would correspond to $n = N_*/2$, whereas for an odd number of electrons it would be $n = (N_* + 1)/2$. If N_* is roughly an order of magnitude larger than unity, which turns out to be generally valid as illustrated hereafter, the two cases yield similar values.

Hence, after adopting $n = N_*/2$ and substituting this into (4), we arrive at

$$\mathcal{E}_{N_*/2} = \frac{h^2N_*^2}{32m_e\ell_*^2(N_* - 1)^2}, \quad (6)$$

which is the highest occupied energy level. The energy required to excite an electron from this level to the next level $n = N_*/2 + 1$, which is unoccupied by construction, is computed by first recognizing that

$$\mathcal{E}_{(N_*/2)+1} = \frac{h^2(N_* + 2)^2}{32m_e\ell_*^2(N_* - 1)^2}, \quad (7)$$

which follows from substituting $n = N_*/2 + 1$ in (4). As a consequence, the theoretical minimum excitation energy $\Delta\mathcal{E}$ is therefore given by

$$\begin{aligned} \Delta\mathcal{E} &= \mathcal{E}_{(N_*/2)+1} - \mathcal{E}_{N_*/2} \\ &= \frac{h^2(N_* + 1)}{8m_e\ell_*^2(N_* - 1)^2}. \end{aligned} \quad (8)$$

It is worth recalling that $\Delta\mathcal{E}$ is the theoretical minimum photon energy needed for the requisite excitation, owing to which the ensuing wavelength represents an upper bound; to put it differently, if the wavelength is greater than λ_{\max} , then electronic excitation ought not be feasible. After substituting this expression into (5) and solving for λ_{\max} , we duly end up with

$$\begin{aligned} \lambda_{\max} &= \frac{8m_e c}{h} \ell_*^2 \frac{(N_* - 1)^2}{N_* + 1} \\ &\approx 65 \text{ nm} \left(\frac{\ell_*}{1.4 \text{ \AA}} \right)^2 \frac{(N_* - 1)^2}{N_* + 1}, \end{aligned} \quad (9)$$

where ℓ_* has been normalized by $1.4 \text{ \AA} \equiv 0.14 \text{ nm}$ since it corresponds to the characteristic spacing between carbon atoms involved in conjugated bonds, in view of the empirical data

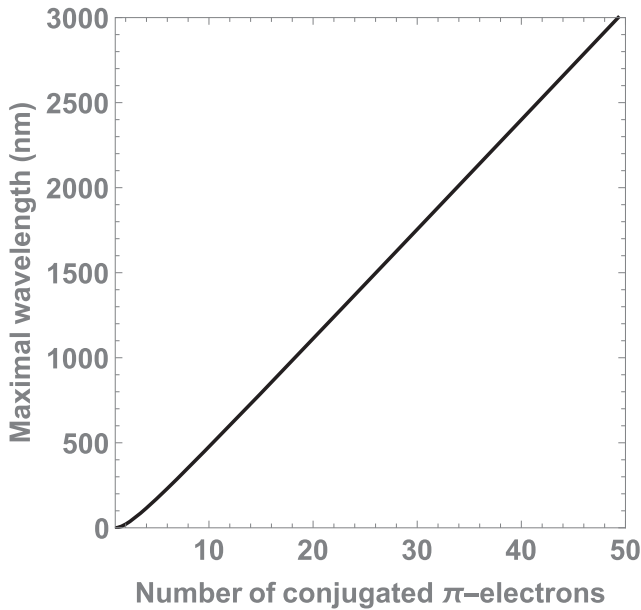


Figure 1. The maximum wavelength that may theoretically permit electronic excitation and photosynthesis (λ_{\max}) as a function of the number of conjugated π -electrons in putative photopigments (N_*) by employing (9).

adumbrated in Falkowski & Raven (2007, pg. 64) and Atkins & de Paula (2009, pg. 498).

In view of the simplifications invoked in deriving (10), it is natural to inquire whether this model is accurate. A bevy of studies have established that the free-electron paradigm constitutes a tenable approximation of more sophisticated treatments (Platt 1949; Simpson 1949; Taubmann 1992). More specifically, we note that this model has been compared against empirical data for molecules such as α -oligothiophenes and exhibited good agreement (de Melo et al. 1999). Furthermore, the quantitative scaling of $\Delta\mathcal{E} \propto 1/N_*$ expected for large N_* —refer to (8)—is confirmed by experiments and density functional theory calculations for pyrroles, thiophenes, and furans (e.g., Hutchison et al. 2003, their Figure 2).

At this stage, it is worth reiterating the significance of λ_{\max} ; it lies in the fact that photons with $\lambda > \lambda_{\max}$ would not possess the requisite energy to excite electrons, and therefore cannot effectuate photosynthesis. We have plotted λ_{\max} as a function of N_* in Figure 1.⁶ It is apparent from inspecting this plot that $\lambda_{\max} \propto N_*$ for $N_* \gg 1$ and that $\lambda_{\max} \approx 1.1 \mu\text{m}$ for $N_* = 20$; we shall return to this latter feature in Section 3. Conversely, if λ_{\max} is deduced through some other empirical or theoretical method, one may potentially utilize Figure 1 to infer N_* of the photopigments.

Until now, we have emphasized $\Delta\mathcal{E}$, which theoretically embodies the minimum energy for electronic excitation. In reality, however, this extreme limit is unlikely to suffice for excitation of electrons due to a number of intricate biochemical and biophysical processes. Laboratory assays suggest that, for the likes of chlorophylls, the excitation energy must be approximately twice that of $\Delta\mathcal{E}$ (Serlin et al. 1975; Grimm 2006; Hedayatifar et al. 2016; Buscemi et al. 2021), which is verifiable after substituting $\ell_* = 1.4 \text{ \AA}$ (Falkowski & Raven 2007, pg. 64) and $N_* = 20$ (Rabinowitch & Govindjee 1969, pg. 110) in (8).

⁶ It is reasonable to hold ℓ_* fixed at its fiducial value because the mean atomic spacing is a property of the fundamental constants of nature (Weisskopf 1975), and is therefore not anticipated to evince significant variation.

Hence, it seems credible to assume that the actual wavelength needed for robust excitation is roughly estimated by means of $\lambda \approx hc/(2\Delta\mathcal{E})$, which is expressible in terms of N_* as

$$\begin{aligned} \lambda &= \frac{4m_e c}{h} \ell_*^2 \frac{(N_* - 1)^2}{N_* + 1} \\ &\approx 33 \text{ nm} \left(\frac{\ell_*}{1.4 \text{ \AA}} \right)^2 \frac{(N_* - 1)^2}{N_* + 1}. \end{aligned} \quad (10)$$

Now, let us consider a few specific photopigments on Earth and assess the reliability of our modeling. To err on the side of caution, we restrict our attention to pigments explicitly involved in photosynthesis. For this reason, we do not explicitly consider microbial rhodopsins (e.g., proteorhodopsins)—which harvest as much (or more) solar energy as chlorophylls in Earth’s marine environments (Gómez-Consarnau et al. 2019; Hassanzadeh et al. 2021)—because they do not take part in photoautotrophy. The rhodopsin family, which exhibits absorption maxima of $\lesssim 550 \text{ nm}$ (Man et al. 2003; Inoue et al. 2021) that are distinctly lower than those corresponding to certain (bacterio)chlorophylls, is posited to have been widespread on early Earth and similar worlds (DasSarma & Schwieterman 2021), and might even be capable of photoautotrophy in principle (Larkum et al. 2018). Since there is no such concrete empirical evidence hitherto for the latter, we do not analyze this pigment hereafter as stated above; however, if and when appropriate, it is straightforward to use the fact that rhodopsin has six conjugated bonds (Sen et al. 2021).

The pigment β -carotene, which is widespread in photosynthetic organisms, is endowed with 11 conjugated bonds (Rabinowitch & Govindjee 1969, Figure 9.6). Therefore, upon specifying $N_* = 22$ in (10), we obtain $\lambda \approx 633 \text{ nm}$, which is ~ 1.5 times higher than the absorption maxima of β -carotene at $\sim 425, 450,$ and 480 nm (Rabinowitch & Govindjee 1969, Table 9.2). Next, on turning our attention toward chlorophyll *a*, a predominant pigment in oxygenic photosynthesis (Nishio 2000), this molecule has 10 conjugated bonds (Rabinowitch & Govindjee 1969, pg. 110). After specifying $N_* = 20$ in (10), we end up with $\lambda \approx 567 \text{ nm}$; this value is broadly compatible with the absorption peaks at $\sim 435 \text{ nm}$ and $\sim 670\text{--}700 \text{ nm}$ documented for chlorophyll *a* (Schwieterman et al. 2018, pg. 684).

Thus, the λ predicted by our approach, and the wavelengths of the absorption peaks of Earth-based photopigments are manifestly not far removed from one another. For the sake of argument, suppose that certain *abiotic* factors govern the wavelengths at which photopigments absorb strongly. If this wavelength regulated by such nonbiological processes (denoted by λ_{opt}) were known, one could accordingly constrain N_* by invoking (10). The premise implicit herein is that these molecules were gradually adapted over the course of evolution such that their eventual absorption was rendered efficacious at λ_{opt} .⁷ Therefore, if we presume that this picture is tenable, it may become feasible to establish a direct connection between putative abiotic phenomena and the structure of extrasolar photopigments, which we examine further in the upcoming Sections 2.2 and 3.

Needless to say, this potential link should not be viewed as exact because evolution is patently not a “perfect” optimization process; in other words, it is by no means assured that N_*

⁷ To put it another way, even if photopigments that can absorb at longer or shorter wavelengths than λ_{opt} (akin to, say, bacteriochlorophylls) are initially favored, molecules with absorption maxima close to λ_{opt} might evolve over time (as outlined in Section 2.2), along the lines of chlorophylls on Earth.

for the potential photopigments would be precisely identical to what one will obtain from (10) after equating it with λ_{opt} .

2.2. Peak Absorption Wavelength of Photopigments

The question of what wavelengths may be typically associated with the absorption peaks of photopigments on exoplanets has not been extensively investigated, barring a few notable publications (Kiang et al. 2007a, 2007b; Lehmer et al. 2018, 2021; Lingam & Loeb 2021a). One key problem is that most of these studies involve several parameters that are currently indeterminate or poorly resolved on other worlds: examples include atmospheric composition, the so-called relative cost parameter of Marosvölgyi & van Gorkom (2010), and the availability of cofactors such as NADP⁺ (Milo 2009). Hence, we opt to construct here a simpler model with no unknown parameters; while it trades some precision, it is still fairly accurate (as expounded hereafter).

The essence of our working hypothesis, paralleling Kiang et al. (2007a) and Lingam & Loeb (2021a, Chapter 4.3.5), lies in positing that the peak absorbance of photopigments occurs in the vicinity of the wavelength where the spectral photon flux (n_λ) of the host star attains its maximal value; the star is treated as a blackbody with temperature T_* . We remark that this criterion is consistent with the penultimate paragraph of Section 2.1 since the abiotic factor would be the stellar electromagnetic spectrum. The spectral photon flux for the star consequently is evaluated using

$$n_\lambda = \frac{2c}{\lambda^4} \left[\exp\left(\frac{hc}{\lambda k_B T_*}\right) - 1 \right]^{-1}. \quad (11)$$

Since λ_{opt} is the maximum of n_λ , it is determined by solving $dn_\lambda/d\lambda = 0$, that simplifies to

$$\lambda_{\text{opt}} \approx 3.67 \times 10^6 \text{ nm} \left(\frac{T_*}{1 \text{ K}} \right)^{-1}. \quad (12)$$

It is necessary to assess how realistic our model is when it comes to actually predicting the peak absorbance of photopigments, which we tackle below.

Naturally the Sun is our fiducial star—on substituting $T = T_\odot \equiv 5780 \text{ K}$ (viz., the temperature of the Sun), we end up with $\lambda_{\text{opt}} \approx 635 \text{ nm}$. This value constitutes a good match with the empirical absorption peaks of $\sim 630\text{--}700 \text{ nm}$ confirmed for chlorophylls *a*, *b*, and *c* (Schwieterman et al. 2018, Table 1). We have emphasized this trio of molecules because they are widely prevalent in oxygenic photoautotrophs. The latter, in turn, comprises the predominant source of biomass on Earth (Bar-On et al. 2018), and the evolution of oxygenic photosynthesis proved to be a major evolutionary innovation that transformed Earth’s biosphere (Knoll 2015). However, it is worth recognizing that the absorption maxima of chlorophyll *d* and *f* occur at slightly longer wavelengths of 710–740 nm (Mielke et al. 2013; Gan et al. 2014; Nürnberg et al. 2018).

Now, let us turn our attention to other stars, with the corresponding spectral type provided in parentheses. By applying (12), we obtain $\lambda_{\text{opt}} \approx 515 \text{ nm}$ for $T_* = 7120 \text{ K}$ (F2V), $\lambda_{\text{opt}} \approx 635 \text{ nm}$ for $T_* = T_\odot$ (G2V), $\lambda_{\text{opt}} \approx 794 \text{ nm}$ for $T_* = 4620 \text{ K}$ (K2V), and $\lambda_{\text{opt}} \approx 1375 \text{ nm}$ for $T_* = 2670 \text{ K}$ (M7V). To put it another way, the absorption peak may switch to bluish wavelengths for hotter stars and near-infrared (near-IR) wavelengths for cooler stars. In order to assess how good a predictor (12) is, we compare the formula with absorption maxima extracted from the detailed

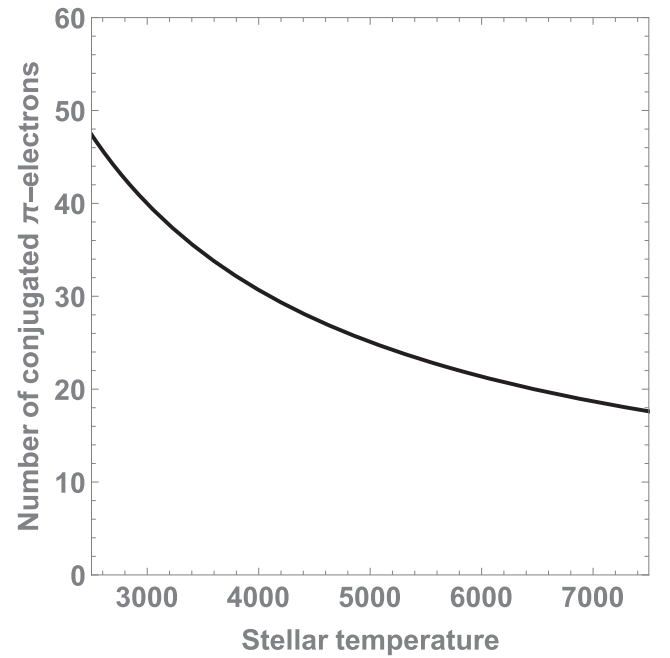


Figure 2. The number of conjugated π -electrons in putative photopigments (N_π) susceptible to excitation as a function of the stellar temperature (T_*). The range of stellar temperatures broadly spans *F*-, *G*-, *K*-, and *M*-type stars.

numerical model of Lehmer et al. (2021, Table 1), which was itself partly predicated on Marosvölgyi & van Gorkom (2010).

The numerical model of Lehmer et al. (2021) cited in the preceding paragraph yielded $\lambda_{\text{opt}} \approx 468$ and 476 nm for $T_* = 7120 \text{ K}$, $\lambda_{\text{opt}} \approx 644$ and 672 nm for $T_* = 5780 \text{ K}$, $\lambda_{\text{opt}} \approx 675$, 711 , and 746 nm for $T_* = 4620 \text{ K}$, and $\lambda_{\text{opt}} \approx 987$ and 1050 nm for $T_* = 2670 \text{ K}$, which clearly agrees with our analytical model. We caution that (12) might be somewhat inaccurate for early *M*-dwarfs (Lehmer et al. 2021, Table 1), although the potential discrepancy is diminished if we compare our calculations instead with Lehmer et al. (2018, Figure 2).

As remarked a couple of paragraphs before, when one considers lower stellar temperatures, λ_{opt} shifts to near-IR wavelengths as per (12), while the opposite tendency is forecast for hotter temperatures. Aside from the quantitative comparison furnished above, we note that this qualitative trend is consistent with previous studies, which have generally suggested that photosynthesis on *M*-dwarfs might operate at near-IR wavelengths and that the spectral edge of photosynthetic organisms may be manifested in this regime (Heath et al. 1999; Wolstencroft & Raven 2002; Kiang et al. 2007b; Lingam & Loeb 2019c); however, refer to Takizawa et al. (2017) and Gale & Wandel (2017) for contrasting takes.

3. Discussion and Conclusions

The first noteworthy result from our analysis is the maximal wavelength theoretically conducive to the excitation of electrons (λ_{max}), an absolute condition for initiating photosynthesis. We determined λ_{max} in (9) and plotted it as a function of N_π in Figure 1. In view of the fact that $N_\pi = 20$ or $N_\pi = 22$ for the principal photopigments of interest—namely, carotenoids, chlorophylls, and bacteriochlorophylls (Rabinowitch & Govindjee 1969; Cong et al. 2008; Phillips et al. 2012)—we end up with $\lambda_{\text{max}} \approx 1.1\text{--}1.25 \mu\text{m}$ from (9).

Hence, for Earth-based photopigments, we anticipate that wavelengths greater than λ_{\max} are ostensibly not suitable for photosynthesis. This prediction from our quantitative model displays excellent agreement with laboratory investigations, which have seemingly failed to excite electrons in primary photopigments such as chlorophylls by means of photons whose wavelengths are $>1.1 \mu\text{m}$ (Kiang et al. 2007a, 2007b; see also Lehmer et al. 2018). Moreover, if extrasolar photopigments are essentially identical to those on Earth, which is, however, not necessarily the case as propounded hereafter, the same limits derived for λ_{\max} in the prior paragraph could prove to be applicable. In this specific scenario, the instantiation of extraterrestrial photosynthesis at wavelengths $>1.1 \mu\text{m}$ may not be rendered viable.

Hitherto, we have centered our attention on λ_{\max} . We will now focus on N_* , and thence explore the possibility that photopigments on other worlds might diverge from those on Earth. We can gauge N_* by substituting (12) into (10), which is tantamount to stating that photopigments are quasi-optimized to operate at wavelengths similar to those where the spectral photon flux of the star is maximized. This procedure generates a quadratic equation for N_* in terms of T_* and ℓ_* :

$$1.1 \times 10^5 \left(\frac{T_*}{1 \text{ K}} \right)^{-1} \approx \left(\frac{\ell_*}{1.4 \text{ \AA}} \right)^2 \frac{(N_* - 1)^2}{N_* + 1}. \quad (13)$$

As per our previous exposition, $N_* \gg 1$ is expected to be quite valid, which allows us to simplify the above equation and thereupon obtain

$$N_* \approx 1.1 \times 10^5 \left(\frac{T_*}{1 \text{ K}} \right)^{-1} \left(\frac{\ell_*}{1.4 \text{ \AA}} \right)^{-2}. \quad (14)$$

Let us specify $T_* = T_\odot$ in (14) and hold ℓ_* fixed at its fiducial value, which accordingly yields $N_* \approx 19$. This estimate is evidently proximate to the number of conjugate electrons in chlorophyll ($N_* = 20$) and β -carotene ($N_* = 22$) (Phillips et al. 2012, pg. 736), thereby lending credence to our analysis and hypothesis; the a priori requirement of $N_* \gg 1$ is also satisfied. On solving the full quadratic equation for N_* given by (13), we arrive at $N_* \approx 22$, which obviously exhibits excellent agreement with the aforementioned molecules.

In Figure 2, we have depicted the variation of N_* with the stellar temperature, whose range encompasses F -, G -, K -, and M -type stars, by employing (13). The first major takeaway from Figure 2 is that N_* is a monotonically decreasing function of T_* . The second, and arguably more crucial, feature is that N_* becomes noticeably high for M-dwarfs, especially for late M-dwarfs. For instance, if we consider the famous TRAPPIST-1 planetary system with $T_* \approx 2566 \text{ K}$ (Agol et al. 2021, Table 7), we duly obtain $N_* \approx 46$ (for $\ell_* \approx 1.4 \text{ \AA}$), which is about twice that of chlorophyll a and β -carotene.

On the basis of these results, we might potentially draw a tentative conclusion. If we posit that our hypothesis is tenable, to wit, that N_* is substantively constrained by the peak absorbance of photopigments—which is presumably close to the peak of the spectral photon flux, as illustrated in Section 2.2—it is not implausible that, if planets around M-dwarfs harbor photopigments, their structures would be very different from those of the widespread chlorophylls. The latter are derived from porphine (and its variants), which is endowed with 11 conjugated bonds ($N_* = 22$), as seen from consulting Rabinowitch & Govindjee (1969, Figure 9.2).

Hence, this value contrasts with N_* determined for late M-dwarfs via Figure 2, which can become almost twice as large compared to the estimate for the Sun when all other factors are held fixed. To put it another way, as per our model, the photopigments on these worlds cannot be simply categorized as canonical chlorophylls and carotenes, both of which are characterized by $N_* \approx 20$. We will not speculate herein about what their structures may resemble, owing to the paucity of concrete data in this regard. It might be possible for the putative photopigments to comprise two porphine molecules linked together in some fashion, which could yield the desired number of conjugated π -electrons.

In contrast, a few notable proposals have advocated that chlorophyll constitutes a “universal pigment” by virtue of its advantages vis-à-vis stability and structure (Wald 1959, 1974; Raven & Wolstencroft 2004). Needless to say, if this school of thought were correct, it would suppress the prospects for novel pigments along the lines intimated above. In this scenario, even on planets orbiting M-dwarfs, one would expect to find chlorophylls and their absorption peaks will occur at $\lesssim 750 \text{ nm}$ if the Earth does represent a suitable benchmark. However, on account of the relative scarcity of such photons, the net primary productivity of these biospheres would be potentially much lower than that of Earth (Pollard 1979; Wolstencroft & Raven 2002; Kiang et al. 2007b; Lehmer et al. 2018; Lingam & Loeb 2019b, 2020, 2021b).

To summarize, there exist a couple of distinct outcomes that merit consideration. On the one hand, as suggested in this paper, extrasolar photopigments may not belong to the group of chlorophylls and these putative molecules could instantiate strong absorption in the near-infrared on M-dwarf exoplanets, which we choose to label hypothesis #1. On the other hand, it is conceivable that chlorophylls are truly quasi-universal in nature and that the absorption peaks of photopigments on planets around all types of stars might therefore transpire at $\lesssim 750 \text{ nm}$. Fortunately, however, it ought to be straightforward to empirically test/falsify our hypothesis by future observations as delineated below.

If the spectral edge (i.e., documented steep change in reflectance) associated with photopigments is nearly independent of the stellar spectral type and transpires in the vicinity of red wavelengths (Seager et al. 2005), data from the reflected light of exoplanets (hosting such biomolecules) garnered by future direct-imaging surveys (Fujii et al. 2018) may effectively suffice to eliminate our model. In contrast, if the spectral edge is manifested in accordance with (12), it could lend credence to our model. However, other paradigms—for example, linking photosystems in series, thereby amounting to multiple Z-schemes operating in tandem (Kiang et al. 2007b), which we christen hypothesis #2—might shift the spectral edge to longer wavelengths on cooler worlds.

It is essential to recognize that these spectral edges are more prominent and detectable for land-based photosynthetic organisms such as embryophytes on Earth (Seager et al. 2005; Cockell et al. 2009). Hence, the ensuing discussion is likely of diminished applicability to ocean worlds (sans landmasses)—which are anticipated to be quite prevalent on the basis of exoplanet surveys (Zeng et al. 2019; Mousis et al. 2020)—since the signatures may not be as pronounced (e.g., Schwieterman et al. 2018, Figure 10) and water additionally modulates the spectral niches of photosynthesis (Stomp et al. 2007; Holtrup et al. 2021; see, however, the simulations by O’Malley-James & Kaltenecker 2018, 2019).⁸

⁸ Moreover, certain characteristics of aquatic photosynthesis (e.g., euphotic zone depth and net primary productivity) are sensitive to the spectral type of the star (e.g., Lingam & Loeb 2020, 2021b).

Thus, coupled photosystems predicated purely on Earth-based photopigments (hypothesis #2) may engender near-IR spectral edges on M-dwarf exoplanets, perhaps obviating the necessity for “exotic” photopigments (hypothesis #1) of the kind theorized in this work. It is consequently imperative to come up with diagnostics for differentiating between these two hypotheses. In this context, we highlight that spectral edges at longer wavelengths associated with hypothesis #2 are near-integer multiples of 350 nm (Wolstencroft & Raven 2002, pg. 539), whereas this discrete pattern is not expected for hypothesis #1. Hence, the location of the spectral edge on various worlds could aid in distinguishing between hypotheses #1 and #2. Furthermore, hypothesis #1 allows for shorter wavelengths on hotter worlds, while this does not seem tenable for hypothesis #2.

In view of the significance of photosynthesis on Earth—from both the evolutionary and ecological standpoints (Falkowski & Raven 2007; Blankenship 2014; Knoll 2015)—as well as the fact that it can generate powerful gaseous and surface biosignatures that permit the detection of extraterrestrial life (Schwieterman et al. 2018; Lingam & Loeb 2021a), the importance of gauging the electronic excitation properties of photopigments is readily apparent. A simple theoretical model with a minimal set of unknown parameters, which is proposed, solved, and analyzed in this paper, gives qualitative and quantitative predictions pertaining to the possible relationship between the spectral type of the host star and the nature of suitable biomolecules (analogs of terrestrial chlorophylls) that harness starlight to create biomass. We hope that some parts of this paper will be relevant to the understanding and interpretation of the collective, fast-increasing knowledge of exoplanets.

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References

- Agol, E., Dorn, C., Grimm, S. L., et al. 2021, *PSJ*, **2**, 1
 Atkins, P., & de Paula, J. 2009, *Elements of Physical Chemistry* (5th ed.; New York: W.H. Freeman & Co.)
 Bar-On, Y. M., Phillips, R., & Milo, R. 2018, *PNAS*, **115**, 6506
 Bayliss, N. S. 1948, *JChPh*, **16**, 287
 Blankenship, R. E. 2014, *Molecular Mechanisms of Photosynthesis* (2nd ed.; New York: Wiley)
 Buscemi, G., Vona, D., Trotta, M., Milano, F., & Farinola, G. M. 2021, *Adv. Mater. Technol.*, 2100245
 Claudi, R., Alei, E., Battistuzzi, M., et al. 2021, *Life*, **11**, 10
 Cockell, C. S. 2020, *Astrobiology: Understanding Life in the Universe* (2nd ed.; New York: Wiley)
 Cockell, C. S., Bush, T., Bryce, C., et al. 2016, *AsBio*, **16**, 89
 Cockell, C. S., Kaltenecker, L., & Raven, J. A. 2009, *AsBio*, **9**, 623
 Cong, H., Niedzwiedzki, D. M., Gibson, G. N., et al. 2008, *J. Phys. Chem. B*, **112**, 10689
 Covone, G., Ienco, R. M., Cacciapuoti, L., & Inno, L. 2021, *MNRAS*, **505**, 3329
 DasSarma, S., & Schwieterman, E. W. 2021, *IJAsB*, **20**, 241
 de Melo, J. S., Silva, L. M., Arnaut, L. G., & Becker, R. S. 1999, *JChPh*, **111**, 5427
 Dole, S. H. 1964, *Habitable planets for man* (New York: Blaisdell Pub. Co.)
 Falkowski, P. G., & Raven, J. A. 2007, *Aquatic photosynthesis* (2nd ed.; Princeton, NJ: Princeton University Press)
 Fujii, Y., Angerhausen, D., Deitrick, R., et al. 2018, *AsBio*, **18**, 739
 Gale, J., & Wandel, A. 2017, *IJAsB*, **16**, 1
 Gan, F., Zhang, S., Rockwell, N. C., et al. 2014, *Sci*, **345**, 1312
 Gómez-Consarnau, L., Raven, J. A., Levine, N. M., et al. 2019, *SciA*, **5**, eaaw8855
 Griffiths, D. J., & Schroeter, D. F. 2018, *Introduction to Quantum Mechanics* (3rd ed.; Cambridge: Cambridge University Press)
 Grimm, B. et al. (ed.) 2006, *Chlorophylls and Bacteriochlorophylls: Biochemistry, Biophysics, Functions and Applications* (Berlin: Springer)
 Hassanzadeh, B., Thomson, B., Deans, F., et al. 2021, *Environ. Microbiol. Rep.*, **13**, 401
 Heath, M. J., Doyle, L. R., Joshi, M. M., & Haberle, R. M. 1999, *Orig. Life Evol. Biosph.*, **29**, 405
 Hedayatifar, L., Irani, E., Mazarei, M., et al. 2016, *RSCAd*, **6**, 109778
 Holthrop, T., Huisman, J., Stomp, M., et al. 2021, *Nat. Ecol. Evol.*, **5**, 55
 Hutchison, G. R., Zhao, Y.-J., Delley, B., et al. 2003, *PhRvB*, **68**, 035204
 Inoue, K., Karasuyama, M., Nakamura, R., et al. 2021, *Commun. Biol.*, **4**, 362
 Johnson, M. P. 2016, *Essays Biochem.*, **60**, 255
 Kasting, J. F., Whitmire, D. P., & Reynolds, R. T. 1993, *Icar*, **101**, 108
 Kiang, N. Y., Segura, A., Tinetti, G., et al. 2007b, *AsBio*, **7**, 252
 Kiang, N. Y., Siefert, J., Govindjee, B. R. E., et al. 2007a, *AsBio*, **7**, 222
 Knoll, A. H. 2015, *Life on a Young Planet: The First Three Billion Years of Evolution on Earth* (Princeton, NJ: Princeton Univ. Press)
 Koppurapu, R. K., Ramirez, R., Kasting, J. F., et al. 2013, *ApJ*, **765**, 131
 Kuhn, H. 1948, *JChPh*, **16**, 840
 Kuhn, H. 1949, *JChPh*, **17**, 1198
 Lammer, H., Bredehöft, J. H., Coustenis, A., et al. 2009, *A&ARv*, **17**, 181
 Larkum, A. W. D., Ritchie, R. J., & Raven, J. A. 2018, *Photosynthetica*, **56**, 11
 Lehmer, O. R., Catling, D. C., Parenteau, M. N., & Hoehler, T. M. 2018, *ApJ*, **859**, 171
 Lehmer, O. R., Catling, D. C., Parenteau, M. N., Kiang, N. Y., & Hoehler, T. M. 2021, *FrASS*, **8**, 689441
 Lingam, M. 2021, *IJAsB*, **20**, 332
 Lingam, M., & Loeb, A. 2019a, *RvMP*, **91**, 021002
 Lingam, M., & Loeb, A. 2019b, *MNRAS*, **485**, 5924
 Lingam, M., & Loeb, A. 2019c, *ApJ*, **883**, 143
 Lingam, M., & Loeb, A. 2020, *ApJL*, **889**, L15
 Lingam, M., & Loeb, A. 2021a, *Life in the Cosmos: From Biosignatures to Technosignatures* (Cambridge, MA: Harvard Univ. Press)
 Lingam, M., & Loeb, A. 2021b, *MNRAS*, **503**, 3434
 Lodish, H., Berk, A., Zipursky, S. L., et al. 2000, *Molecular Cell Biology* (4th ed.; New York: W. H. Freeman & Co.)
 Man, D., Wang, W., Sabeji, G., et al. 2003, *EMBO J*, **22**, 1725
 Marosvölgyi, M. A., & van Gorkom, H. J. 2010, *Photosynth. Res.*, **103**, 105
 Mielke, S. P., Kiang, N. Y., Blankenship, R. E., & Mauzerall, D. 2013, *Biochim. Biophys. Acta Bioenerg.*, **1827**, 255
 Milo, R. 2009, *Photosynth. Res.*, **101**, 59
 Mousis, O., Deleuil, M., Aguichine, A., et al. 2020, *ApJL*, **896**, L22
 Nishio, J. N. 2000, *Plant Cell Environ.*, **23**, 539
 Nürnberg, D. J., Morton, J., Santabarbara, S., et al. 2018, *Sci*, **360**, 1210
 O’Malley-James, J. T., & Kaltenecker, L. 2018, *AsBio*, **18**, 1123
 O’Malley-James, J. T., & Kaltenecker, L. 2019, *ApJL*, **879**, L20
 Phillips, R., Kondev, J., Theriot, J., & Garcia, H. G. 2012, *Physical Biology of the Cell* (2nd ed.; New York: Garland Science)
 Platt, J. R. 1949, *JChPh*, **17**, 484
 Pollard, W. G. 1979, *Am. Sci.*, **67**, 653
 Rabinowitch, E. G., & Govindjee 1969, *Photosynthesis* (New York: Wiley)
 Raven, J. A., & Wolstencroft, R. D. 2004, in *Bioastronomy 2002: Life Among the Stars*, ed. R. Norris & F. Stootman, 213 (San Francisco, CA: ASP), 305
 Ritchie, R. J., Larkum, A. W. D., & Ribas, I. 2018, *IJAsB*, **17**, 147
 Rueda, A. 1973, *SLSci*, **4**, 469
 Schwieterman, E. W., Kiang, N. Y., Parenteau, M. N., et al. 2018, *AsBio*, **18**, 663
 Seager, S., Turner, E. L., Schafer, J., & Ford, E. B. 2005, *AsBio*, **5**, 372
 Sen, S., Kar, R. K., Borin, V. A., & Schapiro, I. 2021, *Wiley Interdiscip. Rev. Comput. Mol. Sci.*, e1562
 Serlin, R., Chow, H.-C., & Strouse, C. E. 1975, *JChS*, **97**, 7237
 Simpson, W. T. 1949, *JChPh*, **17**, 1218
 Stomp, M., Huisman, J., Stal, L. J., & Matthijs, H. C. P. 2007, *ISME J*, **1**, 271

Takizawa, K., Minagawa, J., Tamura, M., Kusakabe, N., & Narita, N. 2017, [NatSR](#), **7**, 7561
Taubmann, G. 1992, [JChEd](#), **69**, 96
Wald, G. 1959, [SciAm](#), **201**, 92

Wald, G. 1974, [Orig. Life](#), **5**, 7
Weisskopf, V. F. 1975, [Sci](#), **187**, 605
Wolstencroft, R. D., & Raven, J. A. 2002, [Icar](#), **157**, 535
Zeng, L., Jacobsen, S. B., Sasselov, D. D., et al. 2019, [PNAS](#), **116**, 9723