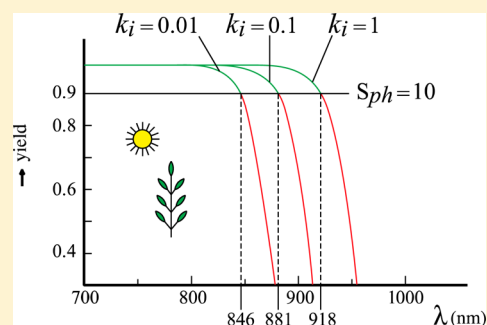


Limits on Natural Photosynthesis

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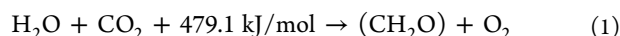
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ABSTRACT: Photosynthesis in nature does not use the far infrared part of the solar spectrum ($\lambda > 900$ nm), comprising about 30% of the incoming solar energy. By simple thermodynamic arguments it is explained that this is due to the unavoidable back reactions during the night. It follows that $\lambda \approx 900$ nm provides a natural limit on artificial photosynthesis. The same limit holds for a two-tandem Si solar cell.



INTRODUCTION

The final result of photosynthesis in nature can be summarized by the well-known equation¹



On the right-hand side the building block of glucose is indicated. It appears that 10 photoabsorptions are required to complete reaction 1 on the molecular scale. One or two photons are used for the formation of ATP, which is needed for cell maintenance. Taking into account some losses, 8 absorptions contribute directly to reaction 1; one finds that each absorption process (reaction 1) ties up 0.60 eV of energy.

The precise mechanism of photosynthesis is complex. In this paper we focus on plants, where there are two photosynthetic centers, PS1 and PS2 in each of which four absorptions occur for one O₂ produced and one CO₂ reduced.^{2,3} In PS2, the following occurs: H₂O is oxidized; electrons move via a complex electron/proton transfer process to PS1; from there on light absorption energy is accumulated to reduce CO₂. One may bypass this complexity by modeling the photosynthetic apparatus in a thermodynamic way like a chemical reactor. This follows earlier work of Almgren⁴ and Duysens⁵ and recent work of the present authors.²

The sun provides the external source of energy of this “chemical reactor”. Figure 1⁶ shows the energy spectrum of the incident solar radiation at the earth’s surface as a function of wavelength λ . Also depicted are the absorption spectra of chlorophylls a and b, which occur in plants, and the spectra of bacteriochlorophylls acting in photosynthetic purple bacteria. It is clear that plant chlorophylls absorb mainly in blue (between 400 and 500 nm) and red (around 650 to 680 nm). Plants also contain carotenoids such as β -carotene and lutein, which absorb somewhat to the red of the main chlorophyll b transition at 460 nm. There is however only little absorption in the green (around 530 nm). This allows green light to be scattered out of the leaf, which explains its green color. Much of

the green light will be scattered inward and subsequently be absorbed as well.

A second point of interest is that there is a considerable part of the solar spectrum to the right of 700 nm, which is not absorbed in plants and, in a sense, is wasted for plant photosynthesis. Bacteriochlorophylls do absorb in the infrared but hardly in the visible region. It seems that there is room for “improvement” of photosynthesis by better covering the whole spectral range of solar light. In Blankenship et al.⁷ (Figure 3), it was suggested to use visible photons to excite PS2 while PS1 is re-engineered; it is to be excited by near-infrared photons (700–1200 nm).

The research question of the present paper is to investigate the efficiency and stability of photosynthesis with water splitting in a red-shifted absorption spectrum. The thermodynamic analysis will provide the answer to what extent re-engineering PS1 will make sense. It appears that it is also possible to draw conclusions on photovoltaic energy conversion in the infrared.

THERMODYNAMIC MODEL

The thermodynamic model is summarized in Figure 2 where the level scheme of chlorophyll is depicted on the left. On excitation, the chlorophyll, indicated by Chl, goes to one of the excited states Chl*. It quickly relaxes to the lowest Chl* state, indicated by E_r. This lowest excited state is driving many biochemical reactions, which finally lead to a product, state P. A single arrow in Figure 2 models this complex process. In order to produce one building block of glucose (reaction 1), one needs 8 product compounds P; that process is much slower than the formation of P. Therefore, P may be regarded as a provisional final state for the analysis.

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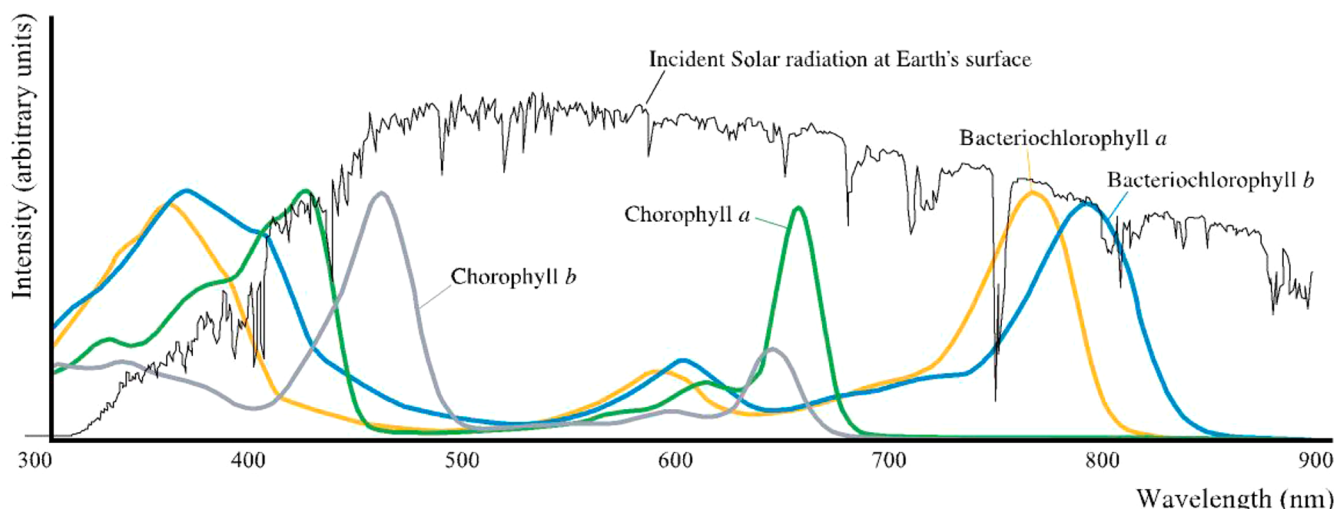


Figure 1. Incident solar energy spectrum at ground level as a function of wavelength and the absorption by chlorophylls a and b (in plants) or bacteriochlorophylls a and b (in bacteria). Adapted with permission from Figure 1A in ref 6. Copyright 2010 Elsevier.

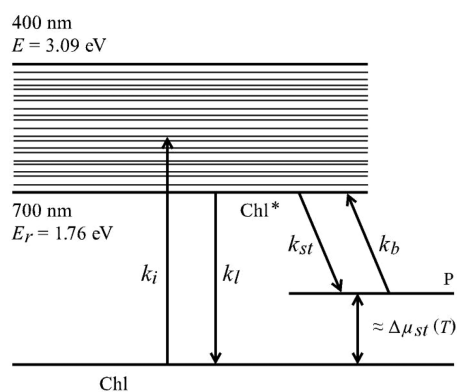


Figure 2. Excitations of chlorophyll between 400 and 700 nm relax quickly to the lowest “red” state indicated by E_r . Also, excitations of carotenoids (not shown) lead to this state. Together this is summarized by a rate k_i . The excited state may return to the ground state with a loss rate k_l or, by many intermediate steps, may fill a product or storage state P with rate k_{st} . The latter state may return with rate k_b . The chemical potential of storage $\Delta\mu_{st}$ depends on temperature but is indicated symbolically on the right.

From Figure 1, it follows that chlorophyll absorbs between wavelengths of 400 and 700 nm. With the well-known formula $E = h\nu = hc/\lambda$, one finds that these wavelengths correspond with excitation energies of 3.09 and 1.76 eV.

As mentioned before, carotenoids also absorb in the intermediate spectral region. Those excitations are quickly transferred to chlorophyll. All levels very quickly, within 1 ps, relax to the lowest “red” level, indicated by $E_r = 1.76$ eV. All excitations together for a single chlorophyll molecule in a leaf are summarized by a rate k_i s⁻¹, of which the numerical value depends on the intensity of the solar light, while the subscript i refers to “incident”.

For the lowest “red” level there are two possibilities: it may return to the ground state with a rate k_l (the subscript l means “loss”) or it may, by many intermediate steps, go to a product state P. The loss rate may be estimated from the fluorescence lifetime^{8,9} of about 4 ns as $k_l \approx 0.25 \times 10^9$ s⁻¹. The decay of the lowest “red” level takes place in about 33 ps for PS1¹⁰ and about 150 ps for PS2,¹¹ in both cases mainly to the product state P, considerably longer than the relaxation time of 1 ps for

going to this state. Therefore, the relaxation and the subsequent decay and formation of the product state may be considered to be independent. The rate by which the product state is reached is indicated by k_{st} , where the subscript st obviously means “storage”. The two decay times mentioned correspond to rates $k_{st} = 30 \times 10^9$ s⁻¹ and $k_{st} = 7 \times 10^9$ s⁻¹; for the average we use the round-off value of $k_{st} = 20 \times 10^9$ s⁻¹. The rate by which this state eventually returns to Chl* is indicated by k_b ; here, the subscript b refers to “back”.

Typical values for the photosynthetic rates are given in Table 1. The loss rate and storage rate have been estimated above.

Table 1. Typical Rates for Photosynthesis^a

| | |
|-------------------------|--------------------|
| k_i (bright sunlight) | k_i (overcast) |
| 10 | 10^{-4} |
| k_l (loss rate) | k_{st} (storage) |
| 0.25×10^9 | 20×10^9 |

^aUnits: s⁻¹ molecule⁻¹.

The excitation rate for bright sunlight may be calculated from the number of photons in the red region, which interact with chlorophyll for an insolation of 250 W m⁻². It is assumed that for this insolation all absorbed photons give an excitation. The light intensity for a very cloudy, overcast day is measured as 5 orders of magnitude lower. The data should only be used for order of magnitude estimates.

With reference to the back reaction it may be clear and will be shown below that it will be largest for small energy differences between Chl* and P. This is an extra argument to consider only the lowest “red” level for the back reaction.

The chemical potential of the product state P with respect to the ground state Chl* is indicated on the right-hand side of Figure 2 as $\Delta\mu_{st}(T)$. It is not drawn to scale as it depends on temperature.

The chemical potential of a substance in a dilute solution like chlorophyll with concentration [Chl] mol/L usually is approximated by (see Appendix in Blankenship¹)

$$\mu_{\text{mol}}(\text{Chl}, T) = \mu_{\text{mol}}^0(\text{Chl}) + RT \ln[\text{Chl}] \quad (2)$$

Here, T is the absolute temperature, and R is the universal gas constant in units J K⁻¹ mol⁻¹. Also, μ_{mol}^0 is the free energy per

mol of substance at temperature $T = 0$. Free energy is a macroscopic concept, and that remains the case, but the model is written on a molecular scale. Therefore, eq 2 is divided by Avogadro's number N_A , which is the number of molecules/mol with units mol^{-1} . This leads to

$$\mu(\text{Chl}, T) = \mu^0(\text{Chl}) + kT \ln[\text{Chl}] \quad (3)$$

where the subscript mol now is omitted. Here, $k = R/N_A$ is the Boltzmann constant with units J/K. For the excited state a similar equation can be written

$$\mu(\text{Chl}^*, T) = \mu^0(\text{Chl}^*) + kT \ln[\text{Chl}^*] \quad (4)$$

The difference of chemical potential between the excited state and the ground state is found by subtracting

$$\begin{aligned} \Delta\mu &= \mu(\text{Chl}^*, T) - \mu(\text{Chl}, T) = \mu^0(\text{Chl}^*) - \mu^0(\text{Chl}) \\ &+ kT \ln \frac{[\text{Chl}^*]}{[\text{Chl}]} \end{aligned} \quad (5)$$

It follows from the definition of chemical potentials that the energy difference ΔU between two states of a system may be written as

$$\Delta U = -p\Delta V + T\Delta S + \sum_i \mu_i \Delta n_i \quad (6)$$

This equation can be applied to the energy difference between the lowest excited "red" state of chlorophyll and the ground state at temperature $T = 0$. It is assumed that in these compact structures no volume change occurs ($\Delta V = 0$) and one finds

$$\begin{aligned} E_r &= \Delta U = \mu_{\text{exc}}^0 \Delta n_{\text{exc}} + \mu_{\text{ground}}^0 \Delta n_{\text{ground}} \\ &= \mu^0(\text{Chl}^*) - \mu^0(\text{Chl}) \end{aligned} \quad (7)$$

In the last equality, upon excitation the excited state's population increases by 1 and the ground state population decreases by 1. By combining eqs 5 and 7 one obtains

$$\Delta\mu = E_r + kT \ln \frac{[\text{Chl}^*]}{[\text{Chl}]} \quad (8)$$

In the absence of light there will be equilibrium between the two states: $\Delta\mu = 0$. This leads to

$$\frac{[\text{Chl}^*]}{[\text{Chl}]} = e^{-E_r/kT} \quad (9)$$

which is the well-known Boltzmann equation.

Storage Equations. The equations determining storage of light energy will be derived in two steps. The first step considers storage without back reaction $\text{P} \rightarrow \text{Chl}^*$; the second step includes the back reaction albeit with certain assumptions.

Upon absorption of light without a back reaction, steady state is reached when the formation of Chl^* equals the sum of its decays to the ground state Chl and the product state P . This implies

$$k_i[\text{Chl}] = (k_1 + k_{\text{st}})[\text{Chl}^*] \quad (10)$$

The efficiency ϕ_{st} of a storage process is defined as 1 minus the probability of return to the ground state divided by the probability of formation from the ground state. In other words, it is the relative probability of not returning to the ground state. Ignoring the back reaction is indicated by a superscript 0; this gives

$$\phi_{\text{st}}^0 = 1 - \frac{k_1[\text{Chl}^*]}{k_i[\text{Chl}]} = 1 - \frac{k_1[\text{Chl}^*]}{(k_1 + k_{\text{st}})[\text{Chl}^*]} = \frac{k_{\text{st}}}{k_1 + k_{\text{st}}} \quad (11)$$

For photosynthesis to work, one should have $k_{\text{st}} \gg k_1$ or $\phi_{\text{st}}^0 \approx 1$. Table 1 shows that this is indeed the case in nature.

In the second step of deriving the storage equations, the back reaction with rate k_b is taken into account. In the argument below a few assumptions will be made by which the back rate is eliminated from the equations.

During the day light energy is absorbed to form the excited state Chl^* . This state is very short-lived, and for the largest part, it decays to state P where the energy is stored. To some extent the excited Chl^* state is also filled by the back reaction. We now first consider a night and then the following day.

During the night, light is absent, and only the back reaction is filling Chl^* from P ; state Chl^* again may decay to the ground state (rate k_1) or return to state P (rate k_{st}). In steady state the concentration of Chl^* during the night is indicated by $[\text{Chl}^*]_{\text{dark}}$ and its formation equals its decay. This gives

$$k_b[\text{P}] = (k_1 + k_{\text{st}})[\text{Chl}^*]_{\text{dark}} \quad (12)$$

Since $k_{\text{st}} \gg k_b$, eq 12 may be approximated by

$$k_b[\text{P}] = k_{\text{st}}[\text{Chl}^*]_{\text{dark}} \quad (13)$$

which looks like a thermodynamic equilibrium between P and $[\text{Chl}^*]_{\text{dark}}$. Therefore, to a good approximation their chemical potentials will be the same:

$$\mu(\text{Chl}^*)_{\text{dark}} = \mu(\text{P}) \quad (14)$$

Finally, consider the day following this night. The excited state, now called $[\text{Chl}^*]_{\text{light}}$ is filled by excitations and back reactions. In steady state its formation again equals its decay, and instead of eq 12, one obtains

$$k_i[\text{Chl}] + k_b[\text{P}] = (k_{\text{st}} + k_1)[\text{Chl}^*]_{\text{light}} \quad (15)$$

The efficiency of storage in steady state including the back reaction is indicated by $\phi_{\text{st}}^{\text{ss}}$. Again, it is defined as 1 minus the probability of return to the ground state divided by the probability of formation from the ground state:

$$\phi_{\text{st}}^{\text{ss}} = 1 - \frac{k_1[\text{Chl}^*]_{\text{light}}}{k_i[\text{Chl}]} \quad (16)$$

Photosynthesis in nature is a matter of many days or weeks. It is therefore reasonable to assume that $[\text{P}]$ only slowly changes with time, which means that $[\text{P}]$ during the night from eq 12 may be taken equal to $[\text{P}]$ during the subsequent day which appears in eq 15. In that case one finds from eqs 16, 15, and 12

$$\begin{aligned} \phi_{\text{st}}^{\text{ss}} &= 1 - \frac{k_1[\text{Chl}^*]_{\text{light}}}{k_i[\text{Chl}]} = 1 - \frac{k_1}{k_i[\text{Chl}]} \left(\frac{k_i[\text{Chl}] + k_b[\text{P}]}{k_{\text{st}} + k_1} \right) \\ &= 1 - \frac{k_1}{k_{\text{st}} + k_1} - \frac{k_1}{k_i[\text{Chl}]} \left(\frac{(k_1 + k_{\text{st}})[\text{Chl}^*]_{\text{dark}}}{k_{\text{st}} + k_1} \right) = \phi_{\text{st}}^{\text{ss}} \\ &= \phi_{\text{st}}^0 - \frac{k_1[\text{Chl}^*]_{\text{dark}}}{k_i[\text{Chl}]} \end{aligned} \quad (17)$$

In deriving this equation it was also assumed that the concentration $[\text{Chl}]$ is so big that changes may be ignored.

One may get rid of the ratio $[\text{Chl}^*]_{\text{dark}}/[\text{Chl}]$ by looking at the chemical potentials. From eqs 4 and 7 one finds

$$\begin{aligned}\mu(\text{Chl}^*)_{\text{dark}} &= \mu^0(\text{Chl}^*)_{\text{dark}} + kT \ln[\text{Chl}^*]_{\text{dark}} \\ &= \mu^0(\text{Chl}) + E_r + kT \ln[\text{Chl}^*]_{\text{dark}}\end{aligned}\quad (18)$$

and for the ground state

$$\mu(\text{Chl}) = \mu^0(\text{Chl}) + kT \ln[\text{Chl}]\quad (19)$$

Subtracting eq 19 from eq 18 gives

$$\mu(\text{Chl}^*)_{\text{dark}} - \mu(\text{Chl}) = E_r + kT \ln \frac{[\text{Chl}]_{\text{dark}}}{[\text{Chl}]}\quad (20)$$

According to eq 14 $\mu(\text{Chl}^*)_{\text{dark}} = \mu(\text{P})$, which gives, from eq 20

$$\ln \frac{[\text{Chl}^*]_{\text{dark}}}{[\text{Chl}]} = \frac{\mu(\text{P}) - \mu(\text{Chl}) - E_r}{kT} = \frac{\Delta\mu_{\text{st}} - E_r}{kT}\quad (21)$$

Here the Gibbs free energy stored is indicated by

$$\Delta\mu_{\text{st}} = \mu(\text{P}) - \mu(\text{Chl})\quad (22)$$

From eqs 17 and 21 it follows that

$$\phi_{\text{st}}^{\text{ss}} = \phi_{\text{st}}^0 - \frac{k_1}{k_i} e^{-(E_r - \Delta\mu_{\text{st}})/kT}\quad (23)$$

From the data in Table 1 it is clear that the ratio k_1/k_i is very large. Therefore, also the exponent $(E_r - \Delta\mu_{\text{st}})/kT$ should be very large in order to produce a very small exponential function; then, one would obtain steady state storage close to 1 and an excellent photosynthesis performance.

Before making a quantitative analysis it is illuminating to look at another concept related to storage: stability. This quantity will appear to have the same exponential as eq 23; therefore, the two will be discussed together later.

Stability. Suppose that during a time Δt , which may comprise many days, Gibbs free energy G_{st} (in Joules) is stored by photosynthesis. This amount may be expressed as

$$G_{\text{st}} = k_i(\Delta t)[\text{Chl}]\phi_{\text{st}}^{\text{ss}}\{\mu(\text{P}) - \mu(\text{Chl})\}\quad (24)$$

Relation 24 is easily understood. The excitation rate (s^{-1}) is given by $k_i[\text{Chl}]$. To obtain the total amount of excitations it should be multiplied by the time of storage Δt . The steady state storage $\phi_{\text{st}}^{\text{ss}}$ is the relative amount stored; the total amount of free energy stored is then obtained by multiplying with $\{\mu(\text{P}) - \mu(\text{Chl})\}$.

In the dark, during the night, free energy is lost through the back reaction. Its rate R_1 (in Joule per second) is given as

$$R_1 = k_1[\text{Chl}^*]_{\text{dark}}\{\mu(\text{P}) - \mu(\text{Chl})\}\quad (25)$$

The time t_1 in which all stored free energy would be lost follows from

$$t_1 R_1 = G_{\text{st}}\quad (26)$$

It follows that

$$t_1 = \frac{G_{\text{st}}}{R_1} = \frac{k_i(\Delta t)[\text{Chl}]\phi_{\text{st}}^{\text{ss}}}{k_1[\text{Chl}^*]_{\text{dark}}}\quad (27)$$

The stability S_{ph} of the process of photosynthesis can then be defined as

$$S_{\text{ph}} = \frac{t_1}{\Delta t}\quad (28)$$

Assuming a reasonable stability $S_{\text{ph}} = 10$, it then follows that $t_1 = 10\Delta t$; in other words, the time during which the complete free energy would be lost is 10 times its formation time. So, during the night 1/10 of the energy, stored the previous day, is lost due to unavoidable back reactions. From eqs 27 and 28 and using eq 23 it follows that

$$\begin{aligned}S_{\text{ph}} &= \frac{t_1}{\Delta t} \\ &= \phi_{\text{st}}^{\text{ss}} \frac{k_i}{k_1} \frac{[\text{Chl}]}{[\text{Chl}^*]_{\text{dark}}} \\ &= \left\{ \phi_{\text{st}}^0 - \frac{k_1}{k_i} \frac{[\text{Chl}^*]_{\text{dark}}}{[\text{Chl}]} \right\} \frac{k_i}{k_1} \frac{[\text{Chl}]}{[\text{Chl}^*]_{\text{dark}}} \\ &= \phi_{\text{st}}^0 \frac{k_i}{k_1} \frac{[\text{Chl}]}{[\text{Chl}^*]_{\text{dark}}} - 1\end{aligned}\quad (29)$$

Using eq 21 but noting that the ratio in eq 29 is upside down gives for the stability of the process of photosynthesis

$$S_{\text{ph}} = \phi_{\text{st}}^0 \times \frac{k_i}{k_1} \times e^{+(E_r - \Delta\mu_{\text{st}})/kT} - 1\quad (30)$$

From Table 1 it follows that the ratio k_i/k_1 is very small; therefore, the exponential $(E_r - \Delta\mu_{\text{st}})/kT$ should be large in order to get a sufficiently large value of the stability S_{ph} . This is consistent with eq 23 where the same exponential enters with a minus sign.

This consistency becomes even clearer by combining eqs 30 and 23. One finds easily

$$\phi_{\text{st}}^{\text{ss}} = \phi_{\text{st}}^0 \left(1 - \frac{1}{S_{\text{ph}} + 1} \right)\quad (31)$$

One will notice that for large stability S_{ph} the steady state storage $\phi_{\text{st}}^{\text{ss}}$ will approach ϕ_{st}^0 . Because of the exponential function in eq 30 the stability may reach very large values; therefore, it is more transparent and more relevant to plot values of the steady state storage.

RESULTS

Natural photosynthesis is interplay between reaction centers PS1 and PS2. In the simplest approach each one is excited by a photon. Ross and Calvin¹² estimate that the stored free energy for each photon is about 0.8 eV. With eq 23 and Table 1, one may then calculate the steady state storage $\phi_{\text{st}}^{\text{ss}}$ as a function of the wavelength λ of the lowest red level E_r . In Figure 3 the result is shown for three values of the excitation rates k_i , viz., $k_i = 0.01, 0.1, \text{ and } 1 \text{ s}^{-1}$ per molecule. In Figure 3 the stability $S_{\text{ph}} = 10$ is indicated as well. To the left of the intersections of the line $S_{\text{ph}} = 10$ with the curves of the excitation rates; the stability will be larger than 10 for that excitation rate.

For photosynthesis an absorption rate of about $k_i = 0.1 \text{ s}^{-1}$ or somewhat larger is considered to be optimal; for brighter sunlight, plants gradually switch off photosynthesis in order to prevent damage. In fact, at most latitudes early morning or late afternoon is the most suitable for photosynthesis. Values such as $k_i = 10 \text{ s}^{-1}$ given in Table 1 are seldomly realized. From Figure 3 one may conclude that, for wavelengths larger than about 900 nm, the stability of photosynthesis becomes too low to be interesting for harnessing solar energy. Note that the curves go down steeply after the indicated intersection points.

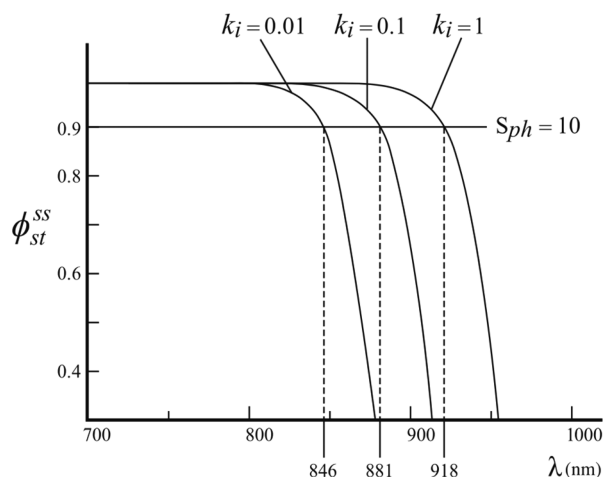


Figure 3. Steady state storage as a function of the wavelength of the lowest red level for three values of the absorption rate per molecule $k_i = 0.01$, 0.1 , and 1 s^{-1} . In eq 23 the value $\Delta\mu_{st} = 0.8 \text{ eV}$ is inserted. The ambient temperature is taken as 290 K .

This implies that for a lower stability the useful wavelengths do not become much larger.

In order to determine whether by artificial means the value $\Delta\mu_{st} = 0.8 \text{ eV}$ may be lowered in order to have stability at larger wavelengths, one has to look at the final product of photosynthesis, glucose. For processes like photosynthesis with $\Delta p = \Delta T = 0$ the free energy difference ΔG between glucose and the initial chlorophyll can be written as²

$$\Delta G = \Delta U + p\Delta V - T\Delta S \quad (32)$$

From eq 1 it follows that $\Delta U = 0.60 \text{ eV}$. From Atkins¹³ (p 151), one finds $T\Delta S = -0.01 \text{ eV}$; the value for $p\Delta V$ will be of the same order of magnitude. Therefore, $\Delta G \approx 0.60 \text{ eV}$. In plants the free energy difference of 0.2 eV between P and glucose is used to drive the many reactions of the Calvin cycle (Blankenship,¹ Chapter 9; Boeker and Van Grondelle,² Figures 5.29 and 5.33) leading from product P to glucose. Suppose that one is by artificial means able to reduce this driving power to 0.1 eV and make $\Delta\mu_{st} = 0.7 \text{ eV}$. It is then easy to draw a figure similar to Figure 3. With $k_i = 0.1 \text{ s}^{-1}$ and $S_{ph} = 10$, one finds the wavelength 948 nm above which photosynthesis does not make sense.

It is interesting to note that this conclusion is also valid for organic photocells. There the two functions, light absorption and charge transfer, are physically separated, just as in photosynthesis. In fact, a picture similar to Figure 2 describes the organic cell schematically (Boeker and Van Grondelle,² Figure 5.25; O'Regan and Grätzel¹⁴). Also here, wavelengths $\lambda \geq 900 \text{ nm}$ will not contribute to store solar energy in organic materials.

DISCUSSION

In the model, presented in this paper, the photosynthetic process is reduced to the interplay between excited chlorophyll states and a storage product state P. Differences between the two reaction centers PS1 and PS2 are only taken into account by using an average value for their loss rates. In this way the filling up of state P during the day and the subsequent inverse reaction during the night are easily analyzed. As always with chemical reactions it is the Gibbs free energy which controls the process. That free energy depends on the ambient temperature;

this gives rise to an exponential function in the expression for the final steady state storage, analogous to a similar exponential in the Boltzmann equation.

The research question of this paper is whether it makes sense to design plants or artificial photosynthetic systems, which use the considerable part of solar energy in the infrared, in other words systems with the E_r level of Figure 2 shifted to lower energies. The answer, shown in Figure 3, is that for wavelengths larger than 900 nm this does not make sense. The mathematical reason for the sharp cutoff is the occurrence of the exponential in steady state storage. The physical reason is that the distance in the energy levels of Chl^* and P in Figure 2 ($E_r - \Delta\mu_{st}$) has to compete with the thermal motion (kT); above 900 nm the thermal motion supports the back reaction too much.

Other authors have not answered the same research question. As to the method, the work of Ross and Calvin¹² comes closest. Their Figure 2b is similar to our Figure 2, but they focus on the maximum amount of free energy stored, without considering wavelength dependence in their calculations. Almgren's⁴ assumptions are similar to ours, and his Figure 1 is essentially the same as our Figure 2. In his calculations several loss levels are assumed which lead to his conclusion that wavelengths smaller than $600\text{--}800 \text{ nm}$ are optimal for photosynthesis. Our Figure 3 gives a more definite answer, dependent on incident light.

Regarding other approaches, we mention that Parson¹⁵ focused on redox potentials, while recently Marosvölgyi and van Gorkom¹⁶ studied the energy costs to grow and maintain the photosynthetic apparatus. They showed that the absorption spectra of chlorophyll and the bacteriochlorophylls peak at wavelengths which optimize their growth versus costs.

None of the papers mentioned here used an analysis of photoexcitation and back reactions to calculate the stability of the reaction products and curves like Figure 3 with a cutoff around 900 nm .

Finally, architectures for photosynthesis consisting of 3 photosystems can always be summarized in a level scheme like our Figure 2. The method presented in this paper still will apply. The data of Table 1 may change somewhat, as would, consequently, Figure 3. We expect our general conclusion about cutoff at large wavelengths to hold.

CONCLUSION

In this paper it is shown that in re-engineered photosynthesis the part of the solar spectrum with wavelengths $\lambda \geq 900 \text{ nm}$ does not lead to sufficiently stable products like, ultimately, carbohydrates. Re-engineering does make sense in harnessing the spectrum between 700 and 900 nm , which at present is not covered.

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