Fundamental limits of concentration in luminescent solar concentrators revised: the effect of reabsorption and nonunity quantum yield: supplementary material

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1. SECONDARY SOURCES DUE TO REFLECTIONS

We consider a radiation field propagating in the positive z direction which is characterized by a radiance $\mathcal{L}^+(z)$ and its reciprocal field $\mathcal{L}^-(z)$ propagating in the negative z direction. The dielectric-air interfaces at $z = 0$ and $z = d$ form a cavity in which multiple reflections occur, Fig. S1. In order to determine the total fields being built inside the LSC the superposition of all these reflections needs to be considered. If we abbreviate with I_0 the photon flux confined within the element of solid angle $d\Omega'$ that reach the top and bottom boundaries then $I_0 = \mathcal{L}_0 d\Omega' \cos\theta'$ with $\mathcal{L}_0 = \mathcal{L}^+(d) = \mathcal{L}^-(0)$. As shown in Fig. S1, the net reflected field $S_2^+(\theta'; z)$ propagating upwards is

$$S_2^+(\theta'; z) = \sum_n [R^n(\theta') e^{-\alpha_2 n d}] I_0 R(\theta') e^{-\alpha_2 z} = \frac{R(\theta')}{1 - e^{-\alpha_2 d} R(\theta')} I_0 e^{-\alpha_2 z} \quad (\text{S1})$$

where the attenuation per unit length, α_2 , in the optical path of the beam was introduced. To calculate the total flux $S_2^+(z)$ we need to integrate (S1) over the solid angle $d\Omega'$. By taking into account that for isotropic fields $\partial \mathcal{L}^\pm(z) / \partial \theta' = 0$ we can derive $S_2^+(z)$ as

$$S_2^+(z) = \int S_2^+(\theta'; z) d\Omega' \cos\theta' = \mathcal{L}_0 \zeta e^{-\alpha_2 z} \quad (\text{S2})$$

with,

$$\zeta = \int R(\theta') / (1 - e^{-\alpha_2 d} R(\theta')) d\Omega' \cos\theta'. \quad (\text{S3})$$

Fig. S1. Origin of $S_2^\pm(z)$ source. Multiple reflections of $\mathcal{L}^\pm$ at the boundaries $z = 0$ and $z = d$ result in a feedback photon flux generated in the LSC. The situation resembles a Fabry-Perot cavity with the difference that the fields here are incoherent and so phases need not be taken into account.

A similar expression holds for $S_2^-(z)$ by application of the reflection rule in (S2).

2. CHEMICAL POTENTIAL CALCULATION WITH FREQUENCY SHIFT

The objective of this Appendix is to calculate the local chemical potential of the fluorescent system shown in Fig. 1 when it is excited by some radiation field $S_1(z)$ at ω_1 and from this to deduce the field emitted by the photoexcited chemical system at ω_2 . We first consider the LSC in the dark in which case the system is in thermal equilibrium at the ambient temperature T_0 . If for simplicity we ignore stimulated emissions, the rate equation describing the chemical equilibrium is given by

$$[\epsilon(\omega_2)S(\omega_2; T_0) + \epsilon(\omega_2)S(\omega_1; T_0)]n_g^0 = An_g^0 \quad (\text{S4})$$

where $S(\omega_{1,2}; T_0)$ is given by (2), A corresponds to the spontaneous emission rate from the excited to the ground state and n_g^0 and n_e^0 are the population densities of the ground and excited states correspondingly. We now switch on the external radiation $S_1(z)$ which results in an excited electron population described by a chemical potential $\mu \neq 0$. As was shown by Ruppel [1], a radiation field in equilibrium with a system at a chemical potential μ , is characterized by a radiance

$$S(\omega; \mu) = \frac{8\pi\omega^2}{c^2} \frac{1}{e^{(h\omega - \mu)/KT_0} - 1}. \quad (\text{S5})$$

Under normal terrestrial conditions we can drop the factor 1 in the denominator of (S5) and so approximate the equilibrium field with

$$S(\omega; \mu) = S(\omega; T_0) e^{\mu/KT_0}. \quad (\text{S6})$$

Writing rate equations for the excited system then gives

$$[\epsilon(\omega_2)S(\omega_2; \mu) + \epsilon(\omega_1)S_1(z)]n_g = An_e, \quad (\text{S7})$$

where again stimulated emissions were not taken into account. Implicit in the above equation is the assumption that the absorption cross-sections do not depend on the chemical potential of the system which is, in general, accurate for diffuse, non-concentrated by lenses, mirrors or other means radiation [2]. From (S4) and (S6)-(S7) we can deduce that

$$\frac{n_e}{n_g} \frac{n_g^0}{n_e^0} \equiv e^{\mu/KT_0} = \frac{\epsilon(\omega_2)e^{\mu/KT_0}S(\omega_1; T_0) + \epsilon(\omega_1)S_1(z)}{\epsilon(\omega_2)S(\omega_2; T_0) + \epsilon(\omega_2)S(\omega_1; T_0)} \quad (\text{S8})$$

this equation can be solved for e^{μ/KT_0} and be combined with (S6) and (2) to give for the emitted field

$$S(\omega_2; \mu) = \left(\frac{\omega_2}{\omega_1}\right)^2 e^{h(\omega_1 - \omega_2)/KT_0} S_1(z). \quad (\text{S9})$$

3. SOLUTION OF MASTER DIFFERENTIAL EQUATION

For $q \neq 1$ the system of differential equations (10) is coupled. To solve this system, we first differentiate (10b) and replace in (10a) to derive

$$\frac{d^2 v(z)}{dz^2} = \alpha_2^2 (1 - q) v(z) - f(z) \quad (\text{S10})$$

where we have abbreviated,

$$f(z) = -\frac{q\alpha_2}{\pi} [S_2(z)\alpha_2 + \left(\frac{\omega_2}{\omega_1}\right)^2 e^{h(\omega_2 - \omega_1)/KT_0} S_1(z)\alpha_1] \quad (\text{S11})$$

This has now been transformed to a non-homogeneous, second order, linear differential equation which can be solved with the method of Green's functions [3]. The solutions $h^+(z)$ and $h^-(z)$ of the corresponding homogeneous equation are

$$h^+(z) = e^{-\alpha_2 \sqrt{1-q}z}, \quad h^-(z) = e^{-\alpha_2 \sqrt{1-q}(d-z)}. \quad (\text{S12})$$

The particular solutions $p^+(z)$ and $p^-(z)$ can then be derived by the solutions of the homogeneous problem as

$$\begin{aligned} p^+(z) &= h^-(z) \int_0^z \frac{h^+(t)f(t)}{W(h^+, h^-)} dt, \\ p^-(z) &= h^+(z) \int_z^d \frac{h^-(t)f(t)}{W(h^+, h^-)} dt. \end{aligned} \quad (\text{S13})$$

In S13, $W(h^+, h^-)$ is the Wronskian of h^+ and h^- , $W(h^+, h^-) = (h^+)'h^- - h^+(h^-)'$. The general solution of (S10) can then be

expressed as a linear combination of the homogeneous and particular solutions

$$v(z) = C^+ h^+(z) + C^- h^-(z) + p^+(z) + p^-(z). \quad (\text{S14})$$

Remembering that $v(z) = (\mathcal{L}^-(z) + \mathcal{L}^+(z))$ and noting from the reflection rule that $v(d-z) = v(z)$ we immediately infer that $C^+ = C^- = C$. The solution for $u(z)$ is then obtained from (10b) as

$$u(z) = \frac{1}{\alpha_2} \frac{dv(z)}{dz}. \quad (\text{S15})$$

The definitions for $u(z)$ and $v(z)$ in (9) can then be used to convert back to $\mathcal{L}^\pm(z)$. The constant C still remains unknown but can be calculated by imposing the symmetrical boundary condition $\mathcal{L}^+(0) = \mathcal{L}^-(d) = 0$ which finally renders (11).

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