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Citation: *J. Appl. Phys.* **111**, 076104 (2012); doi: 10.1063/1.3702815

View online: <http://dx.doi.org/10.1063/1.3702815>

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Photon reabsorption in fluorescent solar collectors

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(Received 6 February 2012; accepted 13 March 2012; published online 11 April 2012)

Understanding photon transport losses in fluorescence solar collectors is very important for increasing optical efficiencies. We present an analytical expression to characterize photon reabsorption in fluorescent solar collectors, which represent a major source of photon loss. A particularly useful universal form of this expression is found in the limit of high reabsorption, which gives the photon reabsorption probability in a simple form as a function of the absorption coefficient and the optical *étendue* of the emitted photon beam. Our mathematical model predicts fluorescence spectra emitted from the collector edge, which are in excellent agreement with experiment and provide an effective characterization tool for photon transport in light absorbing media. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.3702815>]

Understanding photon reabsorption (also known as recycling) is key to the design and optimum operation of devices such as solar cells, semiconductor lasers, or light emitting diodes.^{1–5} Arguably, the clearest exposition of this subject has been presented with application to fluorescent solar collectors (FSC).^{6–9} Fluorescent solar collectors—in the form of a transparent plate medium, such as glass or PMMA doped with fluorescent dyes—represent useful structures for the study of reabsorption, since a large fraction of the re-emitted photons are trapped inside the collector and can be observed when emitted from the edge. In media with high absorbance, photons undergo multiple reabsorption and reemission or simply photon recycling and gradually enter thermodynamic equilibrium with the light absorbing media before exiting the collector edge.¹⁰ Thermodynamic theories of such processes have been developed by Kennard¹¹ and Stepanov¹² for molecular structures and by van Roosbroeck and Shockley¹³ for radiative recombination in semiconductors. In this paper, we propose a new theoretical expression for the edge fluorescence of a FSC and show that this model agrees well with experiment. A particularly useful universal form of this expression is found in the limit of high reabsorption.

The classical theory used to predict the photon flux, which enters the solar cell at the edge of the fluorescent collector, was developed by Weber and Lambe (W&L).⁶ As this flux exits the collector from a full hemisphere, it cannot be observed by an observer in a medium with refractive index lower than that of the collector. As shown in Fig. 1, only the photons re-emitted in the edge escape cones (EEC) can escape from the collector and be detected by an observer at the collector edge. Photons which exit from the top and bottom surface escape cones are considered as loss. Assuming the fluorescence emitted by the dyes to be isotropic, the probability of photons emitted inside the EEC will be $P = 1 - \cos \theta_c$, where θ_c is the critical angle for total internal reflection at the collector-air interface.

For a uniform distribution and irradiation of dye molecules with isotropic emission inside the FSC, the spectral photon reabsorption probability $r(\lambda)$ can be obtained by using Beer-Lambert's law and can be written as

$$1 - r(\lambda) = \int_{(V_0)} \frac{dV}{V_0} \int_{(\Omega_0)} \frac{d\Omega}{\Omega_0} e^{-\alpha(\lambda)l}, \quad (1)$$

where V_0 is the volume of the FSC, Ω_0 is the relevant solid angle, $\alpha(\lambda)$ is the absorption coefficient, and l is the path length traveled by the photon. In W&L's theory, the edge solar cell is assumed to be fully optically coupled to the FSC edge; thereby, the spectral reabsorption probability of photons emitted out from the FSC edge is calculated using the solid angle representing the complement of the top and bottom surface escape cones, i.e., $\Omega_0 = 4\pi(1 - P)$, and can be obtained from Eq. (1),

$$1 - \{r(\lambda)\}_{\text{WL}} = \frac{1}{4\pi(1 - P)} \int_0^\pi d\phi \int_{\theta_c}^{\pi-\theta_c} \frac{\sin \theta \sin \phi}{\alpha(\lambda)L} \times \left\{ 1 - \exp \left[\frac{-2\alpha(\lambda)L}{\sin \theta \sin \phi} \right] \right\} \sin \theta d\theta, \quad (2)$$

where $\{r(\lambda)\}_{\text{WL}}$ is the spectral reabsorption probability for photons considered to be collected in W&L's theory and L is the length of the FSC. For the photon flux observed by a detector, however, the solid angle is given by the escape cone for photons emitted from the edge, i.e., $\Omega_0 = 4\pi P$. A simple calculation using Eq. (1) then gives

$$1 - \{r(\lambda)\}_{\text{EEC}} = \frac{1}{2P\alpha(\lambda)L} \times \int_0^{\theta_c} \left\{ 1 - \exp \left[-\frac{2\alpha(\lambda)L}{\cos \theta} \right] \right\} \cos \theta \sin \theta d\theta, \quad (3)$$

where $\{r(\lambda)\}_{\text{EEC}}$ is the spectral reabsorption probability for the photons emitted in the EEC and the other symbols have identical meaning as in Eq. (2).

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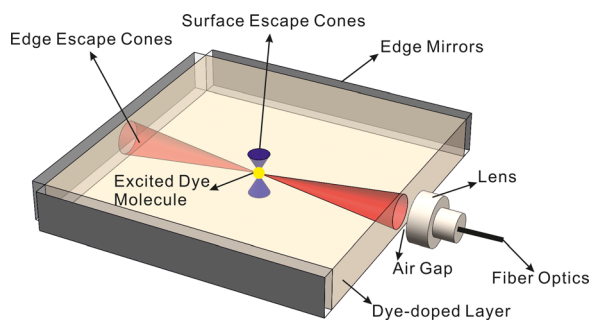


FIG. 1. FSC structure and photon flux observed at the edge.

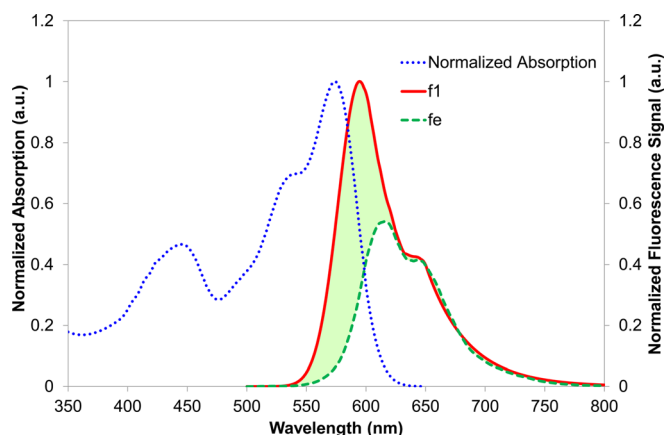
In the limit of high reabsorption, thermodynamic equilibrium between the medium and the fluorescent radiation is rapidly established, which requires that the photon absorption rate of the medium equals to the edge-emission rate, and thereby, photon reabsorption is limited. Using the concept of optical *étendue*,¹⁴ this reabsorption limit can be obtained by setting the limit of $\alpha(\lambda)L \gg 1$ to Eq. (2) or Eq. (3) and is given by

$$1 - \{r(\lambda)\}_{\text{limit}} = \frac{\varepsilon}{\alpha(\lambda)n^2V_0\Omega_0}, \quad (4)$$

where $\{r(\lambda)\}_{\text{limit}}$ is the limit for reabsorption, ε is the optical *étendue* of the photon beam emitted from the FSC edge, and n is the refractive index of the dye-doped layer of the FSC. Noting that the term $(1/V_0\Omega_0)$ is equal to the probability of photon emission per unit volume per unit solid angle, Eq. (4) shows that, in the high reabsorption limit, the reabsorption probability for a photon beam emitted from the edge depends only on its size, i.e., its optical *étendue*, the absorption coefficient, and the refractive index of the medium. We shall thus call it the universal reabsorption limit.

The theoretical expression in Eq. (3) was compared with experiment. BASF Lumogen F Red 305 dye was mixed with PMMA (MICRO CHEM 950 PMMA C 10), and the mixture was placed in an ultrasonic bath for 1 h to aid dissolution of the dye. The dye-doped PMMA solution was dropped onto glass substrates (Menzel, 20 × 20 × 1 mm, clear cut edges) and spin coated. The spin-coating speed was set to 500 rpm, with acceleration of 100 rpm/s for all the samples in order to maintain identical PMMA film thickness. The spin coated samples were left at room temperature for 24 h to consolidate before spectral measurements. The molar mass of BASF red dye is not specified by the manufacturer; thus, the units of the dye concentrations were mg/L. The spectra were obtained using a Bentham (absorption) and an Avantes (AvaSpec-2048, fluorescence) spectrometer and have been described previously.⁷ The excitation light source was a Xenon lamp with a 440-nm bandpass filter (Melles Griot, 10-nm bandwidth). Experimental data on a similar system were recently reported in Ref. 15.

By using the experimental characterization method in Ref. 7, the spectra reabsorption probability was obtained by scaling the edge fluorescence spectrum (f_e) to the fluorescence spectrum without reabsorption. This is obtained by observing fluorescence from the top of the FSC samples with low dye concentration and low absorbance, $A < 0.06$

FIG. 2. Normalized absorption (BASF Red 305 samples), normalized first generation fluorescence spectrum (f_1 , 40 mg/L), and scaled-edge fluorescence spectrum (f_e , 200 mg/L).

(referred to as the first generation fluorescence spectrum, f_1). This method is illustrated in Fig. 2. We note that f_e fits well with f_1 at the low absorption wavelength range, which is used to normalize the edge spectra. The shadowed area equals to the total reabsorption probability.

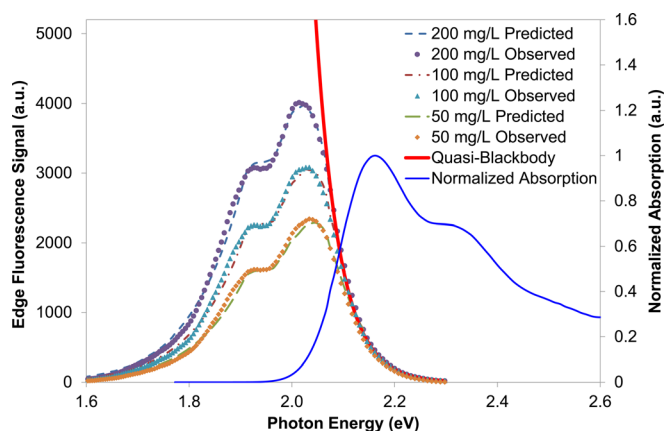
Figure 3 compares the experimentally observed edge fluorescence spectra with the predicted results given by

$$f_e(\lambda) = f_1(\lambda)[1 - \{r(\lambda)\}_{\text{EEC}}]. \quad (5)$$

Also shown are the quasi-blackbody radiation spectra, with temperature T^* given by the Kennard-Stepanov relationship, and chemical potential μ_{flux} of the photon flux exits the FSC edge, obtained following the method described in Ref. 10.

Figure 3 shows an excellent agreement between the shape and position (redshift) of the predicted and observed f_e . At the high absorption photon energy range, photons enter thermal equilibrium before exiting the FSC edge; thus f_e at this range resembles the quasi-blackbody radiation spectrum. In contrast, at the low absorption photon energy range, f_e is proportional to the dye concentration.

Figure 4 compares the experimentally obtained spectral reabsorption probability (symbols) with W&L's theory (red solid line) and the EEC model (thicker blue solid line), given

FIG. 3. Experimentally observed and predicted edge fluorescence spectra (f_e) of BASF Red samples and a blackbody radiation spectrum with $T^* = 500$ K and $\mu_{\text{flux}} = 2.42$ eV.

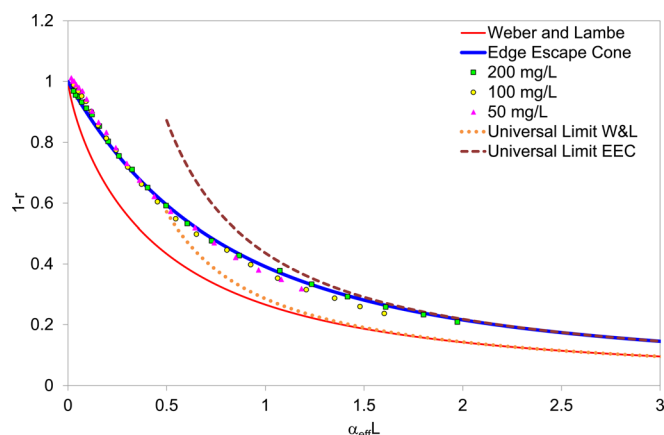


FIG. 4. Experimental spectral photon reabsorption probability for different dye concentrations' FSC samples compared with modeling results.

by Eq. (2) and Eq. (3), respectively. It shows an excellent agreement of the EEC model with the experimental results. In Fig. 4, α_{eff} is an effective absorption coefficient averaged over the thicknesses of the dye-doped PMMA film and the glass substrate and L is the length of the FSC.⁷ At high absorption, we observe that the universal reabsorption limit coincides with W&L's theory and the EEC model, whereas, at low absorption, the photon reabsorption probabilities given by W&L and the EEC model are lower than the related universal limit. The reason is that there is a limited number of reabsorption events occurring before the photon flux is emitted from the FSC edge.

We have obtained a new expression to describe the photon flux emitted from the edge of a FSC plate. This expression shows excellent agreement with experimental results and can be used to predict the spectra of the photon flux

emitted from the FSC edges. Based on this analysis, it will be possible to infer the photon flux emitted by the FSC onto a fully optically coupled solar cell, which is not easy to measure experimentally. This general expression is also valid for the new and more complex systems described in Refs. 8 and 9 as long as photon reabsorption exists. This work suggests that the present method represents an effective tool to characterize photon reabsorption in absorbing media and can be used to model and optimize their performance in applications such as fluorescent solar collectors.

This work has benefited from the financial support from SUPERGEN PV21, Faculty of Engineering and the Environment, University of Southampton, and China Scholarship Council.

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