

Luminescent solar concentrators and the reabsorption problem

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The problem of reabsorption in luminescent solar concentrators (LSC) is discussed. A mathematical development is presented which enables the LSC gain to be calculated based on the optical properties of the materials and a random walk formalism. Two- and three-dimensional analyses are used. A detailed set of calculations for a common dye (rhodamine 6G) is used to examine the practicality of employing a single dye. The effects of diameter, thickness, and quantum yield on the LSC output are presented. The spectrum of the LSC output as a function of concentration is calculated. It is suggested that LSCs can be made more efficient with a system which utilizes radiationless electronic excited state transport and trapping as intermediate steps between absorption and reemission. Trap emission substantially avoids the reabsorption problem.

I. Introduction

Several years ago it was suggested that a luminescent solar concentrator (LSC) could be used to augment photovoltaic conversion of solar energy to electricity.¹ The basic device would work as follows. A thin sheet of plastic containing a strongly absorbing and highly fluorescent dye (or dyes) is in contact around its perimeter with a set of photovoltaic cells (PVCs). Light absorbed by the dye is reradiated as fluorescence. Due to total internal reflection at the surfaces of the LSC, fluorescence emerges from the thin edge of the sheet of plastic and strikes the PVCs. Thus, the plastic sheet acts as an optical trap and a 2-D light pipe to the PVCs. Ideally, all the light striking the surface of the plastic sheet is absorbed, reradiated, and totally internally reflected. The maximum amount of solar concentration is the ratio of the surface area of the face to the surface area of the edge of the sheet. For a circular or square plastic sheet the amount of concentration is $d/4h$, where h is the thickness of the sheet and d is the diameter of the circle or the length of the side of the square. The ratio $d/4h$ is the gain of the ideal LSC. If $d = 10$ m and $h = 1$ mm, the gain is 2500. Thus, instead of having to cover a large area with PVCs, a much smaller number could be used and LSC augmented PVCs could become cost effective.

As described above the ideal LSC is far from realizable. Not all fluorescence undergoes total internal reflection. For a plastic with refractive-index 1.5, 25% will hit the surface of the plastic sheet at an angle that will allow it to escape. Also, dyes in general do not have unit quantum yield, i.e., some excitations are lost through radiationless relaxation. A typical number for a dye quantum yield is 0.9. Furthermore, not all the light which strikes the LSC will be absorbed. However, by using highly concentrated solid dye solutions and perhaps several dyes² a large percentage of the incident light can be absorbed. For the sake of illustration let us take this number to be 50%. Then, ignoring reabsorption, 34% of the light incident on the LSC would strike the PVCs. For the dimensions given above this would still result in a very respectable gain of ~ 850 .

Reabsorption has not been treated in detail previously, although it has been recognized as a serious problem.³ In any LSC which is large enough to be useful, the typical photon which is reradiated by a dye molecule will have to travel one to a few meters to reach the edge of the plastic sheet. Extinction coefficients in the region of the spectrum where fluorescence occurs are not negligible, and for concentrations of dyes which are useful to absorb a reasonable amount of sunlight, reabsorption will occur. Once a photon has been reabsorbed, nonunit quantum yield reduces the probability that a photon will be reemitted. Furthermore, the ensemble average reemission will occur in a random direction. This has two consequences. First, 25% of the reemitted photons will be traveling in directions which will not be totally internally reflected and will escape from the LSC. This and the nonunit quantum yield will reduce the LSC gain. Second, a photon which

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had moved closer to the edge of the LSC at the point of reabsorption can be reemitted in a direction which moves it away from the closest edge. A quantum of energy undergoing successive absorptions and emissions will execute a random walk in the essentially 2-D LSC. This will greatly increase the number of steps (absorption-emissions) which are necessary to reach the edge of the LSC.

Consider an LSC in which a photon is absorbed on the average 1 m from the edge. If the average distance traveled before reabsorption is 10 cm, using a simple mean-square-displacement argument the quantum will require ~ 100 steps to reach the edge since the rms displacement in a random walk increases as the square root of the number of steps. For each step in the random walk the probability that a photon will eventually reach the edge of the LSC is reduced by the product of the quantum yield and the probability for total internal reflection. This product is ~ 0.68 for a typical dye. For the example given above $(0.68)^{100} \approx 10^{-17}$, and no significant number of quanta will reach the edge from the interior of the LSC. Although the above simple analysis is not quantitatively correct, it is clear that the random walk nature of the process severely compounds the problem of reabsorption. The LSC reabsorption problem is actually a first passage problem⁴ rather than a mean-square displacement problem. The above considerations are treated in the next section.

II. Reabsorption and the Random Walk

A. Consideration of Single Wavelength Fluorescence

The probability that a quantum initially absorbed by the LSC comes out of the edge is

$$P_{\text{out}} = (QP_{\text{TIR}})^N, \quad (1)$$

where Q is the quantum yield (typically 0.9 for a dye), P_{TIR} is the probability that the photon is reemitted in a direction in which it will undergo total internal reflection (~ 0.75 for randomly oriented dye molecules in the LSC and index of refraction 1.5), and N is the number of times the quantum is emitted before it reaches the edge of the plastic sheet. The exponent in Eq. (1) is +1 if there is no reabsorption at all, i.e., the extinction coefficient $\epsilon(\lambda) = 0$ for all wavelengths of fluorescence, since at least one emission event will occur in the LSC.

The plastic sheet is very thin relative to the other dimensions, so initially we are concerned with motion in a plane. The optical quantum will execute a random walk in two dimensions since the ensemble average reemission occurs in a random direction. This situation actually involves a random walk first passage problem.⁴ The first passage is the average number of steps required for a quantum to first encounter the edge, for on that step the photon escapes and the problem ends. This is closely related to the mean-square displacement. The number of steps required for the rms displacement to equal the radius of a circular sheet goes as $(r/l)^2$, where r is the radius and l is the average step size. We employed a computer simulation to obtain the average number of steps for first passage to the edge. The

Table I. First Passage Results.

| l/r | $a(l/r)$ | $N(l/r)$ |
|-------|----------|-------------------|
| 5 | 28.1 | 1.12 \pm 0.01 |
| 4 | 18.5 | 1.16 \pm 0.01 |
| 3 | 10.9 | 1.21 \pm 0.02 |
| 2.5 | 7.9 | 1.26 \pm 0.02 |
| 2 | 5.3 | 1.32 \pm 0.02 |
| 1.5 | 3.2 | 1.43 \pm 0.03 |
| 1 | 1.7 | 1.70 \pm 0.03 |
| 0.75 | 1.1 | 1.97 \pm 0.05 |
| 1/2 | 0.67 | 2.67 \pm 0.06 |
| 1/3 | 0.42 | 3.74 \pm 0.11 |
| 1/4 | 0.33 | 5.24 \pm 0.15 |
| 1/5 | 0.28 | 6.87 \pm 0.32 |
| 1/6 | 0.24 | 8.69 \pm 0.22 |
| 1/8 | 0.20 | 12.90 \pm 0.35 |
| 1/10 | 0.18 | 18.09 \pm 0.75 |
| 1/20 | 0.15 | 58.54 \pm 1.38 |
| 1/40 | 0.13 | 213.59 \pm 1.72 |

l \equiv average step length.

r \equiv LSC radius.

$a(l/r)$ \equiv the coefficient in Eqs. (3), (5), (6), and (7).

$N(l/r)$ \equiv average number of steps to first passage.

simulation involved the average of a vast number of calculated walks which had random starting points on a disk and random step directions. The step length is randomly chosen from an exponential distribution of step sizes. Thus, a given step could be of any length, but the probability of taking a large step falls off exponentially. Equation (4) gives an expression for l . The step length procedure used in the simulation mimics the Beer's law absorption which will occur in a real LSC.

The simulation procedure gives the average number of steps N (emission-reabsorptions) for escape from the edge of the LSC (first passage). N depends on the ratio l/r , where r is the radius of the LSC and l is the average step length. It is found that for small l/r , i.e., $l/r < 0.025$,

$$N = \sim \frac{1}{8} \left(\frac{r}{l} \right)^2. \quad (2)$$

When Eq. (2) is applicable, N is very large ($N > 200$). As shown in the numerical example above, a large N prevents light from escaping from the edge of the LSC. Thus, we need to know N when the step size is not very small compared with the radius, i.e., $l/r \approx 1$. In this case N is given by

$$N = a(l/r) \left(\frac{r}{l} \right)^2. \quad (3)$$

The coefficients $a(l/r)$ are given in Table I. Enough values are given so that linear interpolation can be used without introducing significant error. When the step size l becomes much larger than the radius r , N becomes 1. This is the case for which reabsorption is negligible and only the first emission event is important. This limit is reached when $l/r > 5$. Therefore, given r and l , N can be calculated for any l/r ratio.

The average step size in the random walk l is the distance traveled by a photon for which the probability of absorption is 0.5. Thus,

$$l = -\frac{\log 0.5}{\epsilon C} = \frac{0.3}{\epsilon C}, \quad (4)$$

where ϵ is the molar extinction coefficient and C is the molar concentration of absorbers. Using this,

$$N = a(l/r)[r\epsilon C/0.3]^2 = 11a(l/r)[r\epsilon C]^2. \quad (5)$$

Fluorescence will occur over a range of wavelengths λ , and ϵ is a function of λ , $\epsilon(\lambda)$. For photons emitted at a particular wavelength

$$N(\lambda) = 11a(l/r)[r\epsilon(\lambda)C]^2, \quad (6)$$

$$P_{\text{out}}(\lambda) = (QP_{\text{TIR}})^{N(\lambda)} = (QP_{\text{TIR}})^{[11a(l/r)r^2C^2\epsilon(\lambda)^2]}. \quad (7)$$

Equation (7) only applies if fluorescence occurs at a single wavelength or over a band of wavelengths for which $\epsilon(\lambda)$ is constant. However, it serves a heuristic purpose in that it is a simple expression which provides insight into the magnitude of the reabsorption effect. For $\epsilon = 20$ and $C = 10^{-3}$ M, from Eq. (4) $l = 15$ cm. Then with $r = 50$, the ratio $l/r = 0.3$. For this l/r , Table I gives $N \approx 4$. Taking $(QP_{\text{TIR}}) = 0.68$, P_{out} drops from 68 to 21%. Thus, with a small ϵ and a relatively small r , reabsorption can have a profound effect on the gain of the LSC. If r is increased to 500 cm, $l/r = 0.03$. Table I gives $N \approx 180$ and $P_{\text{out}} = 0$.

B. LSC: 2-D Simulation

To understand quantitatively the effects of reabsorption on the LSC gain we have considered a hypothetical LSC which uses rhodamine 6G (R6G) as the absorbing and fluorescing dye. First, we determined the absolute quantum yield and found $Q = 0.90 \pm 0.02$.⁵ Next, we took absorption and fluorescence spectra using computer interfaced equipment⁵ so the numerical procedure described below could be handled accurately. In taking the fluorescence spectrum great care was exercised to obtain an absolute spectrum. A black body lamp of known color temperature was used to obtain a correction for the wavelength response of the grating and the phototube. Very low concentration solutions (10^{-7} M) of R6G in ethanol were used to assure that reabsorption of the fluorescence did not affect the spectrum.

The gross features of the absorption and fluorescence spectra are shown in Fig. 1(a).⁶ Clearly, a sizable portion of the fluorescence spectrum overlaps strongly with the absorption spectrum, and for reasonable concentrations and size of the LSC, this part of the fluorescence spectrum will not contribute to the LSC gain. Figure 1(b) displays the R6G extinction coefficients $\epsilon(\lambda)$ to the red of 17,200 cm^{-1} . These are small and for most purposes, such as using R6G as a laser dye, are negligible when compared with a maximum extinction coefficient of $>100,000$ at the peak of the absorption spectrum. However, as illustrated using Eq. (7), an ϵ of 20 can be significant. The red extinction coefficients arise from hot band absorption. As the wavelength becomes longer the Boltzmann factor for the necessary activation energy rapidly decreases, but the density of states rapidly increases. This results in the nonzero ϵ far to the red of the $S_0 \rightarrow S_1$ origin

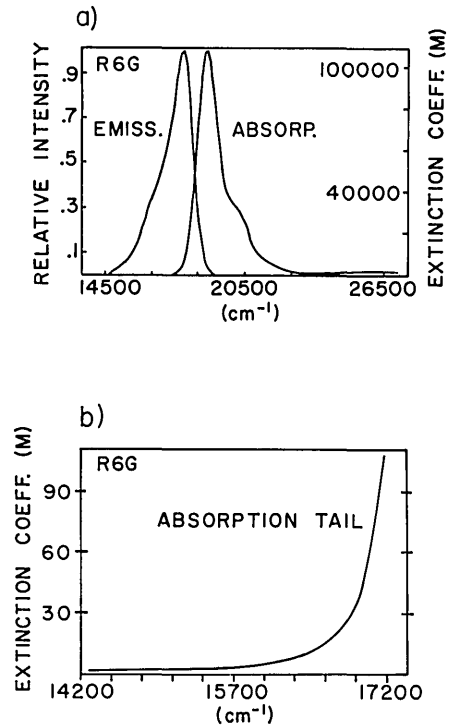


Fig. 1. (a) Absorption and emission spectra of rhodamine 6G. Notice the large overlap between the two spectra. Absorption spectrum has a long tail into the blue for which $\epsilon \approx 1000$. (b) Absorption spectrum far to the red of the origin. Absorption is very weak but can be important for a large diameter or high concentration LSC.

For each wavelength in the fluorescence spectrum there is an extinction coefficient $\epsilon(\lambda)$ which determines the average step size l . Emission in the blue part of the spectrum results in small steps while emission to the red results in larger steps on the average.

To model the LSC a 2-D computer simulation was employed. The LSC is taken to be a 2-D disk of radius r . A pair of random numbers determines the initial absorption point on the disk. Next, a fluorescence wavelength is chosen randomly from a distribution weighted by the fluorescence spectrum. This wavelength gives $\epsilon(\lambda)$ from the absorption spectrum. Using this $\epsilon(\lambda)$ and a Beer's law (exponential) weighted distribution a random number determines the step length. Finally, a direction in the plane of the disk is randomly chosen, and a move is made to the reabsorption point. If this point lies outside the disk, first passage has occurred and the trip stops. If not, successive steps are made, each using the above sequence until first passage occurs. Repeating many thousands of trips yields N , the average number of steps to first passage.

In the 2-D model the LSC properties which affect N are the radius of the LSC, the dye concentration, the dye quantum yield, and the absorption and emission spectra. In the examples given below, R6G spectral properties are used. Then, given the concentration and an LSC radius, N is calculated. As in the example given

Table II. Two-Dimensional Simulation Results, $Q = 0.9$, R6G Spectral Data

| $C(M)$ \ $r(cm)$ | 500 | 250 | 50 | 25 | 5 |
|--------------------|-------|-------|-------|-------|------|
| 5×10^{-3} | 0.003 | 0.010 | 0.061 | 0.089 | 0.20 |
| 1×10^{-3} | 0.020 | 0.061 | 0.15 | 0.20 | 0.31 |
| 5×10^{-4} | 0.061 | 0.089 | 0.20 | 0.25 | 0.35 |
| 1×10^{-4} | 0.15 | 0.20 | 0.31 | 0.35 | 0.44 |

Numbers in the tables are the probability that a photon will emerge from the LSC edge given that a photon has been absorbed by the LSC.

in Sec. II. A, P_{out} is given by Eq. (1) with $Q = 0.9$ and $P_{TIR} = 0.75$. P_{out} is the probability that a photon comes out the edge of the LSC given that a photon is absorbed. The gain of the LSC is P_{out} multiplied by the fraction of impinging solar photons which are absorbed by the LSC. This depends on the thickness as well as the concentration.

Table II gives the results of a series of calculations for a variety of concentrations C and radii r . The table displays for various R6G concentrations and LSC diameters the probability of a photon emerging from the edge of an LSC given that a photon is absorbed. Table II demonstrates that unless the concentration of R6G is low or the diameter is very small only a small fraction of the absorbed light will escape from the edge of the LSC.

If the LSC diameter is 100 cm and the thickness is 1 mm, $d/4h = 250$. For a dye concentration of 10^{-4} M, $\sim 31\%$ of the absorbed photons will escape from the edge. This physical situation would result in an eighty-fold increase in intensity of the absorbed photons. Consulting Fig. 1(a) shows that only a small portion ($\sim 10\%$) of the useful solar photons will be absorbed. Overall the device has a gain of approximately eight, nowhere near the $d/4h$ limit, but nonetheless an enhancement. Again consulting Fig. 1(a), it is seen that R6G has a long absorption tail to the blue which has $\epsilon \approx 1000$. If the LSC thickness is 1 cm and the concentration is 5×10^{-4} M, a greater portion ($\sim 35\%$) of the useful solar photons will be absorbed. For a diameter of 100 cm, $d/4h = 25$. From Table II the fraction escaping from the edge is 20%. When absorption of the solar spectrum is included, the device has a gain of just under two.

The basic problem is that efficient absorption of the solar spectrum requires either high concentration or a thick LSC. High concentration exacerbates the reabsorption problem, while increased thickness reduces the $d/4h$ ratio.

C. LSC: 3-D Simulation

It is clear that the thickness of the LSC is an important design parameter. However, the 2-D model of the last section does not consider the effect of thickness on the reabsorption problem. The LSC thickness enters the problem in two ways. A photon emitted in a wavelength region in which the Beer's length is short compared with the LSC thickness will be reabsorbed before it encounters the face of the LSC. If the photon

were traveling in a direction which would not have resulted in total internal reflection, it would have escaped from the face. Thus, reabsorption can prevent the loss of a photon and provide another opportunity for emission in a direction and with a wavelength that allows escape from the LSC edge. In the 2-D model, this effect could not be included. Any reabsorption event was considered a step which reduced the probability of escaping the LSC edge by both the quantum yield and the probability of total internal reflection. But if reabsorption occurs before the photon strikes a face, only the quantum yield is involved. Therefore, the LSC thickness will influence the reabsorption problem.

A more straightforward consequence of considering the LSC in three dimensions is that the in-plane displacement depends on the angle of reflection from the face for photons which are taking long steps. Long steps involve multiple total internal reflections, and displacement from the starting point is the step size multiplied by the cosine of the angle of incidence.

To include the above features the following simulation procedure was employed. Three random numbers are chosen to determine the starting point inside the LSC. A random number is chosen from a distribution weighted by the quantum yield to determine if a photon is emitted. If a photon is not emitted, the trip ends. Next, using the fluorescence spectrum a step length is chosen as before. Two angles are randomly chosen to determine the direction of the step. If the step length is not long enough to reach a face, reabsorption occurs and the trip continues. If the photon strikes the face at less than the total internal reflection angle, the trip ends. Otherwise, the endpoint of the step after multiple reflections is calculated, and this point is used as the starting point for a new step. The trip continues until a photon either emerges from the LSC edge or is lost out a face or by radiationless relaxation. In this simulation P_{out} is obtained by dividing the total number of photons which come out of the LSC edge by the total number of trips. Equation (1) is not used.

Tables III and IV give the results for various concentrations and radii with thicknesses of 0.1 and 1 cm, respectively. Again, R6G spectral data were used along with the R6G quantum yield of 0.9. The values of P_{out} are affected by thickness. P_{out} can increase substantially when the thickness is increased from 0.1 to 1 cm. It is interesting to note that the more approximate 2-D calculation gives very reasonable values. Also the symmetry of the 2-D table is lost in the 3-D tables. In two dimensions a tenfold increase in radius is offset by a tenfold decrease in concentration as in Eq. (5). However, in the more realistic 3-D case a tenfold increase in both radius and thickness is required to offset a tenfold decrease in concentration. This destroys the diagonal symmetry of the 3-D tables.

Table V demonstrates the effect of quantum yield on the output of an LSC having R6G spectral characteristics. In the absence of reabsorption for unit quantum yield $P_{out} = 0.75$, and if $Q = 0.5$, $P_{out} = 0.375$, a twofold change. When reabsorption is included, the negative influence of the quantum yield is greatly increased. For

Table III. Three-Dimensional Simulation Results: 0.1-cm Thick LSC, $Q = 0.9$, R6G Spectral Data

| $C(M)$ \ $r(cm)$ | $r(cm)$ | | | | |
|--------------------|---------|-------|-------|------|------|
| | 500 | 250 | 50 | 25 | 5 |
| 5×10^{-3} | 0.005 | 0.012 | 0.061 | 0.11 | 0.25 |
| 1×10^{-3} | 0.025 | 0.053 | 0.16 | 0.22 | 0.33 |
| 5×10^{-4} | 0.049 | 0.087 | 0.20 | 0.25 | 0.35 |
| 1×10^{-4} | 0.13 | 0.17 | 0.27 | 0.31 | 0.39 |

Table IV. Three-Dimensional Simulation Results: 1.0-cm Thick LSC, $Q = 0.9$, R6G Spectral Data

| $C(M)$ \ $r(cm)$ | $r(cm)$ | | | | |
|--------------------|---------|-------|-------|------|------|
| | 500 | 250 | 50 | 25 | 5 |
| 5×10^{-3} | 0.009 | 0.015 | 0.081 | 0.14 | 0.28 |
| 1×10^{-3} | 0.029 | 0.062 | 0.19 | 0.25 | 0.38 |
| 5×10^{-4} | 0.062 | 0.11 | 0.25 | 0.30 | 0.41 |
| 1×10^{-4} | 0.16 | 0.21 | 0.33 | 0.37 | 0.46 |

Table V. P_{out} for Various Quantum Yields Q . 1.0-cm Thick LSC, R6G Spectral Data, 3-D Simulation Results

| | $C(M)$ \ $r(cm)$ | $r(cm)$ | | |
|------------|--------------------|---------|-------|-------|
| | | 500 | 50 | 5 |
| $Q = 1.0$ | 5×10^{-3} | 0.018 | 0.16 | 0.48 |
| | 5×10^{-4} | 0.11 | 0.38 | 0.56 |
| $Q = 0.9$ | 5×10^{-3} | 0.009 | 0.081 | 0.28 |
| | 5×10^{-4} | 0.062 | 0.25 | 0.41 |
| $Q = 0.75$ | 5×10^{-3} | 0.004 | 0.041 | 0.16 |
| | 5×10^{-4} | 0.033 | 0.15 | 0.27 |
| $Q = 0.5$ | 5×10^{-3} | 0.001 | 0.017 | 0.066 |
| | 5×10^{-4} | 0.014 | 0.068 | 0.13 |

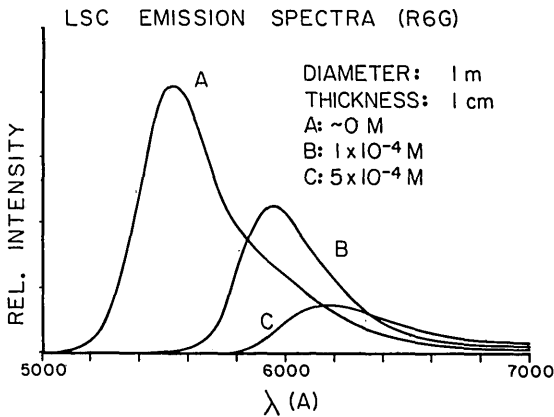


Fig. 2. Curve A: Fluorescence spectrum of R6G in ethanol. Curves B and C: calculated fluorescence spectrum observed at edge of a 50-cm diam, 1-cm thick LSC containing R6G: (B) 10^{-4} M, (C) 5×10^{-3} M. The 3-D simulation calculation was employed, and areas under each curve are proportional to the probability that a photon reaches the LSC edge once absorbed. Note the red-shifts resulting from strong reabsorption of shorter wavelength fluorescence. Only red photons have long step lengths needed to reach the LSC edge.

example, with $r = 50$ cm, $C = 5 \times 10^{-3}$ M and $Q = 1$, $P_{out} = 16\%$. However, if $Q = 0.5$, $P_{out} = 1.7\%$. This roughly tenfold decrease changes a potentially useful device into a nonfunctional one.

Figure 2 illustrates the effect of reabsorption on the LSC spectral output. The curves were calculated using the 3-D simulation, keeping track of the wavelength associated with the escape step in each trip. Curve A is the R6G fluorescence spectrum in the absence of reabsorption. Curve B is the output of a 1-cm thick 50-cm diam LSC with an R6G concentration of 10^{-4} M and $Q = 0.9$. Curve C is for an identical LSC, but $C = 5 \times 10^{-3}$ M. The three curves have the correct relative areas. As the concentration increases, reabsorption becomes more severe and the output is red-shifted and reduced in intensity. Comparing curve C with Fig. 1(b) shows that the spectral peak in the output of the high concentration system occurs at the wavelength where the extinction coefficient first becomes negligible. The LSC spectral output can provide a sensitive experimental test of the 3-D simulation procedure.

The 3-D simulation procedure provides an accurate method for calculating the gain of an LSC with a given set of physical parameters. Here we have used the dye R6G as an example, but any dye or collection of dyes with known spectral characteristics can be investigated. The calculations show the dramatic role that reabsorption plays in reducing the potential effectiveness of large-scale LSCs. However, even with the single dye R6G these calculations show some LSC configurations are useful. For example, from Table III with $C = 10^{-4}$ M, $r = 500$ cm, and a thickness of 0.1 cm, an overall gain (including solar absorption) of ~ 33 is predicted.

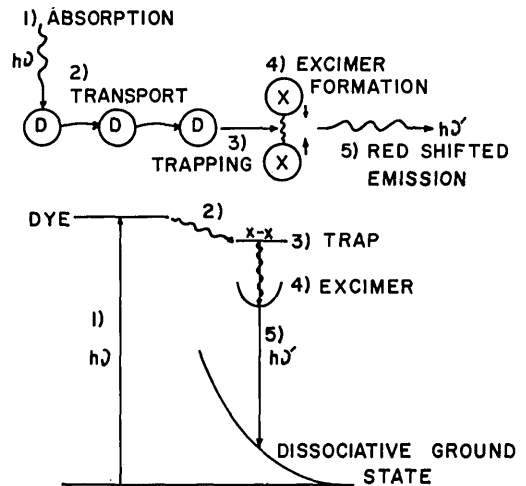


Fig. 3. Schematic representation of the excimer approach to avoiding LSC reabsorption problem: (1) Absorption occurs into concentrated dye system. (2) Radiationless transport brings the excitation to the vicinity of the excimer chromophores. (3) The excitation is trapped on the excimer chromophores. (4) Excimer formation takes place, i.e., the pair of chromophores becomes bound. (5) Strongly red-shifted emission from the excimer avoids reabsorption. Dissociative ground state prevents reabsorption by the excimer chromophores. The lower part of the figure shows the sequence in terms of the energy levels.

III. Transport and Trapping in the LSC

One approach to the solution of the reabsorption problem is to use a molecule with a large Stokes shift. Frequently a large Stokes shift arises because the lowest energy electronic absorption is only weakly allowed. However, because of the weak $S_0 \rightarrow S_1$ transition, quantum yields are low. Large Stokes shifts also occur when there are large changes in molecular geometry upon excitation. Excimer^{7,8} (excited state dimer) formation is an example of intermolecular complex formation upon excitation. An approach using excimers or other suitable traps⁹ is illustrated in Fig. 3. A highly concentrated dye or mixture of dyes efficiently absorbs sunlight. Rapid radiationless spatial transport¹⁰ moves excitations through the dye system. An excitation is then trapped by a linked pair of molecular chromophores. These chromophores undergo excimer formation (exciplex formation if the chromophores differ).

Excimer emission is dramatically red-shifted from the absorption of the individual chromophores. Excimer formation stabilizes the complex and emission occurs to a dissociative ground state. The equilibrium ground state geometry is so different from the excited state geometry that direct absorption from the ground state to the excimer does not occur. Therefore, excimer emission is not reabsorbed even in concentrated systems.

Excimers can have high quantum yields: 9,10-dimethylanthracene excimer in ethanol has a quantum yield of 0.82,⁷ which compares favorably with R6G in ethanol, $Q = 0.9$.³ 9,10-Di-*n*-propylanthracene excimer has a remarkable quantum yield of 0.98.⁷ This compound has an $\sim 6700\text{-cm}^{-1}$ splitting between the onset of strong absorption and the peak of the emission spectrum.⁷ This should be compared with R6G [Fig. 1(a)] in which the peak of the emission spectrum and the onset of strong absorption are virtually coincident in wavelength.

Recent theoretical and experimental studies of electronic excited state transport in solution¹⁰ and transport and trapping by a second species in solution¹¹ have greatly increased our understanding of these processes. In highly concentrated dye solutions, transport and trapping can occur very rapidly. Virtually all the excitations can be trapped on a time scale short compared with the dye molecule's lifetime (a few nanoseconds).¹¹ However, it was found that in highly concentrated dye solutions dimer formation by the dyes can greatly increase the rate of radiationless relaxation of the excited states and quench fluorescence.¹¹ The quenching is reduced in a high viscosity medium.¹¹ It is possible that in plastics used for LSCs, dimers of dye molecules would not present a problem.

Rather than having the dye and excimer-forming compounds dissolved as solutes in a plastic solution, chromophore-containing polymers could be employed. Both dye molecules and the excimer-forming chromophores could be attached to a polymer backbone. The polymer structure would place the dye molecules in positions to inhibit dimer formation while intermixing

the excimer chromophores in configurations to promote excimer formation upon excitation. Excimer formation between chromophores on polymers is well known and is promoted or prevented by the structure of the polymer.¹² The dye absorbers could be clustered on the polymer backbone about the excimer forming chromophores. As in photosynthetic units, this could enhance the overall efficiency of the system.

The chromophores which form the excimer or exciplex should absorb as far to the red as possible since they must act as traps for dye molecular excitations. The trapping and excimer formation will red-shift the emitted spectrum. This results in a loss of energy but not a loss of optical quanta. Since the band gaps of PVCs are in the near IR, the red-shifted excimer emission should not be a problem.

Although excimers provide a path to the elimination of the reabsorption, it could be possible to use a dilute dye as the lowest energy chromophore in a mixture of dyes. Consider a two-component system: a high concentration blue dye and a low concentration red dye. After absorption by the blue dye, radiationless transport among the blue dye molecules can bring the excitation into the vicinity of a lower concentration red dye molecule. The lower energy red dye will trap the excitation. Fluorescence will occur from the low concentration traps, reducing reabsorption, but the low trap concentration necessary for weak reabsorption also results in poor trapping efficiency. Proper selection of absorber and trap molecules for good transport and trapping characteristics and the use of mixed polymer systems with microdomains which cluster the trap and absorber molecules could make this idea viable. However, if the trap is an excimer or other photophysical species that greatly red shifts emission, the trap can be in high enough concentration for efficient trapping without causing reabsorption.

IV. Concluding Remarks

We have presented an analysis of LSCs which utilized a random walk formalism to handle the reabsorption problem. The results provide a method for determining the usefulness of optical chromophores in LSC applications in terms of their absorption and emission spectra and the dimensions of the LSC. It was found that even small extinction coefficients in the spectral region of the fluorescence can greatly diminish the LSC gain.

We proposed that a system using radiationless excitation transport and trapping on excimer-forming chromophores could avoid reabsorption problems. The use of polymers tailored to promote excimer formation could be useful. Clearly, other reversible photophysical processes which strongly red shift emission and have high quantum yields could replace excimer formation, e.g., photoisomerization. It was also suggested that dilute dye traps could be used to red shift the emission if problems of inefficient transport and trapping could be avoided.

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References

1. W. H. Weber and John Lambe, *Appl. Opt.* **15**, 2299 (1976); J. S. Batchelder, A. H. Zewail, and T. Cole, *Appl. Opt.* **18**, 3090 (1979).
2. B. A. Swartz, T. Cole, and A. H. Zewail, *Opt. Lett.* **1**, 73 (1977).
3. W. D. Johnston, Jr., *Solar Voltaic Cells* (Dekker, New York, 1980).
4. S. Chandrasekhar, *Rev. Mod. Phys.* **15**, 1 (1943); E. W. Montroll, *Proc. Symp. App. Math.* **16**, 193 (1964); E. W. Montroll and G. H. Weiss, *J. Math. Phys.* **6**, 167 (1965); E. W. Montroll, *J. Math. Phys.* **10**, 753 (1969).
5. M. D. Ediger, R. S. Moog, and M. D. Fayer, unpublished results.
6. I. B. Berlman, *Handbook of Fluorescence Spectra of Aromatic Molecules* (Academic, New York, 1971).
7. J. B. Birks, *Photophysics of Aromatic Molecules* (Wiley-Interscience, New York, 1970).
8. K. A. Nelson, D. D. Dlott, and M. D. Fayer, *Chem. Phys. Lett.* **64**, 88 (1979).
9. R. Kopelman in "Radiationless Processes in Molecules and Condensed Phases," F. K. Fong, Ed. (Springer, Berlin, 1976), p. 297; A. Blumen and R. Silbey, *J. Chem. Phys.* **70**, 3707 (1979); D. D. Dlott, M. D. Fayer, and R. D. Wieting, *J. Chem. Phys.* **69**, 2752 (1978); R. D. Wieting, M. D. Fayer, and D. D. Dlott, *J. Chem. Phys.* **69**, 1996 (1978).
10. C. R. Gochanour, Hans C. Andersen, and M. D. Fayer, *J. Chem. Phys.* **70**, 4254 (1979); C. R. Gochanour and M. D. Fayer, *J. Phys. Chem.* **85**, 1989 (1981).
11. D. R. Lutz, Keith A. Nelson, C. R. Gochanour, and M. D. Fayer, *Chem. Phys.* **85**, 1989 (1981).
12. C. W. Frank and L. A. Harrah, *J. Chem. Phys.* **61**, 1526 (1974); C. W. Frank and M. A. Oashgari, *Trans. N. Y. Acad. Sci.* to be published (1981).

Meetings Schedule

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- 7-11 September 1981** OPTICS IN BIOMEDICAL SCIENCES, INTERNATIONAL CONFERENCE AND SATELLITE MEETING OF TWELFTH ASSEMBLY, INTERNATIONAL COMMISSION FOR OPTICS, GRAZ Information: Klaus Schindl, C. Reichert Optische Werke AG, Hernalser Hauptstr. 219, A-1170 Vienna, Austria
- 8-11 September 1981** OPTICAL COMMUNICATION, SEVENTH EUROPEAN CONFERENCE, Copenhagen Information: Magnus Danielsen, Technical U. Denmark, Electromagnetics Institute, Building 348, DK-2800 Lyngby, Denmark
- 26-30 October 1981** ANNUAL MEETING OPTICAL SOCIETY OF AMERICA, Kissimmee, Fla. Information: Meetings Department at OSA or CIRCLE NO. 57 ON READER SERVICE CARD
- 9-11 December 1981** OPTICAL FABRICATION AND TESTING WORKSHOP, Anaheim Information: Meetings Department at OSA or CIRCLE NO. 47 ON READER SERVICE CARD
- 6-8 January 1982** INTEGRATED AND GUIDED-WAVE OPTICS, SIXTH TOPICAL MEETING, Asilomar Information: Meetings Department at OSA or CIRCLE NO. 48 ON READER SERVICE CARD
- 8-10 March 1982** LASER TECHNIQUES FOR EXTREME ULTRAVIOLET SPECTROSCOPY, TOPICAL MEETING, Boulder Information: Meetings Department at OSA or CIRCLE NO. 50 ON READER SERVICE CARD
- 13-15 April 1982** OPTICAL FIBER COMMUNICATION, FIFTH TOPICAL MEETING, Phoenix Information: Meetings Department at OSA or CIRCLE NO. 49 ON READER SERVICE CARD
- 14-16 April 1982** CLEO 82, CONFERENCE ON LASERS AND ELECTROOPTICS, Phoenix Information: Meetings Department at OSA or CIRCLE NO. 64 ON READER SERVICE CARD
- 17-21 May 1982** SPRING CONFERENCE ON APPLIED OPTICS, Rochester Information: Meetings Department at OSA or CIRCLE NO. 56 ON READER SERVICE CARD
- 22-25 June 1982** QUANTUM ELECTRONICS, TWELFTH INTERNATIONAL CONFERENCE, Munich Information: Meetings Department at OSA or CIRCLE NO. 51 ON READER SERVICE CARD
- 18-22 October 1982** ANNUAL MEETING OPTICAL SOCIETY OF AMERICA, Tucson, Ariz. Information: Meetings Department at OSA or CIRCLE NO. 58 ON READER SERVICE CARD