

Possibility of Luminescent Quantum Yields Greater than Unity*

D. L. DEXTER

Institute of Optics, University of Rochester, Rochester, New York

(Received June 27, 1957)

It is shown that an excited sensitizer can transfer its energy simultaneously to two activators, under suitable conditions, leading to two emitted photons per incident higher energy photon. The probability of this transfer process is computed, and the process is shown to be experimentally feasible.

THE study of luminescence in inorganic crystals has been largely concerned with luminescent impurity "centers." From the experimental point of view this is a result of two factors: one, that most "pure" inorganic crystals do not luminesce with appreciable efficiency at room temperatures, and two, that the variety of systems obtainable clearly is greatly increased when impurities are added. From the theorist's point of view, the localized "center" is easier to deal with, and may in some cases be considered as an almost isolated atom, perturbed by the host crystal in which it resides.

In the simplest case, excitation of the luminescence does not require the motion of charge through the crystal, the electrons involved in the radiative transitions existing only in bound, localized states. In the following we shall restrict ourselves to examples of this type, with the further restriction that the excitation of the luminescence be by visible or near-visible light. That is, we shall be concerned with photoluminescence in the absence of photoconductivity.

In this conceptually simple problem, the impurity center is raised to one of perhaps several discrete, excited, bound states by excitation with light in a definite energy range corresponding to an absorption band associated with the impurity. From one of these excited states the center returns to its ground state with the emission of a photon, generally less energetic than the exciting light. This degradation of the excitation energy is referred to as the Stokes' shift, the energy difference of course appearing as heat. Such a luminescing center is called an activator.

It sometimes happens that an activator with desirable luminescent properties has no excitation, i.e., absorption band in an energy region for which a convenient light source is available. This may happen for example if the activator has only forbidden transitions in the energy range available, so that the absorption bands, though present, are extremely weak, or it may happen that the particular light source, e.g., a mercury lamp, has very little intensity at wavelengths as long as the activator's principal absorption bands. In such cases it is sometimes possible to excite the activator by the incorporation in the host crystal of an

additional impurity, called the sensitizer, which is able to absorb the light from the source and transfer its excitation energy to the activator. The resulting luminescence from the activator is called sensitized luminescence. A previous paper¹ contains a discussion of this phenomenon and references to other work.

The total process clearly involves three steps: absorption of light at the sensitizer, transfer of the energy to the activator, and emission at the activator. If the probability of transfer is low, the sensitizer may itself luminesce, so that in general one would expect two emission bands upon excitation of the sensitizer, the one from the sensitizer having undergone a Stokes' shift, and the one associated with the activator at still lower energy because of lattice relaxation on both centers.

It is not essential that the sensitizer be an impurity, if the host crystal itself can absorb light from the source and transfer the energy to the activator. Thus, we may expect host-sensitized and impurity-sensitized luminescence in different systems.

As we have seen, there are certain advantages specific to *sensitized* luminescence: First, we are enabled to use certain activators (such as Mn) which may not be excitable by light directly. Second, the double Stokes' shift may enable us to use a particularly convenient ultraviolet source (such as a mercury lamp) and yet obtain visible luminescence, a shift in energy unlikely to be obtained with a single Stokes' shift. In the present note we point out the possibility of a third decided advantage, namely, the possibility of obtaining quantum yields greater than unity through a "photon-splitting" process.

Getting two visible photons out per ultraviolet photon is energetically possible, of course, and can potentially be achieved by a trivial process on a single activator. All that would be required is that the activator have three energy levels, such that the separation between adjacent levels corresponds to visible light, and that radiative transition probabilities be sizable between adjacent levels and between the ground and second excited levels. The writer is not aware of any examples of this "cascade" process among the common luminophors.

We envisage the process as follows. A sensitizer absorbs a uv photon of energy E_1 , the surrounding

* Research supported in part by the U. S. Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command.

¹ D. L. Dexter, J. Chem. Phys. 21, 836 (1953).

lattice relaxes so that the sensitizer could emit a photon of energy $\sim E_2 < E_1$, this energy is transferred before emission to *two* activators, each activator accepting $\sim E_2/2$, the lattice around each activator relaxes, and finally each activator emits a photon of energy $\sim E_3 < E_2/2$. In the succeeding paragraphs we shall discuss the probability for the occurrence of this energy transfer.

We take as the normalized wave function for the initial state of the system, before energy transfer has occurred, the antisymmetrized product

$$\Psi_I = (6)^{-\frac{1}{2}} [1 - \Theta^2(2,3)]^{-\frac{1}{2}} \times \sum_P (-1)^P P \psi_{S'}(1) \psi_2(2) \psi_3(3). \quad (1)$$

The subscript S refers to the sensitizer, and 2 and 3 refer to the two activators. For convenience, let us define as atom 2 the activator closest to the sensitizer. The prime in $\psi_{S'}(1)$ indicates an excited state, and the arguments 1, 2, 3 are abbreviations for the coordinates of electron 1, 2, 3. $\Theta(2,3)$ is the overlap integral between the normalized atomic wave functions $\psi_2(r)$ and $\psi_3(r)$. We have omitted all terms such as $\Theta^2(S',2)$, since it will be explicitly assumed that the sensitizer's wave function does not overlap the activators' wave functions. (If the sensitizer is very close to one or both of the activators we assume that ψ_S and $\psi_{S'}$ have been orthogonalized to $\psi_2, \psi_2', \psi_3, \psi_3'$.) Similarly we take as the wave function of the system after transfer has occurred the antisymmetrized product

$$\Psi_F = (6)^{-\frac{1}{2}} [1 - \Theta^2(2',3')]^{-\frac{1}{2}} \times \sum_{P'} (-1)^{P'} P' \psi_S(1) \psi_2'(2) \psi_3'(3), \quad (2)$$

where $\Theta(2',3')$ is the overlap integral between $\psi_2'(r)$ and $\psi_3'(r)$. Terms such as $\Theta^2(S,2')$ have again been omitted. It is clear that Ψ_I and Ψ_F are orthogonal if $\psi_i(r)$ and $\psi_i'(r)$ are orthogonal, with our further stipulation of the orthogonality of ψ_S and $\psi_{S'}$ to $\psi_2, \psi_2', \psi_3, \psi_3'$. Overlap integrals between ψ_2 and ψ_3 or ψ_3' are not assumed to be zero, and in fact will be responsible for the energy transfer.

We take into account the fact that the levels are not infinitely sharp, but are broadened by lattice vibrations, by our method of normalization. We normalize $\psi_{S'}, \psi_2, \psi_3$ in the usual way,

$$\int |\psi_{S'}|^2 d\tau = \int |\psi_2|^2 d\tau = \int |\psi_3|^2 d\tau = 1, \quad (3)$$

introducing probability functions $p_{S'}(w_{S'})$ and $p_A(\epsilon)$ for the probabilities that instantaneously the excited sensitizer has energy $w_{S'}$ and the two activators together have energy ϵ . These functions are normalized such that

$$\int p_{S'}(w_{S'}) dw_{S'} = \int p_A(\epsilon) d\epsilon = 1. \quad (4)$$

The functions in the final state wave function, Eq. (2), are normalized on an energy scale, such that

$$\int_w^{w+1} dw_S \int |\psi_S(r, w_S)|^2 d\tau = 1, \quad (5)$$

$$\int_E^{E+1} d\epsilon \int |\psi_2'(r_2) \psi_3'(r_3)|^2 d\tau_{23} = 1.$$

We now compute the matrix element of the perturbation Hamiltonian H between Ψ_I and Ψ_F , where

$$H = \frac{1}{2} \sum_i \sum_j' \frac{e^2}{\kappa r_{ij}} - \sum_i \sum_J' \frac{e^2}{\kappa r_{iJ}} + \frac{1}{2} \sum_I \sum_J' \frac{e^2}{\kappa r_{IJ}}, \quad (6)$$

and κ is the (high frequency) dielectric constant. The lower case indices refer to electronic, the upper case indices to nuclear coordinates, and the prime on the summation symbol excludes the equality of the two summation indices. Equation (6) is merely the sum of the Coulomb interactions among the electrons and nuclei involved. We shall explicitly assume from now on that only one electron on each of the three atoms is involved in the transitions, though more general cases can easily be treated by the same methods. We shall further assume for simplicity that the ground state of each atom is an S state.

The perturbation matrix element of Eq. (6) using Eqs. (1) and (2) is given by

$$\langle H_{IF} \rangle = \frac{-e^2 O(2,3')}{\kappa R_{S2}^3 [1 - \Theta^2(2,3)]^{\frac{1}{2}} [1 - \Theta^2(2',3')]^{\frac{1}{2}}} \times \mathbf{u}_S \cdot \left\{ \mathbf{v}_2 - 3\mathbf{R}_{S2}(\mathbf{v}_2 \cdot \mathbf{R}_{S2})/R_{S2}^2 + \left(\frac{R_{S2}}{R_{S3}} \right)^2 [\mathbf{v}_3 - 3\mathbf{R}_{S3}(\mathbf{v}_3 \cdot \mathbf{R}_{S3})/R_{S3}^2] \right\}, \quad (7)$$

where \mathbf{u}_S is the usual type of dipole matrix element,

$$\mathbf{u}_S = \int \psi_{S'}(\mathbf{r}) \mathbf{r} \psi_S(\mathbf{r}) d\tau, \quad (8)$$

and \mathbf{v}_2 and \mathbf{v}_3 are two-center dipole matrix elements,

$$\mathbf{v}_2 = \int \psi_2(\mathbf{r}) \mathbf{r} \psi_3'(\mathbf{r}) d\tau, \quad \mathbf{v}_3 = \int \psi_3(\mathbf{r}) \mathbf{r} \psi_2'(\mathbf{r}) d\tau. \quad (9)$$

\mathbf{R}_{S2} and \mathbf{R}_{S3} are the vectors connecting the sensitizer nucleus with the two activator nuclei. Because of the normalization procedure $\langle H_{IF} \rangle$ is a dimensionless quantity, not an energy. There may be several degenerate states ψ_2', ψ_3' which can contribute to the energy transfer, and it will be necessary eventually to sum

over all states. In this case $O(2,3')$ and \mathbf{v}_2 and \mathbf{v}_3 will depend on the particular state involved; we suppress explicit indication of this dependence for brevity. A different symbol $O(2,3')$ is used for the overlap integrals, as compared with Eqs. (1) and (2), because the Θ 's are computed with wave functions normalized in the usual way, whereas we use functions normalized according to Eqs. (3) and (5) in calculating $O(2,3')$. $\langle H_{IF} \rangle$ is a function of $w_{S'}$, ϵ , w_S and ϵ' , subject to the condition that energy be conserved during the energy transfer, and the transfer probability is given by

$$P_{SA} = \frac{4\pi e^4 G(\mathbf{R}_{S2}, \mathbf{R}_{S3}) \sum_I \sum_F \int dE \int \mathbf{u}_S^2(w_{S'}, w_{S'} - E) p_{S'}(w_{S'}) dw_{S'}}{3\kappa^2 R_{S2}^6 \hbar g_{S'} [1 - \Theta^2(2,3)]^{\frac{1}{2}} [1 - \Theta^2(2',3')]^{\frac{1}{2}}} \int \mathbf{v}_2^2 O^2(2,3') p_A(\epsilon) d\epsilon, \quad (11)$$

where G is a quantity of the order of or slightly larger than unity depending on the orientations \mathbf{R}_{S2} , \mathbf{R}_{S3} . In the last integral the product $\mathbf{v}_2^2 O^2(2,3')$ is a function of ϵ and $\epsilon + E$, where we have integrated over w_S by means of the Dirac delta function and have substituted E for $\epsilon' - \epsilon = w_{S'} - w_S$.

The second integral in Eq. (11) can be related to the spontaneous emission probability $1/\tau_S$ of the sensitizer, as in reference 1, and the last integral is equal to the product of the probability $f_A(E)$ that the two activators are momentarily in resonance with the sensitizer, the average of the square of the overlap integral $\Theta(2,3')$ computed with wave functions normalized in the usual way, and the square of the two-center dipole matrix element $\mathbf{r}_{23'}$ computed with the same wave functions. Thus, we obtain

$$P_{SA} = \frac{\pi e^2 \hbar^3 c^3 G(\mathbf{R}_{S2}, \mathbf{R}_{S3}) (\mathcal{E}/\kappa^{\frac{1}{2}} \mathcal{E}_c)^2 (g_A')^2}{\kappa^{\frac{1}{2}} R_{S2}^6 \tau_S [1 - \Theta^2(2,3)]^{\frac{1}{2}} [1 - \Theta^2(2',3')]^{\frac{1}{2}}} \times \langle \Theta^2(2,3') \rangle_{\text{av}} \langle (\mathbf{r}_{23'})^2 \rangle_{\text{av}} \int \frac{F_S(E) f_A(E) dE}{E^3}. \quad (12)$$

In this expression $F_S(E)$ is the shape of the emission band of the sensitizer, normalized such that

$$\int F_S(E) dE = 1,$$

and $f_A(E)$ is the similarly normalized probability that the two activators can accept the energy E . If each activator has the normalized shape function $\alpha_A(w)$ for its absorption band, $f_A(E)$ is equal to

$$f_A(E) = \int \alpha_A(w) \alpha_A(E - w) dw, \quad (13)$$

and the integral in Eq. (12) is essentially a statement of the conservation of energy in the transfer process. From a slightly different point of view it is the density of states ρ_E in the familiar expression for transition

$$P_{SA} = \frac{2\pi \sum_I \sum_F \int d\epsilon' \int dw_S \int d\epsilon p_A(\epsilon) \int dw_{S'} p_{S'}(w_{S'})}{\hbar g_{S'} [1 - \Theta^2(2,3)]^{\frac{1}{2}} [1 - \Theta^2(2',3')]^{\frac{1}{2}}} \times |\langle H_{IF}(w_{S'}, \epsilon; w_S, \epsilon') \rangle|^2 \delta[(w_{S'} - w_S) - (\epsilon' - \epsilon)]. \quad (10)$$

We have divided by the factor $g_{S'}$, the degeneracy of the excited sensitizer state, since we subsequently sum over all of these states. We square $\langle H_{IF} \rangle$, average over all orientations of \mathbf{u}_S , \mathbf{v}_2 , and \mathbf{v}_3 with respect to \mathbf{R}_{S2} and \mathbf{R}_{S3} , and insert in Eq. (10), obtaining

probabilities, $P = (2\pi/\hbar) |\langle H \rangle|^2 \rho_E$. In Eq. (12) \mathcal{E}_c is the electric field which would exist at the sensitizer if an electric field \mathcal{E} were applied to the crystal. Neglecting "local field" effects, we may set equal to unity the quantity $(\mathcal{E}/\kappa^{\frac{1}{2}} \mathcal{E}_c)$.

We must now discuss the integral in Eq. (12). Let us assume that the emission band of the sensitizer is approximately a Gaussian, centered about the energy E_0 , with a full width at half maximum given by $U_S = (2 \ln 2)/\beta^{\frac{1}{2}}$, so that

$$F_S(E) = (\beta/\pi)^{\frac{1}{2}} \exp[-\beta(E - E_0)^2].$$

Similarly, if the absorption band of the activator is a Gaussian centered around w_0 with a width $U_A = (2 \ln 2)/\gamma^{\frac{1}{2}}$, the joint shape function for the activators is equal to

$$f_A(E) = \frac{\gamma}{\pi} \int \exp[-\gamma(w - w_0)^2] \exp[-\gamma(E - w - w_0)^2] dw = \left(\frac{\gamma}{2\pi}\right)^{\frac{1}{2}} \exp[-\gamma(E - 2w_0)^2/2]. \quad (14)$$

If the sensitizer and activators be chosen for best resonance, so that $E_0 = 2w_0$, the integral in Eq. (12) is equal to approximately

$$\frac{1}{E_0^3} \int F_S(E) f_A(E) dE = \frac{2 \ln 2}{\pi^{\frac{1}{2}} E_0^3 (2U_A^2 + U_S^2)^{\frac{1}{2}}}. \quad (15)$$

Thus, the effective density of states is reduced by at most a factor $2^{-\frac{1}{2}}$ by the fact that transfer must occur to two activators rather than to one.

In order that appreciable transfer occur before the sensitizer itself luminesces, $P_{SA} \tau_S$ must be greater than or of the order of unity. Thus, for appreciable transfer,

$$1 \lesssim P_{SA} \tau_S = \frac{2\pi^{\frac{1}{2}} (\ln 2) G(\mathbf{R}_{S2}, \mathbf{R}_{S3}) (\hbar c)^3 \left(\frac{e^2}{e^2}\right)^6}{\kappa^{\frac{1}{2}} E_0^3 (2U_A^2 + U_S^2)^{\frac{1}{2}}} \left(\frac{e^2}{R_{S2}}\right)^6 \times (g_A')^2 \langle \Theta^2(2,3') \rangle_{\text{av}} \left\langle \frac{(\mathbf{r}_{23'})^2}{e^4} \right\rangle_{\text{av}}. \quad (16)$$

Where the activators are near to each other, say first- or second-nearest like neighbors, we may expect $\Theta(2,3')$ to be of the order 10^{-1} , and $|\mathbf{r}_{23'}|$ to be perhaps a few times 10^{-9} cm. If we evaluate Eq. (13) for a typical alkali halide, setting $\kappa=2.4$, $E_0=5$ ev, $U_A \sim U_S=0.4$ ev, and choose P states for the excited activator (i.e., $g_A'=3$) we may solve for a characteristic value of R_{S2} , finding that for appreciable transfer to occur, R_{S2} must be less than or of the order

$$R_{S2} \lesssim 12 \text{ \AA}. \quad (17)$$

Thus, we find that if two activators, separated by only one or two lattice distances, are within about 12 \AA of an excited sensitizer, the sensitizer will probably transfer its energy before emitting a photon. If the two activators are farther apart than first- or second-nearest like neighbors, $\Theta(2,3')$ and $\mathbf{r}_{23'}$ will be reduced, and the activators would have to be closer to the sensitizer than we have found in Eq. (14). There are about 160 lattice sites for Na or Cl within a sphere of radius 12 \AA in NaCl, so that we would have a reasonably large probability of achieving these conditions in a crystal doped with activator in excess of one percent.

It is important to note that for this process to occur it is not necessary that the activator's transition of energy $\sim w_0$ be an allowed one. That is, the matrix element $\mathbf{r}_{23'}$ is not the usual dipole matrix element responsible for an allowed electric dipole transition on the activator, but is instead a two-center matrix element which will in general be nonzero regardless of the relative symmetry of ψ_2 and ψ_3' . Hence an activator such as Mn might be perfectly satisfactory in this transfer process, and in fact might work better in this double-transfer process than in the usual single transfer. If the radiative transition in the activator is too weak one may not be able to observe an absorption curve, but the transfer may occur anyway. In this case of course one would not know $\alpha_A(w)$ or $f_A(w)$. In this case also the luminescent decay time from the activator would be long, but this would not necessarily imply a low emission yield.

Once the activators are excited, they will either luminesce or undergo a nonradiative transition to a lower state. We may compute the quantum yield for the activators' luminescence as twice the transfer yield multiplied by the average luminescent efficiency of the activators. The presence of the sensitizer and the other activators will not in general influence greatly the relative probability for emission until the concentration becomes so high that concentration quenching is important. The luminescent quantum yield from the activators will be a function of concentration similar to that in Fig. 1 of reference 1, but with the ordinate scale multiplied by two for good efficient activators. Thus, we obtain the quantum yield for the activator luminescence, a function which monotonically increases with activator concentration, with a critical concentration of about one percent where the yield is unity,

if we use the typical figures leading to Eq. (17). Above this concentration the yield should continue to increase until concentration quenching begins to dominate.

If thermal quenching occurs on the sensitizer so that in the absence of the activators the sensitizer has a luminescent yield of η_S , the criterion for efficient transfer is obtained by replacing the left side of Eq. (16) by η_S . With an efficient sensitizer we would expect η_S to be about unity, and the above results not to be appreciably changed.

The dependence of this transfer process on temperature¹ and on sensitizer concentration² is expected to be similar to that for the usual single transfer, and will not be discussed here.

If the two activators were sufficiently close together and were to interact sufficiently strongly, another point of view would be appropriate, in which the two activators might be considered as a diatomic activator molecule. In such a case, if the energy levels and wave functions of the activators were strongly perturbed, the foregoing arguments might or might not be applicable. For example, the molecular levels might not be in resonance with the excited sensitizer, so that transfer could not occur. Or it might happen that direct excitation of the molecular activator could occur by the absorption of the incident ultraviolet photon, even in the absence of the sensitizer. Similarly, the emission from the activator molecule might occur in the form of one uv photon rather than two visible quanta. A possible piece of evidence indicating the necessity for the "molecular" viewpoint would be the appearance of an appreciably modified absorption spectrum at high activator concentration. On the other hand, if the specific interaction between neighboring activators is not too great, the energy levels would not be greatly perturbed, the absorption spectrum would not be much modified, and the activators could be considered as largely independent. This is the case treated here, which may be expected to be typical in systems in which tight binding is prominent.

In summary, it is proposed that sensitized luminescence measurements be made at high activator concentrations where the activator is in half resonance with the sensitizer. It is expected that quantum yields greater than unity may be obtained in the process of changing uv photons into visible light. A suitable system might be one such as KCl containing 0.1 mole percent Tl and about 3 mole percent Mn.[†]

ACKNOWLEDGMENTS

It is a pleasure to acknowledge helpful discussions with D. Fox and R. S. Knox of this laboratory and with C. C. Klick and J. H. Schulman of the Naval Research Laboratory.

² D. L. Dexter and J. H. Schulman, J. Chem. Phys. 22, 1063 (1954).

[†] Although the discussion has been based on inorganic systems, identical arguments and results obtain for organic crystals and for liquid and gaseous solutions.