THEORY OF PHOTO-INDUCED RATE PROCESSES

IN RIGID GLASS SOLUTIONS

By

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INTRODUCTION

During the last decade or so, extensive and precise studies of luminescence in organic systems have been made and have been reviewed by various workers. In addition to these experimental investigations there has been a parallel development of the wave-mechanical approach to the theory of luminescence in organic molecules. The investigation of the occurrence and characteristics of luminescence in organic molecules has not only increased our general knowledge of such processes but has provided a powerful method of relating photochemical activity and luminescence to the structural form and physical states of molecules. Since molecules are apparently less perturbed by their environment in solid solutions than they are in liquid solutions, most of the luminescence studies of organic molecules have been done in solid solutions or rigid media. The occurrence of luminescence in rigid solutions has been known for a long time, but the systematic study began with the work of Jablonski (2).

Among the primary objectives in luminescence studies have been efforts to find the conditions favorable for the occurrence of luminescence in molecules and the mechanism by which electronically excited molecules lose their energy of excitation. In such considerations, one usually makes use

of potential energy diagrams to describe the normal and
excited states of molecules. The use of molecular energy
level diagrams to explain the emission mechanism was first
given by Jablonski (2) and quantitatively verified by Lewis,
Lipkin, and Magel (7).

The energy level diagram used by Jablonski to arrive at
his theory of the nature of phosphorescence and fluorescence
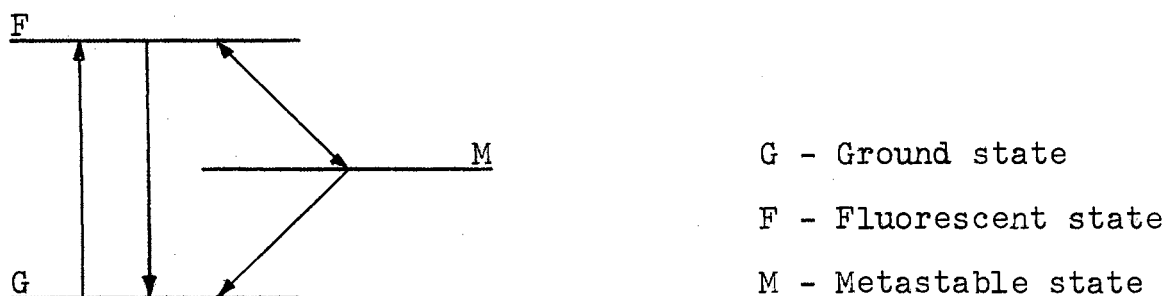emissions is given in Figure 1.

G - Ground state

F - Fluorescent state

M - Metastable state

Figure 1

He assumed that molecules giving phosphorescence have two
electronically excited levels, the F or fluorescent level,
and M or mestastable level. Lewis and Kasha advanced the
theory that the mestastable level is a triplet state of the
molecule and that the fluorescent level is an excited
singlet state (6). These molecules are excited directly to
the F state after which they either emit fluorescence and
return to the ground state by a rapid process, or they pass
over into the M state. Since the M state is metastable, the

molecule remains there for a much longer period of time before it either emits phosphorescence or is thermally activated back to the F state after which it emits fluorescence and passes again to the ground state. The metastable character of the M state causes the phosphorescence to have a much longer lifetime than the fluorescence. Lewis et al., designated the emission produced when molecules undergo a transition to the ground state from the triplet state as beta phosphorescence and the emission produced when molecules in the triplet state return to the ground state via the singlet state as alpha phosphorescence. The spectral character of the alpha phosphorescence is the same as that of the fluorescence. In order for alpha phosphorescence to be emitted, molecules in the triplet state must first absorb heat and be activated to the singlet state; therefore, the rate of the alpha phosphorescence is strongly temperature dependent and usually becomes negligible at low temperatures, while the beta phosphorescence is nearly independent of temperature and undoubtedly would continue down to absolute zero (7). The difference in the temperature dependence of these emissions together with their spectral differences serve to characterize these two types of phosphorescence. A full review of the work of Lewis and others on the metastable triplet state of molecules in rigid media has been given by Kasha (3).

For purposes of understanding the electronic nature of molecules, both in their ground state and in their various

excited states, a knowledge of the values of the transition probabilities for the several processes taking place is of great importance. These transition probabilities are the reciprocals of the respective rate constants. The first attempts to determine transition probabilities of triplet-singlet transitions were made by measuring beta phosphorescence decay lifetimes (8). It was known that such measurements did not take into account non-radiative transitions between these same two states. Later measurements of the quantum yields of fluorescence and beta phosphorescence provided data with which limits could be set on the value of the triplet-singlet transition probability (1). More accurate values of such transition probabilities would permit a surer identification of triplet-triplet absorption bands (9) and a more precise way of identifying perturbing levels in series of similar compounds (8). Furthermore, a more complete understanding of the processes by which a molecule dissipates its energy of excitation will be possible when the values of all the rate constants have been determined. The possibility also exists that rate constants for the non-radiative processes can be correlated with those found from independent photodecomposition experiments.

THEORETICAL STUDY OF THE RATE EQUATIONS

The object of this research is to demonstrate that the rate constants of some types of processes occurring in rigid glasses can be computed if enough relationships between measurable emission parameters can be found. By assuming that Jablonski's explanation of the nature of the emissive levels is correct, and that emission of luminescence by the excited molecules is first order kinetically, we have found it possible to solve for the rate constants in terms of measurable parameters. Experimentally, phosphorescences are found to be first order (8), and Jablonski's scheme is generally regarded to be correct.

There is presented in Figure 2 the energy level diagram used in the present calculations. A similar diagram was used by Koizumi and Kato (4,5) in a study of the quenching of the phosphorescence of absorbed organic dyes. They included rate constants for quenching processes in addition to these shown in Figure 2, but such constants are combined with the rate constants for the non-radiative transitions in the present treatment. Such a treatment appears to be justified because the experiments are considered to be carried out in the same solvent in obtaining a particular set of emission parameters; therefore, the rate constants

for the quenching processes should not vary. Consequently, they can be lumped together with the rate constants for the other non-radiative processes.
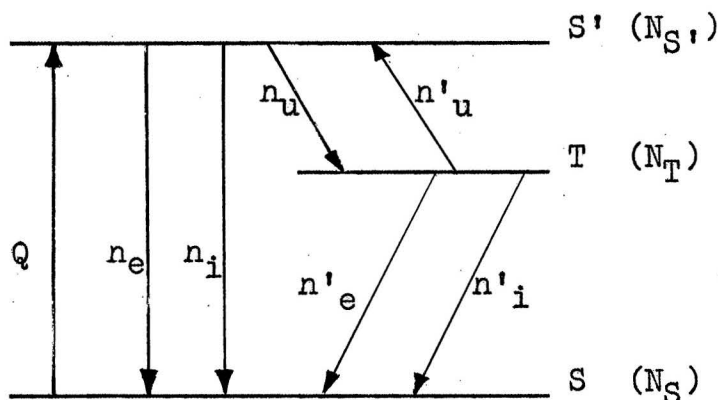

Figure 2

Key to symbols Used:

Q -   number of exciting quanta being
                           absorbed per second.

S, T, and S' -   the ground, excited triplet, and excited
                           singlet levels, respectively.

N_S, N_T, and N'_S - the instantaneous numbers of molecules
                           in the ground, excited triplet, and
                           singlet molecules, respectively.

n_e and n'_e -   the first order rate constants, for the
                           emission processes occurring from the
                           S and T levels, respectively.

n_i and n'_i -   the first order rate constants for the
                           non-radiative transitions to the ground
                           level from the S' and T levels,
                           respectively.

n_u and n'_u -   the first order rate constants for the
                           transitions occurring from the S' to T
                           level, and the T to S' level,
                           respectively.

The rate of decrease of the instantaneous numbers of molecules in the excited singlet and that of in the excited triplet levels during the illumination can be expressed in the following two differential equations:

$$\frac{dN_{S'}}{dt} = Q - (n_e + n_i + n_u) N_{S'} + n'_u N_T, \qquad (1)$$

and

$$\frac{dN_T}{dt} = - (n'_e + n'_i + n'_u) N_T + n_u N_{S'}. \qquad (2)$$

The particular solutions for $N_{S'}$ and N_T are:

$$N_{S'}(0) = \frac{R_T \, Q}{R_S \, R_T - n_u n'_u} \qquad (3)$$

and

$$N_T(0) = \frac{n_u \, Q}{R_S \, R_T - n_u n'_u}, \qquad (4)$$

where

$$R_S = (n_e + n_i + n_u),$$

and

$$R_T = (n'_e + n'_i + n'_u).$$

Equations (3) and (4) give the number of molecules in the excited singlet and in the excited triplet state during the steady state condition, respectively.

For the general solution, one obtains by standard procedures

$$N_S' = \frac{a_1 + \frac{R_T}{n_u}}{} C_1 e^{a_1 t} + \frac{a_2 + \frac{R_T}{n_u}}{} C_2 e^{a_2 t}, \tag{5}$$

$$N_T = C_1 e^{a_1 t} + C_2 e^{a_2 t}, \tag{6}$$

where

$$C_1 = \frac{a_2 \, n_u \, Q}{(a_2 - a_1) \, (R_S R_T - n_u n'_u)}, \tag{7}$$

$$C_2 = \frac{- a_1 \, n_u \, Q}{(a_2 - a_1) \, (R_S R_T - n_u n'_u)}, \tag{8}$$

and

$$a = \frac{1}{2} \left[-(R_S + R_T) \pm \sqrt{(R_S + R_T)^2 + 4(n_u n'_u - R_S R_T)} \right]. \tag{9}$$

a_1 and a_2 correspond to the + and - signs, respectively, in equation (9).

N_S' and N_T represent instantaneous numbers of molecules in the excited singlet and triplet states, respectively, at time t after an interruption of the exciting source.

Considering the fact that the lifetime of the excited triplet state is usually greater than that of the excited

singlet state by the factor of 10^8, and since R_S is also greater than R_T by this factor, a_1 and a_2 can be approximated by

$$a_1 = \frac{n_u n'_u}{R_S} - R_T,\qquad\qquad(10)$$

and

$$a_2 = -(R_S + R_T) - \frac{n_u n'_u - \frac{R_S R_T}{}}{(R_S + R_T)}.\qquad\qquad(11)$$

From equations (10) and (11), $|a_2|$ can be seen to be much larger than $|a_1|$, thus leading one to the conclusion by consideration of equations (7) and (8), that $|C_1|$ is also larger than $|C_2|$ by the same factor. Koizumi and Kato (4,5) derived similar equations in a somewhat different manner in their studies on the quenching of organic phosphors. Consequently, N_S' and N_T can be accurately approximated by the first terms only.

For N_S' one obtains

$$N_S' = \frac{a_1 + R_T}{n_u} C_1 e^{a_1 t}$$

$$= \frac{n_u n'_u/R_S - R_T + R_T}{n_u} C_1 e^{a_1 t}$$

$$= \frac{n'_u}{R_S} C_1 e^{a_1 t}.$$

But

$$C_1 = \frac{a_2\, n_u\, Q}{(a_2 - a_1)\,(R_S R_T - n_u n'_u)} \doteq \frac{n_u\, Q}{R_S R_T - n_u n'_u}$$

And

$$a_1 = \frac{n_u n'_u}{R_S} - R_T,$$

therefore, for t somewhat greater than the average lifetime of the fluorescence (10^{-8} sec.) $N_S{}'$ becomes

$$N_S{}' = \frac{n_u\, Q}{R_S R_T - n_u n'_u}\, \frac{n'_u}{R_S}\, e^{-\left(R_T - \frac{n_u n'_u}{R_S}\right) t}. \qquad (12)$$

For N_T one obtains

$$N_T = C_1\, e^{a_1 t}$$

$$= \frac{n_u\, Q}{R_S R_T - n_u n'_u}\, e^{-\left(R_T - \frac{n_u n'_u}{R_S}\right) t}. \qquad (13)$$

The exponential term, $R_T - \dfrac{n_u n'_u}{R_S}$, in equations (12) and (13) corresponds to the reciprocal of the average lifetime of the phosphorescence or to the decay constant for the α-phosphorescence. If we designate α_p as the decay constant for the α-phosphorescence, then

$$\alpha_p = R_T - \frac{n_u n'_u}{R_S} \qquad (14)$$

This can also be derived in a much simpler manner by applying the stationary state method to the excited singlet state. The rate of the decrease of the number of molecules in the excited triplet states (N_T) and that in the excited singlet state (N_S') after the interruption of the illumination can be given by the following equations:

For S'
$$-\frac{dN_S'}{dt} = R_S N_S' - n'_u N_T = 0, \tag{15}$$

and for T
$$-\frac{dN_T}{dt} = R_T N_T - n_u N_S'. \tag{16}$$

Solving equation (15) for N_S' and substituting into (16), we can easily obtain the solution of (16) as follows:

$$N_T = N_T(0) \exp(-\alpha_p t)$$

$$\alpha_P = R_T - \frac{n_u n'_u}{R_S} \tag{14}$$

Similarly, the decay constant for the fluorescence can be obtained by applying the stationary state method to the excited triplet state.

$$\alpha_F = R_S - \frac{n_u n'_u}{R_S} \tag{17a}$$

Since the term $\frac{n_u n'_u}{R_S}$ is quite small compared with R_S, it may be neglected. Thus, for α_F one obtains

$$\alpha_F = R_S \tag{17}$$

In the foregoing, expressions for the numbers of excited singlet and triplet molecules as a function of time have been derived, and the decay constants have been expressed in terms of rate constants. In the subsequent material, specific expressions for the rate constants in terms of measurable emission parameters will be developed.

In the steady state, the intensity of fluorescence, I_F (0), and that of phosphorescence, I_p (0), can be related to the rate constants by the following valid independent equations:

$$I_F (0) = (4\pi)^{-1} n_e N_S{}' (0), \tag{18}$$

$$I_p (0) = (4\pi)^{-1} n'_e N_T (0). \tag{19}$$

During the decay of the emission, the intensity of the alpha phosphorescence at time t after interruption of the exciting radiation can also be related to the rate constants by the following expression:

$$I_{\alpha - p} (t) = (4\pi)^{-1} n_e N_S{}' \tag{20}$$

Equations (18), (19), and (20) along with equations (14) and (17) form a set of five independent equations. However, these equations contain the six first-order rate constants n_e, n_i, n_u, n'_e, n'_i, and n'_u as unknowns. One more independent equation which expresses the measurable

parameters in terms of the rate constants is needed in order
to solve for their values.

Lewis, Lipkin, and Magel (7) demonstrated that the rate
of the processes which carry molecules from the T to S'
state (Fig. 2) is proportional to $\exp - \epsilon/kT$. Such a
behavior is to be expected because an energy of activation
is clearly required for the process indicated. Hence

$$n_u' = P \, (\exp - \epsilon/kT).$$

Another independent equation is obtained if the temperature
dependence of n'_u can be found. Since n_e, n_i, n_u, n_e', n_i'
refer to processes in which a molecule loses energy, it is
reasonable to expect that these quantities are independent
of temperature. Differentiating, one obtains the expression

$$\frac{\partial \alpha_P}{\partial T} = (1 - \frac{n_u}{R_S}) \, n'_u \cdot \epsilon/kT^2, \tag{21}$$

which constitutes the sixth independent equation.

The summary of these valid independent equations, from
which the rate constants can be solved explicitly, are given
as follows:

$$\alpha_p = R_T - \frac{n_u n'_u}{R_S}, \tag{14}$$

$$\alpha_F = R_S, \tag{17}$$

$$4\pi I_F (0) = \frac{n_e R_T Q}{R_S R_T - n_u n'_u}, \tag{18}$$

$$4\pi I_p (0) = \frac{n'_e n_u Q}{R_S R_T - n_u n'_u}, \tag{19}$$

$$4\pi I_{\alpha-P}(t) = \frac{n_e n_u Q}{R_S R_T - n_u n'_u} \left(\frac{n'_u}{R_S}\right) e^{-(R_T - \frac{n_u n'_u}{R_S})t}, \tag{20}$$

and

$$\frac{\partial \alpha_P}{\partial T} = \left(1 - \frac{n_u}{R_S}\right) n'_u \cdot \frac{\epsilon}{kT^2}, \tag{21}$$

where

$$R_S = n_e + n_i + n_u,$$

$$R_T = n'_e + n'_i + n'_u.$$

EVALUATIONS OF THE RATE CONSTANTS

From equation (18),

$$4\pi I_F (0) = \frac{n_e R_T Q}{R_S R_T - n_u n'_u}.$$

Dividing both nominator and denominator by R_T, one obtains

$$4\pi I_F (0) = \frac{n_e Q}{R_S - n_u n'_u/R_T} \doteq \frac{n_e Q}{\alpha_F}.$$

Therefore

$$n_e = \frac{4\pi I_F (0) \alpha_F}{Q}. \tag{22}$$

From equation (19),

$$4\pi I_p = \frac{n'_e n_u Q}{R_S R_T - n_u n'_u}.$$

Dividing both numerator and denominator by R_S, one obtains

$$4\pi I_p (0) \doteq \frac{n'_e n_u Q}{R_S (R_T - n_u n'_u/R_S)} = \frac{n'_e n_u Q}{\alpha_F \cdot \alpha_p}.$$

Thus

$$n_u = \frac{4\pi I_p (0) \alpha_F \cdot \alpha_P}{Q n'_e}. \tag{23}$$

From equation (20),

$$4\pi I_{\alpha - P}(t) e^{\alpha_p t} = \frac{n_e n_u Q}{R_S R_T - n_u n'_u} \cdot \frac{n'_u}{\alpha_F}.$$

By substituting from equations (22) and (23) for n_e and n_u' respectively and rearranging, n_u' can be expressed by

$$n_u' = \frac{I_{\alpha - P}(t) \cdot e^{\alpha_p t} Q n'_e}{4\pi I_F (0) \cdot I_p (0)}. \qquad (24)$$

From equation (21),

$$\frac{\partial \alpha_P}{\partial T} = \frac{kT^2}{\epsilon} = n'_u - \frac{n_u n'_u}{F}.$$

Substituting n_u' from equation (24) and rearranging, one obtains

$$n_e' = \frac{4\pi I_p (0)\left[\frac{\partial \alpha_P}{\partial T} \cdot \frac{kT^2}{\epsilon} \cdot I_F (0) + \alpha_p \cdot I_{\alpha - P(t)} \alpha_p t\right]}{Q I_{\alpha - P(t)} e^{\alpha_p t}}.$$

$$(25)$$

From equations (25) and (23), one finds n_u to be given by

$$n_u = \frac{\alpha_F \cdot \alpha_p \cdot I_{\alpha - p}(t) e^{\alpha_p t}}{\frac{\partial \alpha_P}{\partial T} \cdot \frac{kT^2}{\epsilon} \cdot I_F (0) + \alpha_p \cdot I_{\alpha_p(t)} e^{\alpha_p t}}. \qquad (26)$$

Since

$$R_S = n_e + n_i + n_u',$$

then

$$n_i = R_S - n_e - n_u,$$

and

$$n_i = \alpha_F - \left[\frac{4\pi\alpha_F \cdot I_F(0)}{Q} + \right.$$

$$\left. \frac{\alpha_p \cdot \alpha_F \cdot I_{\alpha-P}(t)\, e^{\alpha_p t}}{\frac{\partial \alpha_p}{T} \frac{kT^2}{\epsilon} \cdot I_F(0) + \alpha_p \cdot I_{\alpha-P}(t)\, e^{\alpha_p t}} \right]. \tag{27}$$

From equations (25) and (24),

$$n_u' = \frac{\frac{\partial \alpha_P}{\partial T} \cdot \frac{kT^2}{\epsilon} \cdot I_F(0) + \alpha_P \cdot I_{\alpha-P}(t)\, e^{\alpha_p t}}{I_F(0)}. \tag{28}$$

Since

$$\alpha_p = (n'_e + n'_i + n'_u) - \frac{n_u n'_u}{\alpha_F},$$

then

$$n'_i = \alpha_p - n'_e - n'_u + \frac{n_u n'_u}{\alpha_F}$$

results when one substitutes from equations (14) and (17). By substituting the values for n'_e, n_u, and n'_u given by equations (25), (26), and (24) and simplifying, one obtains for the value of n'_i the equation

$$n'_i = \alpha_p - \left[4\pi \left(\frac{\partial \alpha_P}{\partial T} \circ \frac{kT^2}{\epsilon} \circ I_F(0) + \alpha_p \circ I_{\alpha-P}(t) e^{\alpha_p t} \right) \right.$$

$$\left. \left(\frac{I_p(0)}{Q\ I_{\alpha-P}(t) e^{\alpha_p t}} + \frac{I}{4\pi\ I_F(0)} \right) \right] + \frac{\alpha_P \circ I_{\alpha-P}(t) e^{\alpha_p t}}{I_F(0)} \circ \quad (29)$$

The rate constants are, therefore, expressed exclusively in terms of measurable parameters.

The results summarized are

$$n_e = \frac{4\pi \alpha_F \circ I_F(0)}{Q}, \quad (22)$$

$$n_i = \alpha_F - \left[\frac{4\pi \alpha_F \circ I_F(0)}{Q} \right.$$

$$\left. + \frac{\alpha_P \circ \alpha_F - I_{\alpha-P}(t)\ e^{\alpha_p t}}{\frac{\partial \alpha_P}{\partial T} \circ \frac{kT^2}{\epsilon} \circ I_F(0) + \alpha_p \circ I_{\alpha-P}(t) e^{\alpha_p t}} \right], \quad (27)$$

$$n_u = \frac{\alpha_P \circ \alpha_F \circ I_{\alpha-P}(t) e^{\alpha_p t}}{\frac{\partial \alpha_P}{T} \circ \frac{kT^2}{\epsilon} \circ I_F(0) + \alpha_p \circ I_{\alpha-P}(t) e^{\alpha_p t}}, \quad (26)$$

$$n_{e'} = \frac{4\pi\ I_p(0) \frac{\partial \alpha_P}{\partial T} \circ \frac{kT^2}{\epsilon} \circ I_F(0) + \alpha_p \circ I_{\alpha-P}(t) e^{\alpha_p t}}{Q\ I_\alpha - P(t) e^{\alpha_p t}}$$

$$(25)$$

$$n'_i = \alpha_p - \left[4\pi \left(\frac{\partial \alpha_P}{\partial T} \cdot \frac{kT^2}{\epsilon} \cdot I_{F(0)} + \alpha_p \cdot I_{\alpha - P(t)} e^{\alpha_p t} \right) \right.$$

$$\left. \left(\frac{I_{P(0)}}{Q \; I_{\alpha - P(t)} e^{\alpha_p t}} + \frac{I}{4\pi \; I_{F(o)}} \right) \right]$$

$$+ \frac{\alpha_P \cdot I_{\alpha - P(t)} \; e^{\alpha_p t}}{I_{F(0)}} \qquad (29)$$

and

$$n'_u = \frac{\frac{\partial \alpha_P}{\partial T} \cdot \frac{kT^2}{\epsilon} \cdot I_F{(0)} + \alpha_p \cdot I_{\alpha - P(t)} \; e^{\alpha_p t}}{I_{F(0)}} \qquad (28)$$

SUMMARY

Six different rate constants have been expressed exclusively in terms of the measurable parameters under the assumptions that Jablonski's scheme of luminescence is correct and that the rate processes are all first order with respect to the excited species. A few easily justifiable approximations have been introduced in the treatment.

If it is possible to measure, for a given system, the set of parameters appearing in the six equations listed, then calculations of the values of the rate constants can be carried out. The results of such calculations should aid in the testing of the presently accepted theories of rate processes occurring in organic molecules in rigid glass solutions, and they should contribute to a better theoretical understanding of the natures of these processes.

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