



ORGANIC SYSTEMS WITH FLUORESCENCE QUANTUM YIELD DEPENDENT ON EXCITATION WAVELENGTH

Reported results on organic systems whose fluorescence quantum yield depends on the wavelength used for excitation are compared and discussed. A model involving higher excited states of excimers is presented. It is shown that under some definite conditions the model predicts an independence of the shape of the emission spectrum of the excitation wavelength. A more general model, involving a «dissociative state» is also presented and its relation with the excimer model is discussed.

1 — INTRODUCTION

Since the ground state S_0 of aromatic molecules is a singlet state, excitation of an aromatic fluorescent molecule with ultraviolet radiation leads to a higher excited singlet state S_n . It has generally been assumed that with the exception of azulene and derivatives [1, 2] the molecules return to the first excited singlet state S_1 through a rapid, radiationless, internal conversion [3]. Although recent work has shown that in some cases a radiative emission from higher excited states can be detected [4, 5] the quantum yield of this emission is so low that radiationless deactivation must still be considered the main process through which the energy is dissipated. From the first excited singlet state the molecules return to the ground state either through a radiative $S_1 \rightarrow S_0$ emission (fluorescence) or through a radiationless deactivation process, namely a direct $S_1 \rightarrow S_0$ transition or intersystem crossing to the triplet manifold followed by $T_1 \rightarrow S_0$ radiationless transition (the radiative $T_1 \rightarrow S_0$ transition is not usually observed for organic molecules at room temperature).

If the efficiency of the internal conversion $S_n \rightarrow S_1$ is unity the fluorescence quantum yield should be independent of the wavelength of the radiation used for excitation (Vavilov's law [6]). This has been experimentally verified in most cases [7] although some early papers had reported on a few exceptions. Hochstrasser described some cases for which the fluorescence yield obtained upon excitation to the second excited state was lower than that observed where the molecules were excited to S_1 [8]. The effect was attributed either to photodecomposition or to the enhancement of intramolecular energy transfer process competing with internal conversion between singlet states. For the case of dibromo anthracene the conclusion was that the fall-off on fluorescence yield was not caused by significant changes in the rate of internal conversion [9]. FERGUSON [10] also reported on some deviations to Vavilov's law, invoking as possible explanations that some other processes (e. g. predissociation and intersystem crossing) could compete with the internal conversion, even when this process was very efficient. As a matter of fact, the occurrence of $S_n \rightarrow T_n$ intersystem crossing followed by $T_n \rightarrow T_1$ internal conversion should increase the

ratio of the phosphorescence to fluorescence quantum yields. Such a variation has been reported for eosin by PARKER and HATCHARD [11] and also for chrysene and hexahelicene [12].

BRAUN, KATO and LIPSKY presented a detailed study [13, 14] of the variation of the quantum yield with excitation wavelength for benzene, toluene, p-xylene and mesitylene. The quantum yield was found to be lower in the region of high molar extinction coefficient, the wavelength interval studied covering excitation into the first three excited singlet states. Dissociation, internal conversion to the ground state and intersystem crossing were considered as possible explanations, although measurements of the benzene sensitized phosphorescence seemed to indicate that if there was intersystem crossing from higher excited states the triplets so produced did not efficiently internally convert to the lowest triplet state. The findings of Lipsky and co-workers were later confirmed and extended to naphthalene and some of its derivatives [15-17].

In what follows, the « β -effect» will be defined as the relative loss in intensity when the excitation leads the molecules to higher excited singlet states, the value of β representing the quantum yield of fluorescence relative to the yield observed upon excitation into the first excited singlet state S_1 .

The results that were found for benzene and naphthalene derivatives either in pure liquid form or in solution can be summarized as follows:

- a) In all cases the shape of the excitation spectrum is related to the absorption spectrum, β increasing when the molar extinction coefficient decreases. However, for two different wavelengths corresponding to the same extinction coefficient (but in different excited states), the values of β are different.
- b) An interesting result, not observed with the other systems referred before for which variations of the quantum yield with excitation wavelength had been found, is that for high energies, corresponding to excitation into S_3 , the value of β increases, matching the decrease in the molar extinction coefficient.
- c) For pure liquids the magnitude of the β -effect seems to depend on molecular size. The effect

is greater in benzene than in naphthalene and decreases with methyl substitution.

- d) For the same wavelength of excitation and for outgassed solutions, β increases when the fluorescent material is diluted in a non-absorbing solvent such as cyclohexane. In the case of benzene, however, β decreases with dilution. For dilute solutions ($\sim 0.1 \text{ mole.l}^{-1}$) the limiting value is unity for naphthalene and derivatives but seems to be less than unity for the alkylbenzenes (for very dilute solutions the results are not very reliable due to geometrical effects).
- e) For the same wavelength of excitation and for a given fluorescent molecule β is generally greater when the solutions contain oxygen. The effect is more pronounced for the alkylbenzenes than for the naphthalene derivatives. Other quenching agents (e. g. carbon tetrachloride) produce the same effect as oxygen.
- f) In some cases (e. g. with p-xylene) solutions containing oxygen show a decrease in β with dilution. It is to be noted that these measurements were made with air-equilibrated solutions and so oxygen concentration is different from one solution to another.
- g) The presence of a heavy atom in the molecule seems to increase the value of β . Fluoronaphthalene has only a small β -effect. Fluorobenzene still shows a β -effect but less pronounced than benzene.
- h) The presence of impurities also tend to reduce the β -effect. Experiments made with 1.6 dimethylnaphthalene containing an unknown impurity gave excitation spectra with β higher than those obtained with the pure liquid.
- i) At least for 1.6 dimethylnaphthalene the shape of the emission spectrum was found to be independent of the excitation wavelength. In particular, the ratio of monomer to excimer intensities was found to be constant, within the experimental error.
- j) It was found that correction for reflectivity losses which are mainly important in the region of high extinction coefficient was not enough to explain the effect.

The aim of the present work is to present a critical comparison of the explanations that have been

offered for the β -effect as well as a general discussion of kinetic schemes which can be used to analyse the results.

2 — THE INTERPRETATION OF THE RESULTS

To explain the β -effect several mechanisms can in principle be invoked [14, 17].

2.1 — SURFACE EFFECTS

For anthracene, variations in quantum yield with excitation wavelength have been interpreted in terms of a surface quenching effect [18]. According to the theory of this effect [19, 20] if an excitation is produced near the surface it can escape, thus reducing the quantum yield. However, the theory predicts a maximum reduction in quantum yield of 50 % corresponding to absorption at the surface. Now, in the region of high extinction coefficient and at least for benzene and derivatives β reaches values lower than 0.5.

Although the effect of dilution for the alkylbenzenes and naphthalene or naphthalene derivatives is consistent with a surface effect, β increasing with the decrease in concentration, i. e., with the increase in the depth of penetration δ of the exciting radiation, this is not the case with benzene. Furthermore, at least for naphthalene derivatives it is possible to choose two different wavelengths in the second and third absorption bands, corresponding to the same molar extinction coefficient, and so the same δ . However, the values of β are different.

Also an increase in the magnitude of a surface effect should be expected for solutions containing oxygen, leading to a decrease in β , which does not conform with the experimental findings.

This shows that although some surface effects can be invoked [21, 17] this effect alone cannot explain all the results.

2.2 — SINGLET-TRIPLET TRANSITIONS

Upper state intersystem crossing has been predicted on theoretical grounds [22]. As a result, the phosphorescence quantum yield should increase at the expense of the fluorescence emission. However the

transition $S_1 \rightarrow T_1$ is enhanced by the presence of oxygen [23] and the same is to be expected for upper states. Also the presence of heavy atoms in the molecule should increase the triplet population [3].

As referred before the experimental results show that β -effect is less pronounced in fluoronaphthalene than in naphthalene, in fluorobenzene than in benzene and in solutions containing oxygen. Also the effect of dilution is difficult to be understood in terms of an enhancement of upper singlet-triplet transitions.

Finally there is indication that the excitation spectrum of phosphorescence emission is the same as the fluorescence emission spectrum [14, 24]. This shows that upper state intersystem crossing is unlikely to explain the β -effect.

2.3 — TEMPERATURE EFFECTS

If after excitation into higher excited states a molecule undergoes internal conversion to the first excited singlet state the excess energy which is dissipated could lead to an increase in local temperature with a subsequent decrease in quantum yield [25]. Now the β values were found to be independent of the time of irradiation. Also the shape of the emission, at least for 1,6 dimethylnaphthalene which is known to form excimers was observed to be independent of the excitation wavelength. Obviously variations in temperature should alter the relative intensities of monomer to excimer emission [26].

These facts indicate that a local increase in temperature cannot explain the β -effect.

2.4 — PHOTOCHEMICAL DECOMPOSITION

There is experimental evidence [27-29] that higher excited states may be involved in energy degradation processes other than internal conversion to the first excited singlet state and intersystem crossing. Work on the photochemistry of benzene vapour at 1849 Å suggests [30, 31] that photoproducts are formed via a state other than the lowest triplet or singlet excited states.

If upper electronic states undergo photochemical changes there will be variations in quantum yields with the wavelength of the radiation used for excitation. If this is the exclusive mechanism for the

decrease in quantum yield, the results indicate that it is a more efficient process for benzene, decreasing with methyl substitutions. Published data seems to contradict however this prediction, notwithstanding the fact that it is well known that aromatic hydrocarbons undergo decomposition upon irradiation with ionizing radiation or u.v. light. This decomposition is known to be different if the molecules are excited into the first excited singlet state or into higher excited states.

If the explanation of the β effect is to be found solely on a photochemical decomposition it is necessary to discuss the dependence on concentration (taking into account that for benzene the effect of dilution is different from that for the other molecules) and the broad correlation between absorption and excitation spectra, which would seem to point to some differences in the efficiencies of photochemical processes with the vibrational energies. Also it must be explained why for very high energy of excitation an overall increase in the internal conversion efficiency (implying, under the circumstances, a decrease in the yield of the photo-products) is observed.

2.5 — INTERNAL CONVERSION TO THE GROUND STATE

On theoretical grounds this process is considered unlikely [32]. It must be stressed that recent work on isolated molecules has shown the possibility of a large increase in the rate constants for the internal conversion to the ground state upon excitation into high vibrational levels of S_1 [53, 54]. Suggestion has even been made that the same effect could be observed in condensed phase. However, the dependence of the β -effect on concentration seems to suggest that the process is not monomolecular.

It may be argued that since, as referred before, fluorescence from higher excited states has been detected, successive emissions and absorptions, in spite of the low quantum yield of the emission could lead to a degradation of the energy to the ground state which being equivalent to the intramolecular internal conversion would introduce a dependence on concentration. Such a mechanism would correspond to BIRK'S photon cascade theory [33] which has not received much support.

However an internal conversion to the ground state remains a possible explanation for the β -effect [14, 30]. The problem is that the evidence for this radiationless process would come ultimately from the decrease observed in any of the other processes that can be detected.

2.6 — INTERMOLECULAR PROCESSES

As pointed out before, the dependence of β on concentration suggests that more than one molecule may be involved in the process of internal conversion. Since benzene and naphthalene derivatives are excimer forming molecules a possible model would be one involving higher excited states of the excimer. Such a model has indeed already been proposed [17] and it will be discussed more fully later in this paper.

It must be stressed here that the dependence of β on the concentration does not necessarily imply interactions between excited and unexcited molecules of the same kind. On dilution, the depth of penetration of the exciting radiation will be increased and some effects (e. g. the surface effects already discussed) which may contribute to β may vary. Also interactions with solvent molecules may be important.

3 — LATER WORK ON THE β -EFFECT

From the foregoing arguments it is apparent that the complexity of the effect suggest that several factors may be involved. This is indeed the position taken by LAWSON, HIRAYMA and LIPSKY [34, 35]. They assume that when the alkylbenzenes are excited into S_3 (the 1849 Å Hg line being used for excitation) a photochemically generated quencher (fulvene) is present at concentrations much higher than those corresponding to excitation into S_1 (for which excitation with the 2537 Å Hg line was used). Hence a quenching effect on the $S_1 \rightarrow S_0$ fluorescence emission which is wavelength dependent. To obtain the actual value of the internal conversion efficiency it is then in principle necessary to know both the concentration and the quenching constant. To avoid this correction the authors propose that the relative quantum yields must be measured in the presence of high concentrations of an external quencher or a solute to which the alkylbenzenes are

able to transfer its energy. In this way the relative quantum yield will just be the internal conversion efficiency.

The internal conversion efficiencies obtained using this method were found to depend on the solvent and it was observed that the internal conversion is large in solvents where an intense HAM band [6] is observed. According to KOYANAGI [37] the enhancement of the Ham band (the symmetry forbidden 0-0 absorptive transition) requires a solvent perturbation which is effective in mixing the dipole-allowed S_3 state of benzene with the dipole-forbidden S_1 state. On the basis of the observed correlation Lawson, Hirayama and Lipsky suggest that the extent of this mixing is also important to the $S_3 \rightarrow S_1$ internal conversion efficiency.

The effect of dilution is then explained assuming that since the concentration of the generated quencher is reduced β is increased. However, for benzene the solvent perturbation effect in changing from an aromatic to an aliphatic environment is so large that instead there is a reduction in β .

According to this view S_3 has two decay channels, internal conversion to S_1 and internal conversion to S_0 , the solvent playing an important role in modifying the efficiency of the $S_3 \rightarrow S_1$ process by providing the appropriate perturbation for mixing these states.

It is seen that with this method of analysis, to obtain the internal conversion efficiencies it is essential to use energy acceptors at high concentrations. It is then assumed that the energy is only transferred from the S_1 state which is at variance with what has been proposed by other authors either for quenching effects [28] or transfer to a solute [38-40].

FUCHS, VOLTZ and HEISEL presented a detailed study [41-43] of the β -effect in benzene and derivatives. The fluorescence yields were also measured in solutions containing fluorescent solutes but the authors assume that there is transfer from higher excited states and so the internal conversion efficiencies correspond to the relative yields in the absence of solute.

The analysis of the results leads the authors to the calculation of transfer efficiencies and internal conversion efficiencies. They state that the assumption of energy transfer from higher excited states is essential in order that the results can be fully analysed. Also at variance with the assumptions of

Lawson et al., $S_3 \rightarrow S_1$ and $S_3 \rightarrow S_0$ internal conversion transitions are considered negligible compared with $S_3 \rightarrow S_2$ and $S_2 \rightarrow S_1$ nonradiative transitions in accordance with the «energy gap law» [32, 22]. Even so, for molecules excited into S_3 or S_2 there is also the possibility of photodecomposition which represents an alternative route for the energy dissipation.

For high energies of excitation, greater than a characteristic critical value (equal to 7 eV for benzene) the authors conclude that the upper singlet levels decay essentially by autoionization, charge separation being followed by geminate recombination, without spin relaxation, from the lowest charge transfer state to the first excited singlet state. In this way they present an explanation of the increase in the relative quantum yield observed for high energies of excitation.

In the foregoing discussion the two alternative explanations that have been proposed so far for the β -effect since the first reports on the subject were described with some detail since, to the present author's knowledge a critical comparison between them has not yet been published. In both there are processes competing with the $S_n \rightarrow S_1$ internal conversion. However they differ in what regards the possibility of energy transfer from higher excited states, and hence different ways of evaluating the internal conversion efficiencies are proposed.

To explain the effect of dilution on β , Lawson et al. invoke the presence of a photochemically generated quencher, stating that the assumption of higher excited states of an excimer can not be considered since the shape of the emission spectrum is wavelength independent. It will be shown below that this is not necessarily true.

4 — MONOMER-EXCIMER KINETICS

Let us consider a molecule M which can form excimers D^* by interaction between an excited species M^* and a ground state molecule according to the reaction



Let us assume also that if the molecules M are excited into a higher excited singlet state M^{**} they

are able to produce a higher excited state D^{**} of the excimer according to the reaction



the higher excited state of the excimer being able to internally convert to D^* in the same way as M^{**} can internally convert to M^* . We will assume also that D^{**} , M^{**} , D^* and M^* are able to fluoresce and to undergo an internal conversion to the ground state. Since the excimer has not a stable ground state the net result of the «internal conversion to the ground state» for the excimer is the production of two ground state M molecules. The reactions that can take place under the circumstances are indicated in the Table.

For steady state conditions of excitation, the molecules M being excited into M^{**} with light of intensity I_0 (in Einstein sec^{-1}) the concentrations of the excited species obey the equations

$$I_0 + k_{MD}^{(2)}[D^{**}] = (\alpha_M + k_M^{(2)} + k_{DM}^{(2)}c)[M^{**}] \quad (1)$$

$$k_{DM}^{(2)}c[M^{**}] = (\alpha_D + k_D^{(2)} + k_{MD}^{(2)})[D^{**}] \quad (2)$$

$$\alpha_M[M^{**}] + k_{MD}^{(1)}[D^*] = (k_M^{(1)} + k_{DM}^{(1)}c)[M^*] \quad (3)$$

$$\alpha_D[D^{**}] + k_{DM}^{(1)}c[M^*] = (k_D^{(1)} + k_{MD}^{(1)})[D^*] \quad (4)$$

where c is the concentration of the fluorescent molecules and

$$k_M^{(2)} = k_{fM}^{(2)} + k_{iM}^{(2)} \quad (5)$$

$$k_D^{(2)} = k_{fD}^{(2)} + k_{iD}^{(2)} \quad (6)$$

$$k_M^{(1)} = k_{fM}^{(1)} + k_{iM}^{(1)} \quad (7)$$

$$k_D^{(1)} = k_{fD}^{(1)} + k_{iD}^{(1)} \quad (8)$$

From (2)

$$[D^{**}] = \frac{k_{DM}^{(2)}c}{\alpha_D + k_D^{(2)} + k_{MD}^{(2)}} [M^{**}] \quad (9)$$

Substituting into (1) it is easy to obtain

$$[M^{**}] = \frac{k_{DM}^{(2)}c}{(\alpha_D + k_D^{(2)} + k_{MD}^{(2)})(\alpha_M + k_M^{(2)} + k_{DM}^{(2)}c) - k_{MD}^{(2)}k_{DM}^{(2)}c} I_0 \quad (10)$$

and, from (9)

$$[D^{**}] = \frac{k_{DM}^{(2)}c}{(\alpha_D + k_D^{(2)} + k_{MD}^{(2)})(\alpha_M + k_M^{(2)} + k_{DM}^{(2)}c) - k_{MD}^{(2)}k_{DM}^{(2)}c} I_0 \quad (11)$$

Now from (4)

$$[D^*] = \frac{\alpha_D}{k_D^{(1)} + k_{MD}^{(1)}} [D^{**}] + \frac{k_{DM}^{(1)}c}{k_D^{(1)} + k_{MD}^{(1)}} [M^*] \quad (12)$$

By substitution into (3) one gets

$$[M^*] = \frac{\alpha_M(k_D^{(1)} + k_{MD}^{(1)})[M^{**}] + \alpha_D k_{MD}^{(1)}[D^{**}]}{(k_D^{(1)} + k_{MD}^{(1)})(k_M^{(1)} + k_{DM}^{(1)}c) - k_{MD}^{(1)}k_{DM}^{(1)}c} \quad (13)$$

and so from (12)

$$[D^*] = \frac{\alpha_M k_{DM}^{(1)} c [M^{**}] + \alpha_D (k_M^{(1)} + k_{DM}^{(1)} c) [D^{**}]}{(k_D^{(1)} + k_{MD}^{(1)}) (k_M^{(1)} + k_{DM}^{(1)} c) - k_{MD}^{(1)} k_{DM}^{(1)} c} \quad (14)$$

The intensity of the emission from the higher excited state of the monomer, $I_M^{(2)}$ is

$$I_M^{(2)} = k_{fM}^{(2)} [M^{**}] \quad (15)$$

From (10), after some rearrangements one gets

$$I_M^{(2)} = \frac{c_h^{(2)}}{c + c_h^{(2)}} q_M^{(2)} I_0 \quad (16)$$

where

$$q_M^{(2)} = \frac{k_{fM}^{(2)}}{k_M^{(2)} + \alpha_n} \quad (17)$$

represents the fluorescence quantum yield of the higher excited state of the monomer and

$$c_h^{(2)} = \frac{(\alpha_n + k_M^{(2)}) (\alpha_D + k_D^{(2)} + k_{MD}^{(2)})}{k_{DM}^{(2)} (\alpha_D + k_D^{(2)})} \quad (18)$$

corresponds to the half-value concentration usually defined for the monomer-excimer system (see below). On the other hand the intensity of the emission

from the higher excited state of the excimer, $I_D^{(2)}$, is

$$I_D^{(2)} = k_{fD}^{(2)} [D^{**}] \quad (19)$$

Using (11) it is possible to obtain

$$I_D^{(2)} = \frac{c}{c + c_h^{(2)}} q_D^{(2)} I_0 \quad (20)$$

where

$$q_D^{(2)} = \frac{k_{fD}^{(2)}}{k_D^{(2)} + \alpha_D} \quad (21)$$

is the quantum efficiency for the emission from the higher excited state of the excimer.

On the other hand, since the intensity of the emission from the first excited state of the monomer, $I_M^{(1)}$, is

$$I_M^{(1)} = k_{fM}^{(1)} [M^*] \quad (22)$$

we obtain, from (13)

$$I_M^{(1)} = \left\{ \alpha_M [M^{**}] + \alpha_D \frac{k_{MD}^{(1)}}{k_D^{(1)} + k_{MD}^{(1)}} [D^{**}] \right\} \times \frac{(k_{fM}^{(1)} (k_D^{(1)} + k_{MD}^{(1)}))}{(k_D^{(1)} + k_{MD}^{(1)}) (k_M^{(1)} + k_{DM}^{(1)} c) - k_{MD}^{(1)} k_{DM}^{(1)} c} \quad (23)$$

Similarly the intensity of the emission from the first excited state of the excimer, $I_D^{(1)}$ is

$$I_D^{(1)} = k_{fD}^{(1)} D^* \quad (24)$$

and, from (14)

$$I_D^{(1)} = \left\{ \alpha_M [M^{**}] + \alpha_D \frac{k_M^{(1)} + k_{DM}^{(1)} c}{k_{DM}^{(1)} c} [D^{**}] \right\} \times \frac{k_{fD}^{(1)} k_{DM}^{(1)} c}{(k_D^{(1)} + k_{MD}^{(1)}) (k_M^{(1)} + k_{DM}^{(1)} c) - k_{MD}^{(1)} k_{DM}^{(1)} c} \quad (25)$$

Now if the molecules are excited directly into the first excited singlet state S_1 by the use of light of

wavelength λ_1 the intensities of excited monomer and emission are given, respectively, by

$$I_M^{(1)}(\lambda_1) = \frac{k_{fM}^{(1)}(k_D^{(1)} + k_{MD}^{(1)})}{(k_D^{(1)} + k_{MD}^{(1)})(k_M^{(1)} + k_{DM}^{(1)}c) - k_{MD}^{(1)}k_{DM}^{(1)}c} I_0 \quad (26)$$

$$I_D^{(1)}(\lambda_1) = \frac{k_{fD}^{(1)}k_{DM}^{(1)}c}{(k_D^{(1)} + k_{MD}^{(1)})(k_M^{(1)} + k_{DM}^{(1)}c) - k_{MD}^{(1)}k_{DM}^{(1)}c} I_0 \quad (27)$$

It is well known that these expressions can be written as [44]

$$I_M^{(1)}(\lambda_1) = \frac{c_h^{(1)}}{c + c_h^{(1)}} q_M^{(1)} I_0 \quad (28)$$

$$I_D^{(1)}(\lambda_1) = \frac{c}{c + c_h^{(1)}} q_D^{(1)} I_0 \quad (29)$$

where

$$q_M^{(1)} = \frac{k_{fM}^{(1)}}{k_M^{(1)}} \quad (30)$$

and

$$q_D^{(1)} = \frac{k_{fD}^{(1)}}{k_D^{(1)}} \quad (31)$$

are the quantum efficiencies of excited monomer and excimer emissions, respectively, and

$$c_h^{(1)} = \frac{k_M^{(1)}(k_D^{(1)} + k_{MD}^{(1)})}{k_D^{(1)}k_{DM}^{(1)}} \quad (32)$$

is the half-value concentration.

On the other hand, from (15)

$$I_M^{(2)} = \frac{k_{fM}^{(2)}}{\alpha_M + k_M^{(2)}} (\alpha_M + k_M^{(2)}) [M^{**}] \quad (33)$$

and so, taking (17) into account

$$[M^{**}] = \frac{1}{\alpha_M + k_M^{(2)}} \frac{I_M^{(2)}}{q_M^{(2)}} \quad (34)$$

Similarly, from (19) and (2)

$$[D^{**}] = \frac{1}{\alpha_D + k_D^{(2)}} \frac{I_D^{(2)}}{q_D^{(2)}} \quad (35)$$

Noting that the last factors in (23) and (25) are those appearing in (26) and (27) whose final expressions are (28) and (29) and using (16) and (20) into (34) and (35) before substitution into (23) and (25) it is easy to see that (23) and (25) can be written as

$$I_M^{(1)}(\lambda_n) = \left\{ \frac{\alpha_M}{\alpha_M + k_M^{(2)}} \frac{c_h^{(2)}}{c + c_h^{(2)}} + \frac{\alpha_D}{\alpha_D + k_D^{(2)}} \frac{c}{c + c_h^{(2)}} \frac{k_{MD}^{(1)}}{k_D^{(1)} + k_{MD}^{(1)}} \right\} \times \frac{c_h^{(1)}}{c + c_h^{(1)}} q_M^{(1)} I_0 \quad (36)$$

$$I_D^{(1)}(\lambda_n) = \left\{ \frac{\alpha_M}{\alpha_M + k_M^{(2)}} \frac{c_h^{(2)}}{c + c_h^{(2)}} + \frac{\alpha_D}{\alpha_D + k_D^{(2)}} \frac{c}{c + c_h^{(2)}} \frac{k_M^{(1)} + k_{DM}^{(1)}c}{k_{DM}^{(1)}c} \right\} \times \frac{c}{c + c_h^{(1)}} q_D^{(1)} I_0 \quad (37)$$

where $I_M^{(1)}(\lambda_n)$ and $I_D^{(1)}(\lambda_n)$ were written instead of $I_M^{(1)}$ and $I_D^{(1)}$ to mean that excitation has been achieved with ultraviolet light of wavelength λ_n leading to a higher excited singlet state S_n .

If we define the coefficients of internal conversion

$$\beta_M = \frac{\alpha_M}{\alpha_M + k_M^{(2)}} \quad (38)$$

$$\beta_D = \frac{\alpha_D}{\alpha_D + k_D^{(2)}} \quad (39)$$

we obtain

$$I_M^{(1)}(\lambda_n) = \left\{ \beta_M \frac{c_h^{(2)}}{c + c_h^{(2)}} + \beta_D \frac{c}{c + c_h^{(2)}} \frac{k_{MD}^{(1)}}{k_D^{(1)} + k_{MD}^{(1)}} \right\} \times \frac{c_h^{(2)}}{c + c_h^{(2)}} q_M^{(1)} I_0 \quad (40)$$

$$I_D^{(1)}(\lambda_n) = \left\{ \beta_M \frac{c_h^{(2)}}{c + c_h^{(2)}} + \beta_D \frac{c}{c + c_h^{(2)}} \frac{k_M^{(1)} + k_{DM}^{(1)}c}{k_{DM}^{(1)}c} \right\} \times \frac{c}{c + c_h^{(1)}} q_D^{(1)} I_0 \quad (41)$$

Now for benzene and derivatives and naphthalene and derivatives and at room temperature it is known that the monomer-excimer equilibrium is much faster than the monomer and excimer deactivation, i.e., that (45, 46)

$$k_M^{(1)}, k_D^{(1)} \ll k_{MD}^{(1)}, k_{DM}^{(1)}c \quad (42)$$

Under these conditions

$$I_M^{(1)}(\lambda_n) = \frac{\beta_M c_h^{(2)} + \beta_D c}{c + c_h^{(2)}} \frac{c_h^{(1)}}{c + c_h^{(1)}} q_M^{(1)} I_0 \quad (43)$$

$$I_D^{(1)}(\lambda_n) = \frac{\beta_M c_h^{(2)} + \beta_D c}{c + c_h^{(2)}} \frac{c}{c + c_h^{(1)}} q_D^{(1)} I_0 \quad (44)$$

with

$$c_h^{(1)} = \frac{k_M^{(1)} k_{MD}^{(1)}}{k_D^{(1)} k_{DM}^{(1)}} \quad (45)$$

This value of $c_h^{(1)}$ is also the one to be used in

(28) and (29) under conditions (42). Then, from (28), (29), (43) and (44) it is seen that

$$\frac{I_D^{(1)}(\lambda_n)}{I_M^{(1)}(\lambda_n)} = \frac{I_D^{(1)}(\lambda_1)}{I_M^{(1)}(\lambda_1)} = \frac{q_D^{(1)}}{q_M^{(1)}} \frac{c}{c_h^{(1)}} \quad (46)$$

which shows that if conditions (42) are valid the ratio of excimer to monomer intensities is independent of the excitation wavelength even if higher excited states of the excimer intervenes in the energy deactivation when the molecules are excited into higher excited singlet states.

Two further observations must be added here. On one hand, when the molecules are excited into different excited states the intensities of the light used for excitation is usually dependent on wavelength. This means that the values I_0 appearing in (43) and (44) are equal but different from those appearing in (28) and (29). Hence (46) can be written as it is. On the other hand it must be stressed that the relationships so far deduced are valid even if there is no emission from the higher excited states M^{**} or D^{**} . If this is the case $k_{fM}^{(2)}$ and $k_{fD}^{(2)}$ (and hence $q_M^{(2)}$ and $q_D^{(2)}$) are zero and the equations must be modified accordingly.

5 — THE EFFECT OF CONCENTRATION ON THE INTERNAL CONVERSION EFFICIENCY

When measuring excitation spectra, if neither a monochromator nor filters are used to isolate part of the emission, light of all wavelengths emitted by the sample is usually detected by means of a photomultiplier, the intensity of the emission being normalized to that observed when the molecules are excited into S_1 . This means that, for excimer forming molecules, when radiation of wavelength λ_1 is used the measured intensity will be given by

$$G(\lambda_1) = K[I_M^{(1)}(\lambda_1)m_M^{(1)} + I_D^{(1)}(\lambda_1)m_D^{(1)}] \quad (47)$$

where $m_M^{(1)}$ and $m_D^{(1)}$ are the matching factors [47] for monomer and excimer emissions, respectively.

When radiation of wavelength λ_n (leading to the excitation into S_n) is used the intensity will be

$$G(\lambda_n) = K[I_M^{(1)}(\lambda_n)m_M^{(1)} + I_D^{(1)}(\lambda_n)m_D^{(1)}] \quad (48)$$

assuming that any emission from higher excited states is negligible.

In what follows it will be assumed that the intensities are corrected for the different values for the intensities of the radiation used for excitation. Now $G(\lambda_1)$ and $G(\lambda_n)$ can be written as

$$G(\lambda_1) = KI_M^{(1)}(\lambda_1)m_M^{(1)} \left[1 + \frac{m_D^{(1)}}{m_M^{(1)}} \frac{I_D^{(1)}(\lambda_1)}{I_M^{(1)}(\lambda_1)} \right] \quad (49)$$

$$G(\lambda_n) = KI_M^{(1)}(\lambda_n)m_M^{(1)} \left[1 + \frac{m_D^{(1)}}{m_M^{(1)}} \frac{I_D^{(1)}(\lambda_n)}{I_M^{(1)}(\lambda_n)} \right] \quad (50)$$

The internal conversion efficiency is defined as

$$\beta = \frac{G(\lambda_n)}{G(\lambda_1)} \quad (51)$$

It is then seen that if conditions (42) are valid

$$\beta = \frac{I_M^{(1)}(\lambda_n)}{I_M^{(1)}(\lambda_1)} \quad (52)$$

which shows that in this case the experimentally measured internal conversion efficiency is just the ratio of excited monomer intensities.

This analysis is an alternative to that presented in a previous publication [17] where (52) was based on the experimental fact that the shape of the emission spectrum was independent of the excitation wavelength.

If now we use (28) and (43) we may write

$$\beta = \frac{\beta_M c_{h(2)} + \beta_{DC}}{c + c_{h(2)}} \quad (53)$$

It is then seen that $1/\beta$ can be written as [17]

$$\frac{1}{\beta} = \frac{1}{A} \frac{1 + Bc}{1 + Cc} \quad (54)$$

where

$$A = \beta_M = \frac{\alpha_M}{\alpha_M + k_M^{(2)}} \quad (55)$$

$$B = \frac{1}{c_{h(2)}} = \frac{(\alpha_D + k_D^{(2)})k_{DM}^{(2)}}{(\alpha_M + k_M^{(2)})(\alpha_D + k_D^{(2)} + k_{MD}^{(2)})} \quad (56)$$

$$C = \frac{\beta_D}{\beta_M c_{h(2)}} = \frac{\alpha_D k_{DM}^{(2)}}{\alpha_M(\alpha_D + k_D^{(2)} + k_{MD}^{(2)})} \quad (57)$$

and

$$\frac{AC}{B} = \beta_D = \frac{\alpha_D}{\alpha_D + k_D^{(2)}} \quad (58)$$

Taking derivatives with respect to concentration

$$\frac{\partial}{\partial c} \left(\frac{1}{\beta} \right) = \frac{1}{A} \frac{B - C}{(1 + Cc)^2} \quad (59)$$

which is positive (i.e., β decreases when c increases) when $B > C$ and negative (i.e., β increases when c increases) when $B < C$. From (56) and (57)

$$\frac{B}{C} = \frac{\beta_M}{\beta_D} \quad (60)$$

This shows that if $\beta_M > \beta_D$ the value of β is to be expected to increase if c decreases, whereas if $\beta_M < \beta_D$ the value of β is to be expected to decrease with increasing c . It will be recalled that the former situation seems to be the general rule and the latter the case of benzene.

6 — CONCLUSIONS

It must be pointed out that an analysis of the results obtained for the β -effect in terms of an equation of the form (54) has already been presented in a previous publication [17]. It will not be repeated here. The foregoing arguments, however, give a deeper insight into the meaning of the different coefficients (55), (56) and (57) if in fact higher excited states of the excimer are involved in the process.

As a matter of fact, what is important is the presence of two ways for reaching the first excited singlet state S_1 , one depending on concentration and another concentration independent, and also two processes for S_n deexcitation, not leading to S_1 , one concentration independent and another depending on concentration. The relative values of the ratio corresponding to these processes will lead to different variations of the overall efficiency for the internal conversion with the concentration of the fluorescent molecules.

On the other hand, the fact that β seems to be different within a given excited electronic state is an indication that some of the processes involved must accordingly depend on the excitation wavelength.

A rather more general model can be proposed, introducing an unspecified «dissociative state» which could be reached from S_n by two processes, one concentration dependent and another concentration independent. Such a model has indeed been proposed previously [15] and shown to be able to explain qualitatively the main features of the β -effect in what regards the concentration dependence.

This becomes evident from the previous arguments since not only the «dissociative state» could be obtained by the two processes referred above but also $S_n \rightarrow S_1$ transition could proceed directly or involving another molecule, which would amount to an extension of an early suggestion of FRANCK and SPONER [48] regarding energy transfer from higher excited states. It must be noted here that the existence of an excited state (or a set of states) in benzene which does not internally convert to the first excited singlet state has already been proposed [30, 49].

If from the «dissociative state» it is possible to obtain again the higher excited state of the monomer and, furthermore, it is possible to reach the ex-

cimer state directly, the model is equivalent to the model of higher excited states of the excimer discussed before. In this case it is only under conditions (42), which are known to be valid for benzene and naphthalene derivatives, that the experimentally found fact of the shape of the emission spectrum being independent of the wavelength of the excitation radiation can be understood. This is indeed to be expected since conditions (42) correspond to the situation where monomer and excimer deactivation processes are slow compared with the processes of excimer formation and dissociation into an excited monomer and a ground state molecule. Now if higher excited states of the excimer are used to explain the β -effect equations (59) and (60) show that it is the relative values of the internal conversion efficiencies «via the monomer» or «via the excimer» that justifies the different dependence of β on the concentration.

Whatever is the model which is used, it is important to know how to extract the actual values of the internal conversion efficiencies from the experimental results. As discussed before different views have been presented on the subject. In this connection it will be necessary to know what are the photodecomposition processes involved, how they affect the fluorescence quantum yield, and also to what extent they depend on concentration.

Recent work has shown that a β -effect can be detected in other molecules, namely phenol [50] and amino acids [51] for concentrations much lower than those needed to observe the effect in benzene and naphthalene derivatives and this may be relevant for the discussion.

It is also important to understand the effect of solvent not only for benzene but for all the other compounds where a β -effect is detected.

Work is in progress at this Laboratory on these lines [52] and it will be reported soon.

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Table

Reaction	Rate (sec ⁻¹)	Process
$M \rightarrow M^{**}$	1	excitation of higher excited state of the monomer
$M^{**} \rightarrow M^*$	α_n	internal conversion from the higher excited state of the monomer to its first excited state
$M^{**} + M \rightarrow D^{**}$	$k_{DM}^{(2)c}$	formation of the higher excited state of the excimer from the higher excited state of the monomer
$M^{**} \rightarrow M + h\nu_M^{(2)}$	$k_{fM}^{(2)}$	fluorescence from the higher excited state of the monomer
$M^{**} \rightarrow M$	$k_{iM}^{(2)}$	internal conversion from the higher excited state of the monomer to the ground state
$D^{**} \rightarrow M^{**} + M$	$k_{MD}^{(2)}$	dissociation of the higher excited state of the excimer
$D^{**} \rightarrow M + M + h\nu_D^{(2)}$	$k_{fD}^{(2)}$	fluorescence from the higher excited state of the excimer
$D^{**} \rightarrow M + M$	$k_{iD}^{(2)}$	«internal conversion» from the higher excited state of the excimer to the ground state
$D^{**} \rightarrow D^*$	α_D	internal conversion from the higher excited state of the excimer to its first excited state
$M^* + M \rightarrow D^*$	$k_{DM}^{(1)c}$	formation of the first excited state of the excimer from the first excited state of the monomer
$M^* \rightarrow M + h\nu_M^{(1)}$	$k_{fM}^{(1)}$	fluorescence from the first excited state of the monomer
$M^* \rightarrow M$	$k_{iM}^{(1)}$	internal conversion from the first excited state of the monomer to the ground state
$D^{**} \rightarrow M^* + M$	$k_{MD}^{(1)}$	dissociation of the first excited state of the excimer
$D^* \rightarrow M + M + h\nu_D^{(1)}$	$k_{fD}^{(1)}$	fluorescence from the first excited state of the excimer
$D^* \rightarrow M + M$	$k_{iD}^{(1)}$	«internal conversion» from the first excited state of the excimer to the ground state

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RESUMO

Comparam-se e discutem-se resultados publicados para sistemas orgânicos fluorescentes em que a eficiência quântica de fluorescência depende do comprimento de onda da radiação usada para excitação. Apresenta-se um modelo que envolve estados excitados elevados de excímeros. Mostra-se que em determinadas condições esse modelo prevê que a forma de emissão não depende do comprimento de onda da radiação de excitação. Apresenta-se ainda um modelo mais geral envolvendo um «estado dissociativo» e discute-se a sua relação com o modelo que envolve a presença de excímeros.