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The Lifetime of Excimer Fluorescence of Naphthalene

By Tohru AZUMI* and Hiroshi AZUMI

Department of Chemistry, Faculty of Science, Tohoku University, Katahira-cho, Sendai

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The radiative lifetimes of the excimer fluorescence of naphthalene are calculated for excimers of various geometrical configurations. The results vary, to a great extent, with the configurations, but with a previously-suggested configuration the calculated lifetime is 6×10^{-6} sec. This is within a factor of 5 of the experimental results.

The lifetime of the excimer fluorescence has been a subject of dispute for a long time. Williams,¹⁾ in an attempt to interpret the delayed fluorescence he observed from the vapor of several aromatic compounds, assumed the production of an excimer, which, after several milliseconds, dissociates into a monomer ground-state molecule and a monomer excited-state molecule. This idea was also incorporated by Stevens, Hutton, and Porter²⁾ in their interpretation of the delayed fluorescence of phenanthrene species observed from anthracene vapor. These interpretations received some support from the theoretical considerations of Hoijtink,³⁾ who showed that if the excimer has center of symmetry, excimer luminescence is forbidden and that, hence, apart from radiationless conversion to the ground state, the only way of losing its excess energy is the dissociation to monomers. However, this simple treatment does not satisfactorily explain the fact that excimer fluorescence is indeed observed for a number of molecules. Questions have, therefore, arisen as to whether the excimer fluorescence is a dipole-allowed transition or an environmentally-allowed forbidden transition. Azumi and McGlynn⁴⁾ observed delayed excimer fluorescence in rigid glass media, and, in view of their experimental evidence, interpreted this duration as being due to the inherent forbidden character of excimer luminescence. Later work by Smith and McGlynn,⁵⁾ however, revealed that the delayed excimer luminescence is due to an excimer produced by triplet-triplet annihilation; namely, the duration of the excimer luminescence is ascribed to the delay in the production of excimer species, and not to the delay in the luminescence itself. In addition to these studies, recent studies of delayed fluorescence have thrown some doubt on the earlier interpretations given by Williams¹⁾ and by Stevens et al.²⁾ As Azumi and McGlynn⁶⁾ suggested, the vapor-delayed fluorescence reported by these researchers might also be interpreted in terms of triplet-triplet annihilation, in which case there is no necessity of assuming any excimer formation. In this way it became questionable whether an excimer of a long duration really exists or not. Things have, however, become clearer since excellent lifetime measurements of excimer fluorescence were reported by Birks, Dyson, and King.⁷⁾ The resluts show that the lifetime of excimer fluorescence is quite short—in fact, shorter than the lifetime of normal monomer fluorescence.

In a previous paper⁸⁾ the present authors calculated the energy of the excimer luminescence of naphthalene with a variety of geometrical configurations. Starting from the excimer of such a configuration that one of the molecules which constitute an excimer is exactly superposed, at some distance, over the other, the authors examined the effect of the rotation of one molecule with respect to the other on the energy of the excimer luminescence. The principal axes of the two molecules were kept common, and the intermolecular distance was chosen as 3 Å. The excimer configuration for which the calculations were carried out is schematically represented in Fig. 1. It was shown that excimer is stable when the angle, α, of rotation is 75 degrees; this configuration was proposed as the one responsible for excimer fluorescence.

In this paper, the radiative lifetime of naphthalene excimer fluorescence will be calculated for excimers of the same geometrical configurations as in the previous paper⁸⁾ (i. e., those represented in Fig. 1). It will also aim to check if the previously-developed

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1) R. Williams, *J. Chem. Phys.*, **28**, 577 (1958).

2) B. Stevens, E. Hutton and G. Porter, *Nature*, **185**, 917 (1960).

3) G. J. Hoijtink, *Z. Elektrochem.*, **64**, 156 (1960).

4) T. Azumi and S. P. McGlynn, *J. Chem. Phys.*, **39**, 3533 (1963).

5) F. J. Smith and S. P. McGlynn, ibid., **42**, 4308 (1965).

6) T. Azumi and S. P. McGlynn, ibid., **39**, 1186 (1963).

7) J. B. Birks, D. J. Dyson and T. A. King, *Proc. Roy. Soc.*, **A277**, 270 (1964).

8) T. Azumi and H. Azumi, This Bulletin, **39**, 1829 (1966).

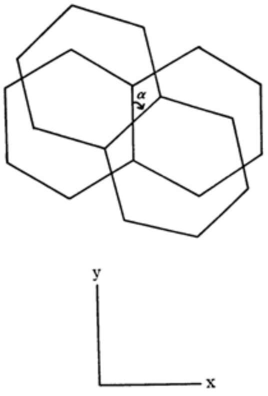

Fig. 1

model of an excimer, which gives satisfactory energy data, also gives reasonable lifetime data.

The Method of Calculation

The general scheme of calculation is identical to that developed in previous papers.[8,9] The highest-occupied and the lowest-vacant molecular orbitals of one ground state molecule (say, molecule A) are designated, respectively, as ϕ_1 and ϕ_2, and the corresponding orbitals of the other molecule (say, molecule B), as θ_1 and θ_2. ϕ_1 and ϕ_2 are orthogonal, as are also θ_1 and θ_2. It is assumed that an orthogonality exists between ϕ_1 and θ_2 and between θ_1 and ϕ_2. The overlap integral between ϕ_1 and θ_1 is designated by S_1.

Wave Functions.—The dimeric wave function for the ground state is:

$$|G\rangle = (1 - 2S_1^2 + S_1^4)^{-1/2}|\phi_1\overline{\phi}_1\theta_1\overline{\theta}_1| \tag{1}$$

The wave function for the excimer state is expressed as a linear combination of four zeroth-order wave functions:

$$|E\rangle = a\psi_A + b\psi_B + c\psi_C + d\psi_D \tag{2}$$

where:

$$\psi_A=\{2(1-S_1^2)\}^{-1/2}\{|\phi_1\overline{\phi}_1\theta_1\overline{\theta}_2|+|\phi_1\overline{\phi}_1\theta_2\overline{\theta}_1|\} \tag{3}$$

$$\psi_B=\{2(1-S_1^2)\}^{-1/2}\{|\phi_1\overline{\phi}_2\theta_1\overline{\theta}_1|+|\phi_2\overline{\phi}_1\theta_1\overline{\theta}_1|\} \tag{4}$$

$$\psi_C=\{2(1-S_1^2)\}^{-1/2}\{|\phi_1\overline{\theta}_2\theta_1\overline{\theta}_1|+|\theta_2\overline{\phi}_1\theta_1\overline{\theta}_1|\} \tag{5}$$

$$\psi_D=\{2(1-S_1^2)\}^{-1/2}\{|\phi_1\overline{\phi}_1\phi_2\overline{\theta}_1|+|\phi_1\overline{\phi}_1\theta_1\overline{\phi}_2|\} \tag{6}$$

The mixing coefficients, *a*, *b*, *c*, and *d*, at different α values were evaluated in a previous paper[8]; they are tabulated in Table I of Ref. 8.

Transition Moment.—The transition moment length for the excimer luminescence is expressed as:

$$\begin{aligned}\mu_E &= \langle G|\boldsymbol{R}|E\rangle \\ &= \{2(1 - S_1^2)/(1 - 2S_1^2 + S_1^4)\}^{1/2} \\ &\quad\times [\langle\phi_1|\boldsymbol{R}|\phi_2\rangle\{(a + b) - S_1(c + d)\} \\ &\quad+ \langle\phi_1|\boldsymbol{R}|\theta_2\rangle\{(c + d) - S_1(a + b)\}]\end{aligned} \tag{7}$$

μ_E is calibrated by taking the experimental transition moment length for the monomer ^{1}A-^{1}L$_a$ transition, μ_M, as a standard, so that the correct transition moment be obtained at an infinite separation of the two molecules. A theoretical evaluation of μ_M yields:

$$\mu_M = \sqrt{2}\,\langle\phi_1|\boldsymbol{R}|\phi_2\rangle \tag{8}$$

μ_E is then calculated by the equation:

$$\begin{aligned}\mu_E = \mu_M{}^{\exp}&\{(1-S_1^2)/(1-2S_1^2+S_1^4)\}^{1/2} \\ &\times[(a+b)-S_1(c+d)+\{(c+d)- \\ &S_1(a+b)\}\langle\phi_1|\boldsymbol{R}|\theta_2\rangle/\langle\phi_1|\boldsymbol{R}|\phi_2\rangle]\end{aligned} \tag{9}$$

where $\mu_M{}^{\exp}$ is the experimental transition moment length for the monomer ^{1}A-^{1}L$_a$ absorption and has the value:

$$\mu_M{}^{\exp} = 0.6923\,\text{Å} \tag{10}$$

The lifetime of the excimer luminescence is then evaluated by the equation:

$$\tau_E = \frac{3h}{64\pi^4\tilde{\nu}^3 e^2\mu_E^2} \tag{11}$$

MO Integrals in Terms of AO Integrals.—The MO overlap integral, S_1, is evaluated by:

$$S_1 = \sum_r\sum_s C_{r1}C_{s1}\langle r_A \mid s_B\rangle \tag{12}$$

where C_{r1} is the Hückel coefficient of the atomic orbital, *r*, in ϕ_1, $\langle r_A|s_B\rangle$ is the overlap integral between the atomic orbital, *r*, in the A molecule and the atomic orbital, *s*, in the B molecule, it is evaluated by the formulas given by Parr and Crawford.[10]

The intermolecular transition moment length $\langle\phi_1|\boldsymbol{R}|\theta_2\rangle$ is expressed as:

$$\langle\phi_1|\boldsymbol{R}|\theta_2\rangle = [\langle\phi_1|\boldsymbol{x}|\theta_2\rangle^2+\langle\phi_1|\boldsymbol{y}|\theta_2\rangle^2]^{1/2} \tag{13}$$

where x and y axes are along the long and short axes of one molecule, as are shown in Fig. 1. The z axes component need not be considered, since the group theoretical treatment[11] shows that the excimer fluorescence is invariably polarized in-plane when the principal axes of the two molecules which constitute an excimer are common. The *x* component is further expressed in the following way:

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[9] T. Azumi, A. T. Armstrong and S. P. McGlynn, *J. Chem. Phys.*, **41**, 3839 (1964).

[10] R. G. Parr and B. L. Crawford, ibid., **16**, 1049 (1948).

[11] T. Azumi and S. P. McGlynn, ibid., **42**, 1675 (1965).

$$\begin{aligned}\langle\phi_1|\boldsymbol{x}|\theta_2\rangle &= \sum_r\sum_s C_{r1}C_{s2}\langle r_\mathrm{A}|\boldsymbol{x}|s_\mathrm{B}\rangle \\ &= (1/2)\sum_r\sum_s C_{r1}C_{s2}\langle r_\mathrm{A}|s_\mathrm{B}\rangle \\ &\quad \times\{x(r_\mathrm{A})+x(s_\mathrm{B})\} \qquad (14)\end{aligned}$$

where C_{s2} is the Hückel coefficient of atomic orbitals in ϕ_2 (or θ_2), and where $x(r_\mathrm{A})$ and $x(s_\mathrm{B})$ are the x coordinates of r_A and s_B respectively. Here, the center of the naphthalene molecule is taken as the origin of the coordinate, and axes are chosen along the molecular axes of the A molecule (Fig. 1). Then,

$$x(s_\mathrm{B}) = \cos\alpha\, x(s_\mathrm{A}) + \sin\alpha\, y(s_\mathrm{A}) \qquad (15)$$

Consequently,

$$\begin{aligned}\langle\phi_1|\boldsymbol{x}|\theta_2\rangle &= (1/2)\sum_r\sum_s C_{r1}C_{s2}\langle r_\mathrm{A}|s_\mathrm{B}\rangle \\ &\quad \times\{x(r_\mathrm{A})+\cos\alpha x(s_\mathrm{A})+\sin\alpha y(s_\mathrm{A})\} \qquad (16)\end{aligned}$$

The y component is obtained similarly:

$$\begin{aligned}\langle\phi_1|\boldsymbol{y}|\theta_2\rangle &= (1/2)\sum_r\sum_s C_{r1}C_{s2}\langle r_\mathrm{A}|s_\mathrm{B}\rangle \\ &\quad \times\{y(r_\mathrm{A})-\sin\alpha x(s_\mathrm{A})+\cos\alpha y(s_\mathrm{A})\} \qquad (17)\end{aligned}$$

The intramolecular transition moment, $\langle\phi_1|\boldsymbol{R}|\phi_2\rangle$, in Eq. 9 is similarly obtained; the result is:

$$\langle\phi_1|\boldsymbol{R}|\phi_2\rangle = 0.8137\,\text{Å} \qquad (18)$$

Results and Discussion

The calculated lifetimes at different configurations are shown in Table I. The only results of any physical significance are those around the stable configurations, $\alpha=75°$ and $\alpha=0°$. The excimer is most unstable around $30°<\alpha<50°$ (see Fig. 4 of the previous paper[8]); the calculated values in Table I for such unstable configurations are those of virtual states and are thus, in fact, meaningless. The fact that quite unreasonable data are obtained around $30°<\alpha<50°$ configurations of the excimer is consistent with the potential energy diagram obtained in the previous paper. At the previously suggested stable configuration, $\alpha=75°$, the calculated lifetime is 6.3×10^{-6} sec.

The lifetimes of the naphthalene excimer fluorescence recently observed by Mataga, Tomura, and Nishimura[12] are $\sim10^{-7}$ sec, but the contribution of the radiative decay is unknown and a direct comparison with the calculated result is impossible. There are, unfortunately, no other experimental data on the lifetime of the naphthalene excimer. However, lifetime data for 1, 6-dimethylnaphthalene were obtained by Birks and King.[13]

TABLE I. LIFETIMES OF EXCIMER FLUORESCENCE AT VARIETY OF GEOMETRICAL CONFIGURATIONS

α	μ_E, Å	Lifetime, sec.
0	0	—
5	-2.69×10^{-2}	2.84×10^{-5}
10	-2.54×10^{-2}	3.18×10^{-5}
15	-2.29×10^{-2}	3.92×10^{-5}
20	-1.89×10^{-2}	5.75×10^{-5}
25	-1.31×10^{-2}	1.20×10^{-4}
30	-5.57×10^{-3}	6.61×10^{-4}
35	-1.57×10^{-5}	8.30×10
40	-8.63×10^{-3}	2.76×10^{-4}
45	-1.53×10^{-3}	8.77×10^{-3}
50	-5.88×10^{-3}	5.94×10^{-4}
55	2.83×10^{-3}	2.57×10^{-3}
60	1.58×10^{-2}	8.25×10^{-5}
65	2.97×10^{-2}	2.33×10^{-5}
70	4.35×10^{-2}	1.08×10^{-5}
75	5.71×10^{-2}	6.30×10^{-6}
80	7.17×10^{-2}	4.00×10^{-6}
85	9.49×10^{-2}	2.28×10^{-6}
90	5.91×10^{-1}	5.89×10^{-8}

Since the excimer fluorescence of dimethyl derivatives of naphthalene behaves quite like that of naphthalene,[14] it is reasonable to assume that the lifetime also does not differ much. Radiative rate parameters for the excimer fluorescence of 1, 6-dimethylnaphthalene[13] is 1.4×10^6 sec^{-1} in an n-heptane solution and 2.2×10^6 sec^{-1} in pure liquid. When calibration is made to a medium whose reflactive index is unity, the rate parameters are 0.73×10^6 sec^{-1} for the former, and 0.85×10^6 sec^{-1} for the latter. These data correspond to radiative excimer lifetimes in vacuo of $1.2-1.4\times10^{-6}$ sec. Hence, the lifetime calculated in this paper, 6.3×10^{-6} sec., is within a factor of 5 of the experimental value. The fairly good agreement with the experimental value is another support of the excimer configuration suggested in a previous paper.[8]

The above consideration is confined to the lifetime at one of the two stable configurations, i. e., $\alpha=75°$. We have disregarded the lifetime at the other stable configuration, i. e., at $\alpha=0°$, since excimer luminescence is forbidden there. It might be argued that the allowed component may arise by the thermal motion of the two molecules of the excimer. In order to check this, let the thermal motion be confined to the thermal vibration needed to change the angle, α. It may then be seen, from the energy data given in the previous paper, that the α which can be changed by the energy of the thermal motion, $1.5\boldsymbol{k}T=$ 0.04eV., is approximately 5°. Even though there is a considerable increase in the transition probability for this change of α, the calculated lifetime

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12) N. Mataga, M. Tomura and H. Nishimura, *Mol. Phys.*, **9**, 367 (1965).

13) J. B. Birks and T. A. King, *Proc. Roy. Soc.*, **A291**, 244 (1966).

14) J. B. Aladekomo and J. B. Birks, ibid., **A284**, 551 (1965).

at $\alpha=5°$ of 3×10^{-5} sec., which is 20 times larger than the experimental value, still can not account for the observed lifetime of the excimer fluorescence.

The present calculations were carried out for excimers in which the two molecular planes are parallel and which have principal axes in common. This is, in fact, rather a freakish situation. To treat the excimers of random orientations, however, is quite difficult, if not impossible, and, at any rate, beyond the range of the present paper. The present treatment may, therefore, only be considered as a prototype calculation. Our suggestion that the excimer of $\alpha=75°$ is responsible for the excimer fluorescence is valid only within the framework of the above specified model. The only conclusion of any general validity may be that the geometrical configuration of the excimer which is responsible for excimer fluorescence is definitely different from the one of the highest symmetry.

The numerical calculations were carried out on the NEAC 2230 at the Computation Center, Tohoku University.

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