BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 1687—1695(1972)

Fluorescence Emission in the Gas Phase of Several Aromatic Hydrocarbons

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(Received December 13, 1971)

The fluorescence and excitation spectra of several condensed aromatic hydrocarbons were measured in the gas phase at low pressures. The emission from the second excited singlet state (S_2 emission) could be observed with some of the compounds studied, in which the first weak absorption band is located close to the second much stronger band. The relative yield of the S_2 emission always increased with the increase in the excitation wavenumber. It has been shown that the occurrence of the S_2 emission can be explained in a qualitative way by the state densities and the radiative rates. In coronene, an emission to be regarded as originating from the third excited singlet state was observed.

It is well known that radiationless transitions from higher excited singlet states to the first excited singlet state in most complex molecules occur with such a high efficiency that usually fluorescence arises solely from the lowest excited singlet state.[1-8] Recent theoretical studies[9-12] have indicated that, in large molecules, internal conversion can take place even in the isolated state. Although the emission from the second excited singlet state (S_2 emission) of a large molecule[8] has been considered to be extremely weak on account of the very fast internal conversion,[4-7] it may be detected in principle by means of a highly sensitive spectroscopic device and by the use of a favorable compound satisfying certain conditions.

The fluorescence originating from the second excited singlet state of pyrene in the gas phase at low pressures

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[7] J. B. Birks, "Photophysics of Aromatic Molecules," Wiley-Interscience, London (1970).

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[9] M. Bixon and J. Jortner, *J. Chem. Phys.*, **48**, 715 (1968).

[10] J. Jortner, S. A. Rice, and R. M. Hochstrasser, "Advances in Photochemistry," Vol. 7, 149 (1969).

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was found independently by Geldof *et al.*[13] and by the present author *et al.*[14] With the aid of a very sensitive emission spectrometer,[15] Geldof *et al.* observed anomalous emission bands in the short-wavelength region of the fluorescence spectrum of a rarified pyrene gas excited in the second absorption band; these bands are to be ascribed to the S_2 emission.[13] They also studied the effect of the inert gas and the temperature on the relative yield of this emission and estimated the rate constants for the internal conversion and the reverse process.[13] On the other hand, the present author *et al.* measured the fluorescence and excitation spectra of pyrene gas, paying special attention to the S_2 emission, and showed a very remarkable increase in its relative quantum efficiency with excitation into successively higher excited singlet states.[14]

It seems to be established that the 'anomalous' emission can be regarded as quite intrinsic and not due to impurities, because no impurity band was detected in the fluorescence and excitation spectra in the solutions of the highly purified sample employed, because its excitation spectrum corresponds well in wavenumber to the absorption spectrum of pyrene gas,[14,16] because its relative intensity is reduced by the vibrational relaxation on the addition of an inert (non-electronically-quenching) gas such as nitrogen[17] and cyclohexane,[16] and further, because such emissions have also been observed with deuteropyrene[17] and methylpyrenes.[18]

Moreover, it has been reported that fluorescence from the second excited singlet state can be observed with 3,4-benzpyrene[13,19] both in the gas phase and in solution, 1,2-benzanthracene[19] in solution, and 1,12-benzperylene[20] in plastics.

In particular, in all of these 'abnormal' molecules, as we can recognize, the very weak first absorption band is situated in the immediate vicinity of the much stronger second band. In this respect, the weakness of the first band should be regarded as more significant than would be desirable for reducing self-absorption.[13,19]

In view of these facts, the following empirical criteria for the occurrence of the S_2 emission may be proposed:

(1) The rate of emission from the second excited singlet is sufficiently large compared to that from the first excited singlet.

(2) The energy separation between the first and second excited singlets is relatively small.

The purpose of this work is to test these criteria on a number of condensed aromatic hydrocarbons by making attempts to detect S_2 emission in the short-wavelength tail of their 'normal' fluorescence spectra. In addition, the influence of the internal conversion rates on the behavior of the S_2 emission has been considered in connection with the vibrational level densities for the relevant states.

Experimental

Naphthalene and phenanthrene were recrystallized from ethanol and zone-refined. 1-Methoxynaphthalene was distilled under reduced pressure. 1-Naphthol was recrystallized from ethanol. Biphenyl was recrystallized from ethanol, zone-refined, and sublimed *in vacuo*. Anthracene was recrystallized from xylene, zone-refined, and sublimed *in vacuo*. Chrysene was recrystallized from benzene and zone-refined. Perylene was chromatographed and sublimed *in vacuo*. Triphenylene, tetracene, 1,2-benzanthracene, 20-methylcholanthrene, 1,12-benzperylene, and coronene were sublimed *in vacuo*. Spectroscopic-grade benzene was used as a solvent without further purification. The purities of the samples were carefully checked by observing the excitation spectra. If, unfortunately, an impurity band was found in the excitation spectrum, the emission spectra were not measured with excitation in the neighborhood of that band.

The fluorescence and excitation spectra were measured with a Hitachi MPF-2A spectrofluorometer, to which an electric furnace was attached in the cell compartment. The square, non-fluorescent quartz cell containing a small amount of the sample was evacuated and sealed off. The furnace in which the gas cell was placed was constructed of brass blocks and was covered with asbestine slates as insulators. It consists of a lower part with two quartz windows and an upper, windowless part; the temperatures of the two parts were separately controlled. The vapor pressure of the compound was assessed utilizing the published data,[21,22] with the temperature of the upper part always set at a somewhat lower temperature. The vapor pressures at which the experiments were carried out were 0.01—1 Torr, except for 1-methoxynaphthalene and biphenyl, whose pressures were raised to 5 Torr.

The fluorescence spectra were corrected for the spectral sensitivity of the instrument by the use of the standard fluorescence spectra of quinine sulfate, 2-naphthol, and phenol.[23-25] The excitation spectra were also corrected using rhodamine B as the standard substance.[25,26]

Results and Discussion

Since the experiments were made at such low vapor pressures that the lifetime of the excited molecule was considerably shorter than the time interval between molecular collisions, during the processes of internal conversion the excitation energy was conserved, with part of it reserved as excess vibrational energy. It may be assumed that the internal conversion to the second excited singlet state from a higher excited singlet state, in which the molecule is initially prepared by

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[13] P. A. Geldof, R. P. H. Rettschnick, and G. H. Hoytink, *Chem. Phys. Lett.*, **4**, 59 (1969).

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[25] C. A. Parker, "Photoluminescence of Solutions," Elsevier, Amsterdam (1968).

[26] W. H. Melhuish, *J. Opt. Soc. Amer.*, **52**, 1256 (1962).

photon absorption, occurs very rapidly and irreversively. The resultant molecule in the high vibronic levels of the second excited singlet state (S_2) either emits the S_2 emission or is isoenergetically converted into the high vibronic levels of the first excited singlet state (S_1), from which it may in turn emit the 'normal' S_1 emission or pass nonradiatively into the highly-excited vibrational levels of the triplet or ground state (S_0). If the radiative lifetime in the high vibronic levels of S_1 is relatively long, then the returning process from S_1 to S_2 can take place.[13] Thus, the yield of the S_2 emission can be considered to be composed of a direct, short-lived component occurring before internal conversion and an indirect, long-lived component derived from the reverse process.[13,16]

By a simple consideration of the kinetics based on this scheme,[16] the ratio of the quantum yield of the S_2 emission, Φ_2, to that of the S_1 emission, Φ_1, is obtained as follows:

$$\Phi_2/\Phi_1 = k_2(k_{1f}+k_{1q}+k_{rp})/k_{1f}k_{1c}, \qquad (1)$$

where k_{1f} and k_2 are the rate constants for the emissions from S_1 and S_2 respectively, where k_{ic} and k_{rp} are those for the internal conversion and the reverse process respectively, and where k_{1q} is the overall rate constant for the nonradiative (quenching) processes from S_1.

The radiative rate constants, k_i, were estimated from the S_0—S_i absorption spectra in solution, using the following well-known equation:[3,4,6,7]

$$k = 2.88 \times 10^{-9} n^2 \bar{\nu}_m{}^2 \int \varepsilon d\bar{\nu}, \qquad (2)$$

or by the aid of a simpler expression:[27]

$$k \sim 8.6 \times 10^{-6} n^2 \bar{\nu}_m{}^2 \varepsilon_{max}, \qquad (3)$$

where ε is the molar extinction coefficient, and n, the refractive index of the solvent.

The rate constant of internal conversion, k_{ic}, can be formulated as:[7,9-12,28]

$$k_{1c} = (2\pi/\hbar)v^2\rho_1, \qquad (4)$$

where v is the coupling matrix element between the zero-order Born-Oppenheimer states for the perturbation inducing internal conversion and where ρ_1 is the density of the final vibronic states (in S_1) at resonance with the initial state (in S_2). For the reverse process, the rate constant, k_{rp}, is expressed in a similar form:[16]

$$k_{rp} = (2\pi/\hbar)v^2\rho_2, \qquad (5)$$

where ρ_2 is the density of states in S_2.

Using these expressions, Eq. (1) can be reduced to:

$$\Phi_2/\Phi_1 = (k_2/k_1)(\rho_2/\rho_1) + k_2/k_{1c}\phi_1, \qquad (6)$$

where ϕ_1 is the quantum yield of S_1 fluorescence caused by excitation in the first excited singlet or within high-pressure limits. It is assumed here that ϕ_1 can be approximated by the quantum yield in solution.

Internal conversion in a large molecule has been thought to occur in 10^{-11}—10^{-13} sec.[1,4-7] Recently, the rate constant, k_{ic}, was estimated for pyrene in the gas phase as $\sim 10^{12}$ sec^{-1} by Geldof *et al.*[13] and as 5.8×10^{11} sec^{-1} by us.[16,29] In the present study, no attempt was made to determine the value of k_{ic}, *e.g.*, by performing the inert-gas experiments[13,16] when S_2 emission could be observed. Instead, for all the molecules under consideration k_{ic} was assumed to take a value similar to that estimated for pyrene, *i.e.*, 10^{12} sec^{-1}.[1,4,7,12] Because of this large k_{ic} value, the contribution of the second term in Eq. (6) may be comparatively small for most 'abnormal' molecules.

The density of vibrational states, ρ, was computed by the use of Haarhoff's formula.[30] As we have no definite knowledge at the present stage about the effectiveness of the vibrational modes in giving rise to radiationless transitions, the contributions of all the modes are taken into account equally. Since the vibrational assignments are not available for most of the compounds studied, a scaling method has been adopted;[31,32] that is, for an aromatic hydrocarbon, C_mH_n, there are n degenerate CH stretching modes assigned at 3050 cm^{-1}, n in-plane CH bending modes at 1100 cm^{-1}, n out-of-plane CH bending modes at 900 cm^{-1}, $m-1$ ring stretching modes at 1500 cm^{-1}, $m-2$ in-plane ring deformation modes at 700 cm^{-1}, and $m-3$ out-of-plane ring deformation modes at 500 cm^{-1}. The values of ρ calculated by this method were compared with those obtained by direct calculation using the observed frequencies; the differences were only 15% for benzene,[33] less than 6 times for naphthalene,[34] and up to 100 times for anthracene[35] and pyrene.[36] Although the difference in ρ increases rapidly with the number of atoms, yet the difference in the ratio between ρ's is satisfactorily smaller, *e.g.*, within a factor of only two for anthracene. It should be kept in mind, however, that the value computed by Haarhoff's approximation becomes inaccurate at smaller energies.[30]

Below, the results of observations of the fluorescence and excitation spectra in the gas phase will be illustrated and the possibility of the appearance of S_2 emission will be investigated by means of the rate constants evaluated in the manner described above.

Naphthalene, 1-Naphthol, and 1-Methoxynaphthalene. Since the lowest excited singlet state (^1L_b), which gives rise to a weak absorption band, is located close to the

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[27] The half-width of an absorption band was taken as 6.0 kK, and the mean wavenumber, $\bar{\nu}_m$, and the maximum extinction coefficient, ε_{max}, were used.

[28] G. W. Robinson and R. P. Frosch, *J. Chem. Phys.*, **37**, 1962 (1962); D. M. Burland and G. W. Robinson, *ibid.*, **51**, 4548(1969).

[29] In this connection, it is of interest to note that k_{ic} seems to vary only slightly with the excess vibrational energy; despite the large difference between the excitation energies (10.5 kK), the value of k_{ic} obtained by Geldof *et al.* is not very different from ours. Since the term for electronic interaction, β, may be assumed to be constant, and since $v^2 = \beta^2\bar{F}$,[7,9,28] the product of the averaged Franck-Condon factor, $\bar{F}$, and the density of states, ρ, can be considered as a relatively slowly-decreasing function of the excitation energy.

[30] P. C. Haarhoff, *Mol. Phys.*, **6**, 337 (1963); **7**, 101 (1963).

[31] R. J. Watts and S. J. Strickler, *J. Chem. Phys.*, **44**, 2423 (1966).

[32] J. L. Richards and S. A. Rice, *Chem. Phys. Lett.*, **9**, 444 (1971).

[33] N. Herzfeld, C. K. Ingold, and H. G. Poole, *J. Chem. Soc.*, **1946**, 316.

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second excited singlet state (^1L_a), which gives rise to a relatively strong band, naphthalene may be considered to meet the aforesaid criteria. The gas-phase fluorescence of naphthalene has thus far been studied by a number of workers,[31,37–39] some of whom attempted, but failed, to detect fluorescence from the second excited singlet state with ordinary exciting light sources.[31,38] The present author also examined the short-wavelength region of the fluorescence spectra, while varying the excitation wavelength, but no emission from an excited singlet state other than the first could be observed. The observed fluorescence and excitation spectra of naphthalene vapor, being similar to those already reported,[31,37,38] will not be presented here.

It can be expected that, by the substitution of an electron-donating group (-OH, -OCH$_3$) into the naphthalene ring, the ^1L_a state will come close in energy to the ^1L_b state, while the absorption intensities of the ^1L_b and ^1L_a bands and, hence, the associated radiative rates will also vary to some extent. In order to observe such substituent effects on the emissivity, the fluorescence spectra of 1-naphthol and 1-methoxynaphthalene were measured. As may be seen from Figs. 1 and 2, no emission from the ^1L_a state could be observed.

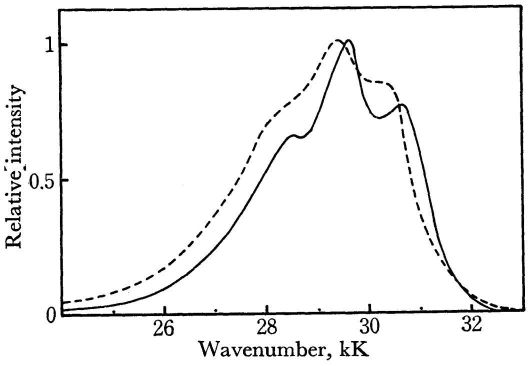

Fig. 1. The gas-phase fluorescence spectra of 1-naphthol. Excitations at 31.8 kK (——) and 35.7 kK (----). At 103°C (~1.7 Torr).

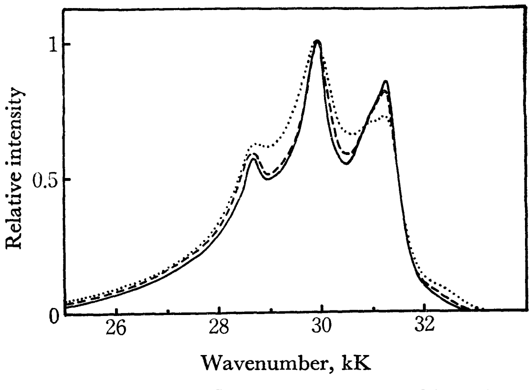

Fig. 2. The gas-phase fluorescence spectra of 1-methoxynaphthalene. Excitations at 32.3 kK (——), 34.5 kK (----), and 40.0 kK (······). At 76°C (<5 Torr).

TABLE 1. THE VALUES GIVEN FOR NAPHTHALENE, 1-NAPHTHOL, AND 1-METHOXYNAPHTHALENE

	Naphthalene		1-Naphthol	1-Methoxy-naphthalene
S_1(kK)	32.0		31.3	31.4
S_2(kK)	36.0		34.1	35.8
k_1(sec^{-1})	5.2×10^6		5.4×10^6	5.8×10^6
k_2(sec^{-1})	4.8×10^7		4.8×10^7	1.1×10^8
ϕ_1[a]	0.19		0.17	0.36
$\bar{\nu}_{exc}$(kK)[b]	36.4	40.0	35.7	40.0
ρ_1(cm)	2.8×10^3	8.9×10^6	2.8×10^3	2.8×10^7
ρ_2(cm)	1.1×10^{-4}	9.5×10^2	2.5×10^{-1}	1.6×10^3
Φ_2/Φ_1 (calc.)	2.5×10^{-4}	1.2×10^{-3}	1.1×10^{-3}	1.4×10^{-3}

a) Ref. 7.

b) Hereafter, $\bar{\nu}_{exc}$ will denote the excitation wavenumber at which the actual observation of the emissions was made.

The reason why S_2 emission could not be found in these compounds can be considered in terms of the estimated values of the radiative rate constants, the densities of states, and the related parameters listed in Table 1. The values of ρ for 1-naphthol and 1-methoxynaphthalene were assumed to be the same as that for naphthalene. As is indicated in Table 1, the calculated quantum yield ratios are so small compared with those of 'abnormal' molecules (*vide infra*) that the intensity of the S_2 emission may be expected to be too weak to be observed with conventional instruments. However, a more sensitive technique may permit its detection. In fact, quite recently Wannier *et al.*[40] could observe the resonance fluorescence from the second excited singlet state of naphthalene in the gas phase by utilizing a laser excitation source. It should be added, however, that the emission mechanism considered by them is very different from ours.[16]

Biphenyl, Phenanthrene, Triphenylene, and Chrysene. The absorption spectrum of biphenyl in solution shows a structureless intense band at about 40.5 kK and a weak band observed as a slight inflection around 36 kK.[41] It is thus interesting to see whether or not S_2 emission occurs in the gaseous state. As is shown in Fig. 3, the 35—42 kK region of the fluorescence spectrum does not vary with an increase in the excita-

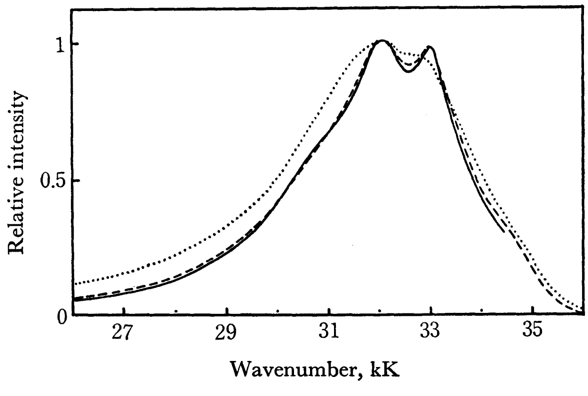

Fig. 3. The gas-phase fluorescence spectra of biphenyl. Excitations at 35.7 kK (——), 37.0 kK (----), and 40.0 kK (······). At 85°C (~2.3 Torr).

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[37] J. O. Uy and E. C. Lim, *Chem. Phys. Lett.*, **7**, 306 (1970).

[38] J. M. Bondeau and M. Stockburger, *ibid.*, **8**, 436 (1971).

[39] U. Laor and P. K. Ludwig, *J. Chem. Phys.*, **54**, 1054 (1971).

[40] P. Wannier, P. M. Rentzepis, and J. Jortner, *Chem. Phys. Lett.*, **10**, 193 (1971).

TABLE 2. THE VALUES GIVEN FOR BIPHENYL, PHENANTHRENE, TRIPHENYLENE, AND CHRYSENE

	Biphenyl	Phenanthrene			Triphenylene		Chrysene		
S_1 (kK)	~37	29.2			29.5		27.6		
S_2 (kK)	42	35.2			35.7		32.5		
k_1 (sec^{-1})	1.2×10^{7}[a]	2.6×10^{6}			3.8×10^{6}		1.7×10^{6}		
k_2 (sec^{-1})	7.7×10^{8}	2.5×10^{8}			3.5×10^{8}		1.2×10^{8}		
ϕ_1[b]	0.15	0.16			0.07		0.12		
$\bar{\nu}_{exc}$ (kK)	45[c]	39.2	41.0	43.5	38.5	41.7	35.0	38.5	40.8
ρ_1 (cm)	4.1×10^{7}	8.8×10^{9}	3.1×10^{11}	2.5×10^{13}	1.5×10^{10}	2.3×10^{13}	2.3×10^{8}	1.3×10^{12}	1.8×10^{14}
ρ_2 (cm)	5.5×10	2.4×10^{3}	5.0×10^{5}	2.3×10^{8}	2.9×10	4.0×10^{6}	7.0	4.0×10^{6}	2.6×10^{9}
Φ_2/Φ_1 (calc.)	5.2×10^{-3}	1.6×10^{-3}	1.8×10^{-3}	2.5×10^{-3}	5.0×10^{-3}	5.0×10^{-3}	1.0×10^{-3}	1.2×10^{-3}	2.0×10^{-3}

a) This value, obtained assuming $\varepsilon_{max}\sim1000$, agrees with that estimated from the quantum yield and lifetime.
b) Ref. 7.
c) An assumed wavenumber at which no fluorescence spectrum was observed.

tion energy. The observed large Stokes shift (4 kK) may be due to the change in the molecular geometry in the excited state.[41] The absence of S_2 emission in biphenyl is considered to be ultimately ascribable to the small ρ_2/ρ_1 values arising from the somewhat large energy separation between the first and second singlet states (~5 kK), as may be seen from Table 2.

Phenanthrene exhibits fairly well-structured fluorescence spectra on low-energy excitation and considerably broadened and red-shifted spectra on high-energy excitation, as is illustrated in Fig. 4. The spectral changes observed are uniform and gradual. In the 29—35 kK range of these spectra, however, no trace of S_2 emission can be found. The fluorescence spectra of triphenylene with excitation at various wavelengths are shown in Fig. 5. As the excitation wavenumber increases, the spectrum gradually becomes broader, and in the 29—35 kK range no S_2 emission is found. The reason for the absence of S_2 emission in phenanthrene and triphenylene is that the energy difference between S_1 and S_2 is quite large (6.0 and 6.2 kK respectively), as is indicated in Table 2.

The emission spectra of chrysene excited at several wavenumbers are shown in Fig. 6. The whole spectrum

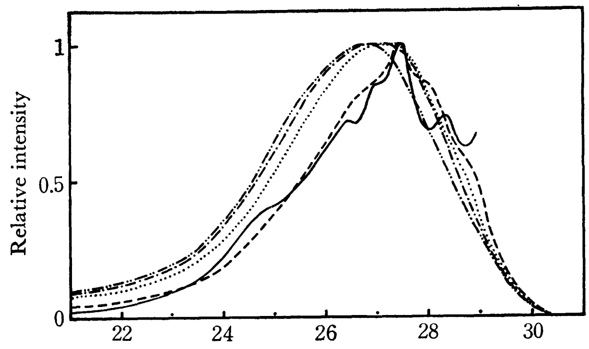

Fig. 4. The gas-phase fluorescence spectra of phenanthrene. Excitations at 30.3 kK (——), 35.2 kK (----), 39.2 kK (······), 41.1 kK (-·-·), and 43.5 kK (-··-). At 113°C (~0.9 Torr).

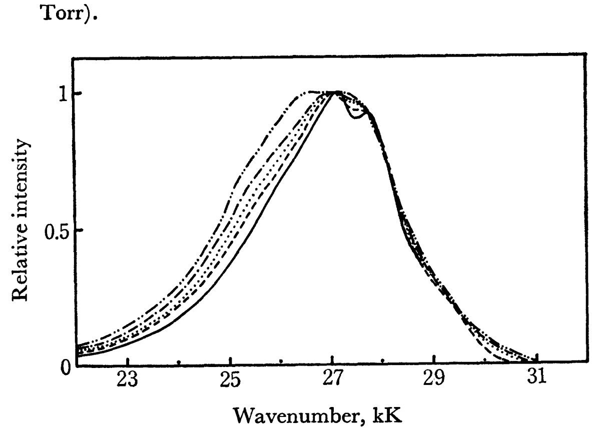

Fig. 5. The gas-phase fluorescence spectra of triphenylene. Excitations at 31.3 kK (——), 33.3 kK (----), 35.7 kK (······), 38.5 kK (-·-·), and 41.7 kK (-··-). At 200°C (~0.032 Torr).

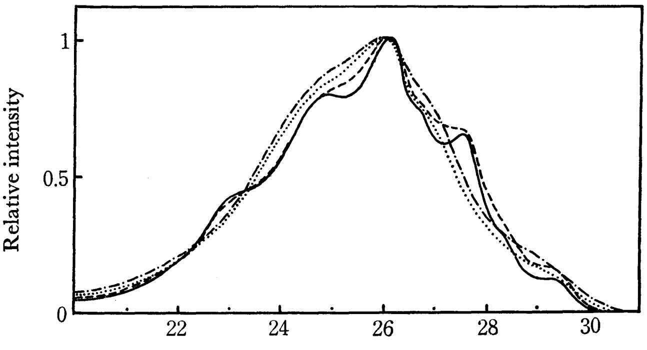

Fig. 6. The gas-phase fluorescence spectra of chrysene. Excitations at 32.5 kK (——), 35.0 kK (----), 38.5 kK (······), and 40.8 kK (-·-·). At 212°C (~0.7 Torr).

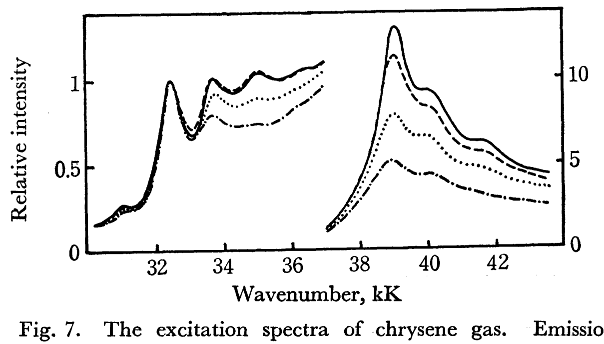

Fig. 7. The excitation spectra of chrysene gas. Emission observed at 25.0 and 26.3 kK (——), 27.5 kK (----), 28.6 kK (······), and 29.2 kK (-·-·). At 210°C (~0.7 Torr).

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[41] H. Suzuki, "Electronic Absorption Spectra and Geometry of Organic Molecules," Academic Press, New York (1967).

becomes more diffuse on excitation at higher energies. The relatively well-resolved band at about 29.3 kK might be assigned to an S_2-emission band. However, this band is situated too far from the position of the second absorption band at about 32.5 kK; further, the behavior of the excitation spectrum is quite anomalous in that its relative intensity decreases with the increase in the monitoring wavenumber, as is shown in Fig. 7. Moreover, Table 2 indicates that the calculated Φ_2/Φ_1 values for chrysene are appreciably smaller than those of, for example, 1,2-benzanthracene (*vide infra*). This is also due to the large S_1—S_2 energy difference (4.9 kK). These facts imply that some impurity is possibly responsible for the emission observed around 29.3 kK.[42]

1,2-Benzanthracene and 20-Methylcholanthrene. As the criteria are well satisfied by 1,2-benzanthracene and its derivative, 20-methylcholanthrene, it is tempting to test the presence of S_2 emission in these molecules. The observation of the emission from the second excited singlet state of 1,2-benzanthracene in *n*-heptane solutions was reported by Easterly *et al.*[19] According to their interpretation, the emission arises from the thermal population of S_2 from S_1.[19] In the present study, the gas-phase fluorescence spectra of 1,2-benzanthracene and 20-methylcholanthrene were measured at various excitation wavenumbers; these are shown in Figs. 8 and 9. The observed spectra are relatively sharp and well-structured with low energy excitations. On excitation at higher wavenumbers, however, the spectrum broadens and shifts to the red, and the intensity on its short-wavelength tail increases appreciably. On the basis of its band position and spectral behavior, the emission appearing in the high-wavenumber region can be assigned to the S_2 emission.

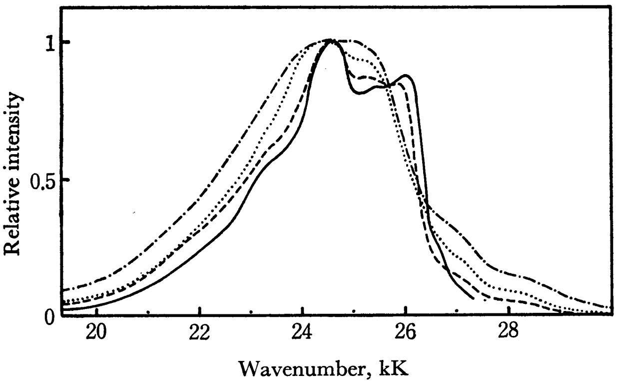

Fig. 8. The gas-phase fluorescence spectra of 1,2-benzanthracene. Excitations at 28.9 kK (——), 31.5 kK (- - -), 36.4 kK (······), and 41.7 kK (-·-·). At 152°C (~0.01 Torr).

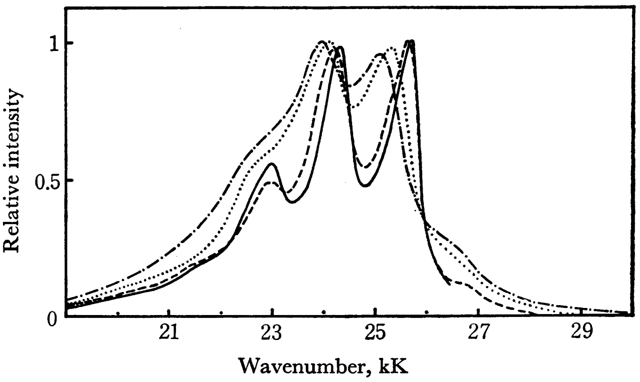

Fig. 9. The gas-phase fluorescence spectra of 20-methylcholanthrene. Excitations at 27.2 kK (——), 28.7 kK (- - -), 35.5 kK (······), and 40.0 kK (-·-·). At 190°C (~0.065 Torr).

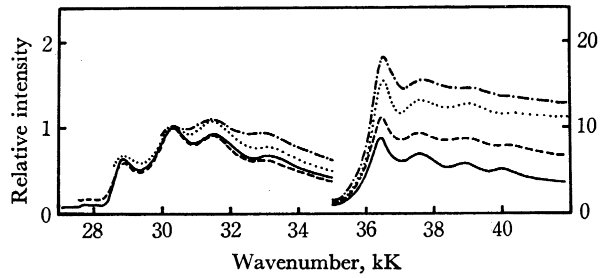

Fig. 10. The excitation spectra of 1,2-benzanthracene gas. Emission observed at 25.0 kK (——), 27.0 kK (- - -), 27.8 kK (······), and 28.6 kK (-·-·). At 167°C (~0.024 Torr).

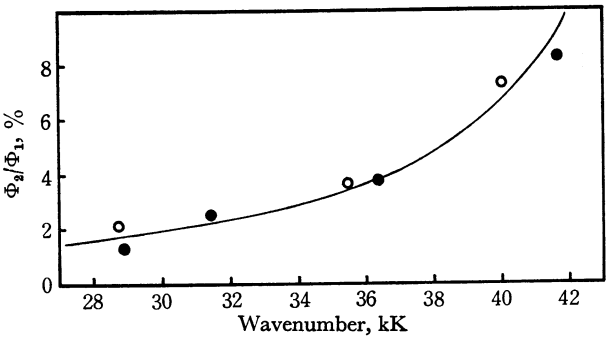

Fig. 11. The observed Φ_2/Φ_1 value *vs.* excitation wavenumber, for 1,2-benzanthracene (●) and 20-methylcholanthrene (○).

Figure 10 shows the excitation spectra of 1,2-benzanthracene, indicating that the relative intensity of the S_2 emission increases with the excitation energy. In Fig. 11, the observed ratio Φ_2/Φ_1 for 1,2-benzanthracene and 20-methylcholanthrene is plotted against the excitation wavenumber, showing the progressive increase in the former with the increase in the latter. Interestingly, the data on 20-methylcholanthrene give almost the same curve as those on 1,2-benzanthracene, as Fig. 11 shows.

The radiative rate constants, state densities, and related parameters are given in Table 3. The ρ values for 1,2-benzanthracene were substituted for those for 20-methylcholanthrene. As is shown in Table 3, the calculated relative yields of the S_2 emission are very large in these molecules, suggesting that the expectation regarding the appearance of the S_2 emission is quite realistic. The great enhancement of the S_2 emission by the substituent effects to be expected with 20-methylcholanthrene was not actually observed, however, as is shown in Fig. 9.

1,12-Benzperylene and Coronene. Dawson and Kropp reported an S_2 emission due to thermal repopulation

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[42] An alternative explanation may be that this band arises from the v—$v-1$ resonance fluorescence and that the anomaly in its excitation spectrum is caused by the considerable broadening of the band.

TABLE 3. THE VALUES GIVEN FOR 1,2-BENZANTHRACENE AND 20-METHYLCHOLANTHRENE

	1,2-Benzanthracene			20-Methylcholanthrene		
S_1 (kK)		26.2			25.7	
S_2 (kK)		28.9			27.1	
k_1 (sec^{-1})		3.3×10^6			4.1×10^6	
k_2 (sec^{-1})		1.1×10^8			1.4×10^8	
ϕ_1		0.19[a]			0.2[b]	
$\bar{\nu}_{exc}$ (kK)	31.5	36.4	41.7	28.7	35.5	40.0
ρ_1 (cm)	4.3×10^5	2.7×10^{11}	1.6×10^{16}	7.3×10	1.1×10^{11}	1.6×10^{15}
ρ_2 (cm)	1.1×10	3.0×10^8	8.0×10^{13}	4.5×10^{-2}	3.3×10^9	9.9×10^{13}
Φ_2/Φ_1 (calcd)	0.001	0.038	0.17	0.022	1.0	2.0
(obsd)	0.025	0.037	0.081	0.022	0.037	0.073

a) Ref. 7. b) The value assumed by reference to that for 1,12-benzanthracene.

with 1,12-benzperylene in a poly (methyl methacrylate) matrix.[20)] 1,12-Benzperylene shows absorption spectra with a very weak first band, followed by a much stronger second band, well satisfying the criteria. In coronene, the first and second absorption bands are extremely weak and closely spaced (α-band), accompanied by an intense third band (*p*-band).[43)] This assignment was made in view of the relatively complicated structure of the 'α-band' and the theoretical results.[44–46)]

The fluorescence spectra of 1,12-benzperylene and coronene measured in the gas phase and in benzene solutions are shown in Figs. 12 and 13. In benzene solutions the spectra exhibit quite distinct vibrational structures, with an enhanced 0—0 band indicative of the so-called Ham effect recently studied by the present author;[47)] this effect can be utilized in the assignment of the vibronic bands.

As may be seen from Fig. 12, the gas-phase fluorescence of 1,12-benzperylene has an interesting feature. On the short-wavelength side of the weak 0—0 band observed as a small peak at 24.6 kK, a band corresponding to the solution band around 25 kK appears at about 25.1 kK, with an appreciably high intensity. In addition to this, another relatively intense band can be observed around 26.4 kK upon excitation at higher wavenumbers.

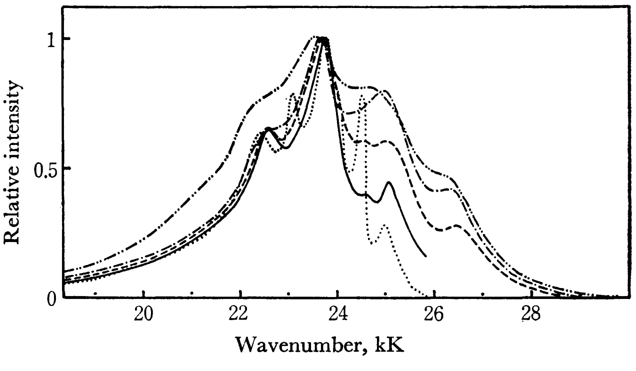

Fig. 12. The fluorescence spectra of 1,12-benzperylene. In the gas phase: excitations at 27.0 kK (——), 29.9 kK (----), 34.5 kK (-·-·-), and 40.0 kK (-··-··-); at 210°C (~0.02 Torr). In the benzene solution: excitation at 28.6 kK (······); at room temperature.

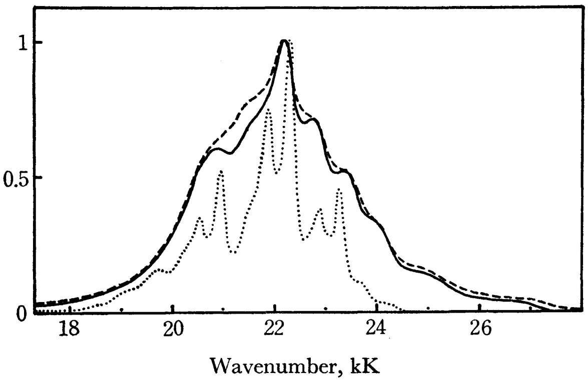

Fig. 13. The fluorescence spectra of coronene. In the gas phase: excitations at 30.1 kK (——) and 34.2 kK (----); at 285°C (~0.09 Torr). In the benzene solution: excitation at 29.5 kK (······); at room temperature.

The excitation spectra monitoring on the three bands is shown in Fig. 14. Though these spectra differ considerably in relative intensity in the high-wavenumber region, their agreement with one another in wavenumber is very good, implying that these three bands originate from the same molecular species and not from impurities.

The emission observed around 25 kK in solution was

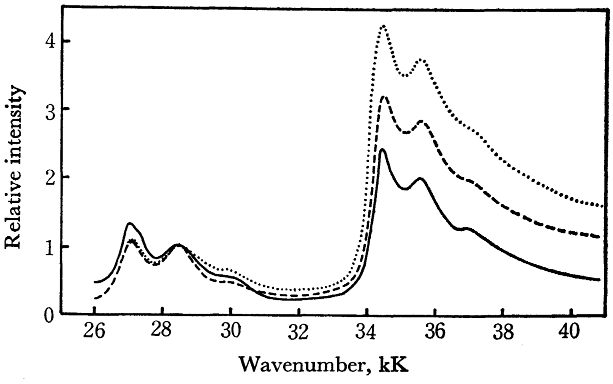

Fig. 14. The excitation spectra of 1,12-benzperylene gas. Emission observed at 23.7 kK (——), 25.0 kK (----), and 26.5 kK (······). At 210°C (~0.02 Torr).

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45) H. Gutfreund and W. A. Little, *Phys. Rev.*, **183**, 68 (1969); *J. Chem. Phys.*, **50**, 4468 (1969).

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47) A. Nakajima, This Bulletin, **44**, 3272 (1971); unpublished data.

TABLE 4. THE VALUES GIVEN FOR 1,12-BENZPERYLENE AND CORONENE

1,12-Benzperylene				Coronene		
S_1 (kK)		24.6		S_1 (kK)	23.5	
				S_2 (kK)	~25	
S_2 (kK)		27.0		S_3 (kK)	29.6	
k_1 (sec^{-1})		6.6×10^6		k_1 (sec^{-1})	1.4×10^6	
				k_2 (sec^{-1})	$\sim6\times10^6$	
k_2 (sec^{-1})		3.9×10^8		k_3 (sec^{-1})	3.4×10^8	
ϕ_1		0.36[a)]		ϕ_1	0.3[b)]	
$\bar{\nu}_{exc}$ (kK)	29.9	34.5	40.0	$\bar{\nu}_{exc}$ (kK)	30.1	34.3
ρ_1 (cm)	1.0×10^6	1.1×10^{12}	3.1×10^{17}	ρ_1 (cm)	1.4×10^8	2.8×10^{13}
ρ_2 (cm)	4.5×10	1.3×10^9	1.8×10^{15}	ρ_2 (cm)	6.8×10^5	5.0×10^{11}
				ρ_3 (cm)	10^{-7}	1.4×10^5
Φ_2/Φ_1 (calc.)	0.004	0.076	0.35	$(\Phi_2+\Phi_3)/\Phi_1$ (calc.)	0.022	0.079
(obs.)	0.24	0.37	0.38	(obs.)	0.097	0.11

a) Ref. 20. b) Ref. 7.

assigned by Kropp and Dawson[20)] to the S_2 emission. If this is true, the bands appearing around 25.1 kK and 26.4 kK might be attributable to the S_2 and S_3 emissions respectively. However, the 0—0 absorption band of the second electronic transition is observed in the gas phase at 27.0 kK (see Fig. 14). Accordingly, it is preferable to assign the 26.4 kK band[48)] to the S_2 emission. The 25 kK band, on the other hand, may be considered to be the 1—0 resonance emission band, overlapped by the higher vibrational components of the S_2 emission. This explanation seems to be consistent with the observation in the condensed phase by Kropp and Dawson of the temperature-dependent anti-Stokes band, which may, in our opinion, occur from an excited vibronic level.

The relative yields of the S_2 emission were estimated from the areas under the emission curves obtained on the assumption of a mirror-image relationship. The observed and calculated yield ratios are given in Table 4, showing that these ratios have appreciably large values and that they increase with the excitation energy.

The fluorescence spectra of coronene are also interesting, as is shown in Fig. 13. Excitation was made at the limited peaks (30.1 and 34.3 kK), because a weak impurity band was observed with excitation at lower wavenumbers and because the purification of coronene is notoriously difficult.[49)] The fluorescence tail extending to the higher-energy region (24—29 kK) may be composed of S_2 and S_3 emissions. Since the relative intensities of these emissions could not be estimated separately, their yields were treated as a sum. As is shown in Table 4, the values of $(\Phi_2+\Phi_3)/\Phi_1$ observed are of a reasonable order of magnitude in comparison with those calculated in the manner described in the Appendix. The calculated value of Φ_3/Φ_1 was relatively small, of the order of 10^{-3}.

Anthracene, Tetracene, and Perylene. Since the second absorption band (^1L_b) in anthracene, tetracene, and perylene is quite weak compared to the first band (^1L_a), this is a case where the criteria are not satisfied. The gas-phase fluorescence spectra of these compounds were also measured, while varying the excitation wavelength, and the absence of any S_2 emission was shown. The spectral results were almost the same as those obtained by other workers[50—55)] and so are not given in this paper. The failure of any S_2 emission to appear can be well understood by the very small values of Φ_2/Φ_1 calculated to be as is shown in Table 5.

TABLE 5. THE VALUES GIVEN FOR ANTHRACENE, TETRACENE, AND PERYLENE

	Anthracene	Tetracene	Perylene
S_1 (kK)	27.6	22.2	23.9
S_2 (kK)	~31	~26	~30
k_1 (sec^{-1})	9.1×10^7	1.1×10^8	4.8×10^8
k_2 (sec^{-1})	$\sim10^7$	$\sim10^7$	$\sim10^7$
ϕ_1[a)]	0.30	0.17	0.78
$\bar{\nu}_{exc}$ (kK)	40	38.5	37.7
ρ_1 (cm)	9.0×10^{11}	7.0×10^{16}	2.5×10^{15}
ρ_2 (cm)	1.1×10^9	4.3×10^{13}	1.1×10^9
Φ_2/Φ_1 (calc.)	1.7×10^{-4}	1.2×10^{-4}	1.3×10^{-5}

a) Ref. 7.

Concluding Remarks

It has been shown that the density of states can play an important role in radiationless transitions; this is in contrast with the view of Siebrand,[56)] who places more emphasis on the Franck-Condon factors. Despite our simple model, the tendency for the relative yield of the S_2 emission to increase with the excitation energy can be interpreted, though qualitatively, in terms of

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48) The band seems to be affected by the reabsorption by the strong second absorption band.

49) S. Iwashima, K. Ohno, T. Kajiwara, and J. Aoki, *Nippon Kagaku Zasshi*, **90**, 884 (1969).

50) E. Bowen and S. Veljkovic, *Proc. Roy. Soc.*, **A236**, 1 (1956).

51) K. H. Härdtl and A. Scharmann, *Z. Naturforsch.*, **12a**, 715 (1957).

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56) W. Siebrand and D. F. Williams, *ibid.*, **46**, 403 (1967); W. Siebrand, *ibid.*, **46**, 440 (1967); **47**, 2411 (1967).

the appropriately evaluated values of the state densities and the radiative rate constants. All the results obtained have proved consistent with the criteria previously mentioned, which can be restated on the basis of the first term in Eq. (6) that the S_2 emission can occur because of the large values of k_2/k_{1f} and ρ_2/ρ_1, the latter of which depends strongly on the energy difference. The contribution of the second term in Eq. (6), on the other hand, has been estimated to be comparatively small ($\lesssim 5\times10^{-3}$). In the case of azulene, it can be considered that k_{rp}/k_{ic} is very small because of the anomalously large S_1—S_2 energy separation, but k_{ic} is nearly comparable to k_2 because of the small Franck-Condon factors, so that the large second term permits the fluorescence emission from S_2. According to our results, in the molecule whose Φ_2/Φ_1 value is evaluated to be larger than about 0.01, there is a possibility for the S_2 emission to occur; this emission is essentially of an indirect nature. A strong laser excitation source would, however, be very useful for detecting a much weaker S_2 emission in a variety of compounds, including those studied in this work.

The participation of the triplet state has been neglected, but the vibrational relaxation by molecular collisions is so fast and complete during the sufficiently long lifetime of the triplet state that the molecule resulting in this state may contribute only to the quenching process.

The discrepancy between the observed and calculated yield ratios and, especially, the too great dependence of the calculated Φ_2/Φ_1 values on the excitation energy may be improved to some extent by considering the differences in the Franck-Condon overlap integrals for the individual vibrational modes; this must be done in a more elaborate study, irrespective of the model assumed.

Attention should be called to the assignment of the S_2 emission, which is generally made on the basis of the observations that it occurs in the short-wavelength region of the normal fluorescence and that its excitation spectrum almost agrees with the absorption spectrum. As has been suggested in the case of 1,12-benzperylene (and chrysene[42]), such behavior can be exhibited by the *v*—*v*—*i* resonance fluorescence in the gas phase or the thermally-excited vibronic band (hot band) in the condensed phase. This possibility requires further investigations designed to establish a method for an unambiguous identification.

In view of the interesting spectral features observed in 1,12-benzperylene and coronene, it seems worthwhile to make further studies of their gas-phase emissions.

The author wishes to express his thanks to Professors Junji Aoki and Hiroo Inokuchi for the gift of the sample of 1,12-benzperylene. His tahnks are also due to Mr. Masakatsu Aoi for his helpful discussions.

Appendix

The kinetics involving the third excited singlet state is considered, in which it is assumed that the direct conversion process between S_1 and S_3 is negligible. In Fig. 15 the radiative and nonradiative processes concerned are represented, along with the definitions of the rate constants. According to this scheme, the rate equations can be expressed as follows:

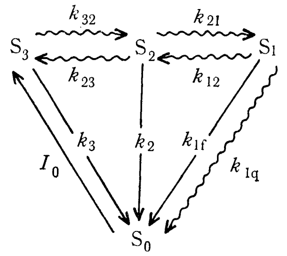

Fig. 15. Three-state scheme, with the rate constants for various radiative (——) and nonradiative (〰) processes.

$$\mathrm{d}S_1/\mathrm{d}t = k_{21}S_2 - (k_{1f}+k_{1q}+k_{12})S_1 \qquad (7)$$

$$\mathrm{d}S_2/\mathrm{d}t = k_{32}S_3 + k_{12}S_1 - (k_2+k_{21}+k_{23})S_2 \qquad (8)$$

$$\mathrm{d}S_3/\mathrm{d}t = I_0 + k_{23}S_2 - (k_3+k_{32})S_3 \qquad (9)$$

where S_i is the concentration of the molecules in S_i. Under photostationary conditions, $\mathrm{d}S_1/\mathrm{d}t=\mathrm{d}S_2/\mathrm{d}t=\mathrm{d}S_3/\mathrm{d}t=0$, from which the following formulae can be obtained:

$$\Phi_2/\Phi_1 = (k_2/k_{1f})(k_{12}/k_{21}) + k_2/k_{21}\phi_1 = \text{Eq. (1)} \qquad (10)$$

$$\begin{aligned}\Phi_3/\Phi_1 &= (k_3k_{12}/k_{1f}k_{21})(k_{23}/k_{32}+k_2/k_{32}) + (k_3k_{23}/k_{21}k_{32} \\ &\quad +k_3k_2/k_{21}k_{32}+k_3/k_{32})(k_{1f}+k_{1q})/k_{1f} \\ &= (k_3/k_{1f})(\rho_2/\rho_1)(\rho_3/\rho_2+k_2/k_{32}) \\ &\quad + [(k_3/k_{21})(\rho_3/\rho_2)+k_2k_3/k_{21}k_{32}+k_3/k_{32}]/\phi_1, \end{aligned} \qquad (11)$$

where the rate constants for the forward and backward conversion processes have been given by

$$k_{ij}/\rho_j = k_{ji}/\rho_i = (2\pi/\hbar)v_{ij}^2. \qquad (12)$$

The Φ_2/Φ_1 ratio obtained by neglecting the S_1—S_3 conversion process and the quenching process from S_2 is identical to that given before for the two-state scheme, as is indicated by Eq. (10). On the basis of these expressions, the quantum-yield ratios for coronene are evaluated using the rate constants and state densities listed in Table 4. It was assumed that $k_{32}\sim k_{21}\sim 10^{12}$ (sec^{-1}).