

Vibronic Quantum Effects in Fluorescence and Photochemistry. Competition between Vibrational Relaxation and Photochemistry and Consequences for Photochemical Control

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Abstract: In this paper we measured the fluorescence quantum yield (Φ_F) and the reaction quantum yield (Φ_{PC}) of a photochromic molecule (flindersine) as a function of the vibronic level (n) excited within a given sequence. We found that Φ_F decreased and Φ_{PC} increased with an increase in the quantum number of the vibronic level excited within a sequence. On the basis of a previously proposed model, this behavior was interpreted as resulting from competition between vibrational relaxation and photochemistry at each vibronic level. This model was broadened, and a new equation developed which, alone, or in combination with fluorescence data, permits determination of (1) the molar extinction coefficient of the partially produced colored form, (2) the quantum yield of vibrational relaxation, Φ_V , and the complementary Φ_{PC} at each vibronic level, (3) the photochemical reaction rate constant, k_{PC} , (4) the nonradiative internal-conversion rate constant from S_1 to S_0 , k_{NR} , and (5) the vibrational relaxation rate constant among the n levels of S_1 , k_V . The k_{PC} value ($1.7 \times 10^{10} \text{ s}^{-1}$) is comparable to k_V ($4.0 \times 10^{10} \text{ s}^{-1}$) and k_{NR} ($2.3 \times 10^{10} \text{ s}^{-1}$). The data and model account for the significant decrease in Φ_F with an increase in the value of n excited. Therefore, from the results here as well as those from our previous works, we propose the theory that for molecules undergoing excited-state photochemistry, there will be a vibronic-level dependence for Φ_{PC} and Φ_F and potentially for the triplet state yield Φ_T as well. It also appears that there can be a vibronic-mode and electronic-state dependence for these parameters. The nature of the photochemistry could also well be mode-dependent.

Introduction

In 1969 one of us published a paper dealing with what was called vibronic effects in photochemistry.¹ This in fact was a conclusion based on vibronic effects in fluorescence which is what was actually measured (relative Φ_F as a function of n , the vibronic quantum number excited within a singlet excited-state S_m). Here¹ we found that for two known photochromic chromenes, 2,2-diethyl-2H-chromene (DEC) and 2,2-dimethyl-5,6-benzo-2H-chromene (DMBC), the Φ_F showed a noticeable progressive decrease when excitation occurred to higher and higher vibronic levels of S_1 and S_2 (and S_3 for DMBC). To the contrary, for an analogue of DEC, 1,2-dihydronaphthalene, which did not undergo photochemistry, the relative Φ_F showed no decrease or change with excitation into two electronic transitions over the range 296–250 nm. Actually, we had made a qualitative observation earlier that the efficiency of fluorescence for DEC decreased as the excitation energy was increased from near the onset to higher values.² On the basis of these observations, a model was proposed which implied that at each vibronic level (n), in a sequence, there was competition between vibrational relaxation to the next lowest vibronic level ($n - 1$) and photochemistry. This of course presented the important revelation that photochemistry was as fast as vibrational relaxation.

We observed similar vibronic effects for Φ_F in some different molecules known to be photochromic, such as indolinospiropyran³ and fulgides⁴ for example. On the other hand, for one of the fulgides not showing photochromism/photochemistry, there was no dependence of the (relative) Φ_F upon the excitation energy over the first transition (410–340 nm).⁴ Furthermore, we⁵ made the important observation, for a fulgide showing photochemistry, that the (relative) Φ_{PC} increased by a factor of ~ 3 -fold with excitation to higher energy ($37\,600 \text{ cm}^{-1}$, 266 nm vs $28\,170 \text{ cm}^{-1}$, 355 nm), whereas the Φ_F decreased over the excitation range of 350–290 nm.⁴ This provided the first real proof that the earlier model (and idea) was, in fact, generally correctly founded.

Later studies of the photochemistry of a polycyclic cyclobutene⁶ and the photoisomerization of 1,3-Dewar naphthalene⁷ were noted to provide additional evidence of the long-standing premise¹ that “hot” excited-state photochemistry could occur. They showed that a decrease in Φ_F correlated to an increase in Φ_{PC} . They⁷ believed that hot (vibrationally) excited-state photochemistry could compete with cooling of large molecules (presumably this would occur via vibronic or vibronic-lattice/solvent relaxation as considered by us¹ and

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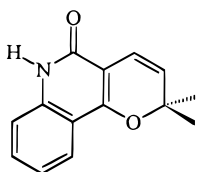
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above). However, they were not at all convinced of vibronic-level or mode selectivity as claimed earlier¹ but believed⁷ that an increase in excitation energy alone was responsible for the increase in Φ_{PC} . In the case of 1,4-Dewar naphthalene, there was no vibronic sequence(s), so in fact, it really was not possible to do an n -dependent determination of Φ_F or Φ_{PC} within a defined vibronic sequence. We have considered the case of benzene, where wavelength-dependent phenomena occur, in our first major work¹ on the subject of this paper. However, no data exists on the quantum yields of emission and photochemistry as a function of vibronic-level excitation.

Given the results of our early works^{1,3-5} on vibronic effects in fluorescence and their association with what we believed to be photochemistry, some parallel results⁷ from other works, and the potential important impact of our earlier results^{1,3-5} on competition of photochemistry with vibrational relaxation, we have done a careful and quantitative study on another molecule showing photochemistry (also photochromic), flindersine (FL):



Not only was Φ_F (absolute vs relative this time) determined as a function of the specific vibronic level excited within a given sequence of S_1 but also Φ_{PC} (absolute vs relative this time) was determined in the same manner. Very importantly, a model similar to that in ref 1 was employed, and from it, an additional and new equation was developed to permit determination of (1) the molar extinction coefficient of the colored form (only partially produced) (2) the Φ_{PC} as a function of the vibronic level excited (3) the vibrational relaxation quantum yield, Φ_V , within a defined sequence of S_1 (4) (with the use of fluorescence data) the photochemistry reaction rate constant, k_{PC} (5) the nonradiative/internal conversion rate from S_1 to S_0 , k_{NR} , and, finally, (6) k_V , the vibrational-relaxation rate constant among the n levels of S_1 . Furthermore, our data were obtained at relatively high temperature, 260 K, and in solution, compared with very low temperatures in a matrix where molecular (vibronic-lattice) cooling is expected to be slower.⁷

Experimental Section

Flindersine (from John Morgan, Forest Products Research Laboratory, England) was used without further purification. The solvent, 3-methylpentane (3MP), a reagent-grade Carlo Erba product, was distilled before use.

Absorption spectra were recorded on a Perkin-Elmer Lambda 16 spectrophotometer or on a Beckman diode array DU 7500 spectrophotometer. For absorption measurements at varying temperatures, a cryostat (Oxford Instruments), equipped with a temperature controller operating between 77 K (if liquid nitrogen was used for cooling) and 500 K, was used. The temperature precision was within ± 1 °C; the accuracy in the temperature control was on the order of ± 0.2 °C.

The irradiation wavelengths ($\lambda_{exc} = 367, 349, 333, 323, 309,$ and 294 nm) were selected for Φ_F using the fluorimeter excitation system with a band-pass of 4–6 nm, and for Φ_{PC} from the emission of a 150-W Xe lamp filtered by a monochromator (Jobin-Yvon H10 UV) with a band-pass of 8–16 nm. For determining Φ_{PC} , the radiation intensity (which was constant during each run) was determined using potassium ferrioxalate actinometry. The intensity of light varied from 8.1×10^{-6} to 3.5×10^{-6} Einstein $L^{-1} s^{-1}$ in the wavelength range of irradiation. A single Gaussian analysis/fit was done for each band of the longest wavelength transition (from ~ 375 to 275 nm) to determine the overlap at the wavelengths and band-passes used for excitation. The true

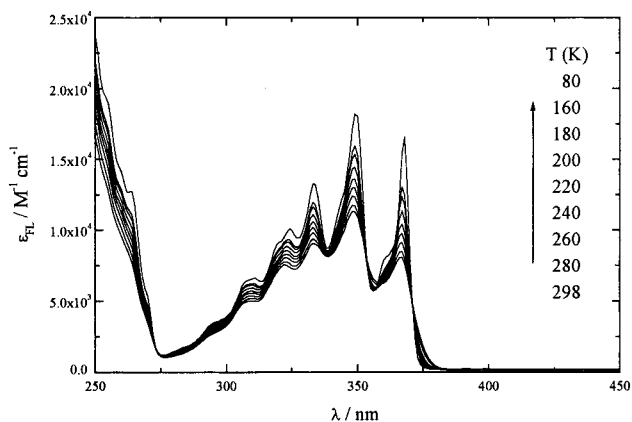


Figure 1. Absorption spectra of FL in 3MP as a function of temperature.

absorption spectrum was then almost perfectly reproduced based on the analysis ($\chi^2 = 7 \times 10^{-5}$). The overlaps ranged from $<1\%$ to 6% for the 4–6 nm band-pass for all of the vibronic levels excited and $<5\%$ ($n = 0, 1$) to $15\text{--}20\%$ ($n = 2\text{--}5$) for the 8–16 nm band-pass. The concentration of FL was on the order of $(2\text{--}7) \times 10^{-5}$ mol L^{-1} , corresponding to absorbances in the range 0.2–0.7 at the irradiation wavelengths. The photoreaction was carried out in a fluorimetric 1-cm path cell containing 1 mL of solution. The irradiation was carried out in the spectrophotometer holder at a right angle with respect to the monitoring beam. The light was homogeneously spread on the cell window; thus, stirring was unnecessary. The increase of absorbance was followed, under stationary irradiation, at 385 nm, where the reactant (FL) does not absorb and the excitation light did not disturb the absorption measurement. The kinetic rate parameter of the back reaction was determined at constant temperature following the disappearance of the photoproduct at the wavelength of analysis after having removed the irradiating source (zero time was $\sim 2\text{--}3$ s after the end of the irradiation).

Corrected emission spectra were recorded using a Spex Fluorolog-2 FL 112 spectrofluorimeter. To measure the emission quantum yield, Φ_F , corrected areas of the standard (benzophenone in CH_3CN , $A = 0.135$ at 333 nm, previously calibrated with quinine sulfate in 0.5 M H_2SO_4 , $\Phi_F = 0.546$)⁸ and the sample ($A \sim 0.137$ at 333 nm) emissions were compared and corrected for the refraction index of the medium. The temperature effect on the refraction index was evaluated using the semiempirical relationship: $n(T_2) = n(T_1) + ca(T_2 - T_1)$, where c and a are solvent constants.⁹ When necessary, the signals were corrected for any solvent contribution.

Results

The room-temperature absorption spectrum of FL in organic solvents shows a vibrationally structured band ($\lambda_{max} \sim 350$ nm, $\Delta \bar{\nu} \sim 1300$ cm^{-1}) and a more intense band in the UV region ($\lambda_{max} = 225$ nm). By lowering the temperature from 298 to 80 K, both the vibrational resolution and absorption intensity increase (Figure 1). Molar extinction coefficients (error limit, $\pm 5\%$), measured in 3MP at room temperature on each absorption peak, are reported in Table 1.

The room-temperature emission from FL is assigned as fluorescence on the basis of its location, its spectral distribution which mirrors the absorption, its similarity to other chromenes,¹ and its calculated lifetime (see below). The excitation spectrum reproduces the absorption spectrum, Figure 2 (with some small loss of intensity on the UV side of the band). The Φ_F is excitation-wavelength dependent and varies between $\sim 10^{-3}$ and 4×10^{-3} , Table 2. The rate constant for the fluorescence was

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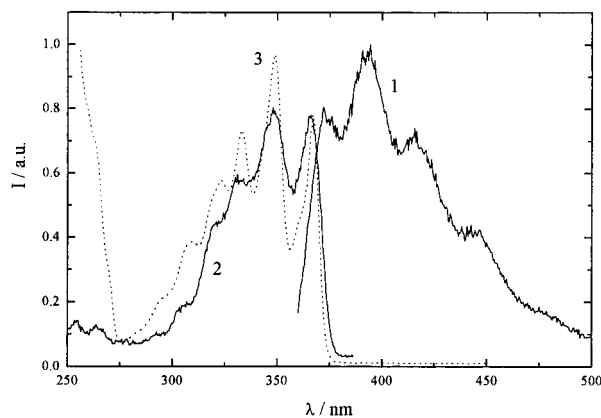


Figure 2. Fluorescence, $\lambda_{\text{exc}} = 340$ nm (1), fluorescence excitation, $\lambda_{\text{em}} = 410$ nm (2), and absorption (3) spectra of FL in 3MP at 180 K.

Table 1. Molar Extinction Coefficients of the Vibronic Bands of FL in 3MP at 298 K

λ_{max} (nm)	ϵ ($\text{L mol}^{-1} \text{cm}^{-1}$)	λ_{max} (nm)	ϵ ($\text{L mol}^{-1} \text{cm}^{-1}$)
367	7750	306	4200
349	11 300	294	2300
333	8600	235	23 400
321	6800		

Table 2. Experimental Fluorescence Quantum Yields, $\Phi_{\text{F}}(n)$, of FL as a Function of Vibronic Level Excited in S_1 in 3MP at 260 K

n	λ_{exc} (nm)	$\Phi_{\text{F}}(n) \times 10^3$
0	367	4.1 ± 0.2
1	349	3.2 ± 0.2
2	333	2.6 ± 0.2
3	323	2.3 ± 0.1
4	309	1.4 ± 0.1
5	294	1.1 ± 0.1

determined by graphical integration of the absorption and fluorescence spectra using the Strickler–Berg equation¹⁰

$$k_{\text{F}} = 1/\tau^{\circ} = 8 \times 1000(\ln 10)\pi c N^{-1} n^2 \frac{\int f(\bar{\nu}) d\bar{\nu}}{\int \bar{\nu}^{-3} f(\bar{\nu}) d\bar{\nu}} \int \frac{\epsilon(\bar{\nu})}{\bar{\nu}} d\bar{\nu} \quad (1)$$

where k_{F} and τ° are the radiative rate constant and the natural lifetime of the singlet state, respectively, c is the speed of light in a vacuum, N is Avogadro's number, n is the refractive index of the medium, and $f(\bar{\nu})$ and $\epsilon(\bar{\nu})$ represent the emission intensity and the molar absorption coefficient at the wavenumber, $\bar{\nu}$ (cm^{-1}), respectively. This equation holds only if the transition is fully allowed and is not accompanied by large changes in the internuclear distances. In the present case both conditions are fulfilled, as can be seen from the ϵ values, Table 1, and the nature of the absorption and emission spectra (Figure 2). The result was

$$k_{\text{F}} = 1.75 \times 10^8 \text{ s}^{-1}$$

Φ_{F} 's were measured by exciting each of the six vibrational bands of the first absorption band, S_1 , see Figure 1. The temperature of 260 K was chosen in order to have good resolution and to match the conditions at which Φ_{PC} was measured (see below). The Φ_{F} values were excitation-wavelength dependent, as previously noted, and depended on the vibronic level excited, Table 2.

To determine the photochemical yield (Φ_{PC}), the kinetic behavior of the photoproduct was evaluated under steady

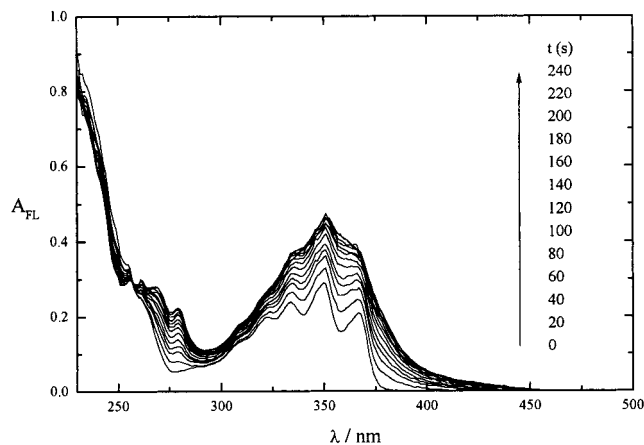
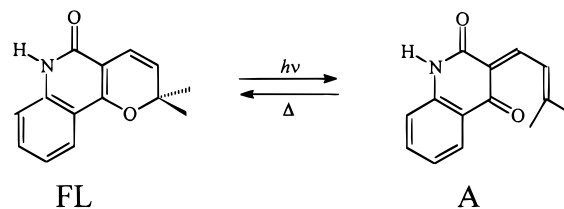


Figure 3. Time course of the absorption spectrum of FL under continuous irradiation.

monochromatic excitation into the six vibronic bands of S_1 . The temperature, 260 K, was chosen as a compromise of the requirement of obtaining reasonable transformation in a realistic time. It was determined that, for short irradiation times, only one species A was produced. As can be seen from Figure 3, an isosbestic point ($\lambda = 257$ nm) is maintained during short irradiation times. The limit spectrum (240 s irradiation) in Figure 3 corresponds to photostationary state attainment under continuous irradiation. The photoproduct is assigned as the “open” colored form resulting from C–O bond breakage as has been shown by us for other pyrans and chromenes (*o*-quinone allide structure, refs 1 and 11).



The production of A upon irradiation of FL is described by means of the following kinetic equation

$$d[A]/dt = I_{\text{FL}} \Phi_{\text{PC}}(n) - k_{\Delta}[A] \quad (2)$$

where $\Phi_{\text{PC}}(n)$ is the quantum yield of the photochemical reaction obtained by exciting the vibronic level $n = 0, 1, 2, \dots$, k_{Δ} is the bleaching parameter of the thermal back reaction, and I_{FL} represents the intensity of the monochromatic excitation light absorbed by FL per time unit (Einstein $\text{dm}^{-3} \text{s}^{-1}$). Since the spectrophotometric method is the most suitable for following the reaction kinetics, this equation is conveniently expressed in terms of the absorbance (A_{A}) and molar extinction coefficient (ϵ_{A}) of the photoproduct. Thus, considering 1-cm path length, the time-dependence of the absorbance of the colored form (A_{A}) at an analysis wavelength is given by

$$dA_{\text{A}}/dt = \epsilon_{\text{A}} \Phi_{\text{PC}}(n) I_{\text{FL}} - k_{\Delta} A_{\text{A}} \quad (3)$$

By expressing I_{FL} as $I^{\circ}[1 - \exp(-2.3A_{\text{FL}})]$, where A_{FL} is the absorbance of FL at the irradiating wavelength, and substituting I_{FL} in eq 3, the following relationship is obtained

$$dA_{\text{A}}/dt = \epsilon_{\text{A}} \Phi_{\text{PC}}(n) I^{\circ} [1 - \exp(-2.3A_{\text{FL}})] - k_{\Delta} A_{\text{A}} \quad (4)$$

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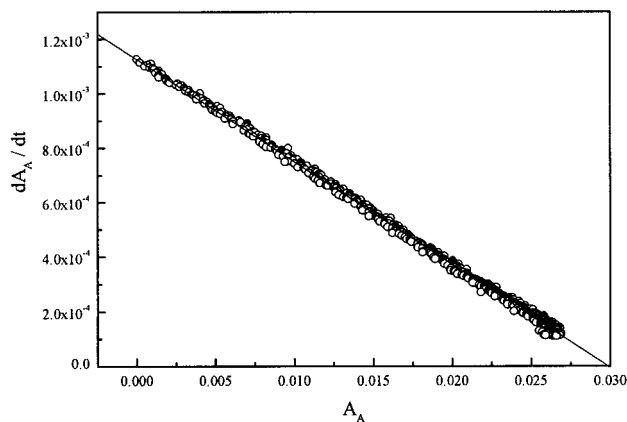


Figure 4. Experimental data treated according to eq 4 (260 K, $\lambda_{exc} = 323$ nm).

Table 3. Experimental Conditions and Data of $\epsilon_A \Phi_{PC}(n)$ as a Function of n Determined Using Equation 5

n	λ_{exc} (nm)	I^0 (Einstein $L^{-1} s^{-1} \times 10^7$)	A_{FL}	$\epsilon_A \Phi_{PC}(n)$ ($L mol^{-1} cm^{-1}$)
0	367	8.14	0.562	1290
1	349	7.98	0.796	1860
2	333	6.89	0.639	2520
3	323	6.00	0.531	2660
4	309	4.81	0.352	2810
5	294	3.51	0.183	3090

From the absorbance/time curves, the product $\epsilon_A \Phi_{PC}(n)$ can be obtained by extrapolating the color-forming rate to zero time (eq 5).

$$\epsilon_A \Phi_{PC}(n) = \frac{(dA_A/dt)_{t \rightarrow 0}}{I^0 [1 - \exp(-2.3A_{FL})]} \quad (5)$$

An example of the data treatment is given in Figure 4: the reaction was followed up to 10% photoconversion. Since ϵ_A is unknown, only the $\epsilon_A \Phi_{PC}(n)$ value can be experimentally obtained from a single measurement. However, see the later discussion where, utilizing a newly developed equation, we can obtain ϵ_A itself.

If the exciting source is removed, the rate parameter of the thermal bleaching, first order kinetics, can be determined spectrophotometrically ($k_A = 0.03 s^{-1}$ at 260 K).

To test the effect of varying the vibronic level excited on the reaction yield, the exciting light was selected corresponding to the six different vibronic peaks. The quanta emitted were measured at each exciting wavelength by ferrioxalate actinometry (see Experimental Section). The data obtained, $\epsilon_A \Phi_{PC}(n)$, were corrected for the change in absorbance. They are reported in Table 3.

Discussion

On the basis of the observations on DEC and DMBC, a model and accompanying equation were developed¹ which related Φ_F , the internal conversion/vibronic relaxation rate constant, which was then denoted as k_{IC} , k_{PC} (photochemistry rate constant), and n . As we will see shortly, it is better to refer to the relaxation process among the S_m states ($m \neq 0$) as vibrational relaxation (k_V) reserving k_{NR} for nonradiative molecular relaxation from S_1 to S_0 .

$$\Phi_F(n) = [k_{IC}/(k_{IC} + k_{PC})]^n \quad (6)$$

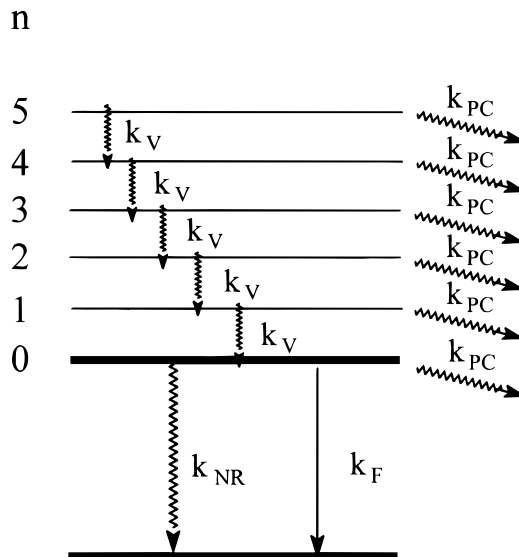


Figure 5. Model for the fate of quanta absorbed into any vibronic level of S_m ($m = 1$ here).

where $n = 0, 1, 2, 3 \dots$ was the vibrational/vibronic quantum number in a given sequence. Using the log of eq 6

$$\log \Phi_F(n) = n \log[k_{IC}/(k_{IC} + k_{PC})] \quad (7)$$

straight lines (eq 7) should be obtained from plots of $\log \Phi_F(n)$ vs. n of a given sequence, as was found.¹ The one missing experimental observation to unequivocally nail down the model¹ was the determination of Φ_{PC} as a function of n . The fact that photochemistry was indeed involved seemed secure since for DEC, DMBC, and several fulgides which were photochromic, the vibronic effect occurred, whereas in the case of 2,2-dihydronaphthalene and one specific fulgide which were not photoreactive the effect did not occur.

In this work we have been able to establish both the absolute Φ_{PC} and Φ_F as a function of n for FL. According to the model originally developed¹ and with the additional consideration of the rate constant k_{NR} , needed to account for the nonradiative and nonreactive paths from the 0 vibronic level of S_1 (Figure 5), a slightly modified equation results

$$\Phi_F(n) = \Phi_F(0) \Phi_V^n \quad (8)$$

where $\Phi_F(0) = k_F/(k_F + \sum k_i)$ is the fluorescence yield from $n = 0$ of S_1 , $\Phi_V = k_V/(k_V + k_{PC})$ is the vibrational relaxation yield, and $n = 0, 1, 2, \dots$. Furthermore, k_V refers to the rate constant for vibrational relaxation, k_{PC} refers to the rate constant for photoreaction, and $\sum k_i = k_{PC} + k_{NR}$. Using the ln of eq 8 we get

$$\ln \Phi_F(n) = \ln[k_F/(k_F + \sum k_i)] + n \ln[k_V/(k_V + k_{PC})] \quad (9)$$

Using the experimental $\Phi_F(n)$ data in Table 2, a plot of $\ln \Phi_F(n)$ as a function of n , Figure 6, yielded a straight line with an excellent correlation coefficient of 0.98. From the slope and intercept

$$\Phi_V = 0.77 \pm 0.02 \quad \Phi_F(0) = 4.3 \times 10^{-3} \quad (\text{experimental } 4.1 \times 10^{-3})$$

By utilizing the k_F value obtained from the Strickler and Berg integration

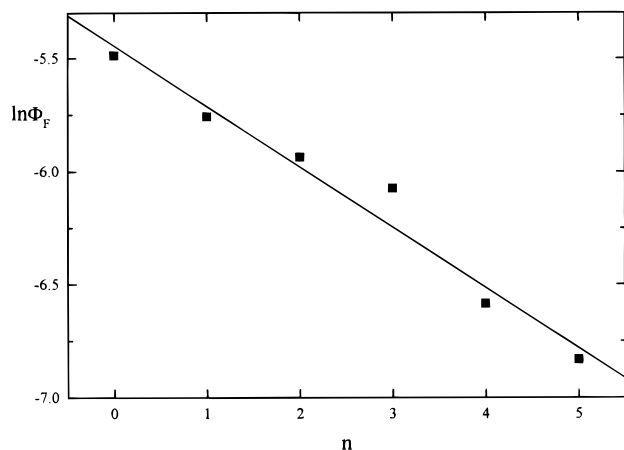


Figure 6. Plot of $\ln \Phi_F(n)$ ($\Phi_F(n)$ from Table 2) versus the vibronic level excited (n).

$$\sum k_i = 4.0 \times 10^{10} \text{ s}^{-1}$$

On the basis of the model, Figure 5, a new relationship was developed to determine Φ_{PC} and its dependence on the vibronic level excited

$$\Phi_{PC}(n) = \Phi_{PC}(0) \Phi_V^n + \Phi_{PC}(1 + \Phi_V + \Phi_V^2 + \dots \Phi_V^{n-2} + \Phi_V^{n-1}) \quad (10)$$

where $\Phi_{PC} = k_{PC}/(k_{PC} + k_V)$ and $\Phi_{PC}(0) = k_{PC}/(k_{PC} + k_F + k_{NR})$.

That is, upon exciting at $n = 0$

$$\Phi_{PC}(0) = k_{PC}/(k_{PC} + k_F + k_{NR})$$

at $n = 1$

$$\Phi_{PC}(1) = \Phi_{PC}(0)\Phi_V + \Phi_{PC}$$

at $n = 2$

$$\Phi_{PC}(2) = \Phi_{PC}(0)\Phi_V^2 + \Phi_{PC}(1 + \Phi_V)$$

and so on. By subtracting the yield corresponding to $(n - 1)$ from that corresponding to n and then taking the logarithm, a linear relationship is obtained

$$\ln[\Phi_{PC}(n) - \Phi_{PC}(n - 1)] = (n - 1) \ln \Phi_V + \ln[\Phi_{PC}(0)(\Phi_V - 1) + \Phi_{PC}] \quad (11)$$

Considering that the experiments give $\epsilon_A \Phi_{PC}(n)$, the plot of $\ln[(\epsilon_A \Phi_{PC}(n) - \epsilon_A \Phi_{PC}(n - 1))] \text{ vs } (n - 1)$ should give a straight line with $\ln \Phi_V$ as slope and $\ln[\epsilon_A \Phi_{PC}(0)(\Phi_V - 1) + \epsilon_A \Phi_{PC}]$ as intercept. Despite the poorer correlation coefficient found (0.65), Figure 7, compared with that for fluorescence, which is due to the intrinsic uncertainty in these kinds of measurements (resulting from actinometry, taking differences between close $\epsilon_A \Phi_{PC}(n)$ values, etc.), the value of Φ_V determined from the slope, 0.7 ± 0.1 , corresponds well to that obtained from the fluorescence measurements ($\Phi_V = 0.77 \pm 0.02$).

Moreover, from the intercept (6.3), the ϵ_A value at an analyzing wavelength can be easily obtained.

$$\epsilon^{\text{intercept}} = \epsilon_A \Phi_{PC}(0)(\Phi_V - 1) + \epsilon_A \Phi_{PC} \quad (12)$$

The Φ_{PC} can be obtained from Φ_V

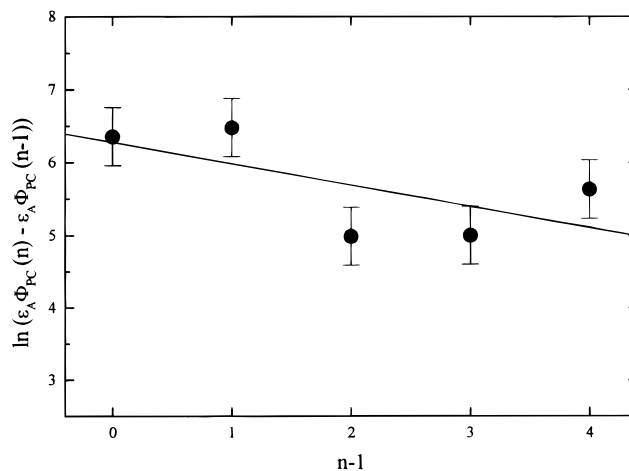


Figure 7. Plot of the experimental parameters of Table 3, last column, treated according to eq 11 to determine Φ_V .

Table 4. Experimental Photochemical Reaction Quantum Yields As a Function of n

n	λ_{exc} (nm)	$\Phi_{PC}(n)$
0	367	0.41 ± 0.02
1	349	0.60 ± 0.02
2	333	0.81 ± 0.03
3	323	0.85 ± 0.03
4	309	0.90 ± 0.04
5	294	0.99 ± 0.04

$$\Phi_{PC} = 1 - \Phi_V = 0.3$$

(0.23 from the fluorescence measurements)

By replacing $\epsilon_A \Phi_{PC}(0)$ with the experimental value, $1290 \text{ L mol}^{-1} \text{ cm}^{-1}$, from eq 12 we obtain

$$\epsilon_A = (545 + 1290 \times 0.3)/0.3 = 3110$$

at 385 nm for the colored form. The determination of ϵ_A allowed the absolute Φ_{PC} as a function of n , $\Phi_{PC}(n)$, to be evaluated (Table 4). From the ratio of $\Phi_{PC}(0)$ (Table 4) to $\Phi_F(0)$ (Table 2), we obtain

$$\Phi_{PC}(0)/\Phi_F(0) = 100 = k_{PC}/k_F$$

and from this equation

$$k_{PC} = 1.7 \times 10^{10} \text{ s}^{-1}$$

using the value of k_F determined earlier ($1.75 \times 10^8 \text{ s}^{-1}$). Thus the vibrational relaxation rate constant, k_V , and the nonradiative rate constant, k_{NR} , can be calculated

$$k_V = 4.0 \times 10^{10} \text{ s}^{-1} \text{ [from } k_V = k_{PC} \Phi_V / \Phi_{PC}]$$

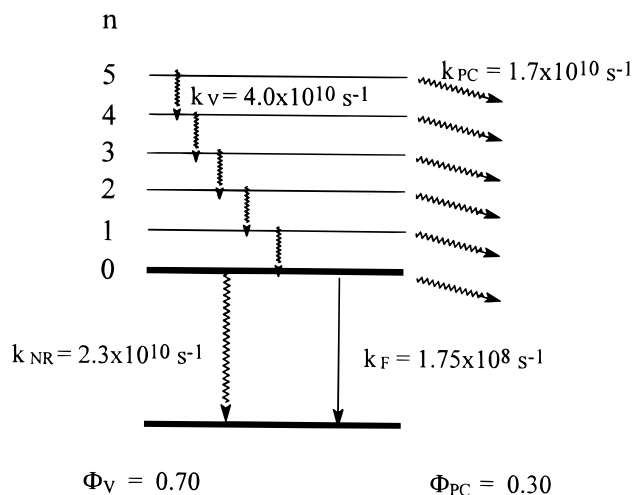
and

$$k_{NR} = 2.3 \times 10^{10} \text{ s}^{-1}$$

(from $\sum k_i = k_{PC} + k_{NR}$, using $\sum k_i$ obtained from the fluorescence measurements).

All of the data obtained fit the model given earlier¹ and here, *vide supra*, and Figure 5, regarding competition between vibrational relaxation and photochemistry at each vibronic level in a sequence. Moreover, using this model and the newly developed equation, eq 10, based on the same model, we were able to determine *all* of the important parameters Φ_V , Φ_{PC} , k_{PC} ,

k_V , and k_{NR} . Thus, in the case of FL, the processes involved and their Φ and k values look as follows



From these data, where the k_{PC} is comparable to k_V , it is clear why, as the excitation occurs from $n = 0$ to $n = 5$, the Φ_F decreases significantly by a factor of 4, Table 2.

Regarding the question of whether the “vibronic effect” found for Φ_F and Φ_{PC} is simply an energy-dependent phenomenon, we can show that this is not the case. In the case of DEC, the value of k_{IC}/k_{PC} (k_V/k_{PC} here) was ~ 3 for one sequence and only 1 for another sequence, that is, 3 quanta of a 280 cm^{-1} (total of 840 cm^{-1}) sequence have essentially the same Φ_F as 1 quantum of a 1300 cm^{-1} sequence¹ although obviously a greater total excitation energy is involved in the latter case.¹ Again, for DEC, the Φ_F resulting from excitation of the 0–0 band at $35\,960\text{ cm}^{-1}$ in the second transition was greater than that obtained from excitation at the lower energy of $32\,995\text{ cm}^{-1}$ (2-quanta of 1300 cm^{-1}) in the first transition.¹ In addition, in the second transition,¹ excitation at $37\,655\text{ cm}^{-1}$ resulted in almost the same Φ_F as that resulting from lower-energy excitation at $36\,290\text{ cm}^{-1}$. For DMBC,¹ the ratio k_{IC}/k_{PC} varied from ~ 3 to ~ 7 depending on the sequence and electronic state (S_1 , S_2 , S_3) involved. For β -naphthoindolinospiropyran, excitation at $29\,020\text{ cm}^{-1}$ (a combination band) and $27\,730\text{ cm}^{-1}$ (1 quantum of 450 cm^{-1}) resulted in almost identical Φ_F values.³ Also, higher-energy excitation at $28\,560\text{ cm}^{-1}$ (1 quantum of $\sim 1290\text{ cm}^{-1}$) as opposed to $27\,730\text{ cm}^{-1}$ (1 quantum of 450 cm^{-1}) resulted in an increase of Φ_F .³ This is also markedly noticeable for excitation at $29\,530\text{ cm}^{-1}$ where Φ_F was greater than at all energies below it (ΔE is as great as 1800 cm^{-1}).³ Finally, recall that, on the basis of the model considered (Figure 5), the new eq 10 (and 11) permits calculation of the extinction coefficient of a partially produced photoproduct and Φ_V (independent of fluorescence) as well as some rate constants. The Φ_V determined is in excellent agreement with that obtained from fluorescence, and the rate constants are in harmony with expectation as well as with literature data on molecules of this size. If Φ_F and Φ_{PC} were simply a function of the energy of excitation, eq 10 would not exist. On the basis of all of the evidence here and elsewhere,^{1,3} we propose the theory that there

is (our case) or can be, in general, a vibronic-quantum-level (and possible mode) dependence for Φ_F and Φ_{PC} .

Regarding the vibronic level dependence, it is clear from the present work that there is a significant enhancement of the total Φ_{PC} as one excites higher and higher vibronic levels. In earlier work,^{1,3–5} we proposed a similar result based on the behavior of the complementary Φ_F . Thus, it is now clearly possible to alter the efficiency of the photochemistry for a molecule by judiciously choosing an excitation energy tuned to a particular level within a mode’s vibronic sequence. This of course represents quite a departure from conventional wisdom that has believed that vibrational relaxation was essentially the only path for de-excitation from any vibronic level (of any mode in any electronic excited state) to the 0 level of S_1 from which photochemistry would occur. Moreover, although it may happen, in general, that excitation into a higher electronic state than S_1 increases the Φ_{PC} , we¹ have seen exceptions involving the 0 level of a next higher electronic state S_2 , although Φ_{PC} did, in fact, then increase again upon excitation into higher vibronic levels of S_2 .

Regarding a potential mode dependence (for photochemistry), we previously found,¹ for example, that excitation into the $\sim 1300\text{-cm}^{-1}$ sequence of DEC compared with the 280-cm^{-1} sequence gave a very different value for the ratio of k_{IC}/k_{PC} —0.7 for the $\sim 1300\text{-cm}^{-1}$ sequence and 2.8 for the 280-cm^{-1} one. A C–O–C asymmetric stretch has approximately the $\sim 1300\text{-cm}^{-1}$ value, and since it is a C–O bond which is broken in photochemistry, this potentially could nicely account for the results observed. Importantly, the presence of a mode dependence would offer the very interesting possibility of being able to change the nature of the photochemistry of a molecule by changing the mode which is excited. Of course the more “photochemically versatile” is the molecule, the more likely it is that such a possibility could become an actuality.

Obviously, either changing the vibronic level or mode excited will have a corresponding effect on the efficiency of fluorescence of a molecule also having a photochemical path. Therefore, in an adverse situation where high-energy excitation was used, the use of a lower energy excitation potentially could result in significantly enhanced fluorescence (by suppression of photochemistry). Also, for parallel reasons and using a parallel technique, it would be potentially possible to alter the efficiency of triplet-state occupation where a competitive photochemical process exists in the singlet manifold.

Finally, the presence of photochemistry in the molecules considered here and elsewhere^{1,3–5} allowed for a unique probe of the molecular dynamic processes of photochemistry, vibrational relaxation, and fluorescence. Although we will not discuss it in this paper, our results here and elsewhere^{1,3,5} (and others in progress) impact the mechanism of vibrational relaxation. We shall consider this in another paper.

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