

Predictions of the Rate Constants of the Radiative Energy Dissipation and the Intersystem Crossing of Some Coumarin Laser Dyes

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ABSTRACT

Dye lasers are commonly used in the optical investigation because their solutions in organic solvents deliver tunable, coherent emission. They exhibit intense fluorescent, owing to some specific spectroscopic characteristics. One drawback of the laser dyes is that it shows excessive Triplet-State Losses (TSLs) the lack of theoretical predictions of fluorescence rates, Inter System Crossing (ISC), and phosphorescence in laser dyes prompted us to report on the predicted rates of radiative and non-radiative transitions of some laser dyes. Structural engineering by some substituents that influence the simulated rates of coumarin laser dye derivatives for an efficient operation was investigated. The NH₂ functional group renders the coumarin 120 more fluorescents with reduced TLS than the other investigated materials.

Keywords: Fluorescence; Intersystem crossing; phosphorescence; Lifetime; Triplet-State loss

INTRODUCTION

Coumarin is one of the very famous organic fluorescent materials. Coumarin derivatives have been widely applied in many fields, such as optical brightening agents, photobiological energy transfer processes, Light-Emitting Devices (LEDs) with the advantages of a sizeable conjugated system and rigid planar structure), laser dyes, medicine, and bio/ chemosensors [1-3].

Previous work noticed that we still lack theoretically predicted spectroscopic characteristics of efficient laser dyes [4]. This paper aims to simulate the missing excited-state dynamic parameters such as fluorescence, ISC, and phosphorescence rates of some coumarin laser dyes induced by different substituents, identified in Figure 1 and Table 1. The varying photophysical properties of coumarin and its various derivatives are sources of motivation that prompted us to study the architecture of the coumarin derivatives, which imparts changes in the electronic distribution within the molecular skeleton. And the effect of substituents on the excited state dynamic rates will be investigated by predicting the rates of fluorescence (k_{flu}), intersystem crossing (k_{ISC}), and phosphorescence (k_{Pho}) in the laser dyes and related molecule (2) given in Table 1. The current study results will pave the way

to highlight the molecular architecture that enables designing efficient laser dyes.

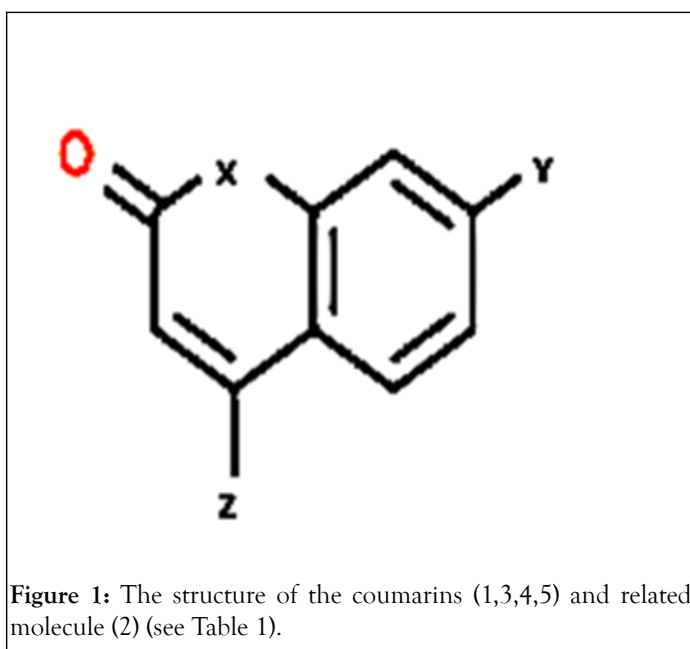


Figure 1: The structure of the coumarins (1,3,4,5) and related molecule (2) (see Table 1).

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Table 1: Dyes studied, ChemSpider ID, and the natural charge on the oxygen atom in position 2 (see Figure 1).

Dye (ChemSpider ID)	X	Y	Z
Carbostyryl 7 (79637)	N	N	CH3
2-quinolinone (168395)	N	N	CF3
Coumarin 120 (83285)	O	N	CH3
Coumarin 151 (90930)	O	N	CF3
Coumarin 4 (4444190)	O	O	CH3

Computations

All calculations were carried out using the ORCA 4.2 (parallel) software package [5]. Structures were optimized using the B3LYP functional and the def2-TZVP (-F) basis set as recommended. The rates and spectra were calculated using the same methods recommended and detailed in the literature [6,7]. We considered the triplet spin-sublevels (1,0, or -1). For the molecules under investigation, we were predicted the kISC as the mean of the sum of the individual kISC (T1), kISC (T2), and kISC (T3). We employed the well-known CPCM model of solvation [5] using ethanol as a solvent. An example of calculating the ISC rate for molecule 1 is given below:

```
!B3LYP DEF2-TZVP(-F) ESD(isc) TIGHTSCF GRID5 GRIDX5
RIJCOSX RI-SOMF(1X) CPCM(ETHANOL)
```

```
%TDDFT NROOTS 5
```

```
SRROOT 1
```

```
TROOT 1
```

```
TROOTSSL 1
```

```
DOSOC TRUE
```

```
END
```

```
%MaxCore 1024
```

```
%scf ConvForced false END
```

```
%SCF MAXITER 300 END
```

```
%GEOM MAXITER 300 END
```

```
%ESD ISCISHES "CARS7-ES.hess"
```

```
ISCFSHES "CARS7-TS.hess"
```

```
USEJ TRUE
```

```
DOHT true
```

```
DELE 28643.09
```

```
END
```

```
%pal nprocs 35 end
```

* xyz 0 1	-3.111222000000	0.001372000000	-2.059050000000
O			
N	-0.889634000000	-0.889634000000	-1.557789000000
N	3.886769000000	-0.096090000000	-0.770116000000
C	-0.078363000000	0.036557000000	0.708754000000
C	0.181047000000	0.016771000000	-0.691451000000
C	-1.458950000000	0.029694000000	1.160873000000
C	1.038929000000	0.052927000000	1.571668000000
C	1.497780000000	-0.000226000000	-1.179933000000
C	-2.469996000000	0.015302000000	0.243292000000
C	2.590167000000	-0.005945000000	-0.301008000000
C	2.338194000000	0.034378000000	1.094272000000

C	-2.242567000000	0.009511000000	-1.199275000000
H	-0.720987000000	-0.002120000000	-2.559905000000
H	4.054014000000	0.173808000000	-1.732364000000
H	4.622857000000	0.190972000000	-0.136162000000
H	0.877614000000	0.081682000000	2.651303000000
H	3.179844000000	0.043742000000	1.791942000000
H	1.667446000000	-0.024418000000	-2.260897000000
H	-3.518228000000	0.004283000000	0.548524000000
C	-1.763582000000	0.031351000000	2.636938000000
H	-1.301041000000	-0.832830000000	3.143320000000
H	-1.367091000000	0.936618000000	3.128295000000
H	-2.847000000000	-0.007917000000	2.817769000000
*			

RESULTS AND DISCUSSION

The predicted spectra of dye 3 (coumarin 120) are depicted in Figure 2 as an example. The theoretically simulated photophysical parameters are summarized in Table 2.

Table 2: Some predicted radiative ($S_1 \rightarrow S_0$, and $T_1 \rightarrow S_0$) and non-radiative (ISC) transitions of the dyes 1-5. Phosphorescence lifetime (τ) in ms is given between parentheses. The percent of the Hertzberg-Teller coupling (HT%) due to vibronic coupling is also p.

Dye	kphos, s ⁻¹ (ms)	HT%	λ_{phos} , cm ⁻¹	kISC, 10 ⁹ s ⁻¹	kflu, 10 ⁹ s ⁻¹	λ_{flu} , cm ⁻¹	*kflu 10 ⁹ s ⁻¹	*knr 10 ⁹ s ⁻¹
1	0.30 (3333.3)	91.1	14807	0.33	0.1	25126	~	~
2	0.62 (1612.9)	98.5	14598	0.18	0.1	23529	~	~
4	5.40 (185.2)	99.5	11854	0.09	0.15	22883	3.65 [10]	54.3 [10]
5	5.80 (172.4)	99.5	16525	0.19	0.11	26810	0.22 [11]	0.94 [11]
3	294 (3.4)	99.9	14116	0.14	0.17	24331	0.12 [12]	1.24 [12]

Referring to Figure 1 and Table 1, architecturally, three important modified positions are observed in the coumarin skeleton for controlling the photophysical properties. One is the 1-position (X in Figure 1), and the second is 7-position (Y in Figure 1), and the third is the 4-position (Z in Figure 1). In this framework, the molecular engineering of these three positions by sensible substituent effect to understand the dominant

deactivation channel and the laser efficiency of coumarin derivatives is addressable. Herein, two members of coumarin derivatives with O and N atoms substituted at the X-position were selected. For now, the rates of deactivation channels were successfully tuned by introducing substituents with various electronic properties at the Y-position (OH and NH₂, Figure 1) and two-electron donor (CH₃) electron acceptor (CF₃) functional groups at the Z-position.

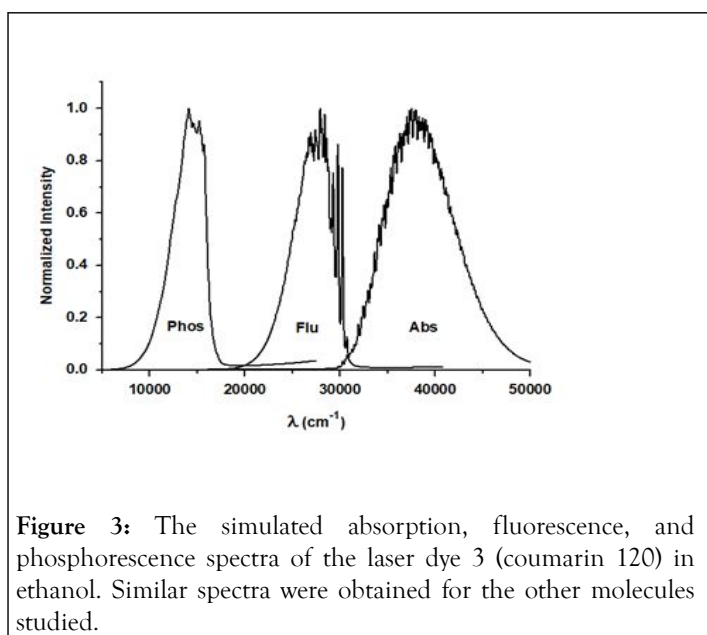


Figure 3: The simulated absorption, fluorescence, and phosphorescence spectra of the laser dye 3 (coumarin 120) in ethanol. Similar spectra were obtained for the other molecules studied.

A glance at Figure 3 reveals the effect of substituents on the non-radiative transition rate k_{ISC} and the radiative k_{flu} . Interestingly, a structural change in Y significantly influenced fluorescence, ICS, and phosphorescence rates (see Table 2). Substituting the OH group in dye 5 by the more electron-donating NH₂ group (dye 3) enhances k_{flu} and k_{pho} and slightly depresses k_{ICS} . The triplet state lifetime is most importantly shortened significantly, decreasing light loss by T → T absorption. In other words, shortening of a triplet-state lifetime due to the replacement of the OH group by the more electron-donating NH₂ group prevents or limits excessive Triplet-State Losses (TSLs) and enhances laser dye efficiency. Moreover, replacing the CH₃ group in 3 with the more electron-withdrawing CF₃ group in 4 further decreases the k_{ICS} value and renders dye 4 less efficient phosphorescent with a longer triplet lifetime dye, enabling considerable TLS.

Astonishingly, the N heteroatom in the X position, as in the carbostyryl 7 (dye 1), significantly depresses both k_{flu} and k_{pho} , noticeably enhances the k_{ISC} value relative to that of dye 3. Consequently, dye 1 should be a less efficient laser dye than dye 3. Molecule 2 behaves similarly to dye 1, indicating that its CF₃ group is of minor influence in this case.

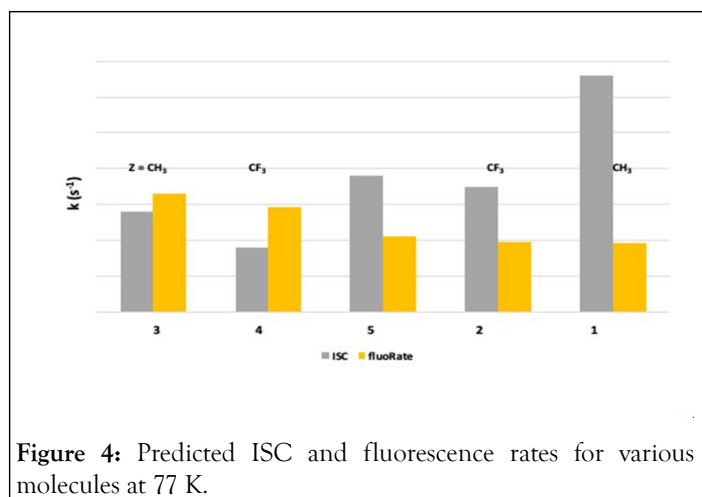


Figure 4: Predicted ISC and fluorescence rates for various molecules at 77 K.

Noteworthy mentioning that the experimentally available photophysical data in the literature [4,8,9-12] match our theoretically predicted parameters (see Table 2). To the best of our knowledge, the triplet state characteristics of all the molecules studied are not reported in the literature [11, 12]. Previous experimental research [11, 12] rolled out the possibility of ISC based on the absence of experimental proofs. However, it was generally assumed that the ISC process is partially responsible for the fast nonradiative deexcitation channel for the fluorescent state of many dyes in nonpolar solvents.

CONCLUSION

This paper aimed to simulate the missing excited-state dynamic parameters such as fluorescence, ISC, and phosphorescence rates of some extensively reported coumarin laser dyes induced by different substituents. Structural substituents that influence the simulated spectroscopic rates of coumarin laser dye derivatives for an efficient operation have been highlighted.

We found that all the NH₂-based dyes (3 and 4) show a much higher fluorescence rate with short-lived triplet-state than those of OH-(dye 5) or -N- heteroatom and NH₂-based molecules (1 and 2). The results obtained pave the way to enable designing new efficient laser dyes.

CONFLICT OF INTEREST

There is no conflict of interest.

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