Fluorescence Spectra and Determination of the Energy of O–O Transitions of Coumarins in Liquid Solutions

A. Bączyński, P. Targowski, B. Ziętek, and D. Radomska
Institute of Physics, N. Copernicus University, Toruń, Poland

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Analytical expressions of absorption and fluorescence spectra of some coumarins in ethyl alcohol at room temperature are given. Satisfactory agreement of measured and calculated spectra is obtained. It was possible to obtain the pure electronic transition energies immediately after excitation (from absorption spectra) and after the thermal and orientational equilibrium is reached (from fluorescence). An optical transition carries a dye-solvent system to a state in which the mutual interaction energy is larger than in the initial state.

Key words: Photoluminescence of solutions, Shapes of molecular spectra, Coumarins.

1. Introduction

Absorption and fluorescence spectra of dye molecules in liquid solutions are usually very broad and show only a few vibrational bands or are even structureless. This broadening is mainly due to the interaction between the dye molecule and the surrounding solvent molecules. In the vicinity of the maxima the spectra are Gaussian, which reflects that the dye molecules are perturbed randomly by many solvent molecules [1].

Usually the luminescent molecule with its nearest neighbourhood is called a luminescence center, the rest of the solution can be treated as a thermal bath. It is obvious that the spectral characteristics of a luminescence center differs considerably from that of the isolated molecule. The course of events after promoting the center to the first excited state is as follows: the absorption of light, which is assumed to be an instantaneous process, initiates photoluminescence accompanied by at least two relaxation processes, the vibrational and orientational relaxations. These relaxation processes are observed in time dependent fluorescence experiments with dyes in polar solutions, showing the characteristic dynamic Stokes shift of the fluorescence [2, 3].

The Stokes shift reflects the change of the energy of the luminescence center due to relaxation processes in its excited state. The transfer of the excess of vibrational energy in the excited state to the surroundings and the redistribution of the excess energy over all degrees of freedom is the reason of vibrational relaxation. The system tends to thermal equilibrium with a Boltzmann energy distribution in the excited state. On the other hand, the orientational relaxation is due to the fact that while the solvents electronic polarization can instantly adjust to a new dipole moment of the solute molecule, the solvents orientational polarization cannot. Therefore the solvent is out of orientational equilibrium and some time is required to reach the equilibrium. This process is accompanied with the minimization of the total energy of the luminescence center. Obviously the above mentioned relaxation processes occur simultaneously, which complicates investigations of excited states of molecules.

The relaxation processes influence not only the position of fluorescence bands but also change the shapes of fluorescence spectra. An experimental confirmation of this statement already exists. By careful examination, such changes of fluorescence spectra obtained by means of time-resolved emission spectroscopy [4, 5, 6] come out.

The time scales of the different relaxation processes are not equal. Assuming that the electronic transition is an immediate event, the vibrational relaxation needs about 10^{-12} s to be completed. On the other hand, the orientational relaxation is in this time scale a rather slow process and depends strongly on external conditions. In low viscosity liquids the orientational equilibrium is reached after a time shorter than the fluorescence lifetime.

Reprint requests to Prof. Dr. A. Bączyński, Institute of Physics, N. Copernicus University, ul. Grudziądzka 5, 87-100 Toruń, Poland.

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The transient behaviour of the fluorescence spectrum can be explained by the stochastic model [7], elaborated in several stochastic theories [3, 8–10]. The use of such models for the description of the behaviour of a dye in solution is justified by the fact that the dye molecule is perturbed by a large number of solvent molecules. The change of the energy difference between the ground and excited states can be thought as a Gaussian-Markovian process.

While stochastic theories in general explain spectral shifts of fluorescence in polar solvents, shapes of fluorescence and absorption spectra need a different description. This is because, independently of environmental effects, shapes of electronic spectra are determined by the dependence of transition moments on vibrational overlap integrals.

In this paper we present a model which takes account of relaxation effects and enables an analytical description of absorption and fluorescence spectra of dyes in polar solutions. In addition, an experimental procedure for the determination of the energy of pure electronic transitions is proposed. This seems to be of special importance because the O–O transition energy is the proper parameter to discuss the time dependence of the Stokes shift. The dynamic Stokes shift is discussed in terms of changes of maxima of fluorescence spectra.

2. Theoretical Background

The general description of electronic transitions in dye solutions is based on the Franck-Condon principle. For a dye-solvent system, because of its complexity, a rigorous quantum-mechanical formulation of this principle (like e.g. in [11]) is hardly useful. In practice, more or less justified approximations are used [12–14]. In the framework of the quasi-molecular model [15], the fluorescence spectrum can be expressed in the form

$$F(\varepsilon) = F_0\, \varepsilon^3 \int P_e(Q)\, \delta[W(Q) - \varepsilon]\, dQ\,. \tag{1}$$

In this formula, $W(Q) = W_e(Q) - W_g(Q)$, where $W_g(Q)$ and $W_e(Q)$ are the Born-Oppenheimer potentials for the ground and excited states, respectively, $P_e(Q)$ is the Boltzmann population distribution in the excited state and ε denotes energy. Such a description, depending only on one variable Q, is used in practice, but by no means should this variable be treated as a real coordinate, like in the configuration coordinate model used to describe luminescence spectra of solids [16]. A similar expression can be formulated for the absorption spectrum:

$$A(\varepsilon) = A_0\, \varepsilon \int P_g(Q)\, \delta[W(Q) - \varepsilon]\, dQ\,, \tag{2}$$

where $P_g(Q)$ is the population distribution in the ground state.

The above description was examined by Kinoshita et al. [1]. In the simplest one-variable model the adiabatic potential curves are parabolas. It was shown that equal shapes of potential functions for the ground and excited states lead to Gaussian shapes of the absorption as well as the emission spectra [1].

In reality, the fluorescence and absorption spectra of dye solutions are never Gaussian. In a more realistic model different parabolas are ascribed to different electronic states. The curvatures of the parabolas reflect the interaction strength between the dye molecules and the solvent. We write:

$$\begin{aligned} W_e(Q) &= c'(Q/Q_0 - 1)^2 + b\,, \\ W_g(Q) &= c(Q/Q_0)^2\,, \end{aligned} \tag{3}$$

where $Q = 0$ and $Q = Q_0$ are the minimum energy positions in the ground and excited state, respectively. The parameters c and c', with $c \neq c'$, fix the curvatures of the respective parabolas. The parameter b denotes the energy of pure electronic transition, equivalent to the energy of the O–O transition.

On integrating (1) with the energy difference $W(Q) = W_e(Q) - W_g(Q)$ defined by (3) and the distribution function in the excited state

$$P_e(Q) = \exp\{-[W_e(Q) - W_e(Q_0)]/kT\}\,,$$

and on integrating (2) with the same energy difference but with the distribution function in the ground state

$$P_g(Q) = \exp\{-W_g(Q)/kT\}\,,$$

the following expressions for the fluorescence and absorption spectra are obtained:

$$F(\varepsilon)/F_0 = \frac{\varepsilon^3}{R(\varepsilon)} \sum_{p=1}^{2} \exp\left\{\frac{-c'}{kT(c'-c)^2}\,[c + (-1)^p R(\varepsilon)]^2\right\}, \tag{4}$$

$$A(\varepsilon)/A_0 = \frac{\varepsilon}{R(\varepsilon)} \sum_{p=1}^{2} \exp\left\{\frac{-c}{kT(c'-c)^2}\,[c' + (-1)^p R(\varepsilon)]^2\right\}, \tag{5}$$

where

$$R(\varepsilon) = \sqrt{c c' - (c' - c)(b - \varepsilon)} \tag{6}$$

and F_0 and A_0 are normalization factors.

The parameters c, c', and b in (4) and (5) can be determined from fluorescence and absorption spectra as well. It turns out that c_a and c_f, c'_a, and c'_f, b_a, and b_f are not equal (subscripts a and f refer to the absorption and fluorescence, respectively). It has to be noted that the typical asymmetries of the fluorescence and absorption spectra of dyes in solutions are accounted for by taking different values of c and c'.

The expression (6) determines frequency intervals of validity of (4) and (5). Thus for fluorescence

$$R_f(\varepsilon) = \sqrt{c_f\, c'_f + (c_f - c'_f)(b_f - \varepsilon)} \tag{7}$$

with $c_f > c'_f$ and $\varepsilon < \varepsilon_{max}$, and for absorption

$$R_a(\varepsilon) = \sqrt{c_a\, c'_a + (c'_a - c_a)(\varepsilon - b_a)} \tag{8}$$

with $c'_a > c_a$ and $\varepsilon > \varepsilon_{min}$.

The unequalities $c_f > c'_f$ and $c_a < c'_a$ result from the Stokes principle. Limits of the spectra are given by the relation

$$\varepsilon_{max,\,min} = b_{f,a} - c_{f,a}\, c'_{f,a}/(c'_{f,a} - c_{f,a}),$$

where the square roots become zero. Such sharp limits of the fluorescence and absorption bands, which do not appear in experimentally obtained spectra, are due to the classical formulation of the Franck-Condon principle, applied in (1) and (2).

3. Experimental

We studied the fluorescence and absorption spectra of alcoholic coumarin solutions. Laser grade coumarins were purchased from Eastman-Kodak. The dyes were used without further purification and dissolved in spectroscopic grade ethanol (purchased from POCH-Gliwice) with a concentration of $5 \cdot 10^{-5}$ M to avoid concentrational effects in the electronic spectra.

The absorption spectra were measured with a commercially available spectrophotometer (Specord UV-VIS Zeiss, Jena). The peak position of the spectrum is reproducible within ± 20 cm^{-1} and the absorption profile uncertainty $\Delta A/A = 0.5\%$. The fluorescence spectra, obtained with a home made fluorimeter [17], were corrected for the wavelength dependent transmittance of the monochromator and the sensitivity of the detector. Stationary fluorescence measurements were made by a photon counting method under excitation with an intensity controlled Xenon lamp. Poisson statistics for the photon counting was assumed, so the error of the fluorescence intensity was estimated from the square root of the number of counts (in our case it was 0.3% of the maximal intensity). The uncertainty of the wavenumber determination in this case was ± 25 cm^{-1}.

A fitting procedure [18] of the analytical expressions (4) and (5) to the experimental spectra, together with χ^2 factor analysis, was applied. The numerical values of the parameters b, c, c' and the χ^2 factors were obtained independently from fluorescence and absorption. The fitting ranges were chosen such that the χ^2 test came out satisfactory.

4. Results and Discussion

Our results are presented in Tables 1 and 2, where the parameters defined in (3), together with the applied fitting ranges and positions of maxima ε_0 of the spectra and their halfwidths $\Delta\varepsilon_{1/2}$ are given. All quantities except χ^2 are in cm^{-1} units. As a representative, the measured and calculated fluorescence and absorption spectra of coumarin 120 in ethyl alcohol are shown in Figure 1. The calculated spectra of the other investigated coumarins coincide similarly well with the experimental ones, except for coumarin 340 where the fluorescence spectrum, shown in Fig. 2, does not coincide with the fitted one.

It is not surprising that the numerical values of the respective parameters presented in Tables 1 and 2 as obtained from absorption and emission spectra, are not equal. This is because of the orientational relaxation. After photo-excitation a nonequilibrated Franck-Condon state is reached while the fluorescence

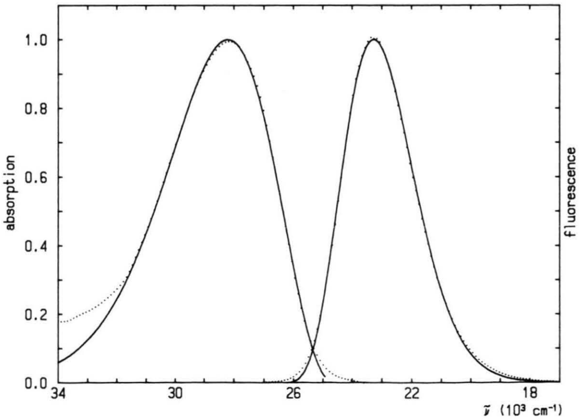

Fig. 1. Normalized absorption and fluorescence spectra of coumarin 120 in ethyl alcohol. Solid lines: spectra calculated from (4) and (5), dots: measured spectra.

Table 1. Spectroscopic parameters of coumarins (from fluorescence spectra).

Coumarin	b_f	c_f	c'_f	Fitting range	$\Delta\varepsilon_{1/2}$	ε_0	χ^2
120	24 701 ± 13	1875 ± 13	854 ± 12	20 000–25 600	2852	23 300	1.14
175	24 555 ± 14	2120 ± 14	1035 ± 15	19 500–25 500	2957	22 900	1.19
2	24 285 ± 11	1850 ± 11	866 ± 12	20 000–25 300	2801	22 900	1.17
138	24 131 ± 15	2153 ± 15	1109 ± 18	19 500–25 000	2918	22 400	0.73
10	22 861 ± 13	1707 ± 12	724 ± 12	19 000–24 000	2771	21 650	1.13
340	21 277 ± 9	1920 ± 8	817 ± 10	17 500–22 400	2926	19 900	7.65

Table 2. Spectroscopic parameters of coumarins (from absorption spectra).

Coumarin	b_a	c_a	c'_a	Fitting range	$\Delta\varepsilon_{1/2}$	ε_0	χ^2
120	25 992 ± 25	775 ± 15	2578 ± 22	25 000–31 500	4368	28 200	0.46
175	25 733 ± 27	752 ± 18	2366 ± 24	24 650–31 000	4071	27 850	0.40
2	25 515 ± 17	628 ± 9	2161 ± 15	24 650–31 000	4039	27 262	0.69
138	25 469 ± 18	745 ± 12	2257 ± 15	24 500–30 000	3898	27 400	1.14
10	24 086 ± 16	768 ± 9	2621 ± 15	23 250–30 500	4467	26 350	1.04
340	22 560 ± 22	775 ± 14	2412 ± 19	21 500–28 000	4099	24 700	0.56

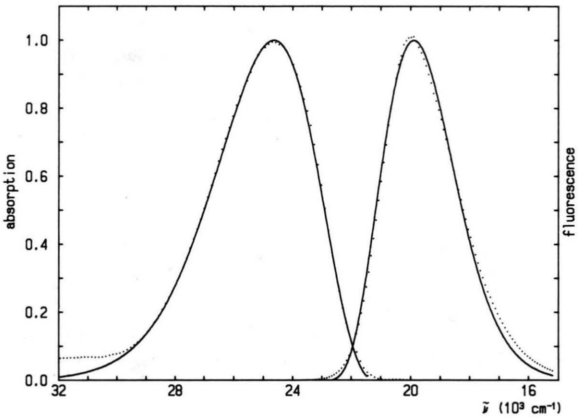

Fig. 2. Normalized absorption and fluorescence spectra of coumarin 340 in ethyl alcohol. Solid lines: spectra calculated from (4) and (5), dots: measured spectra.

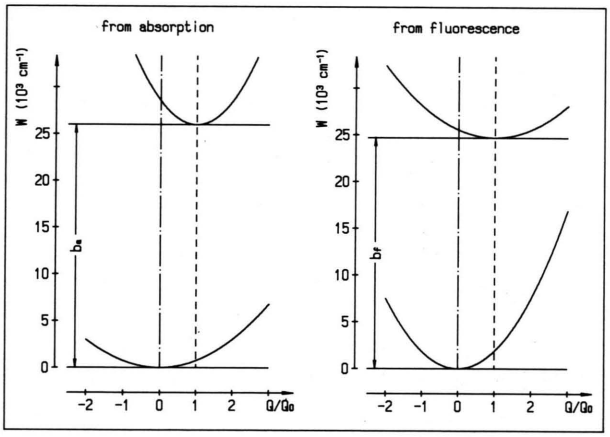

Fig. 3. Potential curves for a dye-solvent system obtained from absorption and fluorescence spectra of coumarin 120.

transition originates from a different, almost relaxed excited state to a nonequilibrated ground state. As a consequence, the parameters *b*, *c*, and *c'* from the two spectra reflect different stages of the environmental relaxation process. The difference in the *b* values is in agreement with the conception of a molecular four level scheme, introduced by Mataga [19].

The two pairs of parabolas, calculated with the parameters for coumarin 120 are demonstrated in Figure 3. They are drawn in the form of two independent schemes because in the framework of the presented model, the relaxation energy in a definite electronic state is not available.

The curvatures of the parabolas of the initial states are smaller than those of the final states, i.e. $c_a < c'_a$ and $c'_f < c_f$. These inequalities are valid for all investigated coumarins. Not the absolute values of the *c* numbers but their mutual relations are responsible for the extension and the halfwidth of the spectrum. Such big halfwidths of the absorption spectra and the differences between c_a and c'_a may be due to the fact that in the case of the investigated dyes, the electronic transition to the first excited state may be accompanied with intramolecular charge transfer [20].

Immediately after excitation the luminescence center will be in a state of orientational non-equilibrium, and from then on will tend to reach the equilibrium. The relation $c'_a > c'_f$, which is also easily noticeable in the tables, suggests that the c parameters describe the state of equilibrium of the system.

The halfwidths of the absorption spectra of the investigated coumarins are almost about 1000 cm^{-1} larger than the halfwidths of fluorescence spectra. No direct correlation exists between the halfwidth of a spectrum and the numerical values of the proper c parameter. However, there exists a correlation between the halfwidth and the ratios c'_a/c_a and c_f/c'_f. It can be stated that the ratios c/c' give information about the change of the interaction of dye molecule with the surroundings followed by an electronic transition.

The revealed disagreement between the calculated and measured fluorescence spectrum of coumarin 340 (see Fig. 2 and Table 1) indicates that in this case either the fluorescence spectrum is due to the emission from more than one fluorescent species, or the vibronic structure of the excited state is displayed. This shows that (4) and (5) are not valid for all the absorbing and emitting dye solutions. However one can expect that investigations of the validity of these formulae in specific systems will deliver new informations about the physical and chemical properties of dyes in liquid solutions.

5. Summary

Analytical expressions for absorption and fluorescence spectra of liquid coumarin solutions are given. It is shown that a quasi-molecular model of the luminescence center with the potential energy difference approximated by function of one variable only, enables a good description of the electronic spectra of coumarins in ethyl alcohol. The energies of O–O transitions immediately after excitation (from absorption spectra) and after thermal and orientational equilibrium is reached (from fluorescence spectra) could be obtained. Such an analysis could give information about the equilibrium of the system when time resolved fluorescence spectra would be available.

The very important result, in agreement with the Stokes principle, is that the c parameters of the final states are always larger than those of the initial ones. It means that, as expected, after an optical transition a dye-solvent system is brought to a state, where the interaction energy is larger than in the initial state. Therefore by no means the system can be brought to exactly the same initial state via fluorescence. This is the reason of the observed asymmetry of the fluorescence and absorption spectra.

The obtained analytical expressions for absorption and fluorescence spectra prove their usefulness for the precise determination of the mean frequencies of absorption and fluorescence. The mean frequencies are used for the determination of correlation functions of Stokes shifts [21].

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