Journal of Fluorescence, Vol. 3, No. 1, 1993

Wavelength Dependence of Fluorescence Spectra of Liquid Coumarin Solutions

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Received March 5, 1993; revised April 1, 1993; accepted April 16, 1993

The excitation wavelength dependence of steady-state fluorescence spectra of low-viscosity dye solutions is reexamined. Measurements are made on some coumarins in methyl alcohol at room temperature. It is found that the fluorescence spectra depend on the excitation energy and their profile changes are due to the excitation wavelength dependence of reorientation processes in the excited state.

KEY WORDS: Photoluminescence of solutions; fluorescence spectra; coumarins.

INTRODUCTION

It has been known since the end of the 19th century that the fluorescence spectra of liquid dye solutions do not depend on the frequency of the excitation light. Such a conclusion was formulated for the first time by Lommel [1,2] on the basis of his experimental results. Later this opinion was justified by the extensive work of Nichols and Merritt [3], by Jabloński [4] and others.

The contemporary measurements based on a more sophisticated photoelectric methods seem to justify such a view, but with some limitations (e.g., liquid solution of some single-component substance [5–7]). Consequently it may be (and it has been) shown experimentally that some well-defined dependence of the fluorescence spectrum profile on the frequency of exciting light does exist and can be easily observed in bicomponent systems [8], in viscous, and in solid dye solutions [9–13]. Similarly dye solutions solidified at low temperatures reveal the same effect [14].

We would like to call a special attention to the fact of a pronounced excitation wavelength dependence of the fluorescence spectra of viscous or solid solutions as compared to the fluorescence spectra of the low-viscosity solutions where the wavelength dependence effect seems to vanish completely. To specify properly the conclusion from the above observation, let us consider briefly the process of absorption and emission taking place in a liquid fluorescing dye solution.

The act of absorption introduces a certain amount of energy into the luminescence center. Therefore it requires, generally speaking, some new equilibrium state to be formed in the electronic charge distribution characteristics for the excited state of the quasi-molecule (center). The quasi-molecule is meant as a dye molecule and its nearest neighborhood. Consequently we may expect some degree of reorientation of the molecules of the solvent with respect to the dye molecule. We may also safely state that reorientation processes, leading the whole system into a new equilibrium state, will be rather difficult to perform in the solid media (solid or solidified solutions). Therefore we may imply that the time constant for such relaxation process may be generally larger as compared to the time constants of the fluorescence process.

On the other hand, the reorientation process in low-viscosity media is rather fast, so that the time constants are few orders of magnitude smaller than the average

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1053-0509/93/0300-0017$07.00/0

decay time of the fluorescence emission. Hence it follows that the experimental evidence seems to indicate clearly on an existence of a very specific correlation between the effect of excitation energy dependence of the fluorescence spectra and the speed of the reorientation process.

In conclusion, we may state the following: if the relaxation processes are slow compared to the fluorescence decay time ($\tau_R > \tau_F$), then this will imply that these processes are sensitive to the frequency of the excitation light, and as a consequence it is expected that the frequency distribution of the fluorescence is also a function of the exciting light energy. The vice versa statement seems also to be true: if by means of an experiment we find some traces of dependence of the spectral profile of fluorescence on the wavelength of the excitation light, then by the same token as above, we conclude that the relaxation processes are also excitation energy dependent. This was demonstrated for high-viscosity solutions of Rh B in glycerol and propylene glycol [13] as well as for low-viscosity solutions of some stilbene derivatives in chlorobenzene, where the excited state mean lifetime $\tau_F < 10$ ps [15].

We further believe that the present degree of precision in experimental techniques of measurements of the spectral distributions of luminescence and related with them computer analysis, simulations, curve fitting, etc., justify a new approach to the old problem. Furthermore, we also hope to employ in our study the quasi-molecular model of luminescence spectra which we developed recently [16,17].

The analysis based on this theoretical approach leads (generally) to a set of molecular parameters proven to be extremely sensitive to some physical changes in a quasi-molecule, due to the absorption-relaxation-emission processes. Therefore we have reason to believe that a combined result of an extremely sophisticated method of measurements as well as a new theoretical approach to the electronic spectra with a brand new tool of interpretation may lead to some new, perhaps more precise results and conclusions on this fundamental topic of absorption-relaxation-emission processes of dye molecules in liquid solvents. As an object in our studies we have chosen some representation of coumarin family dissolved in a polar solvent.

EXPERIMENTAL

The study of fluorescence spectra as a function of the wavelength of exciting light was performed using alcoholic solutions of coumarin 2, coumarin 10, and coumarin 120. Laser grade coumarins (Eastman-Kodak) were dissolved without further purification in a spectroscopic-grade methyl alcohol with dye concentration of $1*10^{-5} M$.

All measurements were performed using a highly modified spectrosopic system described in detail previously [18]. The basic principle of our method of investigation was that of photon counting. By means of cooling of the photomultiplier tube, we obtained some sizable reduction of the background counts, and consequently we were able to obtain a very high dynamics of the measurements. In fact for the maximum intensity of the emission spectrum, we have had on the average $1:10^5$ ratio of the dark counts to the signal counts, which secured a rather high precision of all measurements.

It has to be mentioned that the possible intensity fluctuations of the excitation source was monitored by means of a separate PM tube and corrections via computer were introduced into the final signal-point of the spectral profile. Each spectral curve of fluorescence is defined by means of about 500 experimental points, each of which is processed by a computer procedure including the dispersion of the monochromator, PM-tube sensitivity, etc. The applied fitting procedure of experimental data to an analytical expression of the spectrum provides for numerical values of some molecular parameters determining the spectral profiles. To avoid numerical faults, no smoothing procedures were applied to the spectra.

THEORETICAL BACKGROUND

In the case of polyatomic molecules in polar solvents a classical formulation of the Franck–Condon principle can be used. In this formulation the fluorescence spectrum profile can be expressed as

$$F(\epsilon) = F_0 * \epsilon^3 \int P_e(z)\delta[\Delta V(z) - \epsilon]dz \qquad (1)$$

where $P_e(z)$ is the Boltzmann population distribution in the initial state of fluorescence, $\Delta V(z) = (W_e - W_g)$ is the energy difference between the excited and the ground state, ϵ is the transition frequency, F_0 is the normalization factor, and z is the relative displacement from the equilibrium position.

To derive an analytical expression for a fluorescence spectrum, the existence of some low-energy vibrations in liquid dye solutions was postulated [16]. The recent results of transient spectral hole burning experiments indicate that some phonon-type vibrations in low-viscosity liquids are present in a short distance region [19,20]. These vibrations justify the assumption of the

continuous distribution of sublevels in both the states, the initial and final stages of fluorescence.

It was shown that there exists an analytical expression of spectrum (1) with the energy difference ΔV in harmonic approximation. This expression for the frequency distribution of fluorescence of a quasi-molecule is

$$F(\epsilon)/F_0 = \epsilon^3/N(\epsilon) * \sum_{p=1}^{2} \exp\{-c'[c + (-1)^p N(\epsilon)]^2/kT(c' - c)^2\} \quad (2)$$

with

$$N(\epsilon) = \sqrt[2]{cc' - (c' - c)(b - \epsilon)} \quad \text{for} \quad \epsilon < \epsilon_{\text{lim}} = b + cc'/(c - c')$$

The above parameters are the 0–0 energy difference b, and the parameters determining the coupling of electronic states of the dye molecules with those of the solvent in the ground and excited states c and c', respectively [20]. The frequency interval of the fluorescence distribution given by (2) has a short wavelength limit ϵ_{lim}, where the classical formulation of the Franck–Condon principle can not be used any more. It appears that this frequency limit falls within the short-length wings of the spectra of investigated solutions.

The two contributions to the intensity distribution in (2) are not equally important. The intensity distribution for $p = 1$ contains about 99% of the whole intensity but because the investigated effect was so small, the fitting procedure was carried out with the entire formula.

RESULTS

Fluorescence spectra of alcoholic solutions of investigated coumarins were recorded for different excitation wavelengths in the main absorption bands. Measurements were carried out at room temperature. A nonlinear fitting procedure was applied and the parameters appearing in (2) were determined. These parameters contain some information about the interactions and the relaxation processes occurring in the solution. These results are given in Table I.

The results obtained indicate that the molecular parameters b, c, and c' are, in a limited but observable scope, excitation energy dependent. The numerical values of these parameters depend on the excitation wavelength. They increase when the system is excited to higher sublevels of the first excited state. This effect appears in all the investigated solutions, but the most pronounced effect is observed for the coumarin 10 solution presented in Table I.

The dependence of the parameters on the excitation wavelength is depicted in Figs. 1–3. For the sake of better visualization, a linear fit was applied to the calculated points. The linear fit in this case is to show the tendency of the observed wavelength dependence of the parameters. The unequal changes of these parameters observed for solutions of different dyes (see Fig. 5) indicate that this effect is, to some extent, structure sensitive.

DISCUSSION

The observed excitation wavelength dependence of the fluorescence spectra of liquid dye solutions of coumarins in alcohol leads to the following picture. The excited quasi-molecule is to be found in one of the vibrational states of the produced Franck–Condon state, depending on the excitation energy. It is reasonable to assume that, as in more viscous systems [13], the achieved equilibrated initial state of fluorescence will not remember the way of excitation. Hence the initial state of fluorescence of the equilibrated quasi-molecule is, like the excited Franck–Condon state, a well-defined one.

The different characteristics of the steady-state fluorescence spectra obtained for different excitation energies reflect the production of various nonequilibrated, intermediate states of the system, when excited by different excitation energies. In other words, the excitation wavelength dependence of the fluorescence spectra reflects the fact that several solvent conformations are formed, depending on the excitation energies. Because of the competition between the various relaxation processes in the excited state, a distribution rather than a particular solvent conformation will be formed. The higher the excitation energy, the greater the amount of the solvent conformations that will be present simultaneously in the initial instants after excitation.

A quantitative evaluation of this effect cannot be performed on the basis of the steady-state fluorescence spectra. Nevertheless, the wavelength dependence of fluorescence spectra implies a wavelength dependence of the parameters b, c, and c'. Such behavior of the parameters would be clearly observable in the time-resolved spectral investigations. In the case of the steady-state spectra these parameters represent their mean values lying in between an interval determined, on one side, by the prompt fluorescence parameters and, on the other, by the equilibrated excited-state parameters.

The magnitude of the wavelength dependence of

Table 1. The Excitation Energy Dependence of Molecular Parameters of Investigated Coumarins in Methyl Alcohol

λ_{ex} (nm)	Coumarin 10 (cm^{-1})			Coumarin 2 (cm^{-1})			Coumarin 120 (cm^{-1})			ν_{ex} (cm^{-1})
	b	*c*	*c'*	*b*	*c*	*c'*	*b*	*c*	*c'*	
340	22,909	1,739	694	24,291	1,887	848	24,628	1,817	769	29,412
350	22,886	1,728	692	24,284	1,878	849	24,619	1,815	764	28,571
360	22,844	1,694	662	24,268	1,868	826				27,778
370	22,820	1,674	652	24,257	1,857	818	24,541	1,752	690	27,027
380	22,813	1,672	652	24,264	1,866	830	24,537	1,754	690	26,316
390	22,802	1,663	641	24,264	1,882	837	24,546	1,798	709	25,641
400	22,794	1,651	635	24,224	1,878	814				25,000
410	22,771	1,638	625							24,390
440	22,746	1,624	601							22,727

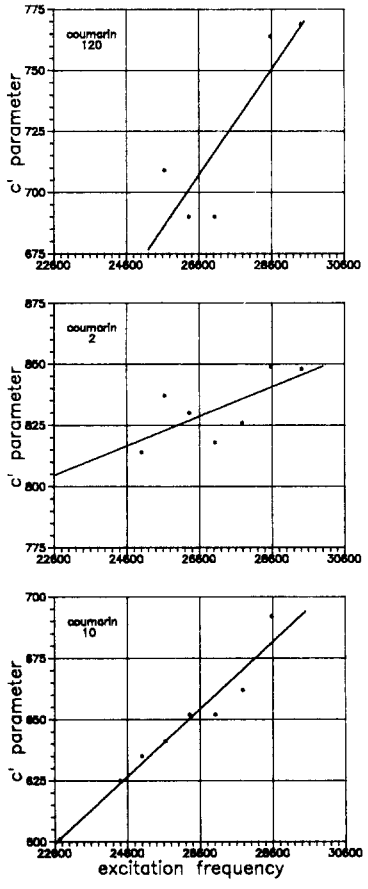

Fig. 1. The excitation wavelength dependence of the coupling parameters of the initial state of fluorescence.

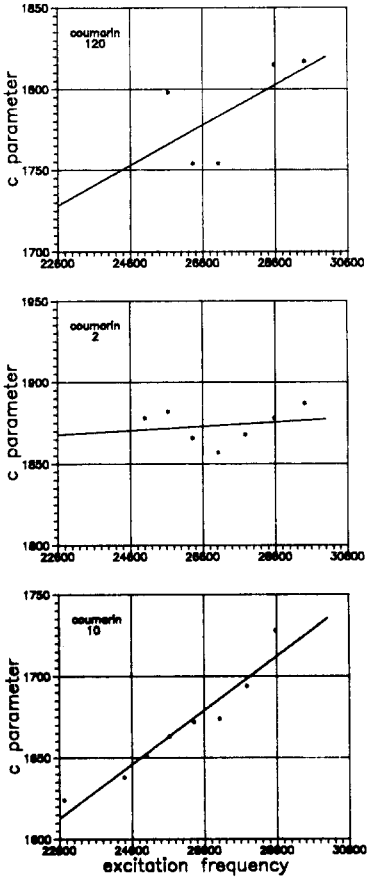

Fig. 2. The excitation wavelength dependence of the coupling parameters of the final state of fluorescence.

stationary fluorescence spectra of liquid dye solutions depends on the relaxation processes occurring in the excited state. The most important ones are the vibrational relaxation, the cooling effect of the quasi-molecule, and the orientational relaxation. The rate constants of these processes are not equal and depend on the kind of the

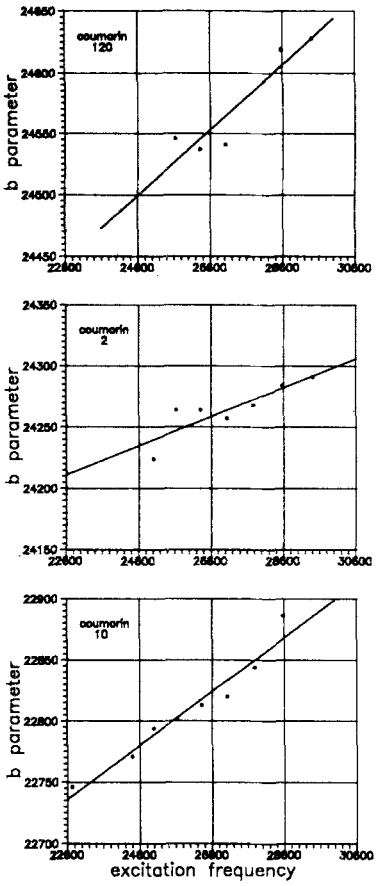

Fig. 3. The excitation wavelength dependence of the 0–0 energy differences of investigated coumarin solutions.

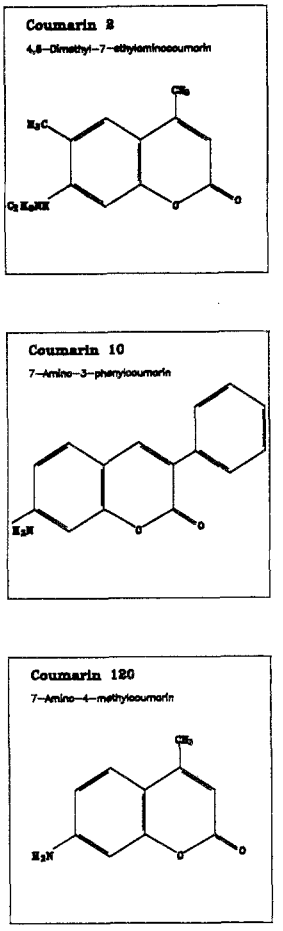

Fig. 5. Structures of dye molecules.

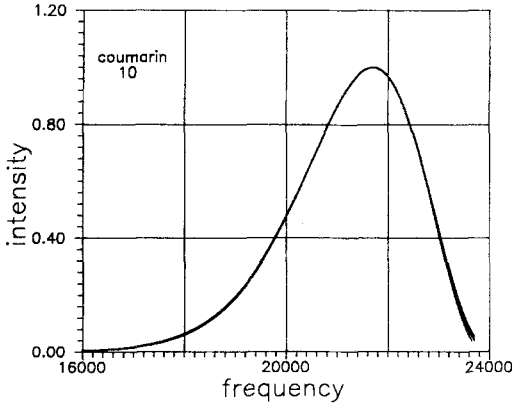

Fig. 4. Normalized fluorescence spectra of a coumarin 10 solution. The applied excitation wavelengths are 340, 380, 400, and 440 nm, respectively.

dye as well as on the properties of the solvent used, and in low-visosity solutions they are usually some orders of magnitude larger than the fluorescence rate constant.

The relaxation processes mentioned above do not influence the spectra in the same way. The vibrational relaxation which ensures the Boltzmann distribution of the population of vibrational sublevels is too fast to be recorded directly in the stationary emission spectra. The same seems to be true for the cooling process, which ensures overall thermal equilibrium of the system. The only process which can be of some importance in differentiating the intermediate states is the solvent relaxation around the dye molecule.

It appears that this reorientation process depends on the excitation energy. It starts before the vibrational and cooling processes are accomplished. Only the short-time values of the excited-state parameters are responsible for the deviation from their means because only in this time interval are the solvent conformations well displaced from

the equilibrium conformation around the excited molecule.

This point of view is in agreement with the conclusions derived by Kawski and his group on the basis of their investigations of the wavelength dependence of stationary fluorescence spectra of some stilbene derivatives in chlorobenzene [15]. This system is rather exceptional because of the extremely short fluorescence decay time, of the order of 10 ps. In this particular case, despite the fact that the solution belongs to the low-viscosity liquids, it behaves like a high-viscosity liquid in the respect that no time is left for reorientation to be completed.

The excitation energy dependence of relaxation processes of the excited state alone would not be able to account for the observed wavelength dependence of the steady-state spectra unless the final states of fluorescence were considered. We would like to refer here to the fact that the appearance of the fluorescence spectra requires that the coupling parameters of the ground and excited states, respectively, always fulfill the inequality relation $c > c'$ [16].

It must be mentioned that the fluorescence spectra are red shifted compared to the prompt spectra. In addition to shifting, it is observed that the spectral bands narrow with time [21]. Such behavior of a polar dye solution is accounted for in the quasi-molecule model of the spectra [17]. This explains the fact that the manifestation of the excitation wavelength dependence of the steady-state fluorescence spectra appears on the short wavelength wings of the spectra, in agreement with observations (see Fig. 4).

Knowing the wavelength dependence of b, c, and c', the fluorescence spectra for different excitation energies were calculated and are depicted in Fig. 4. Such a small effect, lying almost in the line width of the figures, explains why the wavelength dependence of the fluorescence spectra of low-viscosity solutions, with "normal" nanosecond fluorescence decays, was not detected till now. The practical significance of this result is that formula (2) provides an adequate representation of the steady-state fluorescence spectra, despite the fact that they are constituted of contributions from many time intervals.

The main conclusion which can be drawn from this work is that fluorescence spectra depend on the energy of excitation because of the excitation energy dependence of the reorientation processes which follow the promotion of the system to the excited state. It is a matter of the accuracy of spectral measurements only that wavelength-dependent spectral shiftings and broadenings will show up in the steady-state spectra.

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