Franck-Condon States of Coumarins in Alcoholic Solutions

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Z. Naturforsch. **45a,** 1349–1353 (1990); received March 6, 1990

The temperature dependence of the fluorescence spectra of coumarin 2, coumarin 10 and coumarin 120 in ethyl alcohol is investigated. A blue-shift of the spectra with increase of temperature is observed. The blue-shift is explained by means of excited and ground Franck-Condon state parameters obtained by the adjustment of analytical shape factors to experimental spectra.

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

1. Introduction

Several mathematical descriptions of the fluorescence spectra of liquid dye solutions have been proposed [1–6]. Recently we proposed a new one for some liquid coumarin solutions [7], in which we used the concept that the dye molecule, together with the surrounding solvent forms a kind of quasi-molecule. This concept was known for a long time [8]. The total energy of such a quasi-molecule consists of the modified electronic and vibrational energies of the solute molecule and the interaction energy of the solute with solvent molecules in the co-sphere.

The forces acting between solute and solvent molecules are much smaller than the forces between the atoms of the molecules. However, in some cases they are strong enough to force librations of the dye molecules about some equilibrium orientations. Typical separations between resulting energy levels are of the order of few cm^{-1} [9, 10].

There exists another picture, where it is postulated that the energy of a solute molecule, modified by the surroundings, is a stochastic variable. The source of stochasticity is the reservoir's noise, which is assumed to be Gaussian. According to this picture a distribution of solute-solvent interaction energies and the existence of a minimum of the interaction energy in each state is assumed.

In both approaches, the common and basic assumptions are on one hand the existence of some equilibrium orientations, and on the other the existence of closely spaced energy levels. The latter assumption may be considered as experimentally confirmed by the hole burning effect measurements in liquid dye solutions [11]. To get theoretical shape factors of the electronic spectra of dyes in liquid solutions at room temperature, a continuum of sublevels in the ground and excited states with Boltzmann population distribution in both states is postulated. For systems with many degrees of freedom and with closely spaced energy levels, like dye solutions, the application of the classical formulation of the Franck-Condon principle is justified.

The interaction of the quasi-molecule with the electromagnetic radiation field rises the system to a Franck-Condon (F.C.) state. It has to be emphasized that the final state of such a system, reached by prompt fluorescence, is not the initial state just before absorption, but a Franck-Condon ground state in which the solute molecule in the ground state and its surroundings are not adjusted.

The F.C. states, in the excited as well as in the ground states, undergo slow evolution processes. Such evolutions consist mainly in orientational relaxation (see [12] and references therein). The evolution of the excited F.C. states and reorientational times can be measured with time-resolved spectroscopy [13–15].

The aim of this paper is to show how different stages of orientational relaxation in the excited state manifest themselves in the fluorescence spectra and what knowledge can be gained from these spectra about the resulting F.C. ground states. Experimental technique was applied which utilizes the temperature quenching of luminescence. In such a way a shortening of the mean life-time of the excited state can be achieved without drastic changes of chemical properties of the solution. This allows to follow the changes of F.C.

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states in the final stages of their evolution. In addition, further properties of the mathematical model proposed in [7] are discussed.

2. The Model of a Fluorescent Molecule Strongly Interacting with a Polar Solvent

The fact that fluorescence spectra of some alcoholic solutions of coumarins at room temperature can be described by the simple formula

$$F(\varepsilon) = f(\varepsilon)/f(\varepsilon_{\mathrm{m}}) \tag{1}$$

with

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

proves that the model of a fluorescent molecule with its nearest neighborhood, elaborated in [7], is reasonable at least for a particular class of solutions of polyatomic molecules. In this formula, ε is the electronic transition frequency and ε_{m} its value in the emission maximum. c and c' are appropriate parameters of the ground and excited states, respectively, b is the 0–0 transition frequency and

$$R(\varepsilon) = \sqrt{c\,c' - (c'-c)(b-\varepsilon)}\,.$$

For kT, ε and the parameters, the unit cm^{-1} is used throughout. The numerical values of the parameters are obtained by adjustment of (1) to the experimental spectra.

The admission of oscillations of a molecule in the external field of the solvent is equivalent to the acceptance of a momentary dependence of its energy on a parameter $y = Q/Q_0$, giving the displacement from the equilibrium position. For small displacements, the expansion of the energy of the ground and excited states, respectively, yields

$$W_{\mathrm{g}}(y) = W_{\mathrm{g}}(0) + 1/2\,(\partial^2 W_g/\partial y^2)_{y=0}\, y^2, \tag{2}$$

$$W_{\mathrm{e}}(y) = W_e(1) + 1/2\,(\partial^2 W_{\mathrm{e}}/\partial y^2)_{y=1}\,(y-1)^2 \tag{3}$$

with the energy minimum at $Q=0$ or at $y=0$ in the ground and at $Q=Q_0$ or at $y=1$ in the excited state.

Equations (2) and (3) can be rewritten in the form

$$W_{\mathrm{g}}(y) = c\,y^2, \tag{4}$$

$$W_{\mathrm{e}}(y) = c'(y-1)^2 + b, \tag{5}$$

where $c = 1/2\,(\partial^2 W_{\mathrm{g}}/\partial y^2)_{y=0}$, $c' = 1/2\,(\partial^2 W_{\mathrm{e}}/\partial y^2)_{y=1}$ and $b = W_{\mathrm{e}}(1) - W_{\mathrm{g}}(0)$, being the 0–0 transition frequency. This parameter contains the constant part of the interaction energy and also the structure-dependent characteristics of the excited state of the solute molecule. The energies (4) and (5) are similar to those used in [16, 17] except the c parameters in the ground and excited states being not equal. These expressions are the basis to obtain analytical formulae for the absorption and fluorescence spectra of some coumarins in ethyl alcohol [7].

The stochastic theories [18–20] lead to similar analytical expressions for electronic spectra. The main assumption in this approach is a Gaussian distribution of interaction energies with a most probable one identified with the energy in the equilibrium position. In both approaches the energies of the ground and excited states are similar to the energy of a harmonic oscillator [21], but the physical interpretation of the parameters appearing in (4) and (5) would be different.

3. Experimental

The temperature dependence of the shape of the fluorescence spectra of alcoholic solutions of coumarin 2, coumarin 10 and coumarin 120 was investigated. Laser grade coumarins (Eastman-Kodak) were dissolved without further purification in spectroscopic grade ethanol (POCH-Gliwice) with a concentration of $5 \cdot 10^{-5}$ M. The fluorescence spectra were measured in the temperature interval 290–330 K as in [7].

The fitting of the experimental spectra to the analytical expression (1), described in [7], results in the numerical values of the parameters b, c and c'. The calculations were performed by means of an IBM AT computer. The result of the performed analysis depends strongly on the quality of the experimental fluorescence spectra. It appears that the achieved precision of the spectral measurements of dye solutions with stationary excitation [7, 22] is satisfactory.

4. Results and Discussion

In Fig. 1 the fluorescence spectra of coumarin 120 in ethyl alcohol ($5 \cdot 10^{-5}$ M) at 300 and at 340 K are presented, showing the precision of the experimental spectra and the adjustment of the analytical formula. Similar spectra can be easily obtained with the parameters given in Table 1. The experimentally obtained spectra are steady-state ones, so the determined parameters represent time integrated values of the

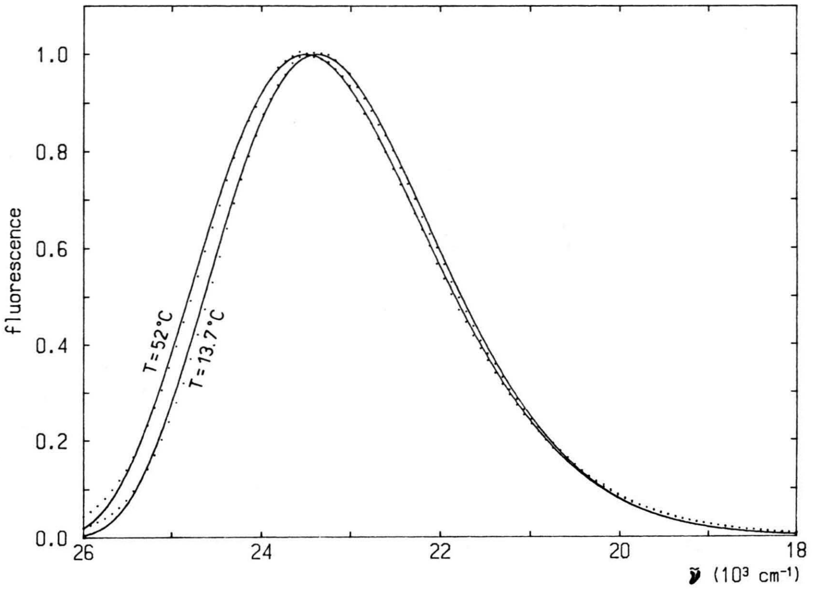

Fig. 1. Fluorescence spectra of cumarin 120 in ethyl alcohol at 13.7 °C and at 52 °C as assigned. Dots: experimental, solid lines: fitted using (1).

Table 1. Temperature dependence of spectroscopic parameters (in cm^{-1}).

	t [°C]	b	c	c'	ε_0	$\Delta\varepsilon_{1/2}$
Coumarin 2	13.1	24 441 ± 10	1909 ± 10	869 ± 10	22 977	2847
	26.8	24 460 ± 11	1873 ± 10	867 ± 11	23 037	2860
	34.7	24 484 ± 11	1903 ± 10	889 ± 11	23 040	2906
	42.7	24 495 ± 11	1875 ± 10	884 ± 11	23 081	2907
	50.8	24 522 ± 12	1893 ± 11	880 ± 11	23 113	2968
Coumarin 10	13.4	22 985 ± 9	1756 ± 8	714 ± 8	21 742	2827
	20.8	22 991 ± 10	1760 ± 9	730 ± 9	21 743	2841
	31.9	23 007 ± 10	1768 ± 9	748 ± 9	21 757	2873
	40.2	23 023 ± 11	1773 ± 9	758 ± 10	21 774	2899
	49.7	23 039 ± 11	1785 ± 10	782 ± 10	21 777	2921
Coumarin 120	13.7	24 757 ± 11	1850 ± 11	792 ± 10	23 382	2868
	23.0	24 780 ± 12	1848 ± 11	805 ± 11	23 410	2888
	33.3	24 802 ± 12	1851 ± 12	815 ± 11	23 438	2922
	42.2	24 829 ± 13	1858 ± 12	829 ± 12	23 463	2949
	52.0	24 866 ± 14	1855 ± 13	839 ± 12	23 508	2972

parameters of the initial and final states of fluorescence with decreasing effective integration time when the temperature is increasing. The 0–0 transition frequencies (the b parameters) and the c parameters increase with increasing temperature.

The most important characteristic of the observed fluorescence is the 0–0 transition frequency and the position of the maximum of the spectrum. Both increase with temperature in the 300 K–340 K interval (Figs. 2 and 3), the latter with a relative blue-shift $\Delta\varepsilon_0/\varepsilon_0 \Delta T \cong 10^{-4}$/K. It has to be emphasized that this blue-shift is not caused by a new distribution of the population when the temperature is raised. The shift of the spectrum due to this effect is smaller and is cared of by (1) separately. The behaviour of coumarins in ethyl alcohol differs considerably from the behaviour of Rh6G in glycerol and eosin in ethyl-glycol, where a red-shift is reported [15].

To explain the shift of the spectra of dyes in solutions with increase of temperature one has to consider two effects:

1) the temperature quenching, which results in the shortening of τ_f,
2) the increase of thermal motions of the system and the decrease of the macroscopic viscosity of the solution.

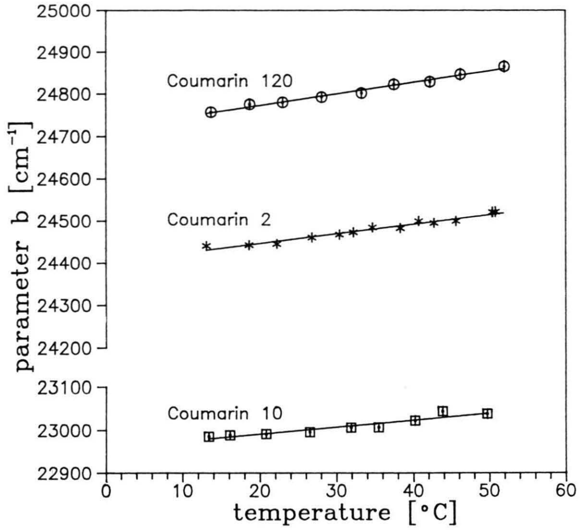

Fig. 2. 0–0 transition frequencies versus temperature.

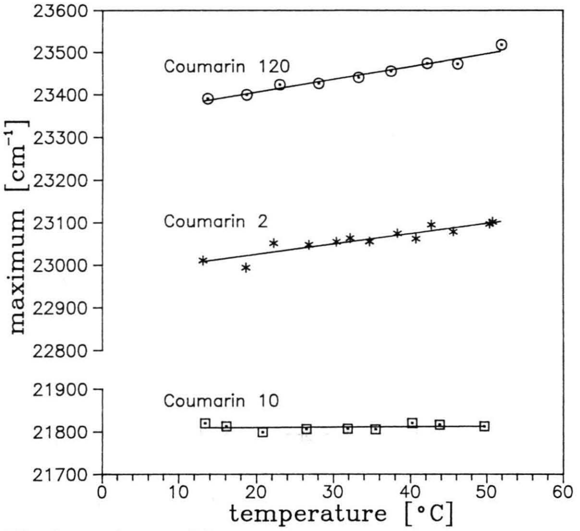

Fig. 3. Maximum of fluorescence spectra versus temperature.

The first effect will cause a blue-shift while the second a red-shift. Most probably the two effects are active simultaneously.

The values of c', the parameter of the excited state, depend on the interaction energy of the dye molecule with the solvent and express the state of adjustment of the excited molecule to its surroundings. The smaller c', the closer is the system to a state of equilibrium. The highest values of this parameter are recorded in the absorption spectra [7].

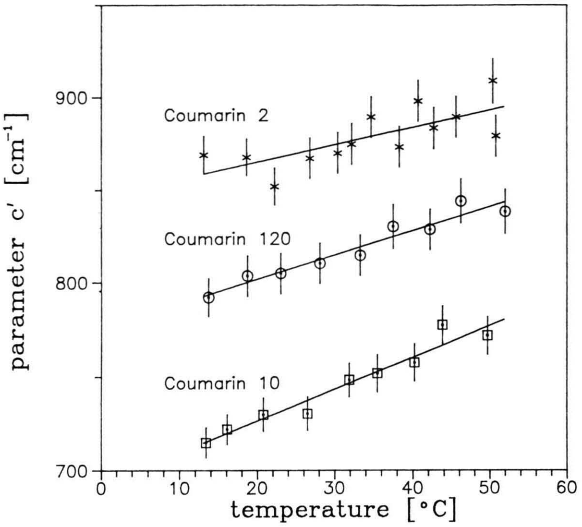

Fig. 4. Parameters c' versus temperature.

The dependence of c' on temperature, given in Fig. 4, helps to chose the effect which is dominantly responsible for the observed solvatochromic effect. In the case of coumarins in ethyl alcohol it seems that the shortening of τ_f is responsible for the observed blue-shift. Evidently, in spite of the fact that the energy diffuses into the solvent after several picoseconds [15], the solvatochromism associated with the change of the transition frequency due to rotation or translation of the polar solvent molecules, is observable in the steady-state fluorescene spectra.

The values of c, the parameter of the ground state, are about three times larger than the parameters of the initial fluorescence states (see Table 1). This means that the F.C. ground state reached by fluorescence is highly out of equilibrium. There is a temperature dependence of c (Figure 5). It follows, however, that in this case the projection of the relaxation process in the excited state is a secondary effect.

From (1) the halfwidths of the spectra can be calculated. It follows that these characteristics depend on the ratios c'/c. Because the c' parameter is more sensitive to temperature changes than c, the halfwidth is increasing with temperature. However the obtained increase is small, of the order of 100 cm^{-1} when the temperature change is 40 °C. The attained precision of the experimental results and the performed analysis has to be notified. Changes of the parameter values of the order of few cm^{-1} can easily be distinguished.

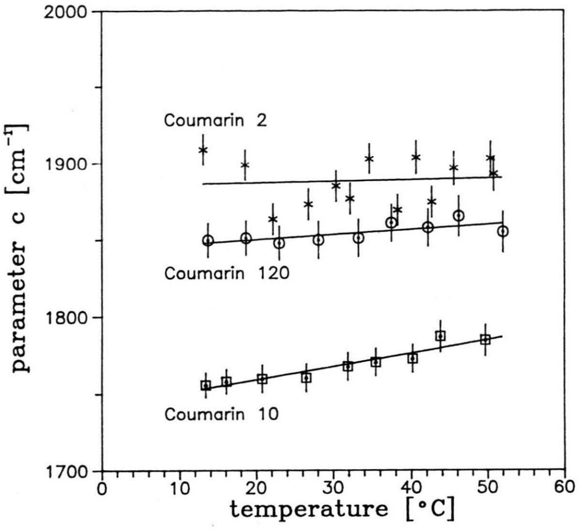

Fig. 5. Parameters *c* versus temperature.

5. Summary

The fluorescence spectra of coumarins in liquid, polar solvents are broad and structureless. It is believed that this broadening can be explained by the coupling of vibrational movements of the solute molecules with the motion of the solvent molecules or by considering the energy difference between the initial and final states of fluorescence as a stochastic quantity. In both cases, closely spaced energy levels are expected. Analytical formulae for shape factors of electronic spectra were obtained and a satisfactory agreement with the experimental spectra was demonstrated. A blue-shift of the fluorescence spectra of coumarins in ethyl alcohol was observed, and the temperature dependence of the parameters characterizing the ground and excited Franck-Condon states were calculated. It has to be noted that the application of such a simple model is limited to systems where intermolecular forces are strong enough, and this is the case of coumarins in polar solvents.

Acknowledgement

This work was carried out under the Polish Research Program CPBP 01.06.

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