

Electronic Spectra of Dye Solutions. I. The Mirror Image Rule

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The main assumptions of the quasi-molecule model of electronic spectra of liquid dye solutions are presented. The derived analytical expressions of the spectra account for the solvatochromic effects present in the solution. Based on the obtained spectral profiles of some coumarins in alcohol, new criteria for the validity of the mirror image rule are formulated.

KEY WORDS: Absorption; fluorescence; shapes of molecular spectra; coumarins.

INTRODUCTION

In spectral distributions of absorption and fluorescence of polar liquid dye solutions, some common features can be observed. One of the common attributes of the absorption and emission spectra are their profiles of transition cross sections, which appear to constitute mutual mirror images symmetrical with respect to a certain frequency. This characteristic feature of the electronic spectra is known as the mirror image rule [1].

Based on the relationship between absorption and emission spectra [2,4], Brand and Heller stated that in condensed phase systems, the mirror image rule holds only at a temperature of 0 K, with the additional condition that oscillation modes in the initial and final states of absorption and emission processes are equal. When these oscillation modes are almost equal, some deviations from the rule will be observed. If they are considerably different, then the mirror image rule breaks down [3].

Based on that reason it cannot be expected that in real molecular systems the mirror image rule will be strictly valid, and therefore a larger or smaller departure

from the rule will be observed. An additional and very important factor which causes a departure from the rule is solvatochromic effects, present in polar dye solutions. They not only cause dynamic Stokes shifts of the spectra, but also influence their profiles.

For a quantitative determination of the deviation from the mirror image rule, analytical expressions of the electronic spectra of a dye solutions should be employed. Such expressions, which relate molecular parameters of the system with the spectral profiles, are derived employing a quasi-molecule model of the spectra. Using these expressions, very precise reproductions of experimentally obtained electronic spectra can be assured [5,6]. However, there is a good reason to reexamine the validity of the mirror image rule if we take into account the solvatochromic effects occurring in polar dye solutions, which may influence dramatically the absorption as well as the fluorescence spectra.

In this paper the main assumptions of the quasi-molecule model of electronic spectra of liquid dye solutions are given and analytical expressions of transition cross sections for absorption and fluorescence processes are presented. Experimental verifications deliver numerical values of some molecular parameters of the system. These parameters enable a quantitative discussion of the validity of the mirror image rule in complex molecular systems, with solvatochromic processes present.

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THE MODEL

The quasi-molecule model of the electronic spectra of polar dye solutions allows us to derive analytical expressions which reproduce the experimentally obtained spectra at least as accurately as the log-normal distribution. The results, which we presented in our recent papers [5,6], lead to some spectral parameters with a simple physical interpretation. In the construction of the model, some reasonable assumptions were employed and the experimental verification serves for their justification. The main assumptions are as follows.

The Quasi-Molecule Concept. The interaction between a polyatomic molecule and the molecules of the polar solvent is assumed to be strong enough so that the coupling between the nuclear vibrational motion of solute molecules and the motion of heavy particles of the solvent does not allow the wavefunctions of the system to be separated into parts describing separately vibrations of the solute and the solvent nuclei. Therefore the description of absorption and emission processes cannot be limited to processes taking place in the solute molecules only. The observed spectroscopic properties of polar dye solutions are evidently due to the properties of dye molecules as well as to the properties of their surroundings. Therefore the dye molecule with its nearest surroundings will be assumed to be a quasi-molecule.

Energy States of Quasi-Molecules Are Functions of a Single Variable. The energy state of a quasi-molecule is determined by the electronic energy of the dye molecule and the interaction energy with the surroundings. It is assumed that in each electronic state of the quasi-molecule, there exists a position of equilibrium, i.e., a situation of the dye molecule in the solution such that the interaction energy will reach its minimum values. Each displacement from such a position will cause an increase in the total energy of the quasi-molecule. In a very crude approximation without a precise description of the interaction, we may assume that for small displacements, the quadratic terms of the Taylor expansion will lead to a parabolic shape of the interaction energy. Hence in each electronic state of the quasi-molecule, the interaction will be represented by a parabola in a certain configurational space, where the configurational coordinates are thought of as displacements from an equilibrium position.

In Each Electronic State of the Quasi-Molecule There Exists a Continuum of Sublevels with a Boltzman Distribution of Their Populations. Despite the fact that each movement in a molecular scale is quantized, the semi-classical description is justified because of the great number of degrees of freedom. Also, a continuum of

sublevels is assumed, evidently obeying the Boltzmann distribution. The last assumption implies time limits on the validity of the model when applied to the description of electronic spectra on the time scale down to the order of picoseconds.

With these assumptions, the transition cross-section distributions for absorption and fluorescence of polyatomic molecules in polar solvents may be expressed in the form

$$\begin{aligned}\sigma_{\alpha}(\epsilon) &= A_0 \int P_g(y) \delta[\Delta V(y) - \epsilon] dy \\ \sigma_f(\epsilon) &= F_0 \int P_e(z) \delta[\Delta V(z) - \epsilon] dz\end{aligned}\quad (1)$$

where $P_g(y)$ and $P_e(z)$ are Boltzmann population distributions in the respective initial states, $\Delta V = (W_e - W_g)$ is the energy difference between the excited and the ground state, ϵ is the transition frequency, A_0 and F_0 are normalization factors, and y and z are relative displacements from equilibrium positions.

According to the above assumptions, the initial ground state and the excited Franck–Condon state of the quasi-molecule read

$$\begin{aligned}W_g^0(y) &= c_{\alpha} y^2 \\ W_e(y) &= c'_{\alpha} (y - 1)^2 + (b_{\alpha})_{t=0}\end{aligned}\quad (2)$$

where $c_{\alpha} = k_g^0(Q_0)_{t=0}^2$ and $c'_{\alpha} = (k_e)_{t=0}(Q_0)_{t=0}^2$. The remaining parameters are k_g^0 and $(k_e)_{t=0}$, the force constants in the ground and excited states at the instant of excitation; $(Q_0)_{t=0}$, the mutual displacement of the potential wells; and $(b_{\alpha})_{t=0}$ the 0–0 transition in absorption spectrum.

The initial and final fluorescence states of the quasi-molecule read

$$\begin{aligned}W_e(z) &= c'_f (z - 1)^2 + (b_f)_t \\ W_g(z) &= c_f z^2\end{aligned}\quad (3)$$

where $c'_f = (k_e)_t(Q_0)_t^2$ and $c_f = (k_g)_t(Q_0)_t^2$. The parameters in these equations, defined similarly to those in Eq. (2), are not determined ones for ever. The slow time dependence of the parameters is due to solvatochromic processes in the excited state. This is directly observable in time-dependent fluorescence experiments with dyes in polar solutions. The evolution of the system from a Franck–Condon to an almost-equilibrated initial state of fluorescence is responsible for the observed dynamic Stokes shift of the spectra.

In steady-state measurements the parameters of the excited state are close to their values in equilibrium. They will determine the initial state of fluorescence under steady-state excitation. It must be emphasized that the energy of the initial state seen in absorption $W_g^0(y)$

Table I. Molecular Parameters of Coumarins in Alcohol Calculated from Absorption and Fluorescence Spectra and from the Respective Mirror Images (cm⁻¹)

Coumarin	(1) $\sigma_\alpha (c_\alpha, c'_\alpha, b_\alpha; \epsilon)$			(2) $\bar{\sigma}_\alpha (\bar{c}_\alpha, \bar{c}'_\alpha, \bar{b}_\alpha; \epsilon)$			(3) $\sigma_f (c_f, c'_f, b_f; \epsilon)$			(4) $\bar{\sigma}_f (\bar{c}_f, \bar{c}'_f, \bar{b}_f; \epsilon)$			ϵ_o
	c_α	c'_α	b_α	\bar{c}_α	\bar{c}'_α	\bar{b}_α	c_f	c'_f	b_f	\bar{c}_f	\bar{c}'_f	\bar{b}_f	
340	775	2,412	22,560	817	1,920	22,483	1,920	817	21,277	2,412	775	21,200	21,880
10	714	2,575	24,151	724	1,707	23,719	1,707	724	22,861	2,575	714	22,429	23,290
138	745	2,257	25,469	1,109	2,153	25,209	2,153	1,109	24,131	2,257	745	23,871	24,670
2	628	2,161	25,515	866	1,850	25,275	1,850	866	24,285	2,161	628	24,045	24,780
175	752	2,366	25,733	1,035	2,120	25,485	2,120	1,035	24,555	2,366	752	24,307	25,020
120	775	2,578	25,992	854	1,875	25,859	1,875	854	24,701	2,578	775	24,568	25,280

is by no means equal to the final state of fluorescence $W_g(z)$, which appears to be the Franck-Condon ground state.

Quasi-molecules in their ground states met in absorption and in the initial states of fluorescence are separate objects because of the different configurations of their surroundings. Therefore the dimensionless variables appearing in Eq. (1)–(3) are not the same, because $y = Q/(Q_o)_{t=0}$ and $z = Q/(Q_o)_t$, where $(Q_o)_t$ is not equal to $(Q_o)_{t=0}$, Q being the displacement from an equilibrium.

In these circumstances the calculated profile of the normalized transition cross section for absorption is

$$\sigma_\alpha(c_\alpha, c'_\alpha, b_\alpha; \epsilon) = a(\epsilon)/a(\epsilon_m) \quad (4)$$

where ϵ is the electronic transition frequency and ϵ_m is its value for the absorption maximum, while

$$a(\epsilon) = \frac{1}{M(\epsilon)} * \exp \left\{ \frac{-c_\alpha}{kT(m-1)^2} * [m - M(\epsilon)]^2 \right\}$$

with

$$M(\epsilon) = \sqrt{m + (m-1)(\epsilon - b_\alpha)/c_\alpha}$$

for

$$\epsilon > b_\alpha - mc_\alpha/(m-1)$$

and $m = c'_\alpha/c_\alpha = (k_e)_{t=0}/k_g^0$ and $b_\alpha = (b_\alpha)_{t=0}$.

Similarly, the normalized cross-section profile for fluorescence can be expressed as

$$\sigma_f(c_f, c'_f, b_f; \epsilon) = f(\epsilon)/f(\epsilon_m) \quad (5)$$

where

$$f(\epsilon) = \frac{1}{N(\epsilon)} * \exp \left\{ \frac{-c'_f}{kT(n-1)^2} * [n - N(\epsilon)]^2 \right\}$$

with

$$N(\epsilon) = \sqrt{n + (n-1)(b_f - \epsilon)/c'_f}$$

for

$$\epsilon < b_f - nc'_f/(n-1)$$

and $n = (k_g)_t/(k_e)_t$ and $b_f = (b_f)_t$.

Table 1, in columns 1 and 3, contains numerical values of molecular parameters of some coumarins, obtained by fitting appropriate cross sections calculated from experimental spectra to formulae (4) and (5). In the last column in Table I the frequency of reflection ϵ_o is given. ϵ_o is defined as the frequency for which the normalized transition cross sections of absorption and emission are equal. It must be noted that the fit of the investigated systems is so congruent that with these parameters calculated, transition cross sections can be recognized as a result of experiment.

The normalized transition cross sections of absorption and fluorescence are presented in Fig. 1 (solid lines). As shown in Fig. 1, instead of frequency, the difference $\epsilon - \epsilon_o$ is used. Knowing the values ϵ_o , it is very easy to convert to the commonly used method of presentation of the spectra. It seems, however, that this method of presentation of the spectra is more illustrative, and the differences in transition cross sections of different coumarins in the same solution are more pronounced. The presentation of the mirror image rule is more pronounced too.

THE MIRROR IMAGE RULE

The mirror image rule requires that

$$\bar{\sigma}_f(\epsilon) = \sigma_\alpha(2\epsilon_o - \epsilon)$$

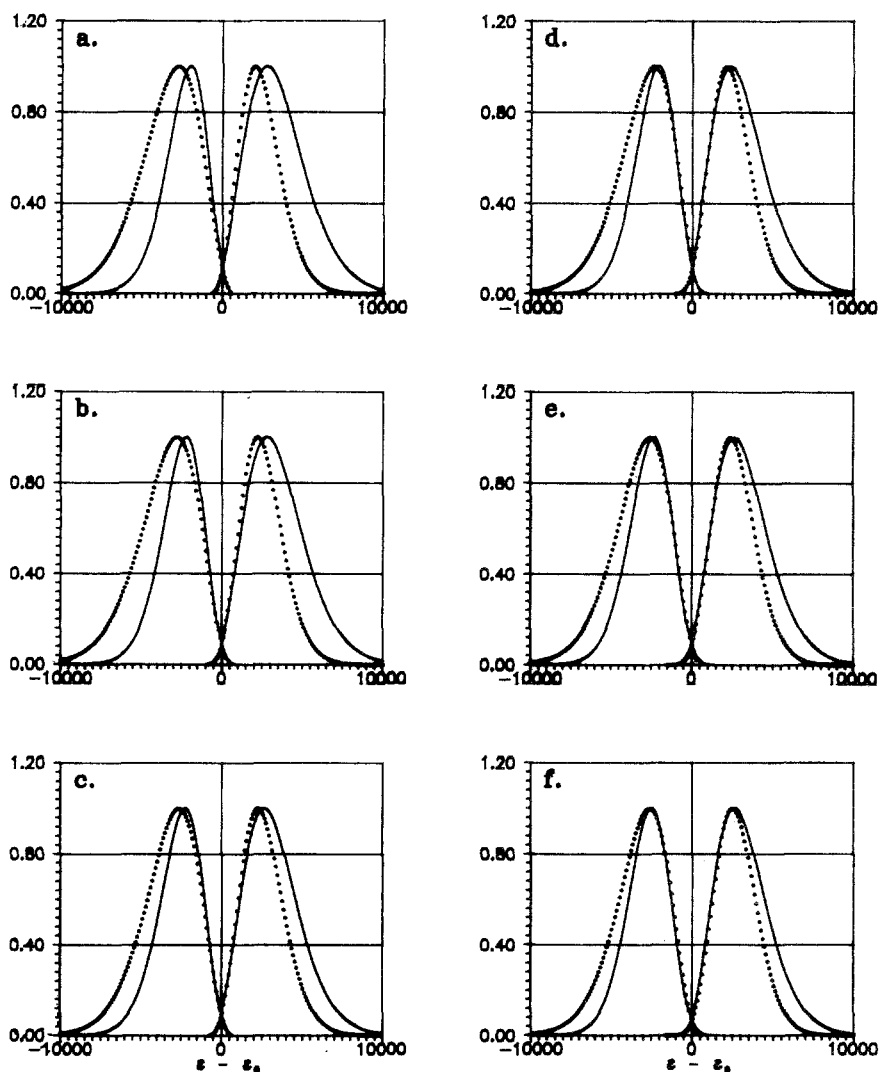


Fig. 1. Normalized transition cross sections of absorption and fluorescence (solid lines) and their mirror images (dotted lines) for coumarins (a) 10, (b) 120, (c) 340, (d) 2, (e) 175, and (f) 138. The negative frequency difference region corresponds to fluorescence, positive to absorption spectra (cm^{-1} units are used).

and that

$$\overline{\sigma}_\alpha(\epsilon) = \sigma_f(2\epsilon_0 - \epsilon)$$

where $\overline{\sigma}_f(\epsilon)$ and $\overline{\sigma}_\alpha(\epsilon)$ are the transition cross-section distributions for fluorescence and absorption, respectively, obtained from their reflections about the frequency ϵ_0 . Knowing the absorption and fluorescence spectra, it is easy to determine the distributions σ_α and ϵ_f , and knowing ϵ_0 , their images as well. Appropriate parameters of the obtained distributions are presented in columns 2 and 4 in Table 1.

The mirror image rule would hold if the relations

$\overline{\sigma}_f(\epsilon) = \sigma_f(\epsilon)$ and $\overline{\sigma}_\alpha(\epsilon) = \sigma_\alpha(\epsilon)$ were fulfilled. This requires that $\overline{c}_f = c'_\alpha$ and $\overline{c}'_f = c_\alpha$ with $\overline{b}_f = 2\epsilon_0 - b_\alpha$ and $\overline{c}_\alpha = c'_f$ and $\overline{c}'_\alpha = c_f$ with $\overline{b}_\alpha = 2\epsilon_0 - b_f$. Transition cross sections of absorption and fluorescence of investigated coumarin solutions (Fig. 1, solid lines) and their respective images (Fig. 1, dotted lines) show that, in all cases, the mirror image rule is violated.

We can formulate the rates of departure from the mirror image rule as the differences $\overline{\sigma}_f(\epsilon) - \sigma_f(\epsilon) = \Delta\sigma_f$ and $\overline{\sigma}_\alpha(\epsilon) - \sigma_\alpha(\epsilon) = \Delta\sigma_\alpha$. These differences are depicted in Fig. 2, calculated for the cases shown in Fig. 1. It appears that the behavior of coumarins 10, 120, and 340 differs from that of the remaining investigated

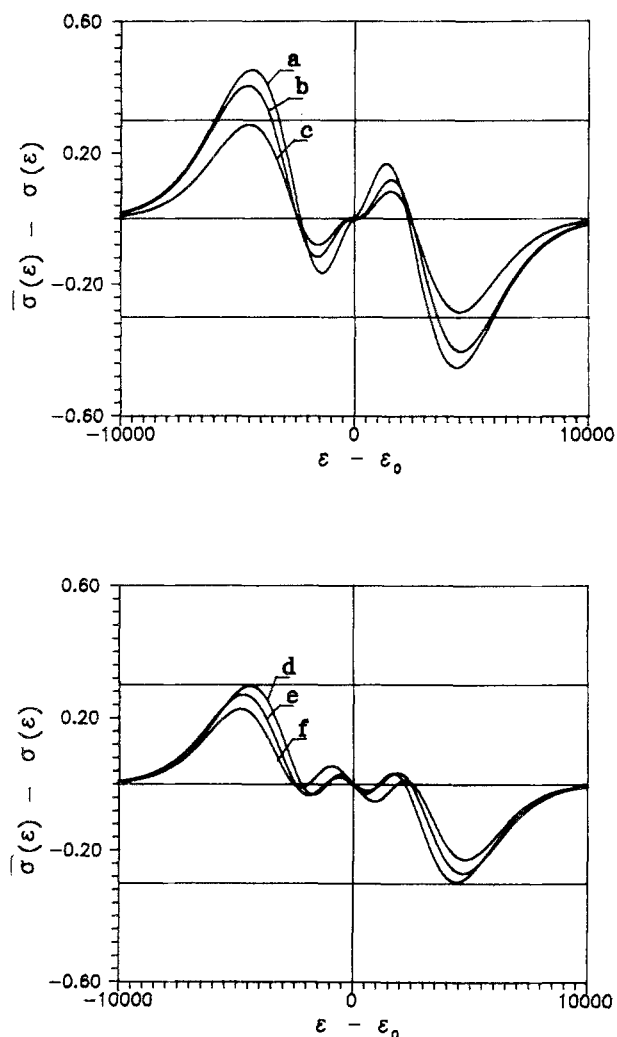


Fig. 2. The differences in transition cross-section distributions of the mirror images and the respective absorption and fluorescence cross sections. Lines are labeled as in Fig. 1.

coumarins. Such a different type of behavior is very hard to notice in the method of presentation used in Fig. 1.

Some further regularities concerning the parameters given in Table I, which seem to be of some importance, can be recognized. For all the investigated coumarins,

$$\begin{aligned} b_{\alpha} &> \bar{b}_{\alpha} > b_f > \bar{b}_f \\ c'_{\alpha} &> \bar{c}'_{\alpha} > c'_f > \bar{c}'_f \\ c_{\alpha} &< \bar{c}_{\alpha} < c_f < \bar{c}_f \end{aligned}$$

These regularities are due to solvatochromic processes occurring in solutions. They show how the system proceeds from the excited Franck-Condon state to the state of equilibrium. Because the initial state of absorption is highly equilibrated, the initial state of fluorescence would

be highly equilibrated too, when only the mirror image rule was fulfilled. In reality, the molecular parameters responsible for the fluorescence spectrum reach values between the parameters of the absorption spectrum and its mirror image. Hence the conclusion can be drawn that the emission takes place from a state where equilibrium could not be attained. This can be either because of the lack of time or because a new charge distribution in the excited state requires a different equilibrium state.

SUMMARY

It is well-known that electronic spectra of many dye solutions are structureless. Therefore to look for some definite oscillation modes in the ground or excited states is useless. This is the reason that a continuum of sub-levels in the ground as well as in the excited state is assumed. It seems reasonable that the population of these levels obeys a Boltzmann distribution.

Solvatochromic processes occurring in polar dye solutions, which influence the shape factors, are due to a characteristic solute-solvent interaction. The knowledge concerning this interaction is not complete; it is assumed here that there exist equilibrium positions of dye molecules among the neighbor solvent molecules. Every displacement of the molecule from equilibrium is connected with the increase in potential energy. The existence of a minimum of interaction energy suggests the quasi-molecular concept of a dye solution. A quasi-molecule is thought of as a dye molecule and its nearest surroundings.

In the simplest approximation the position-sensitive energy of the quasi-molecule is a quadratic function of a single variable. This assumption is merely a result of a compromise to account for the fact that structureless electronic spectra of dye solutions are three-parameter curves.

Based on the above assumptions, analytical expressions for electronic spectra in the Condon approximation were derived and a confrontation with an experiment was possible. By an applied fitting procedure, some molecular parameters were obtained, which could be associated with absorption and fluorescence of the system. Furthermore, some knowledge was gained about the evolution of the system when it proceeds from a Franck-Condon to an equilibrated state. On this basis, a new verification of the mirror image rule was carried out.

For the mirror image rule to be valued, some defined conditions have to be fulfilled. These conditions were recognized by means of a quasi-molecule model of the electronic spectra of dye solutions, with solvato-

chromic effects accounted for. The conclusion is that the mirror image rule would hold strictly if the attained initial state of fluorescence were in a state of equilibrium equal to that of the initial ground state. This seems to be quite unreal because of the difference in charge distributions in the ground and excited states and because of the relaxational processes in the excited state during the transition of the system from the Franck–Condon to an equilibrated state.

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