A Quasi-Molecule Model of Absorption and Fluorescence Spectra of Polar Dye Solutions

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A method for approximating the band shape of electronic spectra of polar dye solutions is described. The band shape is modeled using a modified configuration coordinate model, adapted to liquid dye solutions. In the results some molecular parameters of the solution responsible for the band profile are found. The validity of the use of Condon approximation in the description of spectral profiles of xanthene dye solutions is discussed.

INTRODUCTION

Experimental methods for the determination of electronic spectra of dye solutions are well established. A theoretical description of the spectra of isolated organic molecules is also well known. On the other hand, a complete description of the electronic spectra of dye molecules in organic solvents is still an open question because of the complexity of the system. The electronic spectra of these systems depend on many factors and an analytical representation of the spectra is usually not available. Consequently, experimentally obtained absorption and fluorescence spectra deliver less information about the solution than expected. Very often, only some qualitative conclusions are derived from experimentally obtained spectra.

The structureless profiles of the spectra of polar dye solutions can be roughly approximated by a normal distribution [1]. However, the real spectra are not Gaussian—they are obviously asymmetric. This suggests the utilization of a more sophisticated frequency distribution then the Gaussian one—at least a three-parameter

distribution is required. A known distribution of this kind is the log-normal distribution often used in shaping electronic spectra [2,3]. The disadvantage of this approach is the lack of relations between the spectral distribution and the molecular parameters of the system. The same objection can be raised to the momentum method [4]. Therefore there is a need for a theoretical description of the spectra in which the molecular parameters of the system can be obtained from the parameters of its spectral distribution. This requirement appears to be fulfilled, at least to some extent, by a recently developed quasi-molecule (QM) model of electronic spectra of polar dye solutions [5–10]. The main goal of this model is to provide a new interpretation tool for biophysical and medical applications, where dye molecules are commonly used as luminescent probes. The model may also have some importance for quantum electronics since dye lasers are still in use today.

The QM model of electronic spectra of dye solutions can be recognized as a modification of the configuration coordinate (CC) model. Originally this model was developed for the interpretation of luminescence spectra of color centers and crystalline luminophores [12,13] but was also used for the description of dye solution spectra [11]. Basically the CC model regards the interaction of a multielectron system with the crystalline lattice in sol-

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ids. It is obvious that this model may not be used for the description of electronic spectra of dye solutions without some serious modifications, especially because of the solvatochromic effects present in liquid solutions.

The basis of the CC model can be reduced to the following approximations:

(1) Born–Oppenheimer approximation for wave functions,

(2) Condon approximation for transition moments,

(3) semiclassical formulation of the Franck–Condon principle, and

(4) classical description of heavy particle-dynamics

$$(1)$$

The first two approximations belong to quantum mechanics, while the others make the model a semiclassical one. In consequence, the continuum of vibrational levels in the ground E_g (Q) and in the excited $E_e(Q)$ state is assumed. According to the Born–Oppenheimer approximation, these energies are also potential energies of the movement of heavy particles. In the CC model the configurational coordinates Q seem to be well defined. In the framework of the above four assumptions (1), the spectral distributions of absorption and fluorescence take the form [17]

$$A(\epsilon) = A_0\epsilon \int P_g(Q) \, \delta[\Delta E(Q) - \epsilon] \, dQ \qquad (2)$$

and

$$F(\epsilon) = F_0\epsilon^3 \int P_e(Q) \, \delta[\Delta E(Q) - \epsilon] \, dQ \qquad (3)$$

where $P(Q)$ are the Boltzmann population distributions of appropriate initial vibronic states of absorption (E_g) and fluorescence (E_e), respectively. These energies are related to the coordinates Q in harmonic approximation by the formulae

$$E_e(Q) = k(Q - Q_0)^2 + b \qquad (4)$$

$$E_g(Q) = kQ^2 \qquad (5)$$

and

$$\Delta E(Q) = E_e(Q) - E_g(Q) \qquad (6)$$

where ϵ is the transition energy and A_0 and F_0 are normalization factors which include, according to the Condon approximation, the Q-independent transition moments. The parameter Q_0 is a shift of the excited-state energy minimum in relation to the minimum of the ground-state energy.

Despite the fact that the direct application of the CC model to electronic spectra of solutions of organic compounds was successful [11], it is difficult to assign

some physical meaning for the parameters of the model. The problem of interpretation in this case has its source in the diffusion processes in the ground and excited states and in solvatochromic processes. The latter processes differentiate the excited state achieved directly in the absorption process (called the Franck–Condon state; FC) and the equilibrated excited state reached after some relaxation time. Finally, the spatial coordinates of a dye molecule and its nearest surroundings, called a luminescence centrum or a quasi-molecule, in liquid solutions are not univocally defined. The aim of this work is to remove some of the difficulties in interpretation while adopting the CC model to liquid dye solutions.

THEORETICAL BACKGROUND

In general, the assumptions (1) elaborated for the CC model may be applied to liquid dye solutions but with some modifications introduced because of the specific nature of the system. The spectral distributions for absorption and fluorescence will be similar to distributions (2) and (3) but with new definitions of the physical quantities responsible for the band shapes. The improved spectral distributions now read

$$A(\epsilon) = A_0\epsilon \int P_{ag}(Q) \, \delta[\Delta E_a(Q) - \epsilon] \, dQ \qquad (7)$$

and

$$F(\epsilon) = F_0\epsilon^3 \int P_{fe}(Q) \, \delta[\Delta E_f(Q) - \epsilon] \, dQ \qquad (8)$$

where $\Delta E_a(Q) = E_{ae}(Q) - E_{ag}(Q)$ and $\Delta E_f(Q) = E_{fe}(Q) - E_{fg}(Q)$. Here the energy difference $\Delta E_a(Q)$ is the difference between the FC excited state $E_{ae}(Q)$ and the equilibrated ground state $E_{ag}(Q)$, while the energy difference $\Delta E_f(Q)$ is the difference between the equilibrated excited state $E_{fe}(Q)$ and the FC ground state $E_{fg}(Q)$. By analogy, the population distributions of the initial states of the electronic transitions are denoted $P_{ag}(Q)$ for absorption and $P_{fe}(Q)$ for fluorescence, respectively.

Harmonic Approximation

In order to obtain a theoretical description of experimentally obtained spectra, it is most important to find the proper potential energies for the initial and final states of the electronic transitions. In the harmonic approximation the action of elastic forces is assumed. In this case,

by analogy to formulae (4) and (5), the following potential energies can be applied:

$$E_{ae}(Q) = k_{ae}(Q - Q_{ae})^2 + b_a \qquad (9)$$

$$E_{ag}(Q) = k_{ag}Q^2 \qquad (10)$$

to describe the spectral distributions of absorption and

$$E_{fe}(Q) = k_{fe}(Q - Q_{fe})^2 + b_f \qquad (11)$$

$$E_{fg}(Q) = k_{fg}Q^2 \qquad (12)$$

to describe the spectral distributions of fluorescence. It must be noted that there is no reason to assume that the intermolecular interactions are not sensitive to the particular electronic state of the molecule, therefore $k_{ae} \neq k_{ag}$ and $k_{fe} \neq k_{fg}$. This assures that the spectral distributions will be asymmetric. Otherwise, in the case when $k_{ae} = k_{ag}$ as well as when $k_{fe} = k_{fg}$, the spectral profiles of absorption and fluorescence will be Gaussian.

To describe the absorption distribution, the position of the minimum of potential energy of the ground state is chosen at the origin of the (Q,E) coordinate system, and Q_{ae} accounts for the shift of the equilibria of the FC excited- and the ground-state potentials. The parameter b_a, in accordance with $E_{ae}(Q_{ae}) = b_a$, is the 0–0 transition energy. By analogy, the position of the minimum of the FC ground-state potential is chosen as the origin of the coordinate system used to describe the fluorescence frequency distribution, and the parameter Q_{fe} accounts for the shift of the minima of the initial- and final-state potentials of the fluorescence.

In a liquid solution many different conformations or different quasi-molecules with different force constants k are present. The numerical values of parameters Q_{ae} and Q_{fe} are not known. In consequence, many pairs of potential curves (9)–(12) are responsible for the spectra. By employing the transformations

$$y = \frac{Q}{Q_{ae}} \qquad (13)$$

and

$$y' = \frac{Q}{Q_{fe}} \qquad (14)$$

the potentials (9)–(12) read

$$E_{ae}(y) = c_{ae}(y - 1)^2 + b_a \qquad (15)$$

$$E_{ag}(y) = c_{ag}y^2 \qquad (16)$$

and

$$E_{fe}(y') = c_{fe}(y' - 1)^2 + b_f \qquad (17)$$

$$E_{fg}(y') = c_{fg}(y')^2 \qquad (18)$$

to account for absorption and fluorescence spectra, respectively. The new parameters, which depend on k and Q, are

$$c_{ag} = k_{ag}Q_{ae}^2, \qquad c_{fg} = k_{fg}Q_{fe}^2$$

$$c_{ae} = k_{ae}Q_{ae}^2, \qquad c_{fe} = k_{fe}Q_{fe}^2 \qquad (19)$$

According to transformations (13) and (14), many pairs of potential curves (9)–(12) are replaced by only two pairs of effective potentials, (15)–(18), with parameters which do not depend on a particular conformation of the quasi-molecule. The differences in the values of parameters c and b for absorption and fluorescence are due to the solvatochromic effects present in a dye solution.

Assuming (1) with transformations (13) and (14), one obtains the spectral profiles of absorption and fluorescence spectra

$$A(\epsilon) = A_0\epsilon \int P_{ag}(y) \, \delta[\Delta E_a(y) - \epsilon] \, dy \qquad (20)$$

and

$$F(\epsilon) = F_0\epsilon^3 \int P_{fe}(y') \, \delta[\Delta E_{fe}(y') - \epsilon] \, dy' \qquad (21)$$

respectively, where A_0 and F_0 are new normalization constants. The arguments of the δ functions in (20) and (21) include the energy differences $\Delta E_a(y) = E_{ae}(y) - E_{ag}(y)$ and $\Delta E_f(y') = E_{fe}(y') - E_{fg}(y')$, which are now functions of the relative displacements y and y'. It is obvious that the population distributions in the initial states of the transitions are functions of the relative displacements too. They read

$$P_{ag}(y) = P_{ag}^0 \exp\left[\frac{-E_{ag}(y)}{kT}\right] \qquad (22)$$

and

$$P_{fe}(y') = P_{fe}^0 \exp\left\{\frac{-[E_{fe}(y') - E_{fe}(1)]}{kT}\right\} \qquad (23)$$

In calculations P_{ag}^0 and P_{fe}^0 are embedded in the normalization factors A_0 and F_0.

In liquid dye solutions the absorption process moves the system from the ground equilibrated to an excited FC state. For relatively nonviscous solutions the initial state of the fluorescence is an almost-equilibrated state, and the final state of the emission is again a FC state. The integration of (20) and (21) with potentials (15)–(18) and the population distributions of initial states (22) and (23)

leads to analytical formulae of the spectral distributions of absorption and fluorescence:

$$\frac{A(\epsilon)}{A_0} = \frac{\epsilon}{R_a(\epsilon)} \sum_{p=1}^{2}$$

$$\exp\left\{\frac{-c_{ag}[c_{ae} + (-1)^p R_a(\epsilon)]^2}{kT(c_{ae} - c_{ag})^2}\right\} \qquad (24)$$

and

$$\frac{F(\epsilon)}{F_0} = \frac{\epsilon^3}{R_f(\epsilon)} \sum_{p=1}^{2} \exp\left\{\frac{-c_{fe}[c_{fg} + (-1)^p R_f(\epsilon)]^2}{kT(c_{fe} - c_{fg})^2}\right\} \qquad (25)$$

where

$$R_a(\epsilon) = \sqrt{c_{ag}c_{ae} - (c_{ae} - c_{ag})(b_a - \epsilon)} \qquad (26)$$

and

$$R_f(\epsilon) = \sqrt{c_{fg}c_{fe} - (c_{fe} - c_{fg})(b_f - \epsilon)} \qquad (27)$$

In expressions (24) and (25) the constants $A_o = A(\epsilon_0^a)$ and $F_o = F(\epsilon_0^f)$ are normalization factors, where $\epsilon_0^{a,f}$ are frequencies corresponding to the maxima of the appropriate spectra.

Anharmonic Approximation

Although the description of the initial states of the transitions in harmonic approximation is justified, this is not the case in the description of the final states. Some additional terms that complete potentials (15)–(18) have been suggested [10]:

$$E_{ae}(y) = c_{ae}(y - 1)^2 + c_{ae}^{(anh)} (y - 1)^4 + b_a \qquad (28)$$

$$E_{ag}(y) = c_{ag}y^2 \qquad (29)$$

and

$$E_{fe}(y') = c_{fe} (y' - 1)^2 + b_f \qquad (30)$$

$$E_{fg}(y') = c_{fg} (y')^2 + c_{fg}^{(anh)} (y')^4 \qquad (31)$$

where $c_{ae}^{(anh)}$ and $c_{fg}^{(anh)}$ are additional parameters which account for the anharmonicity. Such a modification of potential curves results in a better fit of the theoretical spectral distributions to the experimentally obtained spectra, especially in the short-wavelength tail region of the absorption spectra and the long-wavelength tail of the fluorescence spectra. With these potentials, integration of Eqs. (20) and (21) can be performed only numerically.

EXPERIMENTAL VERIFICATION OF THE MODEL

Verification of formulae (20) and (21) has been performed using polar coumarin solutions. It was based on the determination of model parameters to reproduce the experimental absorption and emission band profiles. Despite the rough approximations used, the obtained results are surprisingly good. The best-fit nonlinear procedure, described in Ref. 10, has been used to determine model parameters appearing in the theoretical expressions. Appropriate numerical values (cm^{-1}) relating to Eqs. (28)–(31) are given in Table I. The close coincidence of the experimental band profiles and the theoretical fits leads to the conclusion that, in the limit of experimental error, the equation

$$kQ_e^2 = const \qquad (32)$$

holds [compare Eqs. (19)]. This is an important experimental result indicating that the parameters k and Q_e are mutually dependent. Hence, the single pair of potential curves like (28)–(31), which depend on relative variables y and are characterized by c_g and c_e, is equivalent to the whole set of pairs of potential curves (9)–(12) with different values of k_g, k_e, and Q_e, but satisfying Eq. (19). In other words, each pair of potential curves (9)–(10) and (11)–(12) leads to mutually identical band profiles if only k_g, k_e, and Q_e satisfy relations (19), with c_g, c_e,

Table I. Values of Parameters of the Effective Potential Curves for Methanolic Coumarin Solutions $[cm^{-1}]$

| Coumarin	Model	b_a	c_{ag}	c_{ae}	$c_{ae}^{(anh)}$	b_f	c_{fg}	c_{fe}	$c_{fg}^{(anh)}$
120	Harmonic	25,838	970	2,650	160	25,017	1,998	1,285	271
	Anharmonic		1,009	2,717			1,931	1,445	
175	Harmonic	25,576	982	2,361	184	24,806	2,243	1,385	230
	Anharmonic		1,023	2,474			2,153	1,525	
2	Harmonic	25,217	877	2,198	160	24,538	1,907	1,221	241
	Anharmonic		908	2,340			1,882	1,353	
138	Harmonic	24,857	1,271	2,425	449	24,396	2.291	1,485	264
	Anharmonic		1,427	2,400			2.175	1,655	
10	Harmonic	23,873	1,010	2,824	151	22,990	1,670	870	138
	Anharmonic		1,049	2,855			1,723	932	
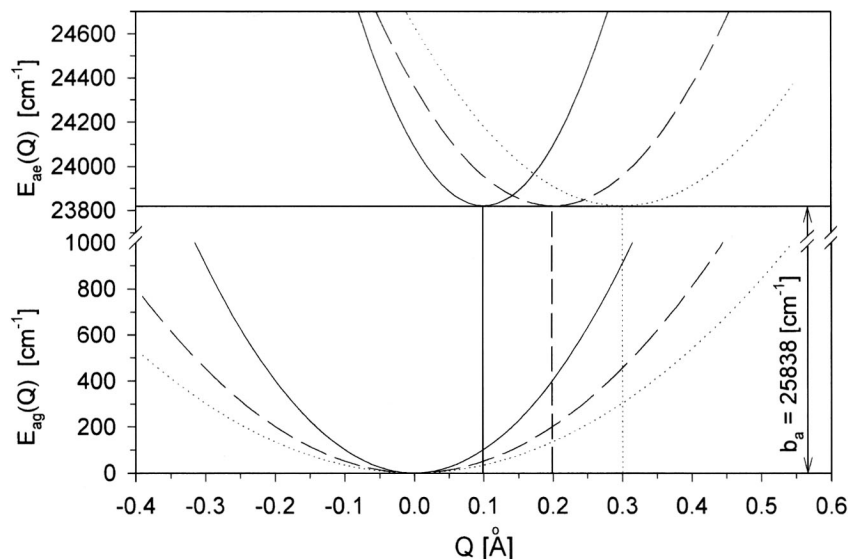
Fig. 1. Pairs of potential curves for equilibrated ground and Franck–Condon excited states of coumarin 120 obtained for $Q_{ea} = 0.1$ Å (——), $Q_{ea} = 0.2$ Å (- - -), and $Q_{ea} = 0.3$ Å (⋯).

and b being constants, characteristic for a given system. This conclusion is valid for absorption as well as for emission bands. As an example, three pairs of such potential curves for coumarin 120 solutions are illustrated in Fig. 1.

The number of curves has been reduced to only three pairs simply to preserve clarity of the picture. They all give rise to the same spectral distributions. Calculations
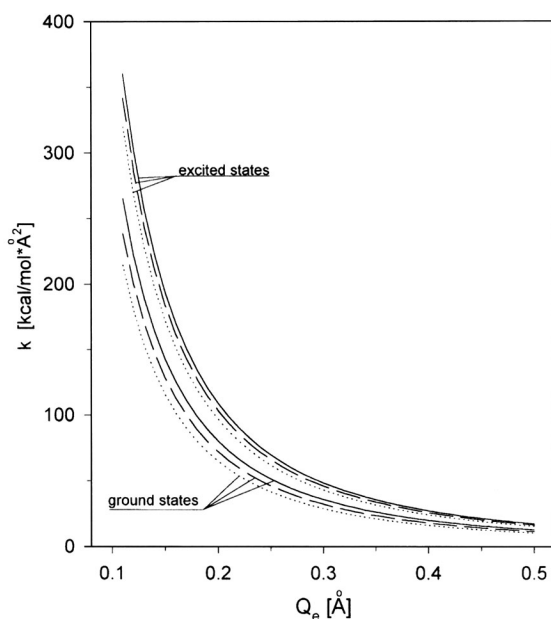

Fig. 2. Force constants in equilibrated states of coumarins vs equilibrium position displacement for coumarin 2 (——), coumarin 120 (- - -), and coumarin 175 (⋯).

were performed based on Eqs. (20) and (21). The values of c_{ag}, c_{ae}, c_{fg}, and c_{fe} obtained are given in Table I.

In Fig. 2 the relationship between the force constants (k) and the potential equilibrium positions (Q_e) are illustrated for several coumarin solutions, based on Eqs. (19) and the parameters c_{ag}, c_{ae}, c_{fg}, and c_{fe} from Table I. It follows from inspection of Table I and Fig. 2 that, for the coumarin solutions studied, the relation $c_{fe} > c_{ag}$ is valid, indicating that (elastic) field forces acting on the dye molecules are always higher in their equilibrated excited states rather than in their equilibrated ground states. This is manifested by the inequality $k_{fe} > k_{ag}$, valid for every value of Q_e over the whole domain of its variation. In addition, the c parameters are related by $c_{fe} < c_{ae}$ and $c_{ag} < c_{fg}$, indicating that appropriate forces (acting on the dye molecule) decrease during reorientational relaxation processes, leading from Franck–Condon states to equilibrated ones. However, the latter conclusion may not be regarded as strictly proven because the variation of Q_e is not known in these processes. In conclusion, one should state that it is not clear whether all properties of coumarin solutions mentioned here are common for all polar dye solutions.

Coumarins, due to their high permanent dipole moments, have structureless absorption/emission bands when dissolved in polar solvents. Many other fluorescing dyes with smaller dipole moments reveal characteristic inflection points in their electronic band profiles.

A good example of this is the absorption bands of xanthene dye solutions, presented in Fig. 3. The appearance of such inflections is often interpreted as traces of
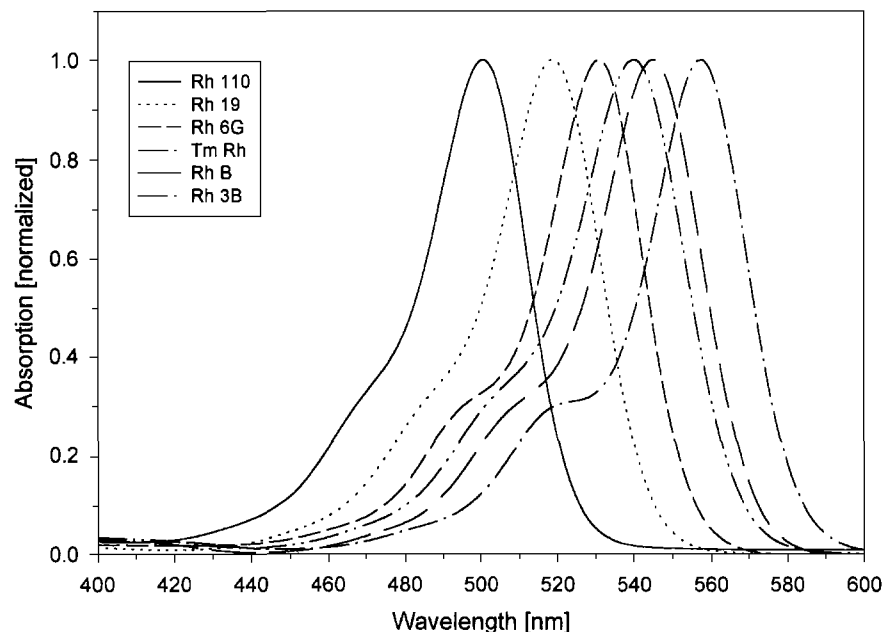
Fig. 3. Absorption bands of xanthene dye solutions.

the vibrational structure of the spectra [18]. Nonetheless, in this work an analysis of the absorption/emission spectra of the xanthene dye solutions was performed according to the same approach as for coumarin solutions in a limited fitting range. Appropriate best-fit values of potential parameters involved in the electronic transitions are collected in Table II, where only the parameters of the equilibrated states are given.

It is clear that the reproducibility of experimental band profiles from the theoretical model functions are worse than in the case of structureless spectra of coumarins. Nevertheless, inspection of the parameters in Table II leads to the conclusion that the main characteristics of the cycle—excitation, relaxation in the excited state, fluorescence, and relaxation in the ground state—are similar for both kinds of solutions.

In Fig. 4 the dependencies between force constants (k) and potential equilibrium positions (Q_e) are demon-

strated graphically for xanthene dye solutions (in analogy to Fig. 2, related to the coumarins). Calculations were made based on Eqs. (20) and (21) and the parameters given in Table II. It must be noted that, according to expectations, the values of the c parameters for xanthene dye solutions differ markedly from those for coumarin solutions. Based on the results illustrated in Figs. 2 and 4, one can conclude not only that the analyses performed allow quantitative comparisons of appropriate force constants, but also that certain qualitative results can be obtained. In the cases considered one can see that the interactions are larger for coumarin than for xanthene dye solutions. In addition, qualitative estimation of the energy differences, related to individual dyes belonging to the same class of dyes, can be determined.

The inflection points (or slightly developed single maxima), appearing in the electronic bands of many dye solutions, are usually interpreted in terms of the vibrational structure. The observed absorption/emission band profiles represent an envelope over the many narrow lines, being the result of vibronic transitions between discrete vibrational energy levels. Such an envelope should not necessarily be structureless, as happens in the case of unsaturated ring hydrocarbons and many other simple dye molecules.

As already mentioned, many dye solutions reveal characteristic inflection points in their spectral profiles. This indicates that some improvements in the quasimolecular model seem to be necessary in this case. A straight-

Table II. Parameters of Effective Potential Curves in the Equilibrated States of Xanthene Dye Solutions [cm^{-1}]

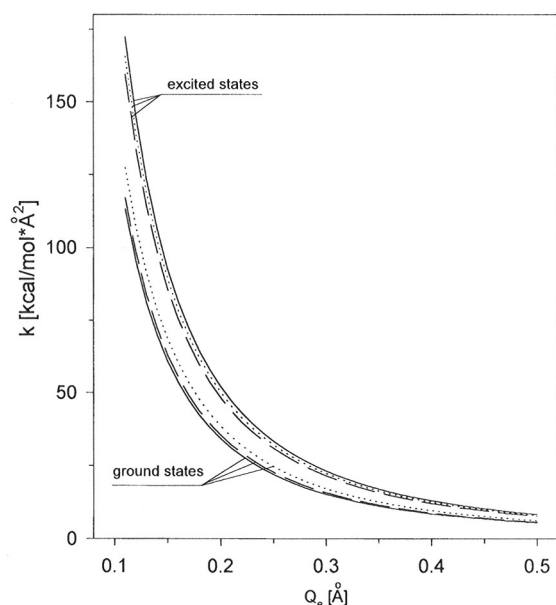| Rhodamine	b_a	c_{ag}	b_f	c_{fe}
Rh 6G	18,880	479	18,645	729
Rh B	18,357	495	17,728	675
Tm Rh	18,511	539	17,864	813
Rh 110	19,938	539	19,329	701
Rh 3B	17,978	461	17,415	727
Rh 19	19,245	534	18,632	719

Fig. 4. Force constants in equilibrated states of rhodamines vs equilibrium position displacement for rhodamine 6G (———), rhodamine B (- - -), and rhodamine 110 (···).

forward solution of this problem is to reexamine the validity of the approximations (1) used. It appears that, unlike the other assumptions (1.1, 1.3, 1.4), the applicability of the Condon approximation is not a crucial feature of the quasi-molecular model. As indicated in Refs. 19–

21, this approximation is not applicable to symmetry-forbidden electronic transitions and may also be inadequate for allowed transitions. When the Condon approximation fails, Eqs. (20) and (21) should be replaced by more general ones:

$$A(\epsilon) = A_0\epsilon \int P_g(y)M_a^2(y) \; \delta[\Delta E(y) - \epsilon] \; dy \quad (33)$$

$$F(\epsilon) = F_0\epsilon^3 \int P_e(y)M_f^2(y) \; \delta[\Delta E(y) - \epsilon] \; dy \quad (34)$$

where $M_{a,f}(y)$ represent electronic transition dipole moments, dependent on the heavy particle positions $y = Q/Q_e$. The spectral analysis performed shows that distributions (33) and (34) well approximate xanthene-like experimental band profiles if the power expansions $M_{a,f}(y) = M_0(1 + a_1y + a_2y^2 + \ldots)$ contain more than just the first term. A good illustration of this statement is Fig. 5, representing the best-fit results obtained for an ethanolic solution of rhodamine B.

The good reproducibility of the experimental results in this case (for the whole fitting range) could be due simply to the presence of the three additional adjustable parameters ($a_1 \ldots a_3$) added to the analysis. However, as was carefully checked, other formally possible modifications of formulae (20) and (21), such as including anharmonic terms (28) and (31), do not lead to desirable results. Therefore, Fig. 5 may indicate the possibility of uncon-
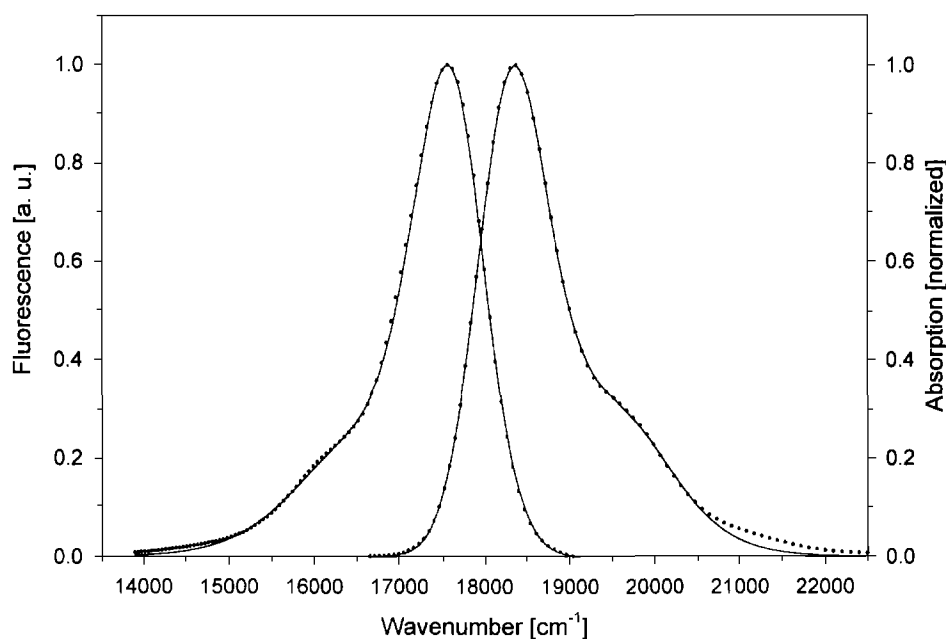

Fig. 5. Absorption and fluorescence band profiles of rhodamine B ethanolic solutions: experimental points (···) and calculated band shapes (———) based on Eqs. (33) and (34), with M^2 depending on y.

ventional interpretation of xanthene dye spectra. For the rhodamine dye solution (RhB in EtOH) analyzed, the best fit of the experimentally obtained spectra to formulae (33) and (34) gives (in addition to parameters presented in Table II) $c_{ae} = 512$ cm^{-1}, $c_{ae}^{(anh)} = 16$ cm^{-1}, $a_{a1} = 0.73$, $a_{a2} = 1.61$, and $a_{a3} = -0.28$ for absorption and $c_{fg} = 578$ cm^{-1}, $c_{fg}^{(anh)} = 40$ cm^{-1}, $a_{f1} = -0.85$, $a_{f2} = 1.52$, and $a_{f3} = 1.2$ for fluorescence. Further consequences of this approach are under investigation.

SUMMARY

A method of approximation of electronic band profiles of polar dye solutions is given. The main idea of the method, called the quasi-molecular model of band profiles, is taken from the configuration coordinate model (developed earlier to describe spectra of crystalline fluorophores), after appropriate adaptation to liquid dye solutions. The quasi-molecule is understood as an object consisting of a dye molecule and its nearest surroundings. The conformation of the quasi-molecule in liquid solution is not specified precisely. For this reason, in the processes of creating electronic spectra many different pairs of interaction potentials are involved. A transformation has been found to replace many pairs of potential curves by just a single pair of some effective potentials in the initial and final electronic states of a given quasi-molecule. The consistency between experimental band profiles and theoretically predicted profiles in the framework of the quasi-molecular model is satisfactory. It is shown that the structureless electronic bands of investigated coumarin solutions fit the model functions well. The more complicated band profiles of xanthene dye solutions can be also described in the framework of the considered model, assuming that the electronic transition dipole moment of the quasi-molecule depends on heavy particle positions (suggesting inadequacy of the Condon approximation).

ACKNOWLEDGMENT

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