Band Shape Analysis of Electronic Spectra of Polar Dye Solutions

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A semiclassical theory of electronic spectra of polar dye solutions is presented and analytical expressions of the spectra are given. A quasi-molecular approach is applied and the quasi-molecule model of the spectra previously published is reanalyzed. It is assumed that a large-amplitude motion plays a key role in the broadening of the spectra of polar dye solutions. An energy-level diagram of a quasi-molecule, considered as a dye molecule with its nearest neighborhood, is presented. In addition, the energy of reorientation in going from a Franck–Condon to an equilibrated state is determined. The orientation energy is equal to that part of the excitation energy given by the difference of the excited Franck–Condon state of a quasi-molecule from that of its equilibrated excited state. It is shown that after excitation, not only is excess vibrational, but also part of the electrostatic interaction energy is transferred to the surroundings. This energy may be obtained directly from absorption and fluorescence spectra of polar dye solutions. Experimental verification is performed on several coumarin solutions. The mean value for the reorientation energy in this case is found to be 645 cm^{-1}.

INTRODUCTION

Many complicated processes occur in liquid dye solutions which reveal themselves in their electronic spectra. The electronic structures of their components as well as thermal motion, translations, and librations influence the positions and profiles of experimentally obtained spectra. To elaborate a method to gain from the profiles of electronic spectra of dye solutions some knowledge about the molecular parameters determining the spectra is a very important task. This can be achieved by means of substantial approximations.

Dye molecules in polar solvents are such complicated systems that a rigorous quantum mechanical description of the dependence of spectral distributions on

a reasonable number of parameters seems to be unrealistic, whereas the experimentally obtained electronic spectra of polar dye solutions appear to be structureless and from the mathematical point of view are two- or three-parameter curves. Thus, many approximations have to be applied to get a theoretical representation of the experimentally obtained electronic spectra. However, the available experimental precision of spectroscopic techniques together with the numerical data processing justify the search for a new approach to the problem of the electronic spectra of polar dye solutions. Recently in a series of papers [1–4] a quasi-molecular model of the spectra was developed. In this model the fluorescence as well as the absorption spectral profiles are related to molecular parameters of a liquid polar dye solution.

In developing the model a commonly known experimental fact was taken into account which states that the positions, on a frequency scale, of the absorption as well as the fluorescence bands depend on the electronic

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structure of the components. In addition, another, often underestimated fact has been taken into consideration. It suggests that band profiles of the spectra of polar dye solutions are only in a limited degree sensitive to the chemical structures of the components. The last fact proves that the formation of electronic spectra of polar dye solutions has a different origin than the electronic spectra of polyatomic molecules in a gaseous phase.

Further it is assumed that the motion of a dye molecule as a whole among the solvent molecules is a decisive factor in shaping the profiles of the absorption and fluorescence spectra of polar dye solutions. The details of their chemical structures play a secondary role. It is self-evident that such a motion differs from the oscillatory movement of the nuclei of atoms in the molecule, especially considering their amplitudes. The dye molecules with their closest neighborhood are treated as quasi-molecules. In the present paper the main assumptions of the quasi-molecule model of the spectra are discussed and analytical expressions of the spectra are given together with molecular parameters responsible for their profiles. An improved version of the energy level diagram of a luminescent dye solution is given and reorientational energies are calculated.

SEMICLASSICAL THEORY OF OPTICAL SPECTRA OF POLAR DYE SOLUTIONS

In isolated polyatomic molecules, as the result of the interaction of an electromagnetic field of optical frequencies, some electronic transitions may take place. The probabilities of such events depend on the square of the matrix element $|\{\tilde{i}|\mu|\tilde{f}\}|^2$, which is the square of a transition moment between the vibronic states $|\tilde{i}\}$ and $|\tilde{f}\}$, where μ stands for the operator of the electric dipole moment. To get an expression for the probability of the absorption (emission) of a fixed energy ε an averaging procedure over the initial states and a summation over the final states has to be performed [5]. As a result one gets for the absorption

$$A(\epsilon)/\epsilon = K_a \sum_i \sum_f P_g |\{\tilde{i}|\mu|\tilde{f}\}|^2 \delta(\Delta E_{if} - \epsilon) \qquad (1)$$

and for the emission

$$F(\epsilon)/\epsilon^3 = K_r \sum_i \sum_f P_e |\{\tilde{i}|\mu|\tilde{f}\}|^2 \delta(\Delta E_{if} - \epsilon) \qquad (2)$$

In these formulas P_g and P_e are the Boltzmann factors of the populations of initial states for absorption and fluorescence, respectively, ΔE_{if} stands for the energy dif-

ference of proper energy levels, and the K's are normalization factors independent of ϵ.

In the adiabatic approximation for wavefunctions and the Condon approximation for transition moments,

$$\{\tilde{i}|\mu|\tilde{f}\} = \mu_e(i|f) \qquad (3)$$

where $(i|f)$ is the Franck–Condon overlap integral of the vibrational wavefunctions of the initial and final states, respectively. In the framework of these approximations the expressions (1) and (2) assume the form

$$A(\epsilon)/\epsilon = K_a |\mu_e|^2 \sum_i \sum_f P_g |(i|f)|^2 \delta(\Delta E_{if} - \epsilon) \qquad (4)$$

for absorption

$$F(\epsilon)/\epsilon^3 = K_r |\mu_e|^2 \sum_i \sum_f P_e |(i|f)|^2 \delta(\Delta E_{if} - \epsilon) \qquad (5)$$

for emission, where

$$\mu_e = \langle I|\mu|F \rangle \qquad (6)$$

In these formulas $|I\rangle$ and $|F\rangle$ describe the electronic states and $|i)$ and $|f)$ the vibrational ones. The Franck–Condon overlap integrals

$$(m|n) = \int e^{-y^2} H_m(y) e^{-(y-1)^2} H_n(y-1) \, dy \qquad (7)$$

for the displaced harmonic oscillators can be calculated using tables of integrals of special functions [6].

In optical spectra of organic dyes in polar solvents a new line broadening mechanism appears which is due to the existence of strong intermolecular interactions. In the field of forces of these interactions dye molecules oscillate about their equilibrium positions. It seems reasonable to assume that amplitudes of such movements are larger than the amplitudes of oscillation of the nuclei of atoms in dye molecules. These movements in quasi-molecules may be attributed to the large-amplitude motion (LAM).

Some examples of LAM are the rotation of the CH_3 group in polyatomic molecules and the torsional vibrations of the C–C bond in ethane [7]. The importance of intermolecular torsional vibrations of LAM type as a band profiling factor in electronic spectra of fluorescence of bianthryl in methyl-butane was recognized recently [8].

In the present paper it is postulated that the large-amplitude motion of due molecules in polar solvents is responsible for the line broadening of electronic spectra of these solutions. The main attribute of LAM is a small oscillation energy and a large anharmonicity. In the case of polyatomic molecules, where the vibrational energy is comparable to or even smaller than the thermal energy kT a semiclassical approach is justified [9]. In particular,

it is justified in the case of LAM in quasimolecules. The LAM potentials in molecular systems have been the subject of many investigations because of their sensitivity to molecular interactions. Their sensitivity to an electronic excitation will be demonstrated further. It is expected that LAM will also influence the dynamics of relaxation processes in polar liquid solutions when excited.

The absorption as well as the fluorescence spectra of flexible molecules are given by a superposition of contributions of the individual conformers and the addition over initial vibronic states in (4) and (5) has to be complemented by an integration over the LAM coordinates. It is expected that in the simplest case only one type of these coordinates may be active. Because of the small energy of the vibrational quanta of the large-amplitude motion the main contribution to the spectra is due to transitions between sublevels characterized by large quantum numbers. It can be demonstrated that the FC overlap integrals $(m|n)$ for large quantum numbers is not seriously frequency dependent. Therefore for the case of one type of active LAM coordinates the spectral distributions (4) and (5) in a semiclassical approximation may be given by

$$A(\varepsilon) = A_o^! \, \varepsilon \int P_g(Q) \, \delta[\Delta E(Q) - \varepsilon] \, dQ \qquad (8)$$

and

$$F(\epsilon) = F_o^! \, \epsilon^3 \int P_e(Q) \, \delta[\Delta E(Q) - \epsilon] \, dQ \qquad (9)$$

where Q represent the acting LAM coordinates. Similar expressions can be found in Ref. 10. It is evident that experimental verification has to be performed to justify the use of the above approximations in every individual case.

The population distributions in the initial ground and excited states are

$$P_g(Q) = P_g^0 \, \exp\{-E_g(Q)/kT\} \qquad (10)$$

and

$$P_e(Q) = P_e^0 \, \exp\{-[E_e(Q) - E_e(Q_0)]/kT \qquad (11)$$

where $P_{g,e}^0$, are Q-independent constants and $E(Q)$ are the LAM potential energies.

To calculate the integrals in (8) and (9) an explicit expressions of the energy difference in the argument of the δ-function is needed. In the hormonic approximation an optical transition occurs between initial and final states, given in the form [9]

$$E_g(Q) = kQ^2 \qquad (12)$$

and

$$E_e(Q) = k(Q - Q_0)^2 + b \qquad (13)$$

where k stands for a force constant, $b = E_e(Q_0) - E_g(0)$ is the energy difference 0–0, and Q is the displacement from a momentary equilibrium position. The minimum energy coordinate in the ground state is chosen to be 0 and in the excited state Q_0.

The numerical value of the quantity Q_0 is not known, but for our purpose the relative values of the displacement are sufficient. For a momentary relative displacement a $y = Q/Q_0$ coordinate may be employed. In the relative coordinates the energy minimum will be found at $y = 0$ in the ground state and at $y = 1$ in the excited state. Then the expressions (12) and (13), as functions of displacments, will read

$$E_g(y) = cy^2 \qquad (14)$$

and

$$E_e(y) = c(y - 1)^2 + b \qquad (15)$$

where $c = kQ_0^2$. Also the distribution functions (10) and (11) have to be expressed as functions of relative coordinates. The expressions (8) and (9) will then read

$$A(\epsilon) = A_0\epsilon \int P_g(y) \, \delta[\Delta E(y) - \epsilon] \, dy \qquad (16)$$

and

$$F(\epsilon) = F_0\epsilon^3 \int P_e(y) \, \delta[\Delta E(y) - \epsilon] \, dy \qquad (17)$$

where A_0 and F_0 are new normalization factors, independent of y.

The parameter c in (14) and (15) is the measure of coupling of electronic states of dye molecules with those of the solvent [11]. There are some similarities between the c parameters and the Huang–Rhys parameters used to describe the luminescence spectra in solids [12]. In liquid polar dye solution some additional solvatochromic processes take place and this is the main reason why the c parameters and the 0–0 energy differences obtained from the absorption and fluorescence spectra are not equal. Because of these effects the excited-state parameters of the Franck–Condon, the equilibrated, and the intermediate states are different excited states of the quasi-molecules.

The energy differences in (16) and (17)

$$\Delta E(y) = E_e(y) - E_g(y) \qquad (18)$$

according to (14) and (15) are equal to

$$\Delta E(y) = b_{af} + c_{af} - 2c_{af}\, y \qquad (19)$$

In these formulas $b_a \neq b_f$ and $c_a \neq c_f$, where the subscript a denotes the parameters obtained from absorption spectra and f those from fluorescence spectra, respectively.

It follows from (19) that the energy difference dependence on relative displacements is linear. This happens to be crucial in the calculation of the integrals (14) and (15). The spectral distributions $A(\epsilon)/\epsilon$ and $F(\epsilon)/\epsilon^3$ calculated with the energy differences (19) are Gaussian and are given by

$$A(\epsilon)/\epsilon = A_0 \exp[-\frac{(\epsilon-\epsilon_0)^2}{4c_a kT}] \qquad (20)$$

and

$$F(\epsilon)/\epsilon^3 = F_0 \exp[-\frac{(\epsilon-\epsilon'_0)^2}{4c_f kT}] \qquad (21)$$

where

$$\epsilon_0 = b_a + c_a \qquad \text{and} \qquad \epsilon'_0 = b_f - c_f$$

The experimentally obtained spectral distributions of polar dye solutions appear to be asymmetric. No wonder that all the attempts to fit them to the formulas (20) and (21) fail. Therefore a modification of the model is necessary.

In the framework of the semiclassical approach presented above, asymmetric spectral distributions may be obtained with the energy differences between the initial and final states being nonlinear functions of displacements. This could be achieved in the harmonic approximation only in the case when the c parameters in (14) and (15) are not equal or when the LAM potentials are anharmonic.

In the simplest case an asymmetric spectral distribution in the harmonic approximation will be obtained when the energy difference (18) is a quadratic function of the displacement. Appropriate LAM potentials in this case may be given in the form

$$V_g^a(y) = c_a\, y^2 \qquad (22)$$

$$V_e^a(y) = c'_a\, (y-1)^2 \qquad (23)$$

and

$$V_g^f(y') = c_f\, y'^2 \qquad (24)$$

$$V_e^f(y') = c'_f\, (y'-1)^2 \qquad (25)$$

The resulting energy differences read

$$\Delta E^a(y) = c'_a\, (y-1)^2 - c_a\, y^2 + b_a \qquad (26)$$

and

$$\Delta E^f(y') = c'_f\, (y'-1)^2 - c_f\, y'^2 + b_f \qquad (27)$$

where b_a and b_f are the 0–0 energy differences related to the absorption and fluorescence spectra, respectively.

The integration of (16) with the energy difference (26) and with the population distribution in the ground state $P_g\,(y) = P_g^0 \exp[V_g^a\,(y)/kT]$, and the integration of (17) with the energy difference (27) with the population distribution in the initial state of fluorescence $P_e\,(y') = P_e^0 \exp\{-[V_e^f\,(y') - V_e^f\,(1)]/kT\}$, yields an analytical formula for the absorption spectrum

$$A(\epsilon)/A_0 = \frac{\epsilon}{R_a(\epsilon)} \sum_{p=1}^{2} \exp\left\{\frac{-c_a[c'_a + (-1)^p R_a(\epsilon)]^2}{kT(c'_a - c_a)^2}\right\} \qquad (28)$$

and for the fluorescence spectrum

$$F(\epsilon)/F_0 = \frac{\epsilon^3}{R_f(\epsilon)} \sum_{p=1}^{2} \exp\left\{\frac{-c'_f[c'_f + (-1)^p R_f(\epsilon)]^2}{kT(c'_f - c_f)^2}\right\} \qquad (28)$$

where A_0 and F_0 are normalization factors which assure that $A(\epsilon_0^a)$ and $F(\epsilon_0^f)$, respectively become unity ($\epsilon_0^{a,f}$ are the frequencies where the appropriate spectra assume their maximum values). Here

$$R_a(\epsilon) = [c_a c'_a - (c'_a - c_a)(b_a - \epsilon)]^{1/2} \qquad (30)$$

and

$$R_f(\epsilon) = [c_f c'_f - (c'_f - c_f)(b_f - \epsilon)]^{1/2} \qquad (31)$$

It appears that the expressions (28) and (29) reproduce sufficiently well the experimentally obtained absorption and fluorescence spectra of many liquid polar dye solutions. Figures 1 and 2 illustrate the usefulness of the analytic representations of the spectra to reproduce the experimentally obtained absorption and fluorescence spectra of several coumarin solutions. A complete set of suitable molecular parameters can be found in Ref. 1.

THE ENERGY LEVEL DIAGRAM

Absorption and fluorescence spectra yield some information about the energy differences between the initial and final states, but not about the distinctive features of the individual states. Yet to build a proper energy level diagram the last information is indispensable. That is why the analysis of electronic spectra of solutions yields only qualitative arguments for the construction of an energy level diagram of a quasi-molecule.

The main contribution to the total energy of a quasi-molecule in a particular electronic state is, besides the electronic part E^{el}, the interaction energy. This interaction energy is of inductive, dispersive, and orientational origin. In polar solvents the inductive as well as
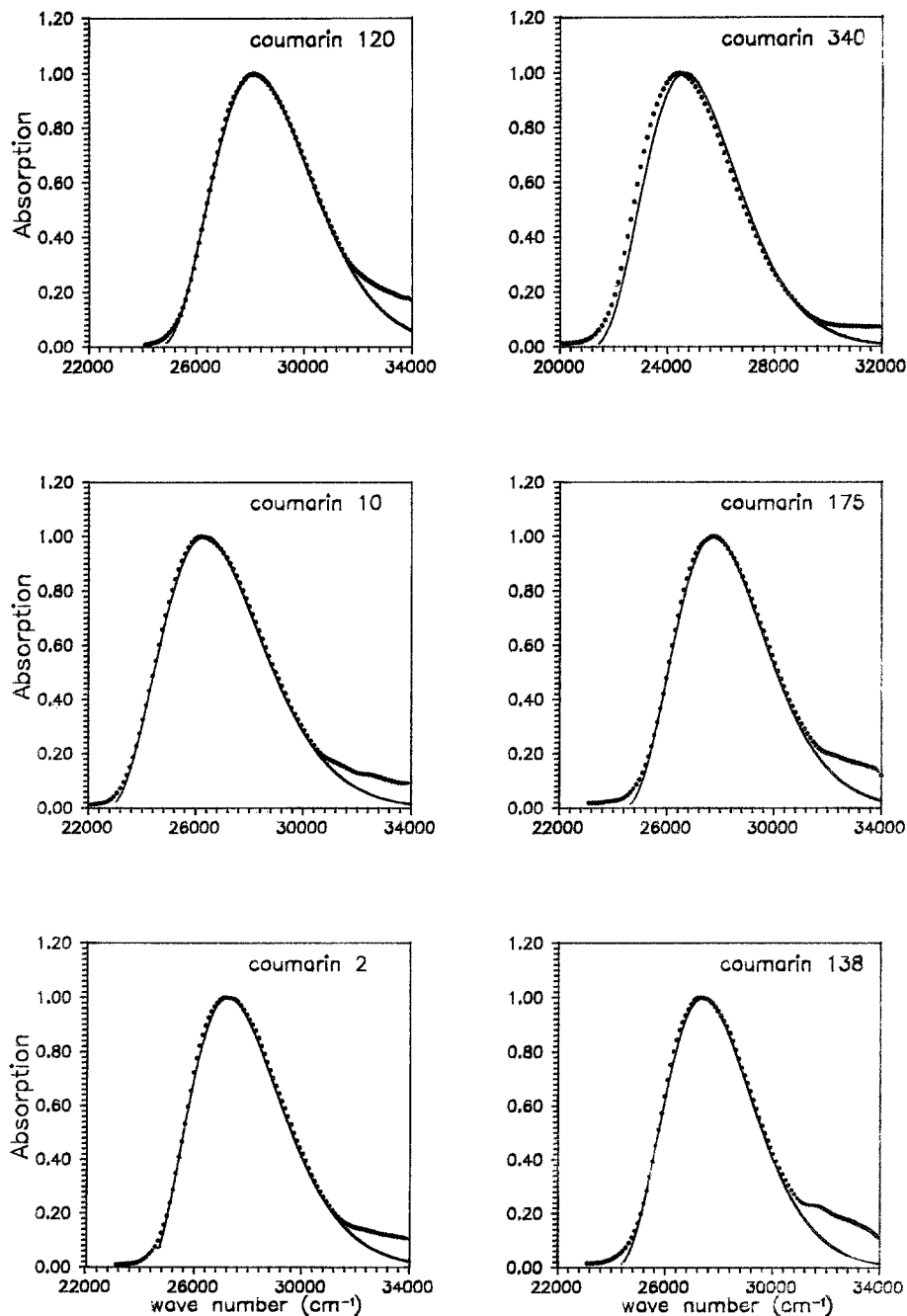
Fig. 1. Experimental (dots) and calculated (solid lines) absorption spectra of coumarin in ethyl alcohol.

dispersive interactions are almost solvent independent [13], whereas the main, orientational part is periodically modulated by the LAM of components in a cosphere of the solute. The appropriate LAM potentials will be designated by $V(y)$. It is convenient to express the energies of the initial and final states of absorption as

$$E_g^a(y) = E_g^{el} + E_g^a + V_g^a(y) \qquad (32)$$

$$E_e^a(y) = E_e^{el} + E_e^a + V_e^a(y) \qquad (33)$$

Similarly the total energies of the initial and final states of fluorescence are

$$E_g^f(y') = E_g^{el} + E_g^f + V_g^f(y') \qquad (34)$$
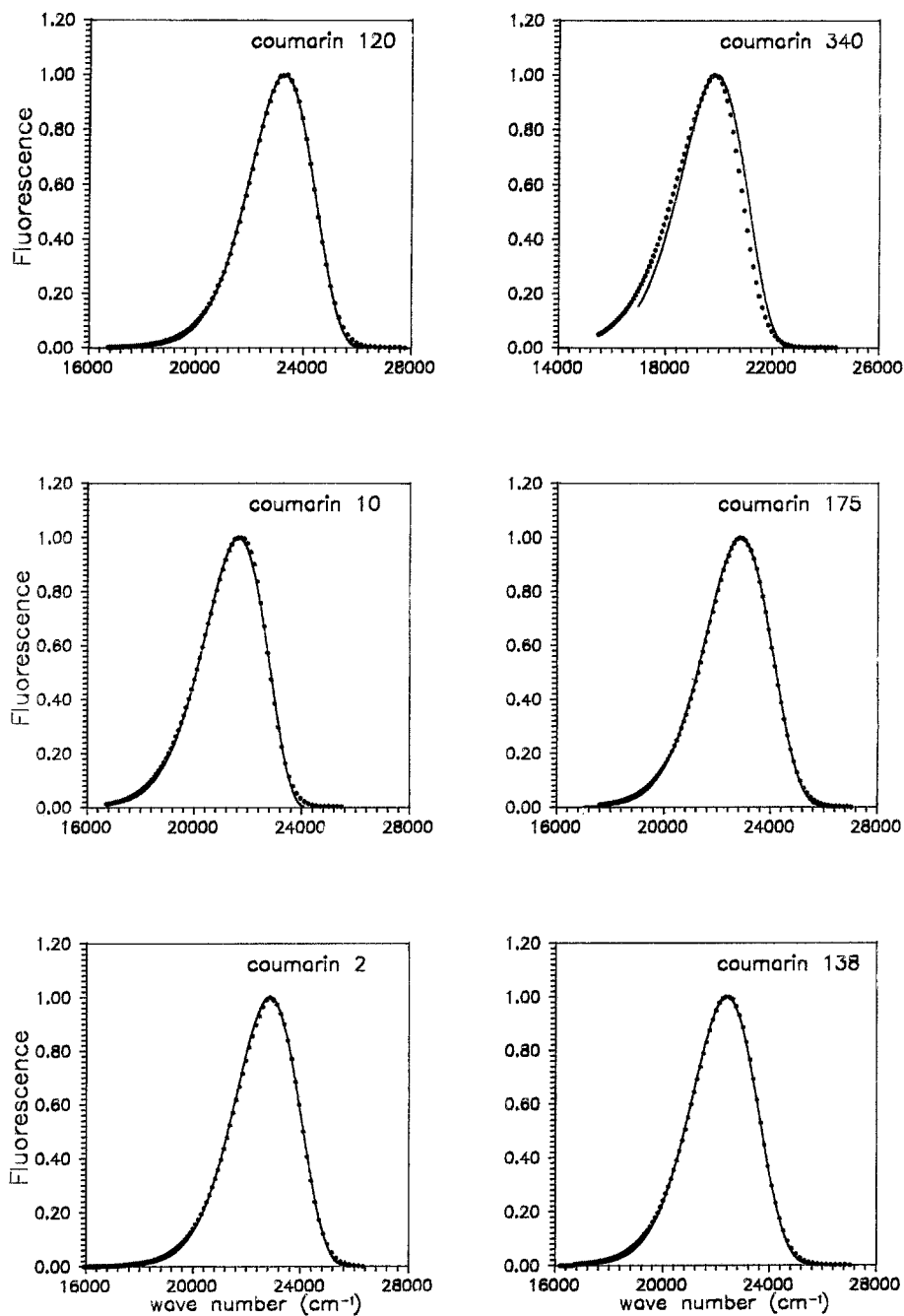
$$E_e^f(y') = E_e^{el} + E_e^f + V_e^f(y') \qquad (35)$$

Fig. 2. Experimental (dots) and calculated (solids lines) fluorescence spectra of coumarin in ethyl alcohol.

According to the assignments used, the 0–0 energy differences will read

$$b_a = E_e^a(1) - E_g^a(0) \qquad (36)$$

and

$$b_f = E_e^f(1) - E_g^f(0) \qquad (37)$$

In a consistant way, according to (32)–(37), one gets new definitions for the 0–0 energy differences:

$$b_a = \Delta E^{el} + \Delta E^a \qquad (38)$$

and

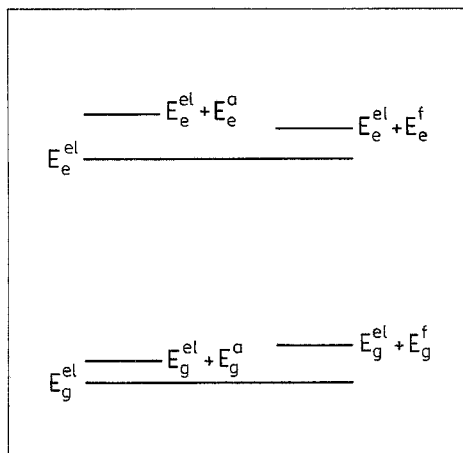$$b_f = \Delta E^{el} - \Delta E^f \qquad (39)$$

Fig. 3. Energy-level diagram of a polar dye solution.

where $\Delta E^{el} = E_e^{el} - E_g^{el}$, being independent of interactions, is common for absorption and fluorescence. The differences $\Delta E^a = E_e^a - E_g^a$ and $\Delta E^f = E_g^f - E_e^f$ in (38) and (39) are measures of the increase of the interaction energies due to the discussed electronic transitions.

As shown in Ref. 1, the energy differences (38) and (39), assigned as 0–0 energy differences, may be obtained from absorption and independently from fluorescence spectra. An appropriate energy level diagram is presented in Fig. 3. There for clarity the contributions of the LAM potentials to the total energy of the quasi-molecule are omitted. This diagram can be thought of as a modification of the previously used ones [13,14]. It has to be emphasized that the interaction energies in the excited as well as in the ground states are treated in the same manner.

DETERMINATION OF THE REORIENTATION ENERGY

In its initial ground state the system is in equilibrium. In this state the reaction field of the solvent and the actual dipole moment of a dye molecule are more or less mutually adjusted. The excitation process, changing the vibronic energy, simultaneously introduces some excess of vibrational energy. This excess is immediately, in a subpicosecond time scale, transferred to the surroundings and the Boltzmann population distribution is ascertained.

The evolution of the system from the Franck–Condon state to an initial state of fluorescence through nonequilibrated excited states and from the Franck–Condon ground state to the primary state through non-

equilibriated ground states is accompanied by reorientations of components of the quasi-molecule. This reorientational process, in terms of the Onsager cavity model, causes some changes of the reaction field of the solvent, especially their orientational part, and introduces some changes of the electric dipole moment of dye molecules. In terms of the quasi-molecule model the relaxation process simply changes the structure of the quasi-molecule.

If we assume that the reorientational process is reversible in the sense that the amount of the energy transferred to the surroundings to ascertain equilibrium in the excited state will be equal to the energy transferred to the surroundings to reestablish the primary ground state, then the following relation will hold:

$$E_e^a - E_e^f = E_g^f - E_g^a \tag{40}$$

This relation is equivalent to

$$E_g^a + E_e^a = E_g^f + E_e^f \tag{41}$$

which indicates that the sum of the LAM coordinate-independent orientational energies in the ground and excited states remain constant in every stage of evolution of the system.

Subtracting (39) from (38) and taking into account (40), one gets

$$E_e^a - E_e^f = (b_a - b_f)/2 \tag{42}$$

This relation shows how a knowledge of the reorientational energy $\Delta E_{ror} = E_e^a - E_e^f$ may be gained by means of the analysis of vibronic spectra of solutions. This energy, like the excess of the vibrational energy, is transferred to the medium [15]. This, however, means that after excitation, a part of the electrostatic interaction energy, previously engaged to form a Franck–Condon state of a quasi-molecule, is transferred to the surroundings. It is obvious that all the processes discussed occur on account of the excitation energy.

It may be concluded that the reorientation energy is equal to that part of the excitation energy which results from the difference of the excited Franck–Condon state of a quasi-molecule from its equilibrated state or, if the emission takes place before the equilibrium is reached, from the state close to it. It may be concluded further that we are not able to determine all of the electrostatic interaction energy acting in the system directly from electronic spectra, but we do are able to determine that part of this energy which is used to reorient molecules in a quasi-molecule to reach an equilibrium state.

For experimental verification of the performed analysis the results of spectral investigations of some coumarin solutions from Refs. 1 and 2 were used. The

Table I. The 0–0 Energy Differences, Half-Widths, and Reorientation Energy of
Coumarin Solutions (in cm^{-1})

Coumarin	b_α	b_f	$\Delta E_{\text{тот}}$	$\Delta\varepsilon^a_{1/2}$	$c'_a - c_a$	$\Delta\varepsilon_{f/2}$	$c_f - c'_f$
120	25992	24701	646	4368	1803	2852	1021
175	25733	24555	589	4071	1614	2957	1085
2	25515	24285	615	4039	1533	2801	984
138	25469	24131	669	3898	1512	2918	1044
10	24151	22861	645	4467	1853	2771	983
340	22560	21277	642	4099	1637	2926	1103

results are collected in Table I. In the table the obtained 0–0 energy differences as well as those from absorption and fluorescence spectra are given and the reorientational energy $\Delta E_{\text{ror}} = E^a_e - E^f_e$ calculated. In spite of the fact that this reorientational energy should be structure sensitive, the dispersion of the values obtained for different coumarin solutions is rather small. The mean value of the reorientation energy for the set of investigated coumarin solutions is equal to 645 ± 45 cm^{-1}. This value is reasonable and differs considerably from that calculated for other kinds of dye solutions, not discussed in this paper.

In addition, Table I also gives the values of the half-widths of the spectra. It has to be noted that in the quasi-molecule model of the spectra these quantities are not essential, for no physical parameters can be connected with them. It appears, however, that a qualitative correlation exists between the half-width of a spectral profile and the $c - c'$ difference. The larger the interaction energy differences of the combining states, the larger the half-widths of the spectral distributions. This conclusion may be of some importance for the determination of initial molecular parameters necessary in the fitting procedure.

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