

# Semiclassical Approach to Fluorescence Spectra of Polar Dye Solutions. Anharmonic Approximation

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On the basis of the quasi-molecule model of electronic spectra of polar dye solutions, a description of structureless fluorescence spectra is accomplished. In the model, parameters of the spectrum have a simple physical interpretation and allow us to specify the dye-solvent interaction potentials in the initial and final states of fluorescence. These parameters for a few coumarin solutions are found by fitting theoretical distributions to the experimentally obtained spectra. A whole fluorescence spectrum can be theoretically reproduced only when the anharmonicity of the motion of molecules in solution is taken into account. However, a main part of the spectrum can also be recovered in harmonic approximation. A criterion for the fitting range in this case is formulated.

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**KEY WORDS:** Electronic spectra; molecular interactions; fluorescence; dye solutions; coumarins.

## INTRODUCTION

Electronic spectra are the most important observables of luminescent dye solutions. There is still a need for an efficient analytical representation of the spectra of solutions. The most important achievement in this field is the configurational model of the spectra elaborated by Williams<sup>(1)</sup> and further improved by Huang and Rhys<sup>(2)</sup> and independently by Pekar<sup>(3)</sup> to account for electronic spectra of solids. This model, without further modification, was used to describe the electronic spectra of dye solutions (e.g., Ref. 4). To represent electronic spectra of dye solutions as well as the method of moments<sup>(5)</sup> the log-normal distribution<sup>(6)</sup> was employed. The methods of mathematical description of the spectra mentioned above have one feature in common: the parameters of the spectra are not related to the molecular parameters of the solution.

Previously we have shown<sup>(7-11)</sup> a quasi-molecular model of structureless absorption and emission spectra

of polar dye solutions. A characteristic way was employed to account for intermolecular interactions in solutions. Dye molecules with their nearest surroundings are thought of as quasi-molecules. This assumption allows replacement of the N-body problem involved in the calculation of molecular interactions in dye solutions by a one-body problem. The problem of molecular interactions is thus reduced to finding an averaged interaction potential. Electronic transitions taking place within quasi-molecules are influenced by vibrations of dye molecules in an averaged force field. It is assumed that these vibrations are a decisive factor in shaping the profiles of electronic spectra of polar dye solutions.

A theoretical treatment of the problem is difficult because of the complexity of the system and calls for some approximations to be used. The adiabatic approximation for the wave-functions, the Condon approximation for the transition moments, and the classical description of vibrations appear to be justified. On the other hand, additional approximations like the harmonic approximation or its anharmonic extension need experimental verification for each particular case.

On the basis of the quasi-molecule model of the spectra a description of structureless electronic spectra

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of polar dye solutions can be accomplished and relations of spectral parameters with those of the system investigated can be demonstrated. To show this, absorption and emission spectra of some coumarin solutions were analyzed and resulted in an analytical description of the spectra of alcoholic solutions of coumarins in the harmonic approximation. Numerical values of the parameters of the spectra, which yield a satisfactory agreement between theory and experiment, could be found. The agreement covers a wide, but not the whole, frequency range of the spectra. This is not surprising since the movement of molecules in solution can be classified as a high-amplitude motion and hence the harmonic approximation is not fully justified. A limitation of the harmonic approximation is the range of the fitting interval, which is unable to cover the whole spectrum without leaving the numerical values of the spectral parameters independent of the fitting range.

In this paper some new criteria for the range of fitting intervals in the harmonic oscillator approximation are formulated and some modifications of the model of the spectra are proposed. To improve the quasi-molecule model of the spectra the anharmonicity in the motion of molecules in solutions is taken into account. It is shown that the new version of the model enables the fitting intervals to cover the whole frequency intervals of experimentally obtained spectra. Within the framework of this new version of the model, more reliable interaction potentials can be obtained. In addition, some details of the fitting procedure are given.

### SEMICLASSICAL THEORY OF FLUORESCENCE SPECTRA IN HARMONIC AND ANHARMONIC APPROXIMATION

The spectral distribution of the fluorescence of dye solutions, defined as

$$F(\varepsilon) = F_0 \varepsilon^3 \sigma_f(\varepsilon) \quad (1)$$

can be obtained experimentally. Herein  $F(\varepsilon)/F_0$  is the relative intensity of fluorescence,  $\varepsilon$  the transition frequency, and

$$\sigma_f(\varepsilon) = \int P_e(y) \delta[f(y, \varepsilon)] dy \quad (2)$$

is a spectral distribution of the transition cross section of fluorescence. In this formula  $P_e(y)$  is the population distribution of the initial state of fluorescence and

$$f(y, \varepsilon) = \Delta E(y) - \varepsilon$$

where the energy difference  $\Delta E(y) = E_e(y) - E_g(y)$ . Here  $E_e(y)$  and  $E_g(y)$  are the energies of the initial and final states of fluorescence, respectively. The dimensionless quantity,  $y = Q/Q_0$ , is a relative displacement from a momentary equilibrium position and is equivalent to the displacement of  $Q$  in  $Q_0$  units.  $F_0$  is a normalization constant independent of  $y$  and  $\varepsilon$ .

According to the properties of the  $\delta$  distribution,<sup>(12)</sup> expression (2) may be written in the form

$$\sigma_f(\varepsilon) = \sum_i^n k[y_i(\varepsilon)] P_e[y_i(\varepsilon)] \quad (3)$$

where

$$k[y_i(\varepsilon)] = \left| \frac{df(y, \varepsilon)}{dy} \right|^{-1}_{y=y_i(\varepsilon)} \quad (4)$$

with  $y_i(\varepsilon)$  being real roots of the equation

$$f(y, \varepsilon) = 0 \quad (5)$$

The summation in (3) must be taken over all real roots of (5) and the  $\delta$ -function in (2) has no meaning when  $f'(y, \varepsilon) = 0$ . Thus the spectral distribution of the fluorescence cross section is the sum of the products of the population distribution of the initial state of fluorescence and the terms  $k[y_i(\varepsilon)]$  represent reciprocals of the gradients of appropriate energy differences of the combining states.

Equation (5) constitutes the relation between the transition frequency  $\varepsilon$  and the relative displacement  $y$ . In the case of a linear equation this relation is a functional one, otherwise, this equation possesses more than one real solution and an univocal relation between  $\varepsilon$  and  $y$  does not exist. The number of solutions of (5) depends both on the order and on the numerical values of parameters of the interaction potentials. For every real root of (5) there exists a definite branch of  $\varepsilon$  on  $y$  dependence.

The spectral distribution (3) depends on the choice of the interaction potentials in both of the combining states of fluorescence. They have to be chosen in such a way that expression (1) may fit the experimentally obtained spectra. Assuming that the redistribution of the population in a low-viscous dye solution takes place *prior* to the emission process,  $P_e(y)$  in (2) is just the Boltzmann population distribution. The unknown potentials may be approximated by a Taylor expansion with the odd terms ignored because of the symmetry.

### The Harmonic Oscillator Approximation

The harmonic oscillator quasi-molecular model is obtained by retaining only the quadratic term in the Taylor expansion of the interaction potentials. This model was discussed in Refs. 7 and 11. In this approximation an optical transition occurs between the initial and the final states of fluorescence expressed as

$$E_e(y) = c_e (y - 1)^2 + b \quad (6)$$

and

$$E_g(y) = c_g y^2 \quad (7)$$

where  $y$  is the relative displacement from the momentary equilibrium position,  $b = E_e(1) - E_g(0)$  is the 0-0 energy difference, and  $c$  parameters are products of  $Q_0^2$  and appropriate force constants or restoring coefficients which govern the vibrational motion of a dye molecule.

In Eqs. (6) and (7) we have chosen  $Q = 0$  for the momentary equilibrium coordinate in the ground state, whereas in the excited state our choice is  $Q = Q_0$ . The numerical value of the quantity  $Q_0$  is not known. However, to describe the spectral profiles only relative displacements  $y = Q/Q_0$  are needed. With these coordinates the energy minimum is found at  $y = 0$  in the ground state and at  $y = 1$  in the excited state, respectively.

In the harmonic oscillator approximation two cases may be distinguished.

1.  $c_g = c_e = c$ . Then  $f(y, \epsilon) = b + c - 2cy - \epsilon$ . In this case  $k[y_i(\epsilon)]$  in (3) does not depend on  $\epsilon$ , and consequently  $\sigma_f(\epsilon)$  is simply a Gaussian distribution. This case strongly disagrees with experimental data.
2.  $c_g \neq c_e$ . In this case, Eq. (5) has two solutions and two branches of  $\epsilon$  on  $y$  dependence should be recognized. The function  $f(y, \epsilon)$  becomes a parabola with a maximum at  $y_m$  calculated from the equation

$$\frac{df(y, \epsilon)}{dy} = 0 \quad (8)$$

In this case the spectral distribution (3) is asymmetric. The  $y_m$  divides the  $y$  axis into two parts for each branch of  $\epsilon$  on  $y$  dependence. Once  $y_m$  is found, the short-wavelength limit of the spectrum  $\epsilon_{lim}$  is given and the transition frequencies  $\epsilon$  fall into an interval  $0 < \epsilon < \epsilon_{lim}$ .

Our previous quasi-molecular model of the spectra in the harmonic oscillator approximation appears to be a useful first-order approximation which allows analysis of electronic spectra of dye solutions over a wide range

of the transition frequencies  $\epsilon$ . However, two limitations arise from our analysis:

- (1) the parameters of the spectra depend somehow on the widths of the fitting intervals,
- (2) the short wavelength limit introduces a singularity in the spectral distribution.

These defects of the model are caused partially by some arbitrariness in the choice of the fitting intervals. In our previous papers<sup>(7-11)</sup> the only criterion for an acceptable value of the fitting quality parameter used was  $\chi^2$ , which should not exceed significantly a value of unity. This version of the quasi-molecule model of the spectra is referred to as model I.

It has to be realized that the harmonic oscillator approximation is justified only in those cases where the relative displacements in both of the states, the initial and final states of fluorescence, are simultaneously smaller than unity. This means that the frequency interval where this approximation is justified should not significantly exceed, according to (5), a frequency interval

$$b - c_g < \epsilon < b + c_e$$

This covers the entire short-wavelength tail of the fluorescence spectrum up to the maximum. This constitutes a new criterion for the choice of the fitting interval. A harmonic approximation model with this new criterion is referred to as harmonic model II. It is obvious that a change of the fitting interval results in a change of the numerical values of the determined molecular parameters.

### The Anharmonic Approximation

The vibrational motion of a dye molecule within a quasi-molecule, arising from the large mass of the molecule and small interaction forces acting in the solution, may be classified as a high-amplitude motion. The idea of extending the quasi-molecular model of the spectra by introducing anharmonicity terms in the interaction potentials is a straightforward consequence of the properties of the high-amplitude motion.<sup>(13)</sup> There are many ways to account for the anharmonicity. However, because the experimentally obtained electronic spectra of polar dye solutions, seen from the mathematical point of view, appear to be distributions, dependent on only a few parameters, modification to the existing model should limit the introduction of new ones.

The simplest improvement of the model can be obtained when the number of parameters increases by only one. Careful examination of the problem results in a modification where the  $c_g$  parameter in (7) is replaced

by a substitution of the type

$$c_g := c_g + c_{an} y^2 \quad (9)$$

where  $c_{an}$  is an anharmonicity coefficient, measured in  $\text{cm}^{-1}$  units. Here the interaction potential for the initial state of fluorescence is left unchanged since most of the transitions initiate from the relaxed excited state, where the amplitudes of the motion are relatively small. This is a crude but necessary approximation required to limit the increase in the number of parameters of the model by one.

The initial and improved final state of fluorescence will read

$$E_e(y) = c_e (y - 1)^2 + b \quad (10)$$

and

$$E_g(y) = c_g y^2 + c_{an} y^4 \quad (11)$$

Formula (3) leads to the analytical form of  $\sigma_f(\epsilon)$  only if an analytical solution of (5) exists. This is not the case in the anharmonic model and calculations of spectral profiles (3) with the potentials (10) and (11) have to be performed numerically.

It is essential for the quasi-molecular model of the spectra that in the final Franck–Condon state, the molecular interaction is larger than in the initial equilibrated state. For fluorescence this leads to the relation

$$c_g > c_e \quad (12)$$

Additionally, for the anharmonic approximation,  $c_{an} > 0$  for all of the examined spectra, leading to the inequality

$$\frac{\partial^2 f(y, \epsilon)}{\partial y^2} < 0 \quad (13)$$

for both harmonic and anharmonic approaches. This means that  $f(y, \epsilon)$  has one and only one *maximum* with respect to  $y$ , at  $y_m$ —calculated from (8). In the harmonic case,

$$y_m = -\frac{c_e}{(c_g - c_e)} \quad (14)$$

whereas in the anharmonic case,

$$y_m = \frac{1}{\sqrt{3}} \cdot 2^{\frac{2}{3}} \cdot \frac{P^2 - 2^{\frac{1}{3}} \cdot (c_g - c_e)}{\sqrt{c_{an}} \cdot P} \quad (15)$$

with

$$P = [\sqrt{2 \cdot (c_g - c_e)^3 + 27 \cdot c_e^2 \cdot c_{an}} - 3^{\frac{3}{2}} \cdot c_e \cdot \sqrt{c_{an}}]^{\frac{1}{2}}$$

Consequently the limiting value  $\epsilon_{lim}$  may be calculated

from the relation

$$\epsilon_{lim} = \Delta E(y_m) \quad (16)$$

Because  $\epsilon_{lim}$  in the anharmonic approximation falls far beyond the short-wavelength edge of the fluorescence spectrum, the fitting procedure may be performed with a satisfactory result for the whole spectral distribution of fluorescence.

## EXPERIMENTAL VERIFICATION

All versions of the quasi-molecule model of the spectra discussed, harmonic models I and II as well as their anharmonic extension, need experimental verification. Results of the analyses of fluorescence spectra for a series of coumarins in ethyl alcohol are presented in Table I. In Table I, in addition to the usual molecular parameters  $b$ ,  $c_g$ , and  $c_e$  for the two harmonic models, a parameter  $c_{an}$  is added to account for the anharmonicity. The limits of the fitting intervals  $\epsilon_{min}$  and  $\epsilon_{max}$ , the  $\chi^2$  parameters, and the short-wavelength limits of the spectra  $\epsilon_{lim}$  for each version of the model are also included.

It should be noted that the short-wavelength limitation of the fluorescence spectrum in harmonic model II is shifted considerably toward high frequencies outside the spectrum and the singularity in the spectral distribution falls outside the range of interest. The price we pay is the slightly larger values of the  $\chi^2$  parameters compared to that in harmonic model I. This comes from the fact that a long-wavelength part of the spectrum is not considered in the fitting procedure.

Further, the values of the 0-0 energy differences show minor disagreement from each other in harmonic model II and the anharmonic one in all of the investigated cases. The same may be said about the  $c_g$  parameters. However, in the case of the  $c_e$  parameters, where the anharmonic correction was not introduced, this is not so and causes a serious increase in their numerical values. The anharmonicity coefficients are positive in all of the cases investigated and therefore indicate an increase in the interaction forces with the increase in the vibration energy.

The improvement of the fit in the case of the anharmonic version of the model is evident. It has the advantages of both the harmonic versions of the model, namely, a wide fitting range and a lack of singularity. Additionally, the fitting range in the new version of the model covers the whole fluorescence spectrum. Figure 1 is an illustration of the improvement of the quasi-molecule model of fluorescence spectra made by introducing anharmonicity. As an example, in Figs. 1a, b, and c the

**Table I.** Molecular Parameters of Alcoholic Coumarin Solutions Calculated in the Framework of Quasi-molecule Models of Fluorescence Spectra

Model	$\epsilon_{\min}$	$\epsilon_{\max}$	$b_r$	$c_g$	$c_e$	$c_{an}$	$\epsilon_{im}$	$\chi^2$
Coumarin 120								
Harmonic I	20,000	25,600	24,715	1,888	849		26,244	1.11
Harmonic II	22,753	26,490	25,017	1,998	1,285		28,613	1.3
Anharmonic	17,513	26,490	25,039	1,928	1,501	295	28,916	0.33
Coumarin 175								
Harmonic I	19,500	25,510	24,567	2,132	1,027		26,550	1.06
Harmonic II	22,247	26,455	24,806	2,243	1,385		30,066	0.66
Anharmonic	17,007	26,455	24,869	2,156	1,676	290	29,278	0.15
Coumarin 2								
Harmonic I	20,000	25,315	24,313	1,876	872		25,945	1.26
Harmonic II	22,422	26,212	24,538	1,907	1,221		27,932	1.24
Anharmonic	16,502	26,212	24,523	1,882	1,318	227	27,730	0.47
Coumarin 138								
Harmonic I	19,500	25,000	24,144	2,166	1,098		26,375	0.66
Harmonic II	21,906	26,525	24,396	2,291	1,485		28,611	0.7
Anharmonic	16,807	26,525	24,488	2,169	1,907	362	29,797	0.13
Coumarin 10								
Harmonic I	19,010	24,010	22,873	1,717	718		24,109	1.23
Harmonic II	21,008	24,600	22,990	1,670	870		24,810	0.91
Anharmonic	16,821	24,600	22,963	1,713	890	118	24,711	0.51

calculated spectra according to harmonic model I, harmonic model II, and the anharmonic model, respectively, are compared with the experimentally obtained fluorescence spectrum of a coumarin 2 solution (dots). Only in Fig. 1a can the singularity induced by the short-wavelength limit of the calculated spectrum be demonstrated. In the two other versions it falls far beyond the region of the spectrum.

## DISCUSSION

The quasi-molecular model of the spectra appears to be effective in describing electronic spectra of polar dye solutions. This was demonstrated in detail for the absorption and fluorescence spectra of ethanolic solutions of some coumarin molecules.<sup>(11)</sup> An important conclusion may be drawn: all the investigated spectral profiles are not very sensitive to the individual, specific chemical structure of the components and the same theoretical formula is able to reproduce spectral profiles of absorption and fluorescence of polar dye solutions. The result of the analyses of the spectra performed are numerical values of some important molecular parameters of a dye solution.

The main concept of the quasi-molecular model, which describes the spectra, originates from the liquid solution structure.<sup>(14)</sup> Under normal conditions there is always the possibility of the existence of some order in

a mutual distribution of components. The intermolecular distances between dye molecules and the closest neighboring solvent molecules are assumed to be not less than the diameter of the molecule. This assumption may be drawn from the analysis of the interaction forces of repulsion. It is also assumed that distances much larger than the molecular diameter are statistically less probable and hence all such contributions are ignored. It is understood that such assumptions introduce certain regularity into the intermolecular distance scales. As a result of the said regularity, which is the basis of the model discussed, we can further assume that each dye molecule resides long enough within its particular environment. The fluctuating field acting on each of the solvated dye molecules within a quasi-molecule can be replaced by an average field of spherical symmetry.

If the interaction between a dye molecule and a single molecule of the solvent is known, the interaction potential of the dye molecule with all neighboring solvent molecules may be obtained after some averaging procedure over all two-particle potentials. The energy of interaction is then a function of distance only. The averaged potential can be approximated by a Taylor series. Leaving just the first term of the expansion, we obtain the harmonic approximation, while the next higher term leads to anharmonic representation.

The forces of interaction of dye molecules with the molecules of the solvent are much weaker than the chemical binding forces. Therefore, due to the large

masses of the molecules, the energy of oscillation quanta are small. Hence, the quasi-continuous distribution of oscillatory sublevels and the semiclassical approximation seem to be well justified. The large value of the molecular masses and relatively small elastic forces of the system allow us to assume that the molecular oscillations are characterized by high amplitudes even in cases of energies less than  $kT$ . Consequently this leads to a limitation of the utilization of harmonic approximation.

Normalized fluorescence spectra of dye molecules with large dipole moments dissolved in polar solvents are, as a rule, structureless. From a mathematical point of view such spectral profiles are four-component curves. Analysis of fluorescence spectra of polar solutions of coumarins indicated that an exact computer fit by the harmonic approximation to experimentally obtained spectra cannot be performed. This justifies the necessity of an extension of the harmonic approximation. It also makes clear the important role which is played by the high-amplitude oscillations in the formation of the profiles of electronic bands.

In the anharmonic approximation, if the temperature is not taken into account, the description of fluorescence spectra depends on four parameters,  $b_p$ ,  $c_g$ ,  $c_e$ , and  $c_{an}$ . The latter arises from a compromise: the initial state of fluorescence is not modified according to the anharmonic model. However, such a compromise leads to a change of the parameter  $c_e$  taken from the anharmonic model compared with the value of this parameter in harmonic models. Hence, the physical value of this parameter has qualitative meaning only. For all investigated cases the anharmonic parameters are positive, which means that with an increase in the amplitude of oscillations, the force of interaction increases faster than linearly. In the theory of vibrations such a case is described as a hard interaction. This result has to be understood as a limited motion of a dye molecule among the molecules of the solvent.

The question now arises if exact knowledge of potentials of high-amplitude motion is necessary at this stage of investigation. From the expression of interaction energy for a pair of molecules, the average potential can be deduced, but the reverse procedure is rather questionable. It seems, however, that the parameters of averaged potentials received experimentally may possibly be connected to the parameters of assumed bimolecular potentials. It is also obvious that in such a process the result of an assignment to a particular model will make a great difference. Such a problem, however, calls for separate studies.

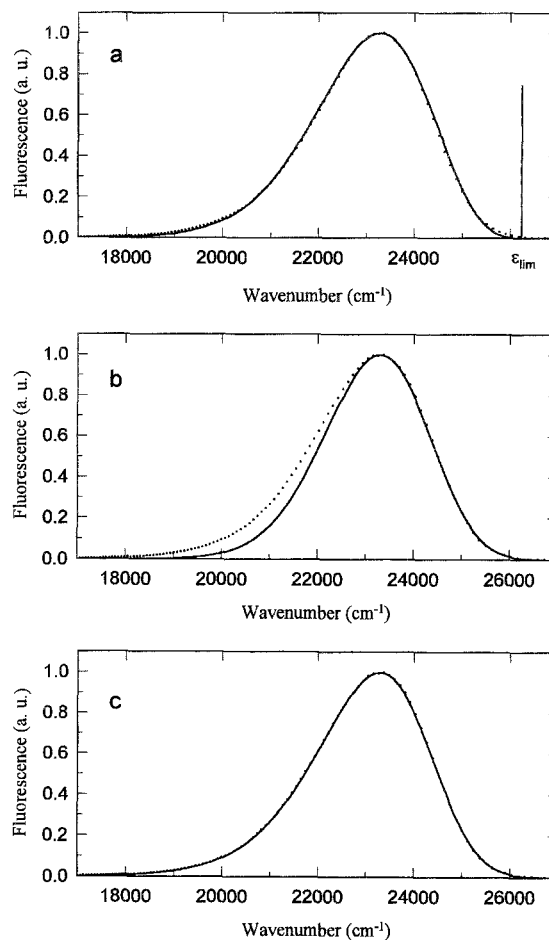


Fig. 1. Fluorescence spectra of coumarin 120 in ethyl alcohol calculated (solid lines) according to model I (a), model II (b), and the anharmonic case (c), together with experimental spectrum (dots).

## COMPUTATIONAL ASPECTS

Spectral parameters of a dye solution may be found by fitting the theoretical spectral distribution represented by (3) to the experimentally obtained spectrum using a nonlinear least-squares search. It is not important what particular algorithm is utilized. We used a noncommercial program written in Turbo Pascal 6.0 by Borland Int. according to the simple algorithm described in Ref. 15. To calculate the spectral distribution the coefficients  $k$  [ $y_p(\epsilon)$ ] in (3) for every  $\epsilon$  must be found. To get at this the algebraic equation (5) must be solved and its real solutions determined. Once found, the spectral distribution for the interaction potentials (6) and (7) reads

$$\sigma_f(\epsilon) = \sum_{p=1}^2 \frac{\exp \{-c_a[y_p(\epsilon) - 1]^2/kT\}}{|2(c_g - c_e)y_p(\epsilon) + 2c_e|} \quad \text{for } \epsilon < \epsilon_{lim} \quad (17)$$

and for the potentials (10) and (11),

$$\sigma_f(\epsilon) = \sum_{p=1}^2 \frac{\exp\{-c_e[y_p(\epsilon) - 1]^2/kT\}}{|4c_{an}y_p^2(\epsilon) + 2(c_g - c_e)y_p(\epsilon) + 2c_e|} \quad \text{for } \epsilon < \epsilon_{lim} \quad (18)$$

where  $y_p(\epsilon)$  are real roots of Eq. (5) for a given  $\epsilon$ . And in both cases,

$$\sigma_f(\epsilon) = 0 \quad \text{for } \epsilon \geq \epsilon_{lim} \quad (19)$$

It is worthwhile to note that for the anharmonic case, in order to calculate  $\sigma_f(\epsilon)$ , the fourth-degree equation must be solved for every  $\epsilon$ . In the harmonic case the analytical formula for  $\sigma_f(\epsilon)$  is known,<sup>(7)</sup> which simplifies and accelerates the calculations. Therefore, it may be convenient to use this approximation in certain cases, remembering its limitations.

Since the experimental data are known with well-defined accuracy, appropriate statistical weights must be ascribed. Only a few hundred experimental points for every *structureless* spectrum of dye solution may be considered.

In the case of the *harmonic approximation* three physical parameters ( $b$ ,  $c_g$ ,  $c_e$ ) must be recovered. In the *anharmonic case* described above there is one more parameter ( $c_{an}$ ) to be found. Finally, according to formula (1) the constant number  $F_0$  links the spectrum profile  $\sigma_f(\epsilon)$  and the experimental spectrum  $F(\epsilon)$ . The particular value of  $F_0$  carries no importance in this study, comprising, among other factors, the specific apparatus sensitivity. Nevertheless, it must be recovered. Consequently in the harmonic case four parameters, and in the anharmonic case five parameters, must be found. It should be noted that there is no correlation observed

between parameters for such structureless spectra as observed for coumarins. In conclusion, such featureless spectra carry information about anharmonic effects, and in addition, this information may be successfully recovered using our new model.

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## REFERENCES

1. F. E. Williams (1951) *J. Chem. Phys.* **19**, 457.
2. K. Huang and A. Rhys (1951) *Proc. Roy. Soc. (L)* **204**, 404.
3. S. I. Pekar (1950) *Zhur. E. T. Fiz.* **20**, 510.
4. S. Kinoshita, N. Nishi, A. Saitoh, and T. Kushida (1987) *J. Phys. Soc. Japan* **56**, 4162.
5. B. I. Stepanov and V. I. Gribowskij (1968) *Theory of Luminescence*, Iliffe Books, London.
6. D. B. Siano and D. E. Metzler (1969) *J. Chem. Phys.* **51**, 1856.
7. A. Bączyński, P. Targowski, B. Ziętek, and D. Radomska (1990) *Z. Naturforsch.* **45a**, 618.
8. A. Bączyński, P. Targowski, B. Ziętek, and D. Radomska (1990) *Z. Naturforsch.* **45a**, 1349.
9. A. Bączyński, T. Marszałek, D. Radomska, P. Targowski, and B. Ziętek (1992) *Acta Phys. Polon.* **82**, 413.
10. A. Bączyński and D. Radomska (1992) *J. Fluoresc.* **2**, 91.
11. A. Bączyński and D. Radomska (1995) *J. Fluoresc.* **5**, 91.
12. A. Messiah (1961) *Quantum Mechanics*, John Wiley and Sons, New York, p. 469.
13. M. Ito (1987) *J. Phys. Chem.* **91**, 517.
14. I. Prigogine (1957) *The Molecular Theory of solutions*, North-Holland, Amsterdam.
15. S. Brand (1970) *Statistical and Computational Methods in Data Analysis*, North-Holland, Amsterdam.