

Electron-vibrational interactions in polyatomic molecules

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We review the literature on electron-vibrational interactions in polyatomic molecules. The analysis is based on an adiabatic theory that employs a single universal small parameter of the molecules, viz., the Born–Oppenheimer parameter. The principal results of the theory of electron-vibrational spectra are summarized. Special attention is paid to the results that follow from a general analysis that is not based on concrete model. The theory is compared with experimental data for a wide range of chemical compounds (hydrocarbons with various structures, heterocyclic compounds, dyes). Possible mechanisms of broadening the electron-vibrational line in liquid and solid solutions are discussed. Experimental data that demonstrate the role of various broadening mechanisms in concrete cases are cited. It is demonstrated by means of a number of examples (induced optical activity, dimers, excimers) that the adiabatic theory is significant in the analysis of the influence of intermolecular interactions on the spectral characteristics of the molecules. The theoretical analysis is illustrated with experimental data. The role of the adiabatic theory in the description of nonradiative transitions in polyatomic molecules is briefly considered. Particular attention is paid to a discussion of the role of chemical processes that accompany nonradiative transitions. Some additional problems faced by theory and experiment are indicated in the conclusion.

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1. INTRODUCTION

Interest in the problem of electron-excited states of polyatomic molecules is constantly increasing. This is due to a variety of causes—the use of organic dyes in laser technology and in motion pictures, extensive use of optical methods in chemistry and biology, the rapid development of research on the molecular mechanisms of photosynthesis, vision, cell damage by radiation, etc.

On the whole, the problem has a vast multitude of various aspects. One of the most common aspects, essential for a great variety of application, is the determination of the role of the vibronic interactions in various spectral and other properties connected with excited electronic states.

The purpose of this review is a systematic exposition of the theory of vibronic interactions in polyatomic molecules and its comparison with experiment. Some of the considered questions are closely related to the theory of crystal impurity-center spectra, which has been treated in detail in a number of reviews and monographs^[1–5]. In the analysis of impurity centers in crystals, however, principal attention is paid to the interaction of the impurity molecule with the lattice vibrations. We, on the other hand, will concentrate our attention on intramolecular vibrations, which play a decisive role in most cases. The problem of vibronic spectra of polyatomic molecules was touched upon relatively recently in the review^[6]. We present a much more complete exposition of this question, as well as a review of the experimental data. In addition, we con-

sider a number of other aspects of the problem of vibronic interaction, such as the mechanisms of line broadening, the spectra of circular dichroism, the luminescence of excimers, and nonradiative transitions.

During the course of the exposition we shall distinguish throughout between deductions that follow rigorously from the general analysis, on the one hand, various model concepts that are based on experimental data obtained for concrete classes of molecules, on the other. The basis for this general analysis of vibronic interactions is an adiabatic theory that uses a single universal small parameter of the molecule, viz., the Born–Oppenheimer parameter $\kappa = (m/M)^{1/4}$, where m is the electron mass and M is the characteristic mass of the nucleus. A large number of examples will be used to demonstrate the effectiveness of using the adiabatic theory to obtain well-founded theoretical results and estimates.

A few words concerning the structure of the article. It is written so that a reader interested only in the traditional applications of the theory can turn immediately to Chaps. 4, 5, and 7, where the main conclusions of the theory (developed in Chaps. 2 and 3) are briefly summarized and where the experimental situation is discussed. Chapter 6 presents the results of the application of the adiabatic theory of vibronic interactions to the investigation of certain particular effects of intermolecular interactions. The experimental data are discussed in that chapter at the end of each of the sections.

2. SCHRÖDINGER EQUATION FOR A MOLECULE

The most important circumstance that follows from the smallness of the quantity $\kappa = (m/M)^{1/4}$ is the validity of the adiabatic approximation. In order for our analysis to be consistent, we present here estimates of the limits of applicability of the adiabatic approximation, although this question has been considered in numerous reviews and monographs (see, e.g., [7]).

We write down the Hamiltonian of the molecule:

$$\hat{\mathcal{H}} = \hat{T}_e + \hat{T}_N + U(r, q), \quad (1)$$

where \hat{T}_e and \hat{T}_N are the kinetic energy operators of the electrons and nuclei, respectively, and $U(r, q)$ is the total potential energy of the molecule and depends on the aggregate of the electronic (r) and nuclear (q) coordinates.

The wave function is written in the form

$$\Psi(r, q) = \psi(r, q) \varphi(q).$$

We do not assume for the time being any properties of the functions $\psi(r, q)$ and $\varphi(q)$, so that this notation is quite general.

The Schrödinger equation takes the form

$$\hat{T}_e \psi + \hat{T}_N \psi \varphi + U \psi \varphi = E \psi \varphi. \quad (2)$$

We introduce an operator \hat{L} defined by the equation

$$\hat{L} \psi \varphi = \hat{T}_N \psi \varphi - \psi \hat{T}_N \varphi. \quad (3)$$

Substituting $\hat{T}_N \psi \varphi$ from (3) in (2) and dividing both parts of the equation by $\psi \varphi$, we obtain

$$\frac{1}{\psi} \hat{T}_e \psi + U + \frac{1}{\psi \varphi} \hat{L} \psi \varphi = E - \frac{1}{\varphi} \hat{T}_N \varphi.$$

We denote the right-hand side of this equation, which depends only on the nuclear coordinates, by $V(q)$; we then get

$$(\hat{T}_e + U + \frac{1}{\psi} \hat{L} \psi) \psi = V \psi, \quad (4)$$

$$(\hat{T}_N + V) \varphi = E \varphi. \quad (5)$$

Equations (4) and (5) are completely identical with the initial Schrödinger equation $\mathcal{H} \Psi = E \Psi$. They have only been rewritten in terms of the new formally introduced functions $\psi(r, q)$ and $\varphi(q)$.

The adiabatic approximation corresponds to neglect of the term $(1/\psi) \hat{L} \psi$, called the nonadiabaticity operator, in Eq. (4).

The system of adiabatic equations is

$$[\hat{T}_e + U(r, q)] \psi_j = V_j(q) \psi_j, \quad (6)$$

$$[\hat{T}_N + V_j(q)] \varphi_{jn} = E_{jn} \varphi_{jn}. \quad (7)$$

The solution of the electronic Schrödinger equation (6) yields a system of electronic wave functions and energy levels that depend on the nuclear coordinates q as parameters. The electronic energy $V_j(q)$ serves as the potential function for the motion of the nuclei. The complete wave function in the adiabatic approximation is the product

$$\Psi_{jn}(r, q) = \psi_j(r, q) \varphi_{jn}(q). \quad (8)$$

To ascertain the conditions under which the adiabatic approximation is valid, it is necessary to calculate the corrections that appear in the electronic energy and in the wave function when account is taken of the nonadiabaticity operator in Eq. (4). We shall label the eigenfunctions (6) by the index "0" and denote the integra-

tion over the electronic coordinates symbolically by angle brackets. Let us calculate the matrix element¹⁾

$$\left\langle \psi_j^{(0)} \left| \frac{1}{\psi} \hat{L} \psi \right| \psi_j^{(0)} \right\rangle = \left\langle \psi_j^{(0)} \left| \frac{1}{\psi} \hat{T}_N \psi \right| \psi_j^{(0)} \right\rangle - \langle \psi_j^{(0)} | \psi_j^{(0)} \rangle \frac{1}{\psi} \hat{T}_N \psi.$$

Recognizing that $T_N = -\sum_q \frac{\hbar^2}{2M} \frac{\partial^2}{\partial q^2}$, we obtain

$$\left\langle \psi_j^{(0)} \left| \frac{1}{\psi} \hat{L} \psi \right| \psi_j^{(0)} \right\rangle = \langle \psi_j^{(0)} | \hat{T}_N | \psi_j^{(0)} \rangle - \sum_q \frac{\hbar^2}{M} \frac{1}{\psi} \frac{\partial \psi}{\partial q} \left\langle \psi_j^{(0)} \left| \frac{\partial \psi_j^{(0)}}{\partial q} \right. \right\rangle. \quad (9)$$

We note that at all values of q the electronic wave functions are normalized by the condition

$$\langle \psi_j^{(0)} | \psi_j^{(0)} \rangle = \delta_{jj'}.$$

Differentiating this equation with respect to q at $f = f'$, we get

$$\left\langle \psi_j^{(0)} \left| \frac{\partial \psi_j^{(0)}}{\partial q} \right. \right\rangle = 0.$$

The first-order correction to the electron energy given by Eq. (6) is therefore

$$V_j^{(1)} = \langle \psi_j^{(0)} | \hat{T}_N | \psi_j^{(0)} \rangle. \quad (10)$$

To estimate matrix elements of the type (9) and (10) it must be recognized that the electronic wave function is significantly altered, when the nuclear coordinates change, over distances on the order of the nuclear distance a :

$$\frac{\partial \psi_j}{\partial q} \sim \frac{\psi_j}{a}.$$

It follows therefore that

$$\left| \frac{V_j^{(1)}}{V_j^{(0)}} \right| \sim \kappa^4. \quad (11)$$

However, even this correction to the electron energy, which is small in itself, still does not violate the adiabatic approximation, since the quantity $V_f^{(1)}$ is fully defined if one knows the solution of only the electronic Schrödinger equation (6). The adiabatic approximation is violated in the analysis of the electronic energy only in second-order perturbation theory. The corresponding correction to the energy is given by

$$V_j^{(2)} = \sum_{f'} \left| \langle \psi_j^{(0)} | \hat{T}_N | \psi_f^{(0)} \rangle - \sum_q \frac{\hbar^2}{M} \frac{1}{\psi} \frac{\partial \psi}{\partial q} \left\langle \psi_j^{(0)} \left| \frac{\partial \psi_f^{(0)}}{\partial q} \right. \right\rangle \right|^2 / (V_j^{(0)} - V_f^{(0)}). \quad (12)$$

Recognizing that the vibrational wave function varies over distances on the order of the amplitude l of the nuclear vibrations ($l \sim \kappa a$), we obtain

$$\frac{\partial \varphi}{\partial q} \sim \frac{\varphi}{\kappa a}, \quad (13)$$

from which we get (assuming that $V_f^{(0)} - V_f^{(0)} \sim \hbar \omega_e$, where ω_e is the characteristic frequency of the electronic transitions)

$$\left| \frac{V_j^{(2)}}{V_j^{(0)}} \right| \sim \kappa^6. \quad (14)$$

In the calculation of the correction to the electronic wave function, the nonadiabatic term appears already in first-order perturbation theory:

$$\psi_j^{(1)} = \sum_{f'} \frac{\langle \psi_j^{(0)} | \hat{T}_N | \psi_f^{(0)} \rangle - \sum_q \frac{\hbar^2}{M} \frac{1}{\psi} \frac{\partial \psi}{\partial q} \left\langle \psi_j^{(0)} \left| \frac{\partial \psi_f^{(0)}}{\partial q} \right. \right\rangle}{V_j^{(0)} - V_f^{(0)}} \psi_f^{(0)}. \quad (15)$$

The correction $\psi_f^{(1)}$ is of the order of

$$|\sim \kappa^2. \quad (16)$$

Thus, the adiabatic approximation is valid accurate to terms of fifth order (inclusive) in κ for the electronic

energy and to terms of second order for the wave function.

This statement, however, is valid for not all values of the nuclear coordinate. One must not forget that the nonadiabatic corrections (12) and (15) contain in the denominator the q -dependent differences $V_f^0 - V_f^{(0)}$, which can turn out to be quite small at certain values of q . Therefore near the intersection points of the electronic terms the adiabatic approximation does not work at all. Moreover, cases are possible when the electronic terms lie close to one another practically at all q . A special analysis is then necessary, which would not be based on perturbation theory, which is not applicable in this case. In this review we confine ourselves mainly to an exposition of the vibronic spectra in the adiabatic approximation. Questions connected with violation of the adiabatic approximation are considered most fully in [8].

The significance of the adiabatic theory is not limited to finding when the total wave function can be represented in the form (8). The use of the small parameter $\kappa = (m/M)^{1/4}$ permits, when calculating various characteristics in the adiabatic approximation, to separate terms that make the largest contribution and to estimate the order of magnitude of the next terms of the expansion. In many cases, when spectral manifestations of the vibronic interaction are considered, we can confine ourselves to the so-called crude adiabatic approximation, in which the total wave function is represented in the form

$$\Psi_{fn}(r, q) = \psi_f(r, q_0) \varphi_{fn}(q),$$

where q_0 is a fixed value of the vibrational coordinates. The use of the exact adiabatic wave functions in the form (8) corresponds to allowance for the next higher terms of the expansion in the small parameter κ , and results in most cases in only small additions to the sought quantities. It must be emphasized, however, that there exist many situations in which the use of the crude adiabatic approximation is utterly insufficient and it is necessary to take into account the next higher terms of the adiabatic expansion. These situations will be considered specially later on (see Chaps. 3, 6, and 7).

3. FORM OF MOLECULE ABSORPTION OR EMISSION BAND (THEORY)

As already noted in the introduction, the question of the intensity distribution in the vibronic spectrum was considered in many reviews as applied to the spectra of impurity centers in crystals [1-5].

In this review we confine ourselves to consideration of only those formulas that play an essential role in the analysis of the intramolecular oscillations.

The electromagnetic field of a light wave can produce in a molecule transitions either between the vibrational levels of the same electronic state, or between vibronic (electron-vibrational) levels of different electronic states. We are interested in the second type of transitions. If $\hat{\mu}$ is the electric dipole-moment operator, then the probability of a transition between the stationary states $\psi_g \varphi_{gn_g} \rightleftharpoons \psi_u \varphi_{un_u}$, where g is the ground electronic state and u is the excited state, is determined in the adiabatic approximation by the square of the matrix element

$$|\langle n' | \mu_e(q) | n \rangle|^2, \quad (17)$$

where

$$\begin{aligned} \mu_e(q) &= \langle \psi_u(r, q) | \hat{\mu} | \psi_g(r, q) \rangle, \\ |n\rangle &\equiv \varphi_{gn_g}, \quad |n'\rangle \equiv \varphi_{un_u}. \end{aligned} \quad (18)$$

It is clear that if the temperature is not equal to zero, then a contribution of equal energy to the absorption (emission) can be made by transitions from different vibrational levels of the initial state. To obtain an expression that describes the probability of transitions with absorption (emission) of a fixed energy $\hbar\omega$, it is necessary to average (17) over the initial state and sum it over the final states, taking the energy conservation law into account. We then have for absorption²⁾

$$\mathcal{X}_a(\omega) = K_a \sum_{n, n'=0}^{\infty} P_n |\langle n' | \mu_e(q) | n \rangle|^2 \delta(E_{un'} - E_{gn} - \hbar\omega); \quad (19)$$

and respectively for emission

$$\mathcal{X}_r(\omega) = K_r \sum_{n, n'=0}^{\infty} P_{n'} |\langle n | \mu_e(q) | n' \rangle|^2 \delta(E_{gn} - E_{un'} + \hbar\omega). \quad (20)$$

In these formulas, P_n are the Boltzmann factors for averaging over the initial states, and K are constants that will incorporate henceforth all the inessential constant multipliers. The dependence of \mathcal{X} on ω yields the form of the emission or absorption band.

Generally speaking, if we wish to calculate the form of the band rigorously within the framework of the adiabatic approximation, then we must take into account the expansion of $\mu_e(q)$ up to second order in q , and calculate $\varphi_{fn}(q)$ by solving the Schrödinger equation of the vibrational problem (7), expanding $V_f(q)$ up to fifth order in q inclusive:

$$\mu_e(q) = \mu_e(q_0) + \sum_q \left. \frac{\partial \mu_e}{\partial q} \right|_{q=q_0} \Delta q + \dots, \quad (21)$$

$$V_f(q) = V_f(q_0) + \sum_q \left. \frac{\partial V_f}{\partial q} \right|_{q=q_0} \Delta q + \frac{1}{2} \sum_q \sum_{q'} \left. \frac{\partial^2 V_f}{\partial q \partial q'} \right|_{q=q_0} \Delta q \Delta q' + \dots, \quad (22)$$

where q_0 are the equilibrium positions of the nuclear coordinates for an arbitrary but fixed electronic state.

The approximation in which one confines oneself to the zeroth order of the expansion of $\mu_e(q)$, i.e., $\mu_e(q) = \mu_e(q_0)$, is called the Condon approximation. It means that the probability of the transition between various electronic states is considered within the framework of the crude adiabatic approximation. We note that since the kinetic energy operator of the nuclei is of the order of $\hbar\omega_e \kappa^2$, it follows that allowance for the term containing the second derivative with respect to q in the expansion (22) is essential, since it is also of the order of $\hbar\omega_e \kappa^2 \sim \hbar\Omega$ (Ω is the characteristic vibration frequency of the nuclei). If we confine ourselves to this term, then the vibrational wave functions obtained by this method are called the harmonic-approximation functions. Within the framework of these approximations, the square of the matrix element in (19) and (20) takes the form $|\mu_e(q_0)|^2 \langle n' | n \rangle^2$. Assume that we have calculated $\mathcal{X}_a(\omega)$ and $\mathcal{X}_r(\omega)$ by using this matrix element. The corrections that must be introduced into these expressions as a result of expanding $\mu_e(q)$ in powers of $q - q_0$, i.e., the deviations from the Condon approximation and allowance for the next higher terms of the expansion of $V_f(q)$ (anharmonicity), as follows from the general analysis in the introduction, will be of order of smallness of κ and higher. Thus, for example, allowance for the first term of the expansion of $\mu_e(q)$ and for the third term of the expansion of $V_f(q)$ leads

to corrections of first order in κ . There is a difference, however, between them. As to the anharmonicity, this correction always appears against the background of the principal contribution, and can be disregarded in most cases for absorption and emission processes that affect, as a rule, not too high vibrational levels of either the ground or the excited electronic states. The anharmonicity becomes quite appreciable in processes in which highly-located vibrational levels take part, i.e., where the oscillation amplitudes corresponding to a given level greatly exceed the amplitudes of the zero-point oscillations. This takes place when nonradiative electronic transitions are considered (see Chap. 7).

The correction due to the deviation from the Condon approximation is also of order of smallness κ , although the situation here is different. The point is that the matrix element $\mu_e(q_0)$ can have a numerical order of smallness for various accidental causes, e.g., it can be equal to zero by symmetry (forbidden transitions). Then the contribution to $\mathcal{X}(\omega)$ due to the expansion of $\mu_e(q)$ no longer appears against the background of the principal term, but is the first nonzero term.

a) Principal model. Thus, let us consider first expressions (19) and (20) within the framework of the following model (principal model):

1) We confine ourselves to the zeroth term of the expansion of $\mu_e(q)$ in powers of q (the Condon approximation).

2) We confine ourselves in the expansions of $V_g(q)$ and $V_u(q)$ to terms of first order in q (the harmonic approximation).

3) We assume that the only consequence of the electronic excitation for a nuclear subsystem is the shift of the equilibrium position of the normal coordinates, and neglect the changes of the natural frequencies and of the normal-coordinate system itself.

It must be emphasized here that the first two assumptions of the principal model are based on an expansion in powers of κ and are practically always valid for radiative transitions, except for the special case of forbidden transitions. On the other hand, the third assumption is quite arbitrary, since it is not based on an expansion on the single small parameter κ , and deviations from it can exert an appreciable influence on the shape of the bands.

The Hamiltonians of the vibrational problem take, in the framework of the indicated approximations, the form

$$\hat{\mathcal{H}}_g = \hat{T}_N + \frac{1}{2} \sum_k M_k \Omega_k^2 Q_k^2, \quad (23)$$

$$\hat{\mathcal{H}}_u = \hat{T}_N + \frac{1}{2} \sum_k M_k \Omega_k^2 (Q_k - \Delta Q_k^{(0)})^2 + \hbar \omega_{ug}, \quad (24)$$

where $\hbar \omega_{ug}$ is the energy of the pure electronic transition, summed over k , and signifies summation over all the normal oscillations, while M_k , Ω_k , and Q_k are the reduced masses, natural frequencies, and normal coordinates, respectively. By $\Delta Q_k^{(0)}$ we denote the change of the equilibrium position along the k -th normal coordinate following electronic excitation.

The expression for the form of the absorption band becomes

$$\mathcal{X}_a(\omega) = K_a |\mu_e|^2 \sum_{n, n'} P_n |\langle n' | n \rangle|^2 \delta(E_{un'} - E_{gn} - \hbar \omega). \quad (25)$$

It follows immediately from the form of the Hamilton-

ians (23) and (24) that the Franck-Condon factor $\langle n' | n \rangle^2$, which determines in the Condon approximation the form of the band, breaks up into a product of factors for each normal vibration

$$|\langle n' | n \rangle|^2 = \prod_k |\langle n'_k | n_k \rangle|^2, \quad (26)$$

with

$$\langle n_k | n'_k \rangle = \int dQ_k \xi_{n'_k}(Q_k) \xi_{n_k}(Q_k - \Delta Q_k^{(0)}), \quad (27)$$

where ξ are the wave functions of the harmonic oscillators. We introduce the quantities $\nu_k = n'_k - n_k$, and then obtain for $\mathcal{X}_a(\omega)$

$$\mathcal{X}_a(\omega) = K_a |\mu_e|^2 \sum_{v=-\infty}^{+\infty} \delta(\omega_{ug} + \sum_k \Omega_k \nu_k - \omega) W_v, \quad (28)$$

where

$$W_v = \prod_k W_{v_k} = \prod_k (1 - \alpha_k) \sum_{n_k=0}^{\infty} \alpha_k^{n_k} |\langle n_k + v_k | n_k \rangle|^2, \quad (29)$$

with $\alpha_k = \exp(-\hbar \Omega_k / kT)$.

We consider first the case $\nu_k \geq 0$. Writing down the functions $\xi(Q)$ in explicit form in terms of Hermite polynomials (see, e.g., [9]) and using formula (7.377) of [10], we obtain an expression for the square of the overlap integral

$$|\langle n_k + v_k | n_k \rangle|^2 = e^{-y_k^2} \frac{n_k!}{(n_k + v_k)!} y_k^{2v_k} |L_{n_k}^{v_k}(y_k^2)|^2, \quad (30)$$

L_n^v is a Laguerre polynomial

$$y_k = \sqrt{\frac{M_k \Omega_k}{2\hbar}} \Delta Q_k^{(0)}. \quad (31)$$

We now substitute (30) in (29) and sum using (8.976.1) of [10]. We then have for W_v

$$W_v = \prod_k \exp\left(-y_k^2 \frac{1 + \alpha_k}{1 - \alpha_k}\right) \alpha_k^{-v_k/2} I_{v_k}\left(\frac{2y_k^2 \sqrt{\alpha_k}}{1 - \alpha_k}\right), \quad (32)$$

where I_v is a Bessel function of imaginary argument. For $\nu_k < 0$ we can obtain an identical expression, except that the Bessel function takes the form $I_{-\nu_k}$. Since, however, $I_v = I_{-v}$, expression (32) is valid for all values of ν_k . Substituting (32) in (28) we obtain a final expression for the intensity distribution in the molecule absorption spectrum within the framework of the principal model. W_v is the probability that the molecule will go over, under the influence of the radiation, from the ground electronic state to an excited one with a change of the aggregate of the vibrational quantum numbers v . The analogous expression for emission is

$$\mathcal{X}_r(\omega) = K_r |\mu_e|^2 \sum_{v=-\infty}^{\infty} \delta(\omega_{ug} - \sum_k \Omega_k \nu_k - \omega) W_v, \quad (33)$$

where W_v is defined as before by (32). It follows therefore directly that in the approximation of the principal model the absorption and emission spectra have mirror symmetry relative to the frequency of the pure electronic transition ω_{ug} . We note that formula (32) was derived many times by various methods (see [1-3]). For cases when $\hbar \Omega_k \gg kT$, it suffices to retain only the first term of the expansion of the Bessel function in powers of its argument, and this yields

$$W_v = \prod_k e^{-y_k^2} \frac{y_k^{2v_k}}{v_k!}. \quad (34)$$

In the opposite limiting case $\hbar \Omega_k \ll kT$, using the asymptotic expansion of the Bessel function, we have

$$W_v = \prod_k \frac{1}{\sqrt{2\pi \sigma_k}} \exp\left[-\frac{(v_k - \bar{v}_k)^2}{2\sigma_k^2}\right], \quad (35)$$

where

$$\bar{\nu}_k \approx y_k^2, \quad \sigma_k^2 \approx 2y_k^2 \frac{kT}{\hbar\Omega_k}.$$

Thus, at low temperatures the distribution of the intensity in the spectrum constitutes an aggregate of Poisson distributions for each normal vibration. At high temperatures, the spectrum takes the form of an aggregate of Gaussian distributions. A detailed discussion of the application of the obtained expression to the analysis of the experimental data will be given in Chap. 4.

We have found above that the probability of a transition in which the molecule energy changes by an amount $\hbar(\omega_{ug} + \sum_k \Omega_k \nu_k)$ is $K_a |\mu_e|^2 W_v$. We consider now several integral characteristics of this probability distribution.

It is convenient to use for this purpose the well known expression for the generator of a Bessel function of imaginary argument:

$$S(z, t) = \exp\left[\frac{z}{2}\left(t + \frac{1}{t}\right)\right] = \sum_{\nu=-\infty}^{\infty} t^{\nu} I_{\nu}(z). \quad (36)$$

We calculate first the summary probability of the transition, i.e., in fact the zeroth moment (m_0) of the distribution W_v . We have

$$m_0 = K_a |\mu_e|^2 \sum_v W_v. \quad (37)$$

We put in formula (36)

$$t_k = \frac{1}{\sqrt{\alpha_k}}, \quad z_k = \frac{2y_k^2 \sqrt{\alpha_k}}{1 - \alpha_k};$$

and then obtain for m_0

$$m_0 = K_a |\mu_e|^2 \exp\left(-\sum_k y_k^2 \frac{1 + \alpha_k}{1 - \alpha_k}\right) \prod_k S(z_k, t_k). \quad (38)$$

Hence

$$m_0 = K_a |\mu_e|^2. \quad (39)$$

Formula (39), incidentally, is obvious beforehand, since it is the consequence of the condition for the normalization of the probability distribution W_v . Formula (39) means that the total absorption intensity, within the framework of the principal model, does not depend on the parameters of the vibrational problem and is determined only by the electronic-transition oscillator strength. The mean value $\bar{\omega}$ of the frequency can be expressed for the distribution $K_a(\omega)$ in the form

$$\bar{\omega} = \omega_{ug} + \sum_k \Omega_k m_1^{(k)}, \quad (40)$$

and its variance in the form

$$\Delta^2 = \sum_k \Omega_k^2 [m_2^{(k)} - (m_1^{(k)})^2], \quad (41)$$

where

$$m_p^{(k)} = \sum_{\nu_k=-\infty}^{\infty} (\nu_k)^p W_{\nu_k}. \quad (42)$$

Using the relations

$$m_1^{(k)} = \exp\left(-y_k^2 \frac{1 + \alpha_k}{1 - \alpha_k}\right) t_k \frac{\partial S(t_k, z_k)}{\partial t_k}, \quad (43)$$

$$m_2^{(k)} = \exp\left(-y_k^2 \frac{1 + \alpha_k}{1 - \alpha_k}\right) t_k \frac{\partial}{\partial t_k} \left(t_k \frac{\partial S(t_k, z_k)}{\partial t_k} \right), \quad (44)$$

we obtain

$$\bar{\omega} = \omega_{ug} + \sum_k \Omega_k y_k^2, \quad (45)$$

$$\Delta^2 = \sum_k \Omega_k^2 y_k^2 \frac{1 + \alpha_k}{1 - \alpha_k} = \sum_k \Omega_k^2 y_k^2 \operatorname{cth} \frac{\hbar\Omega_k}{2kT}. \quad (46)$$

The expressions for emission are similar in form, but

the second term of (45) has a negative sign. We see that the mean value of the frequency and the variance depend strongly on the displacements of the equilibrium positions y_k , and the variance of the bands has furthermore a definite temperature dependence.

b) Deviations from the principal model. 1) Changes of the natural frequencies and of the system of normal coordinates. We have already noted that the most essential assumption of the principal model, not based on the expansion in the parameter κ , is the condition that there be no changes in the natural frequencies and in the normal-coordinate system itself. Let us analyze this question in greater detail.

In the harmonic approximation, the adiabatic Hamiltonians of the vibrational problem take in the general case the form (cf. (23) and (24))

$$\hat{\mathcal{H}}_g = \hat{T}_N + \frac{1}{2} \sum_k M_k \Omega_k^2 Q_k^2, \quad (47)$$

$$\hat{\mathcal{H}}_u = \hat{T}_N + \frac{1}{2} \sum_k M_k \Omega_k^2 Q_k^2 + \hbar\omega_{ug}. \quad (48)$$

The normal coordinates of the electronic ground state can be expressed in terms of the normal coordinates of the excited state in the following manner:

$$Q_k = \sum_j A_{kj} Q'_j + \Delta Q_k^{(0)} \quad (49)$$

where A_{ki} are the elements of the matrix $A = R^{-1}R'$, the columns of the matrices R and R' being the forms of the normal vibrations in the ground and excited states, i.e., R and R' are the matrices for the transition from the generalized (natural) coordinates to the normal ones. Thus, if d_j is the change of the equilibrium value for some natural coordinate, then we have for the change of the equilibrium value of the k -th normal coordinate

$$\Delta Q_k^{(0)} = \sum_j (R^{-1})_{kj} d_j. \quad (50)$$

The intensity distribution is determined as before by Eq. (25), but the overlap integral takes the form

$$\langle n | n' \rangle = \int dQ'_1 \dots \int dQ'_N \xi_{n_1}(Q'_1) \dots \xi_{n_N}(Q'_N) \xi_{n'_1}(Q'_1) \dots \xi_{n'_N}(Q'_N), \quad (51)$$

where N is the number of independent degrees of freedom of the molecule. In the principal-model approximation we have assumed that $(R^{-1}R')$ is a unit matrix, in which case the Franck-Condon factor can be written in the form of a product in the normal coordinates. In the general case the problem reduces to a calculation of the N -dimensional integral (51). The elements of the matrices R^{-1} and R' , the natural frequencies, and the reduced masses for each electronic state are determined independently from the solution of the standard normal-vibration problems (see, e.g., [11]). The quantities d_j , which are also necessary for the calculation of (51), can be determined by the methods of quantum chemistry. Knowing all the indicated quantities, we can calculate the integral (51) by numerical methods with a computer. This approach, while encountering considerable difficulties, can nevertheless be quite effective in the calculation of the vibronic spectrum of a particular compound, but it is impossible to obtain for it the general laws governing the changes that occur in the spectra in the case of deviations from the principal model.

It was established in the preceding section that the absorption and emission spectra have mirror sym-

metry within the framework of the principal model. Deviations from the principal model will always lead to violation of the mirror symmetry. At the same time it is known from experiment that for a very wide class of compounds the spectra do indeed have mirror symmetry, the deviations from which have the character of perturbations (see Chap. 4). This indicates that additional small parameters exist for a large class of real situations.

In actual fact we must ascertain the conditions under which the integral (51) can be calculated by perturbation, taking the principal model as the zero-order approximation. This question was investigated in^[12], where it is shown that the principal model is a good zero-order approximation if one uses in addition to the Born-Oppenheimer parameter an additional small parameter corresponding to the condition that the change in the force constants of the bonds between the atoms of the molecule be small in the case of electronic excitation. This condition takes the form

$$\Delta g \ll g, \quad (52)$$

where g is the force constant and Δg is its change under electronic excitation. In^[12] we calculated the correction to the first model in first order in $\Delta g/g$.

The condition (52) is an additional assumption that depends, generally speaking, on the concrete properties of the ground and excited electronic states. Its validity can be verified only by comparing the experimental data with the conclusions that follow from the model (see Chap. 4). Situations can occur in which the condition (52) is violated, for example in transitions to high-lying electronic level or to states for which, say, one of the double interatomic bonds becomes single, etc.³⁾ Perturbation theory can no longer be used in this case, and the integral (51) must be calculated exactly.

It is of interest, at the same time, to obtain an analytic expression for the intensity distribution in this case. Such an expression was obtained in^[13] for zero temperatures.

Sharp and Rosenstock^[14] have proposed for a numerical calculation of the spectra a different approach based on the fact that the overlap integral (51) can be represented in the form of a coefficient of the expansion of a certain generating function for which an analytic expression can be obtained. This method does not reveal the general character of the intensity distribution, but is quite effective when it comes to obtaining numerical values of the Franck-Condon factors for transitions to low-lying vibrational levels, and was used in^[15] to calculate the vibronic spectra of a number of organic molecules.

2) Forbidden transitions. We now dwell on deviations from the Condon approximation. This deviation from the principal model is quite different in character than the deviation considered above. Since the Condon approximation is based on an expansion in the parameter κ , it follows that allowance for the next higher terms should lead, generally speaking, only to small corrections. Significant deviations from the Condon approximation may turn out to be caused by random factors, owing to the numerical smallness of the quantity $\mu_e(q_0)$, i.e., for transitions that are forbidden (or almost forbidden) by symmetry.

Thus, consider an electronic symmetry-forbidden

transition. The first nonzero term of the expansion of $\mu_e(q)$ in powers of κ is

$$\mu_e(q) = \sum_a \left. \frac{\partial \mu_e}{\partial Q_a} \right|_{Q_a=0} Q_a, \quad (53)$$

where the summation is carried out only over the non-fully-symmetrical normal coordinates (a). It is obvious that for all fully-symmetrical coordinates (s) we have $\partial \mu_e / \partial Q_s = 0$. We now use the remaining premises of the principal model, i.e., we assume that in the case of electronic excitation a change takes place in the equilibrium positions of the nuclei, but there is no change in the frequency and form of the normal vibrations. Moreover, we assume that electronic excitation alters the equilibrium values of only the fully-symmetrical coordinates. This assumption is of far-reaching significance and will be discussed in detail in Chap. 4.

Within the framework of the assumptions made, we obtain for the absorption probability the expression

$$\begin{aligned} \mathcal{K}_a(\omega) = K_a \sum_s \sum_{\nu_s} \left| \frac{\partial \mu_e}{\partial Q_a} \right|_{Q_a=0}^2 \frac{\hbar}{2M_a \Omega_a} \frac{1}{1 - \alpha_a} \left[\delta(\omega_{ug} + \sum_s \Omega_s \nu_s + \Omega_a - \omega) \right. \\ \left. + \alpha_a \delta\left(\omega_{ug} + \sum_s \Omega_s \nu_s - \Omega_a - \omega\right) \right] W_{\nu_s}. \end{aligned} \quad (54)$$

In this expression, $\alpha_a = \exp(-\hbar \Omega_a / kT)$, and W_{ν_s} is the intensity distribution for the fully-symmetrical normal vibrations of the molecule and is given in the general case by expression (32). The singularities to which (54) leads will be analyzed in the next section, using the long-wave band of benzene as an example.

4. COMPARISON OF THEORY WITH EXPERIMENT

a) Main conclusions of the theory. Let us summarize the theoretical results and deduce from them certain consequences that are useful in the analysis of the experimental data.

The main result of the theoretical analysis is the conclusion that a consistent use of the single universal small parameter of the problem, namely the Born-Oppenheimer parameter $\kappa = (m/M)^{1/4}$, and also of the additional assumption that the electronic excitation produces a small change of the strength functions, lead to the principal model of the theory of vibronic spectra.

Within the framework of the principal model, the vibronic absorption and luminescence spectra have the following properties:

- 1) The intensity distribution in the absorption spectrum of a polyatomic molecule is described by formulas (28) and (32).
- 2) The law of mirror symmetry of the absorption and fluorescence spectra is satisfied.

When considering the question of mirror symmetry, it must be recalled that the radiation is always assumed to stem from the same electronic level on which absorption takes place. This is actually valid only for the very lowest singlet excited state (see Chap. 7). In organic molecules, on which most experiments on vibronic spectra have been performed, electronic excitation leads principally to changes in the lengths of the bonds C-C, C=C, C-N, and C=O. At the same time, the potential curves are shifted for the relatively "rigid" normal vibrations, for which the inequality $\hbar \Omega \gg kT$ is satisfied. In this case formula (28) goes over into the simple formula (see (34))

$$\mathcal{H}_a(\omega) = K_a |u_a|^2 \sum_v \delta(\omega_{ag} + \sum_k \Omega_k v_k - \omega) \prod_k e^{-y_k^2} \frac{y_k^{2v_k}}{v_k!}, \quad (55)$$

where the y_k are given by (31).

For one normal vibration (Fig. 1), the relative intensity distribution is given by

$$\frac{W_v}{W_0} = \frac{y^{2v}}{v!}, \quad (56)$$

where $y = \sqrt{M\Omega/2\hbar} \Delta Q^0$.

Formulas (55) and (56) are the most important ones in the analysis of the intensity distribution in the vibrational spectra of polyatomic molecules.

As indicated above, in order for the principal model to be valid it is necessary that electronic excitation change the force constant little. More accurately speaking, this calls for the satisfaction of the inequality

$$\frac{\Delta g}{g} \ll \kappa, \quad (57)$$

where g is the force constant.

The simplest experimental criterion for the satisfaction of this inequality is that the extent to which the mirror-symmetry law is satisfied. Since $\kappa \sim 10^{-1}$, the inequality (57) means that the deviations from mirror symmetry should not exceed about 10%.

This criterion, however, is valid only for the very lowest singlet electronic states. A more universal criterion is therefore the correspondence between the experimental distribution of the intensity in the absorption and luminescence spectra, on the one hand, and formulas (55) and (56) on the other.

Let us consider the condition (57) from a somewhat different point of view. This means that the excitation causes small relative changes in the lengths and angles of the bonds. In other words, condition (57) is equivalent to the requirement that the individual structure of the molecule be preserved under electronic excitation. When the condition (57) is violated, one can say that when a quantum is absorbed the molecule undergoes photochemical transformations. Electronic transitions to low-lying vibrational levels and directly accompanied by photochemical transformations have a rather low probability, owing to the smallness of the Franck-Condon factors for these transitions. Therefore electronic states for which the condition (57) is not satisfied do not manifest themselves in practice in the absorption spectra.⁴⁾ Only after excitation to one of the electronic levels for which the condition (57) is satisfied can the molecule experience a photochemical trans-

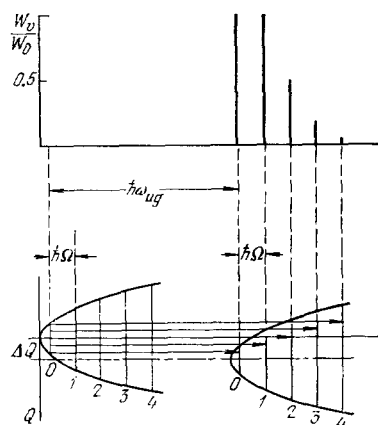


FIG. 1. Potential curves of a molecule. Q is the normal coordinate in the ground and excited electronic states. The shift ΔQ corresponds to $y = 1$. The upper part of the figure shows the relative intensity distribution for transitions from the zero vibrational level (formula (56)).

formation. This question will be considered in detail in Chap. 7. In this section we confine ourselves to the consideration of transitions to levels for which the condition (57) is satisfied.

It was shown in the preceding section that, within the framework of the principal model, the system of normal coordinates is not altered by electronic excitation, and only the equilibrium values of the coordinates can change. The invariance of the normal coordinates means, in particular, conservation of their symmetry properties. Consequently, within the framework of the principal model, electronic excitation cannot cause a change in the equilibrium values of the non-fully-symmetrical normal coordinates, for this would mean a lowering of the molecule symmetry, leading inevitably to a change in the system of normal coordinates. Thus, within the framework of the principal model, the displacement of the equilibrium positions of the nuclei of the molecule following electronic excitation is possible only along fully-symmetrical normal coordinates. This selection rule for the appearance of oscillations in the electronic spectrum limits significantly the number of normal coordinates that manifest themselves primarily in the electronic spectra of polyatomic molecules. We note, finally that the inequality (57) leads to $y \leq 1$.

These are the main results of the theory in the case of the principal model. It must be emphasized, however, that the expansion parameter κ , which is used for the justification of the principal model, is not very small, of the order of 0.1. Therefore the deviations from the model have perfectly measurable values, even for the lower excited states.

The deviations from the principal model manifest themselves primarily in violation of the rigorous mirror symmetry of the absorption and fluorescence spectra, a violation that manifests itself both in a change in the frequencies of the normal vibrations, and in a change of the intensity distribution.

When comparing theory with experiment, a distinction must be made between two levels of rigor of the theoretical predictions. So far we have referred only to a rigorous theory based on expansion in the Born-Oppenheimer parameter. Its conclusions have therefore a very wide range of validity (if the condition (57) is satisfied). However, although this theory does lead to important formulas (such as (38), (55), and (56)), it answers by far not only questions that arise in the analysis of the experimental data. In fact, in this theory the dimensionless values of the displacements of the normal coordinates, which occur following electronic excitation (y_k in formula (55)) enter as the parameters of the theory, and these parameters must be determined from experiment. This theory cannot explain how the structure of the molecule affects its vibronic spectrum. To answer this question we must be able to calculate the y_k . Calculations of this kind cannot be carried out rigorously in principle, in view of the absence of a small parameter, and are inevitably based on one numerical method or another. The degree of reliability of the results depends principally on the perfection of the methods used to calculate the electronic energy of the molecule as a function of the coordinates of the nuclei, a problem that belongs to quantum chemistry.

b) Use of the theory of vibronic spectra to interpret the experimental data. As already noted, the main

formulas of the theory of vibronic spectra were derived in the early Fifties^[1]. These formulas soon found extensive application in the interpretation of the experimental data on impurity centers in crystals (see, e.g.,^[4]). To interpret the spectra of organic molecules in solutions and vapors, these relations came into use only in the early Sixties. Of particular significance in this connection is the widely known paper of McCoy and Ross^[16], in which formula (56) was used to analyze the vibrational progression of the long-wave absorption band of a series of aromatic hydrocarbons. Somewhat earlier, Kuhn^[17] used formula (56) for an analysis of the spectra of metalloporphyrins.

Formulas (55) and (56) were subsequently used for an analysis of the vibronic spectra of hydrocarbons, as well as of a large class of organic dyes^[22-25]. Many attempts were made^[15,16,19,20,21] to calculate the quantities y_k , which determine the form of the vibronic spectrum of the molecule, by starting from the molecular structure. We shall summarize briefly in this section the main results of the cited papers.

1) **Hydrocarbons.** In all the investigated cases, good agreement was observed between the experimental intensity distribution and formula (55). The parameters y_k were regarded as empirical and determined from experiment.

By way of example, Fig. 2 shows the experimental absorption spectrum of benzene, and also the intensity distribution (in a different scale) calculated from (56) with $y = 1.25$. The value of y^2 is determined from the ratio of the intensities of the first two peaks of the band, after which the intensities of the remaining peaks are calculated. Figure 2 demonstrates the good correspondence between theory and experiment. A detailed strictly quantitative comparison of the experimental distribution of the intensity with theory is made difficult (as also in other cases considered below) by the fact that each peak has a noticeable width and the peaks overlap. As is well known, the long-wave band of benzene shown in Fig. 2 (in the region $\lambda = 260$ nm) corresponds to the symmetry-forbidden electronic transition $A_{1g} \rightarrow B_{2u}$ and appears only as a result of a non-fully-symmetrical vibration (see, e.g.,^[26a], p. 175 of the Russian translation).

The main contribution to (54), i.e., to the "allowing" of the forbidden transition in benzene, is made by the non-fully-symmetrical vibration e_{2g} with frequency 608 cm^{-1} in the ground state and 522 cm^{-1} in the excited state. The small peak in the long-wave region (near 37400 cm^{-1}) corresponds to a transition to the zero level ($n'_a = 0$) of the excited electronic state, i.e., it is shifted relative to ν_{ug} (the position of the pure electronic transition is marked by the arrow in Fig. 2) by

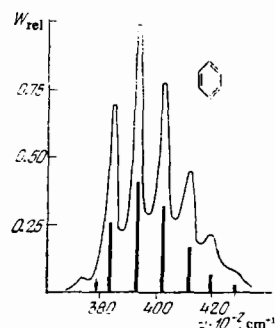
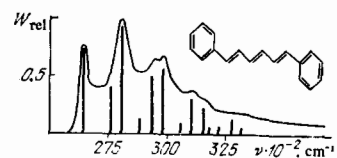


FIG. 2. Absorption spectrum of benzene in a solution of isopropyl alcohol at 293°K. [18] The theoretical progression is shown near the experimental spectrum (in a different scale) and is based on formula (56) with $y = 1.25$.

FIG. 3. Absorption spectrum of diphenylhexatriene at 77°K [21]. The spectrum reveals two vibrations with frequencies $\Omega_1/2\pi = 1670 \text{ cm}^{-1}$ ($y_1 = 1.1$) and $\Omega_2/2\pi = 1210 \text{ cm}^{-1}$ ($y_2 = 0.7$). An expansion of the spectrum with the aid of formula (55) is given.



608 cm^{-1} towards the long-wave side (it corresponds to the second term in the square brackets of (54)). At the same time, the entire progression is shifted relative to ν_{ug} to the short-wave side by 522 cm^{-1} (the first fundamental term in (54)).

An estimate of α_a shows that at room temperature the intensity of the long-wave spike should be approximately 6% of the intensity of the first appreciable maximum; this is in good agreement with experiment (see Fig. 2).

It follows also from (54) that the intensity distribution in the progression due to the fully-symmetrical vibrations should have the usual form (56). From the point of view of the theory of vibronic spectra, benzene is the simplest example of a polyatomic molecule, for in view of its high symmetry it has only one fully-symmetrical (a_{1g}) normal vibration connected with the deformation of the carbon core (a "breathing" vibration having a frequency 995 cm^{-1} in the ground state and 925 cm^{-1} in the excited state). As noted above, following electronic excitation one should expect shifts of the potential curves, primarily along the fully-symmetrical normal coordinates, as is indeed observed in the case of benzene.

The experimentally observed value $y = 1.25$ for the a_{1g} vibration agrees well with quantum-chemical calculations based on the scheme described above (formulas (55), (31), and (50); for details see^[21]).

Appreciable contributions to the spectra of other aromatic hydrocarbons, and also polyenes, which have a lower symmetry, are made simultaneously by several normal vibrations, a fact also in accord with quantum-chemical calculations (see^[15,16-21]). By way of example, Fig. 3 shows the spectrum of diphenyl hexatriene and the result of its analysis with the aid of (55).

The vibronic spectrum of hexatriene was calculated in^[15] by the method of Sharp and Rosenstock^[14] with allowance for the anharmonicity and for the change in the force constants. The results agree better with experiments than calculations within the framework of the principal model^[21]. This difference, however, does not exceed 10% and must be attributed not to deviations from the principal model but apparently to the use of better quantum-chemistry methods in^[15].⁵⁾

2) **Dyes.** Another extensive class of compounds, besides hydrocarbons, for which an analysis was carried out of the intensities of the vibronic spectra, is that of organic dyes. The spectra of these molecules are very weakly resolved at room temperature, and to resolve the vibrational structure the investigations must be carried out at low temperatures. Investigations of this kind have shown^[22-24] that the spectra in these compounds also agree with (55). By way of example, Fig. 4 shows the spectrum of pinocyanol. By measuring the excitation spectra, Ivanov et al.^[27] have analyzed the vibronic progression of the cyanin dyes and have demonstrated the validity of (56) up to the sixth maximum.

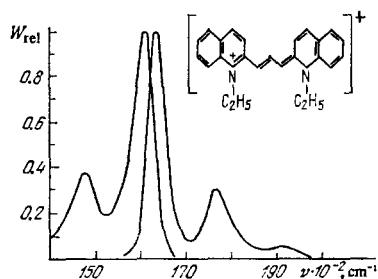


Fig. 4. Absorption and luminescence spectra of pino-cyanol at 77°K [22].

A characteristic feature of the vibrational structure of the electronic spectra of dyes is that the main contribution to the progression is made by only one normal vibration, but even for this vibration the value of y is small. For most dyes we have $y \approx 0.5$.^[23,24]

In many of the cases considered above, the fluorescence spectra were measured in parallel with the absorption spectra. As a rule, no noticeable deviations from mirror symmetry were observed. Where noticeable deviations did exist, more careful investigations have always led to the conclusion that the emission takes place in this case not from the same electronic level to which the molecule is excited. In some cases this is connected with the formation of excimers (or exciplexes (see^[28])), and in others with the presence of a lower-lying weak electronic transition^[29], etc.

Thus, the conclusions of the theory are in full agreement with experiment. In all the investigated cases the intensity distribution in the vibrational progression follows formula (55). As expected, the reliability of the predictions based on quantum-chemical calculations of the values of y_k is much lower, but even these calculations result in a correct semiquantitative (and sometimes even quantitative) picture of the connection between the structure of the molecule and its vibronic spectrum.

5. THE PROBLEM OF THE VIBRONIC LINE WIDTH

A striking feature of the experimental spectra is the large width of each peak corresponding to different values of the vibrational quantum number. This width, as a rule, exceeds the radiative width by several orders of magnitude. There exists a method with which it is possible to obtain narrow quasilines for a number of molecules. We have in mind Shpol'skiĭ's well known method, the use of which calls for placing the investigated molecules in a paraffin matrix. The Shpol'skiĭ effect has been investigated in detail and explained on the basis of the theory of impurity centers of crystals (see^[4,30]). We shall dwell in here in greater details on the possible mechanisms responsible for line broadening in solutions.

a) Mechanisms of broadening of spectral line.

1) "Soft vibrations. This broadening mechanism is illustrated by Fig. 5, which shows the spectrum of a hypothetical molecule whose equilibrium positions of the nuclei is produced by electronic excitation for two normal vibrations—"hard" with frequency $\Omega_1/2\pi = 1000 \text{ cm}^{-1}$ and $y_1^2 = 1$, and "soft" with $\Omega_2/2\pi = 100 \text{ cm}^{-1}$ and $y_2^2 = 3$. The spectrum was calculated from formula (55), i.e., for the case of low temperatures ($\hbar\Omega_1$ and $\hbar\Omega_2 \gg kT$). Owing to the presence of several frequencies of soft vibrations, and also owing to other broadening mechanisms, the fine structure corresponding to "soft" vibrations can vanish completely. The

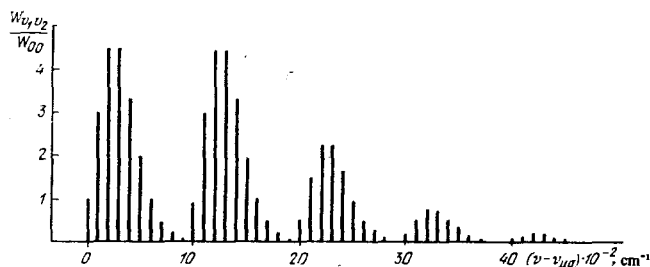


FIG. 5. Absorption spectrum calculated from formula (55) for the case of two normal vibrations, $\Omega_1/2\pi = 1000 \text{ cm}^{-1}$ ($y_1^2 = 1$) and $\Omega_2/2\pi = 100 \text{ cm}^{-1}$ ($y_2^2 = 3$).

experiment will reveal only the envelope of the spectrum shown in Fig. 5. With increasing temperature, the dispersion of the intensity distribution in an individual peak corresponding to a given quantum number for the "hard" vibrations should vary in accord with formula (46). For the considered model of one "soft" vibration, we obtain

$$\Delta = \Omega y \sqrt{\frac{\hbar\Omega}{\text{cth} \frac{\hbar\Omega}{2kT}}}. \quad (58)$$

It follows from this formula that the width of the peak will first remain constant with increasing temperature, and then, at $T \approx \hbar\Omega/k$, it begins to increase, with $\Delta \propto \sqrt{T}$ at $T \gg \hbar\Omega/k$.

The form of the intensity distribution in the peak is also changed thereby. At low T it takes the form of a Poisson distribution, and at high T it is Gaussian (see formula (35)).

2) Phonons. The phonon broadening mechanism is particularly important in crystals, but it can play a noticeable role also in frozen solutions. This mechanism is discussed in a large number of articles, reviews, and monographs (see, e.g.,^[4,5]), so that there is no need to dwell on a detailed description here. We recall only that the fundamental fact in this region is the existence of a very narrow no-phonon line, the intensity of which decreases sharply with rising temperature. It is precisely because of the existence of this no-phonon line that resonance photon absorption and emission effects are observed (the Mössbauer and Shpol'skiĭ effects). With increasing temperature, the intensity is transferred from the no-phonon line into a diffuse phonon wing having a width on the order of the Debye frequency of the phonon spectrum, i.e., $\sim 100 \text{ cm}^{-1}$. The width of the phonon wing increases with rising temperature.

3) Inhomogeneous broadening. This broadening mechanism is particularly important for solutions in which different molecules of dissolved matter turn out to be in different local environments, and the absorption frequencies are changed as a result. The observed spectrum is a superposition of ideal spectra that are slightly shifted relative to one another.

The magnitude of the effect of inhomogeneous broadening of a spectral line should in general depend on the temperature. In fact, we assume for the sake of argument that the absorption frequency $\nu(n)$ is a certain function of the local density n of the solvent in the vicinity of the absorbing (or luminescent) molecule. Assuming the $\nu(n)$ dependence to be weak enough, we confine ourselves to the first term of the expansion of this function in a Taylor series:

$$\nu = \nu_0 + A(n - n_0), \quad (59)$$

where n_0 is the equilibrium density of the solvent near

the dissolved molecules. According to the definition of the quantity n_0 , the energy of the region in question near the impurity molecules is determined by the expression

$$E = E_0 + B(n - n_0)^2. \quad (60)$$

The probability of the density fluctuations is given by

$$W(n) \propto e^{-E/kT} \propto e^{-B(n-n_0)^2/kT},$$

from which we obtain for the shape of the absorption (or emission) line

$$\mathcal{K}(\nu) = \mathcal{K}_0 e^{-(\nu-\nu_0)^2/2\Delta^2}, \quad (61)$$

where $\Delta = A\sqrt{kT/2B}$.

Thus, the mechanism under consideration leads to lines of Gaussian shape, with a half-width proportional to \sqrt{T} . If vitrification of the solvent takes place with decreasing temperature, then the density fluctuations that take place in the vitrification interval become quenched, and no further decrease of the line width will occur. As a result, the $\Delta(T)$ may turn out to be quite close to that resulting from the mechanism of line broadening by "soft" vibrations. This hinders significantly the identification of the line-broadening mechanism that is decisive in the real case.

4) **Stereoisomerization.** This process is closely related to the considered inhomogeneous-broadening by a solvent, although it is not quite as general. Its gist is that if the molecule can exist in several stereoisomeric forms and if the corresponding absorption spectra are shifted relative to one another, then the superposition of spectra of these forms leads to a broadening of the observed bands. Thus, whereas in the preceding section we dealt with an inhomogeneity in the disposition of the solvent near the dissolved molecule, we are dealing here with inhomogeneity of the structure of the molecules themselves. In order for this mechanism to lead to a noticeable effect, a large number of different stereoisomers must be present. Consequently, the role of this mechanism increases with increasing dimensions of the considered molecules, and it can be particularly significant in the case of polymers.

5) **Interaction with other electronic states.** A special situation arises when two electronic states of a molecule have close energy (degenerate or quasidegenerate electronic states). The vibronic spectra undergo in this case particularly significant changes if both electronic levels have close oscillator strengths. Then to find the intensity distribution it is necessary to have an approach that is not based on the adiabatic approximation (see, e.g., [81]). A different situation takes place when the transition to one of the closely-located electronic levels is forbidden, or has a small oscillator strength. From the fact that the exact vibronic wave function corresponding to this energy level can always be written in the form of a linear combination of the corresponding adiabatic functions that pertain to different electronic levels, it follows (in view of the weakness of one of the electronic transitions) that the intensity distribution in the band corresponding to the strong electronic transition is of the same form as in the adiabatic approximation.

The foregoing does not mean, however, that the widths of the vibronic lines remain unchanged in this case. To the contrary, a molecule entering in a state described by an incorrect wave function has a large (for this case) probability of going over into other states

corresponding to the given energy (see Chap. 7). It is this which causes the line broadening due to the non-adiabaticity. In a number of cases this line-broadening mechanism can predominate. It is clear that this mechanism is not universal, since it cannot take place only in the case of "accidental" quasidegeneracy, when a weak absorption band appears alongside the strong one. At the same time, its significance must not be underestimated, since it is well known that a weak $n \rightarrow \pi^*$ transition appears quite frequently alongside a strong $\pi \rightarrow \pi^*$ transition, especially in the case of heterocyclic compounds. The role of this mechanism was first clearly demonstrated in the brilliant studies of Hochstrasser^[31,32], which will be considered in the next section.

b) **Discussion of experimental data.** Some of the possible vibronic-line broadening mechanism were considered already long ago (see, e.g., the series of articles by Neporent^[33] and the earlier papers cited therein), but there are few investigations in which any particular broadening mechanism is convincingly proved. Progress in this direction is strongly hindered by the fact, which has become clear in recent years, that there is no universal line-broadening mechanism that is decisive in all cases. Moreover, as will be seen subsequently, broadening of the spectral line of one and the same molecule can be due to different causes when the external conditions (temperature, solvent, etc.) are altered.

The most prevalent broadening, which appears to be present in all cases when solutions are investigated, is inhomogeneous broadening, even though this mechanism is far from making the largest contribution to the observed effect. The role of the inhomogeneous broadening was investigated by Personov and co-workers^[34]. They have shown that if frozen solutions of various molecules are excited in the region of the pure electronic transition by a narrow laser-emission line, then luminescence spectra are observed, consisting of narrow vibronic lines with half-widths reaching fractions of a cm^{-1} . Figure 6 shows the emission spectra of 3, 4, 8, and 9-dibenzopyrene in ethyl alcohol at 4.2°K, obtained by ordinary excitation (a) and by laser excitation (b). There is an obvious narrowing of the spectral lines in the case of laser excitation. This effect is attributed in^[34] to the fact that laser irradiation excites only a small fraction of the molecules absorbed in the narrow frequency band of the laser radiation, after which these molecules luminesce. These experiments have demonstrated convincingly the presence of the inhomogeneous broadening effect.

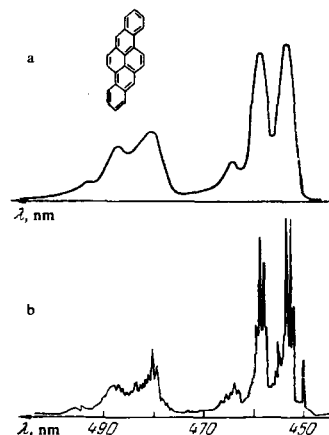


FIG. 6. Fluorescence spectra of 3, 4, 8, and 9-dibenzopyrene in ethanol at 4.2°K under ordinary excitation (a) and after excitation by a cadmium laser with $\lambda = 4415.6 \text{ \AA}$ (data of [34]).

At the same time, it is seen from the spectra shown in Fig. 6 that an individual peak of the initial spectrum, after the lifting of the inhomogeneous broadening effect, turns out to consist of an entire series of narrow lines corresponding to low-frequency ("soft") vibrations. It appears that the total width of the peak in Fig. 6a is determined just by the "soft" vibrations, and the role of the inhomogeneous broadening reduces to a smearing of the fine structure at extremely low temperatures, when the role of the phonon mechanism of broadening is still small. Personov and co-workers^[34] have shown that in analogy with the situation in crystals, when the temperature is raised one observes in frozen solutions a rapid decrease in the intensity of the no-phonon lines, and the phonon broadening mechanism comes into play. It is possible that this mechanism plays at increased temperatures (several dozen degrees Kelvin and higher) a more significant role than the effect of inhomogeneous broadening. Thus, even at a temperature of several dozen degrees Kelvin the spectrum is transformed into a set of peaks with an unresolved fine structure, and the width of each peak is determined by the soft vibrations (see Fig. 6a).

A picture of this type is in good agreement with the hypothesis advanced in^[22-25] to explain the temperature dependence of the half-width of the individual peaks of the vibronic spectra of dyes. In these studies, a comparison was made of the experimentally observed temperature dependence of the principal peak (corresponding to the 0-0 transition in accord with the "hard" progression) with formula (58), which corresponds to broadening due to "soft" vibrations. The result of such a comparison is shown in Fig. 7. The values of the parameters γ and Ω were chosen such as to ensure the best agreement between the theory and experiment.

The experimental data agree thus with the assumption that the "soft" vibrations play the decisive role in the broadening of the vibronic bands of molecules of various classes. The data shown in Fig. 7 can by themselves be interpreted also on the basis of the inhomogeneous-broadening effect, since this effect, as shown above (see formula (61)), can lead to an analogous temperature dependence of the line width. This interpretation, however, contradicts a number of other data. In particular, Serdyukova^[35] has shown that the peaks have a Gaussian form only at high temperatures (where a linear dependence of Δ on \sqrt{T} is already observed), while at low temperatures there is a noticeable deviation of the band shape from Gaussian. This agrees well with the mechanism of broadening due to "soft" vibrations (we recall that in accordance with formulas (34) and (35) the peak should be Gaussian at $\hbar\Omega \ll kT$ and of the Poisson type at $\hbar\Omega \gg kT$), and does not agree with

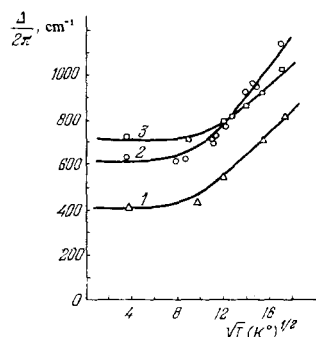


FIG. 7. Temperature dependence of the width of the long-wave maximum of the absorption bands of pinacyanol (1), rhodamine C (2), and brilliant green (3) in alcohol. Points—experiment, curves—theory (formula (58) [^{25,35}]).

the inhomogeneous-broadening mechanism, according to which the peak should be Gaussian at all temperatures. In addition, according to the data of Personov et al.^[34], the inhomogeneous-broadening effect is small.

Nonetheless, further research is needed for a more definite assessment of the validity of the proposed interpretation.

If the notion that the decisive role is played by "soft" vibrations turns out to be true, there will still remain the completely unanswered important question concerning the nature of this vibration. The available data do not make it possible, in most cases, to ascertain unequivocally whether these are intramolecular vibrations or vibrations of the solvent molecules. Moreover, in a number of cases it is necessary to make use of the hypothesis that we should be dealing here with vibrations of the solvent in the field of the dissolved molecule. Only this hypothesis can explain the dependence of the characteristics of this vibration on both the properties of the dissolved molecule and on the properties of the solvent, in the case of dye solutions (see^[25,35]).

In any case, the most probable at present in the following hierarchy of broadening mechanisms in most cases: "soft" vibrations > phonons > inhomogeneous broadening. The last two mechanisms change placed at very low temperatures. This can give rise to a fine structure due to soft vibrations. This picture may turn out to be quite general. However, even now there are known cases when the principal mechanisms are quite different.

We have in mind the last two broadening mechanisms indicated in the preceding section. Neither can claim, in principle, to be general, since one of them requires the existence of stereoisomers, and the other can be realized only in the case of "accidental" quasidegeneracy of the electronic terms.

The broadening mechanism due to stereoisomerization is resorted to in^[36] to explain the anomalously broad band of retinal in comparison with compounds related to it. This explanation is quite plausible, since retinal contains alternating double and single bonds and rotation can take place around the latter.

Very convincing examples of band broadening due to quasidegeneracy of electronic terms of different types (one corresponding to strong absorption and the other to weak absorption) were demonstrated by Hochstrasser^[31,32]. Figure 8 shows one such example, in the form of pyridine in two solvents, water (a) and pentane (b). It is known that the spectra are usually much better resolved in nonpolar solvents than in water^[3].

In this case, the inverse picture is observed—the

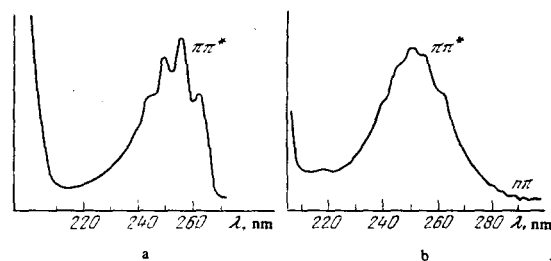


FIG. 8. Absorption spectra of pyridine in water (a) and pentane (b) according to [3].

spectrum is better resolved in water. According to Hochstrasser^[31], this effect is due to the fact that the $n\pi^*$ level of the pyridine shifts in water and turns out to be higher than the $\pi\pi^*$ level. As a result, the broadening of the $\pi\pi^*$ -band vibronic levels due to quasidegeneracy does not take place in water but does take place in pentane, where the $n\pi^*$ level lies somewhat lower than the $\pi\pi^*$ level. Hochstrasser presented also a large number of very convincing examples of an effect of this type^[31].

In addition to its importance in principle, the Hochstrasser effect is also of great interest because it can become significant for the explanation of the spectral characteristics of a large class of heterocyclic compounds, including also molecules that are of great importance in application, such as nitrogenous bases and amino-acids.

6. ADIABATIC THEORY AND INTERMOLECULAR INTERACTIONS

We have reported above the results of the application of the adiabatic theory to isolated molecules (chromophores). We consider now several examples that illustrate the conclusions that can be drawn by applying the adiabatic theory (i.e., by consistently using the Born-Oppenheimer parameter κ) to intermolecular interactions. By "molecule" we mean here not necessarily an individual chemical compound, but also an arbitrary chromophoric group, i.e., a part of a complex chemical compound and having sufficiently individual spectral characteristics. The interaction between the considered chromophoric group and the remainder of a large molecule can therefore be treated by perturbation theory.

a) **Vibrational structure of circular-dichroism spectra.** The spectrum of the circular dichroism (i.e., the difference between the absorption coefficient of right- and left-polarized waves is usually similar to the absorption spectrum, and its vibrational structure is described by the same relations as in the case of ordinary spectral^[37]. As first noted by Moffitt and Moskowitz^[38], however, in the case of weak optical activity, which arises when a symmetrical chromophoric group is placed in a weak asymmetrical field, a noticeable difference between the circular-dichroism (CD) and the absorption spectrum can be observed. This question was subjected in^[39] to a detailed analysis based on the use of adiabatic theory, and also on symmetry considerations, which play in this case a rather significant role.

The following expression was obtained in^[39] for the form of the circular-dichroism band:

$$R_a(\omega) = K_a \sum_{\nu} \left[A + \sum_a B_a Q_a^{(g)} + \sum_a C_a y_a \left(1 - \frac{v_a}{y_a^2} \right) \right] W_{\nu} \delta \left(\omega_{u\nu} + \sum_k \Omega_k \nu_k - \omega \right). \quad (62)$$

The quantities W_{ν} and y_k take as before the forms (32) and (31), respectively. Summation over a means summation over all the normal coordinates that are anti-symmetrical with respect to the operations of inversion and reflection in a plane. $Q_a^{(g)}$ is the displacement of the equilibrium positions of the nuclei along the given normal coordinate in the electronic ground state under the influence of an asymmetrical field. The quantities A , B_a , and C_a are expressed in terms of the matrix elements of the magnetic and electric dipole moments^[39].

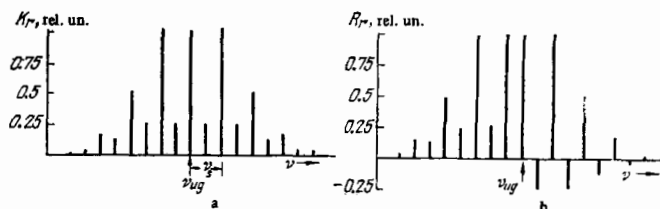


FIG. 9. Absorption and luminescence spectra (a) and circular dichroism luminescence and circular polarization spectra (b) calculated from formulas (28), (33) and (62), (63) respectively in the limit $\hbar\Omega_i \gg kT$ for a hypothetical molecule with one fully-symmetrical vibration $y_s^2 = 1$ and with one asymmetrical vibration $y_a^2 = 0.5$ ($\Omega_a = \Omega_s/2$). For simplicity, the relations between the parameters were assumed to be the following: $A + B_a Q_a^{(g)} = C_a y_a$ and $A' + B'_a Q_a^{(u)} = C'_a y_a$.

Formula (62) yields an expression for the distribution of the intensity in the CD band induced in the molecule by the asymmetrical field in first-order perturbation theory and in the adiabatic approximation. It follows from it that there are three methods by which an asymmetrical field induces optical activity. The first term A corresponds to asymmetrization of the electron motion in the case of symmetrical disposition of the nuclear core. This is the only term usually taken into account in the analysis of induced optical activity^[40]. The second and third terms correspond to asymmetrization of the nuclear core of the molecule in an asymmetrical field. The second term $\sum_a B_a Q_a^{(g)}$ corresponds to asymmetrization of the molecule in the electronic ground state. The third term $\sum_a C_a y_a [1 - (v_a/y_a^2)]$ corresponds to the contribution that arises if the asymmetrized molecule has different equilibrium values of the asymmetrical normal coordinates in different electronic states. This difference is determined by the quantity y_a .

It is important that all three terms in (62) are of the same order of magnitude and generally speaking there are no grounds whatever for discarding any of them. This is demonstrated in^[39] by an estimate of the terms of expression (62) in general form.

We examine now the correspondence between the intensity distributions in an isolated absorption band of the molecule and in the band of its induced CD. It is seen from (62) that the contribution made by the first two terms to the CD has the same dependence on the vibrational quantum numbers ν as in the case of absorption. Therefore, if there is no change in the equilibrium values of the asymmetrical normal coordinates Q_a following the excitation ($y_a = 0$), then the CD spectrum of the isolated band should be perfectly similar to its absorption spectrum. The third term in (62) makes a contribution of an essentially different character. Starting with a certain value of v_a (equal to unity if $y_a < 1$), the contribution given by this term reverses sign (Fig. 9). As shown in^[39], the total contribution from this term, summed over all the v_a , vanishes by virtue of the rotation.

It is easy to show, by a procedure analogous to that used in^[39] for the CD spectra, that the spectrum of the circular polarization of the luminescence should be of the form^[41]

$$R_r(\omega) = K_r \sum_{\nu} \left[A' + \sum_a B'_a Q_a^{(u)} - \sum_a C'_a y_a \left(1 - \frac{v_a}{y_a^2} \right) \right] W_{\nu} \delta \left(\omega_{u\nu} - \sum_k \Omega_k \nu_k - \omega \right), \quad (63)$$

where $Q_a^{(a)}$ is the change of the equilibrium position of the normal coordinate in the excited electronic state under the influence of the asymmetrizing field. A' , B'_a and C'_a differ from the corresponding expressions for A , B_a , and C_a in that the indices are permuted. An essential difference between (63) and (62) is the change of the sign of the third term. This should lead to the absence of mirror symmetry in the CD spectra and in the circular polarization of the luminescence, a symmetry that should occur if $C_a = C'_a = 0$. The usual absorption and emission spectra retain in this case their mirror symmetry (see Fig. 9).

The possibility of contributions of opposite signs in an isolated electronic CD band was first noted in^[42]. This conclusion was based, however, on the erroneous statement that the asymmetrical vibrations of a symmetrical molecule can by themselves lead to a nonzero summary contribution to the CD, just as vibrations lift the symmetry-forbiddenness in absorption spectra. This contribution was obtained in^[42] as a result of the quadratic terms of the expansion of the product of the electric and magnetic moments in powers of the displacements of the normal coordinates. An analysis^[39] shows that these terms are strictly equal to zero from symmetry considerations. A term analogous to the last term of (84) was obtained in^[43,44]. There, however, just as in^[42], no use was made of the symmetry properties, nor were the obtained terms estimated.

Even though the premise in^[42] was wrong, the main conclusion drawn there agrees with our conclusion based on a rigorous analysis. That study stimulated experimental research on the fine structure of CD spectra^[45-47]. Unfortunately, attempts to observe experimentally the theoretically predicted differences between the CD and absorption spectra have not yet succeeded. The reason is that the presence of various conformers of the given compound in the solution hinders the interpretation of the spectra. The first experiments in which circular polarization of the luminescence of weakly asymmetrical molecules have been reported recently^[48,49]. There are grounds for hoping that a parallel investigation of the spectra of CD and of the circular polarization of radiation of molecule, using the difference between (62) and (63) for the interpretation of the data, will help clarify this important question.

b) Vibronic interactions in dimers. The most complete analysis of this question was carried out by Fulton and Gouterman^[8,50] (see also^[51,53] and the review^[6]). The theory makes use of two parameters, the quantity y for the intramolecular vibration of a monomer and the dimensionless parameter ϵ that characterizes the magnitude of the interaction between monomers in a dimer. The most interesting predictions are given by the theory in the case of strong intermolecular coupling, where $|\epsilon/y| \gg 1$. In this case, a strong exciton splitting of the electronic levels should take place, and the intensity distribution in each of the two newly produced bands ("+" and "-") should obey the usual formulas (55) and (56), but with a new value $y_{\pm} = y/\sqrt{2}$.

The theory was subjected to a detailed experimental verification in^[27,54,55], where they investigated a number of "intramolecular dimers," i.e., molecules made up of two identical chromophoric groups. The investigated dimers had different values of the parameter $|\epsilon/y|$, but larger than unity for all of them. It turned out that the predictions of the theory of Fulton and

Gouterman^[8,50] are rigorously satisfied only at $|\epsilon/y| \approx 1$, but a significant deviation from the theory occurs when this parameter increases.

As shown in^[55], the cause of the discrepancy between theory and experiment is that in the theory of Fulton and Gouterman the matrix element of the operator of the interaction of the monomers in the dimer was considered only within the framework of the crude adiabatic approximation. Allowance for the succeeding terms of the adiabatic expansion leads to the expression

$$y_{\pm} = \frac{y}{\sqrt{2}} - \delta y_{\pm}.$$

The value of the additional term δy_{\pm} was estimated in^[55] in terms of the Born-Oppenheimer parameter: $|\delta y_{\pm}| \sim \kappa |\epsilon|$. It is seen from this estimate that the deviation from the simple formula $y_{\pm} = y/\sqrt{2}$ should increase with increasing strength of the intermolecular bond. This regularity, and also certain more definite conclusions that follow from the adiabatic theory, have found full experimental confirmation (see^[54,55,27]).

The briefly considered question of the effects of the vibronic interaction in dimers in the case of strong coupling is instructive in the following respect: It serves as an example of a situation wherein, on top of the universal small parameter κ , there appears also a small parameter peculiar to the given theory ($1/\epsilon$ in the present case), and the additional term that characterizes the deviation from the crude adiabatic approximation turns out to be of the order of the ratio of these two parameters. The real danger inherent in a situation of this kind lies in the insufficient smallness of κ (≈ 0.1). Consequently the additional term may turn out to be comparable with or even larger than the term obtained within the framework of the crude adiabatic approximation.

c) Width of excimer emission band. An excimer is defined as a dimer made up of identical molecules, produced in an excited electronic state, and decaying as the system goes over to the ground state^[28,56]. The presence of excimers is revealed by a characteristic "excimer" luminescence that differs from ordinary luminescence in two basic features: large Stokes shift (about 5000–6000 cm^{-1}) and broad structureless band. To describe an excimer state one considers a model^[28,56] in which the potential of the system in the excited state has a minimum with respect to the intermolecular coordinate, and in the ground state the potential is assumed to be purely repulsive (see Fig. 10).

A theoretical analysis of the excimer luminescence band has been the subject of many papers^[57-59]. In

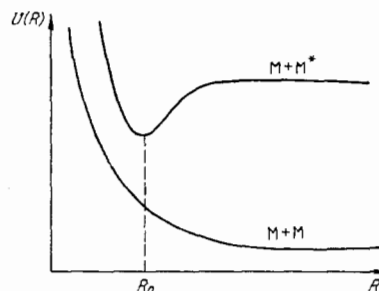


FIG. 10. Potential curves for an excimer. R —distance between molecules in the excimer. Upper curve—state in which one of the molecules is excited, lower curve—both molecules are in the ground electronic state (for simplicity, the curve is assumed to be pure repulsive).

these papers, however, they considered only certain special models of potential curves within the framework of the quasiclassical approximation. A consistent quantum-mechanical solution of the problem was obtained in^[60] for an arbitrary ground-state potential, using an expansion in the Born-Oppenheimer parameter. We repeat below the reasoning of^[60].

Using the Born-Oppenheimer parameter for the potential function of the excited excimer state, we confine ourselves to the harmonic approximation. Then the adiabatic Hamiltonian of the excited state takes the form

$$\hat{\mathcal{H}}_u = \hat{T}_N + \frac{M\Omega^2}{2}(R - R_0)^2 + \hbar\omega_{ug}, \quad (64)$$

and in the ground state we have

$$\hat{\mathcal{H}}_g = \hat{T}_N + V_g(R), \quad (65)$$

where \hat{T}_N is the operator of the kinetic energy of the relative motion of the monomers, R is the distance between the monomers, R_0 is the equilibrium distance between the monomers in the excimer, and M and Ω are the reduced mass and the natural frequency of the intermolecular oscillation in the excimer. In the Condon approximation, the square of the moment of the transition from the excited state to the ground state, normalized to unity, is given by (cf. (28))

$$\mathcal{X}_r(\omega) = (1 - \alpha) \sum_{n_u=0}^{\infty} \alpha^{n_u} \sum_{n_g=0}^{\infty} | \langle n_g | n_u \rangle |^2 \delta(E_{gn_g} - E_{un_u} + \hbar\omega), \quad (66)$$

where $\alpha = \exp(-\hbar\Omega/kT)$. In the case of a continuous spectrum of the states, the summation over n_g is replaced by integration.

We shall continue the calculations using Lax's method^[61]. Taking the Fourier transforms of both halves of (66) and using the rules for matrix multiplication we obtain, following^[61],

$$\int_{-\infty}^{\infty} \mathcal{X}_r(\omega) e^{-i\omega t} d\omega = \tau(t), \quad (67)$$

where

$$\tau(t) = \left\langle \left\langle \exp\left(\frac{i}{\hbar} \hat{\mathcal{H}}_g t\right) \exp\left(-\frac{i}{\hbar} \hat{\mathcal{H}}_u t\right) \right\rangle \right\rangle, \quad (68)$$

with $\langle \dots \rangle$ denoting averaging over the vibrational levels of the excited electronic state, i.e.,

$$\tau(t) = (1 - \alpha) \sum_{n_u=0}^{\infty} \alpha^{n_u} \langle n_u | \exp\left(\frac{i}{\hbar} \hat{\mathcal{H}}_g t\right) \exp\left(-\frac{i}{\hbar} \hat{\mathcal{H}}_u t\right) | n_u \rangle. \quad (69)$$

The moments of the distribution function $\mathcal{X}_r(\omega)$ are calculated from the formula

$$M_k = \int_{-\infty}^{\infty} \omega^k \mathcal{X}_r(\omega) d\omega = (-i)^k \left. \frac{\partial^k \tau(t)}{\partial t^k} \right|_{t=0}, \quad (70)$$

whence

$$M_1 = \frac{1}{\hbar} \langle \langle \Delta \hat{\mathcal{H}} \rangle \rangle, \quad (71)$$

$$M_2 = \frac{1}{\hbar^2} \langle \langle (\Delta \hat{\mathcal{H}})^2 \rangle \rangle + \frac{1}{\hbar^2} \langle \langle [\hat{\mathcal{H}}_u, \hat{\mathcal{H}}_g] \rangle \rangle, \quad (72)$$

where $\Delta \hat{\mathcal{H}} = \hat{\mathcal{H}}_u - \hat{\mathcal{H}}_g$, and $[\hat{\mathcal{H}}_u, \hat{\mathcal{H}}_g]$ is the commutator of the operators $\hat{\mathcal{H}}_u$ and $\hat{\mathcal{H}}_g$. The variance of the distribution $\mathcal{X}_r(\omega)$ is

$$\Delta^2 = M_2 - M_1^2. \quad (73)$$

We introduce, as usual the dimensionless coordinate

$$x = \sqrt{\frac{M\Omega}{\hbar}} (R - R_0). \quad (74)$$

We then obtain

$$\Delta \hat{\mathcal{H}} = \hbar\Omega \frac{x^2}{2} - V_g(x) + \hbar\omega_{ug}. \quad (75)$$

In the calculation of (71) and (72) it is convenient to change from averaging over vibrational energy levels to averaging over the vibrational coordinate. We then have, as is well known (see, e.g.,^[62]), for the arbitrary function $f(x)$

$$\langle \langle f(x) \rangle \rangle = \frac{1}{\sqrt{2\pi\sigma}} \int_{-\infty}^{\infty} f(x) \exp\left(-\frac{x^2}{2\sigma^2}\right) dx, \quad (76)$$

where

$$\sigma^2 = \frac{1}{2} \frac{1+\alpha}{1-\alpha} = \frac{1}{2} \operatorname{cth} \frac{\hbar\Omega}{2kT}. \quad (77)$$

To calculate expressions (71) and (72), we expand the function $V_g(R)$ in a series about the point $x = 0$:

$$V_g(x) = V_g^{(0)} + \hbar\Omega \left(Y_1 x + \frac{1}{2} Y_2 x^2 + \dots \right), \quad (78)$$

where

$$Y_k = \frac{1}{\hbar\Omega} \left. \frac{\partial^k V_g}{\partial x^k} \right|_{x=0}.$$

The quantity $V_g(x)$ will be averaged with a Gaussian distribution having a variance on the order of unity (see (76) and (77)). At the same time, the coefficients Y_k decrease rapidly with increasing index k . Indeed, inasmuch as the potential $V_g(x)$ changes significantly over distances on the order of internuclear distances, the ratio Y_k/Y_{k+1} is of the order of the ratio of the amplitude of the nuclear vibrations to the internuclear distance. In other words, the expansion in (78) is in terms of the Born-Oppenheimer parameter κ . Since we assume the potential in the excited state to be harmonic, it follows that we need retain in (78) terms not higher than of second order. It is known that the mean value of the commutator $[\hat{\mathcal{H}}_u, \hat{\mathcal{H}}_g]$ is rigorously equal to zero^[61].

Since

$$\Delta \hat{\mathcal{H}} = \hbar\omega_{ug} - V_g^{(0)} - \hbar\Omega \left[Y_1 x - (1 - Y_2) \frac{x^2}{2} \right], \quad (79)$$

it follows that by using the relations $\langle \langle x \rangle \rangle = 0$, $\langle \langle x^2 \rangle \rangle = \sigma^2$, $\langle \langle x^3 \rangle \rangle = 0$, and $\langle \langle x^4 \rangle \rangle = 3\sigma^4$, we obtain ultimately

$$\Delta^2 = \Omega^2 \left[Y_1^2 \sigma^2 + \frac{5}{4} (1 - Y_2)^2 \sigma^4 \right]. \quad (80)$$

The first term in (80) is determined by the slope of the potential function of the ground state at an equilibrium position of the monomers in the excimer. In the case of intramolecular vibrations, we have $Y_1 \lesssim 1$ as a result of the small difference between the equilibrium positions of the nuclei of the ground and excited states. The concrete value of Y_1 cannot be estimated beforehand in this case, and depends to a strong degree on the concrete form of the vibration under consideration. To calculate Y_1 it is therefore necessary to use the methods of quantum chemistry, to which we referred in Chaps. 3 and 4 above. The second term in formula (80) for the intramolecular vibrations is usually much smaller than the first, inasmuch as electronic excitation causes small changes in the force constants, i.e., $|1 - Y_2| \ll 1$.

In the case of excimers, when considering the intermolecular coordinate for which the potential of the ground state is practically pure repulsive, the values of Y_1 and Y_2 can be estimated in general form. In fact, using (74), we get

$$Y_1 = \frac{1}{\hbar\Omega} \left. \frac{\partial V_g}{\partial x} \right|_{x=0} = \frac{1}{\hbar\Omega} \frac{\partial V_g}{\partial R} \sqrt{\frac{\hbar}{M\Omega}}.$$

Further, inasmuch as the potential $V_g(R)$ changes by an amount on the order of the energy of the electronic excitation $\hbar\omega_e$ over distances on the order of the internuclear distance $\sqrt{\hbar/m\omega_e}$, it follows that

$$Y_1 \sim \frac{\omega_e}{\Omega} \sqrt{\frac{m\omega_e}{M\Omega}} \sim \sqrt{\frac{M}{m}} = \kappa^{-1}. \quad (81)$$

Analogously we have

$$Y_2 \sim 1. \quad (82)$$

Thus, whereas the second term is of the order of unity in the case of an excimer, the first term turns out to be quite large, of the order of κ^{-2} . For the band width expressed in terms of the frequencies of the molecular vibration of the excimer we have

$$D = Y_1 \sigma = D_0 \sqrt{\frac{\hbar\Omega}{2kT}}, \quad (83)$$

which is practically exact, with $D_0 = Y_1/\sqrt{2}$. It follows from (81) that

$$D_0 \sim \kappa^{-1}. \quad (84)$$

Thus, the excimer luminescence bandwidth can be estimated in terms of a universal molecular constant, the Born-Oppenheimer parameter κ . The concrete characteristics of the excimer can affect the numerical value of D_0 , but cannot change its order of magnitude⁷⁾.

Thus, the obtained estimate is $D_0 \sim 10$. This estimate agrees well with the experimental data, according to which (see^[28,56]) $D_0 \approx 13$. As to the temperature dependence given by formula (83), it is of the same form as in the case usually considered in the theory of vibronic spectra, when $Y_1 \lesssim 1$ and $Y_2 = 1$ (see (58)). As shown by experiment^[28,56], this dependence holds true also for the excimer luminescence band.

7. NONRADIATIVE TRANSITIONS

Vibronic interactions in polyatomic molecules play the decisive role in the nonradiative relaxation of the energy of excited electronic states.

The adiabatic theory makes it possible not only to describe completely the processes occurring in molecules following absorption and emission of photons, but also serves as the basis for the understanding of nonradiative transitions between various electronic states.

Modern development of the theory of nonradiative transitions started in the early Sixties, i.e., simultaneously with the publication of the first papers on the quantitative investigation of vibronic spectra of polyatomic molecules. McCoy, Ross, and co-workers^[63,64] and Robinson^[65] have called attention to the fact that the equilibrium positions of the nuclei of the ground and first-excited electronic states are shifted very little relative to each other. In fact, an analysis of the entire assembly of experimental data (see Chap. 4) shows that for rigid oscillations we have $y \lesssim 1$, meaning that this shift is close in value to the amplitude of the zero-point oscillations, i.e., it is of the order κa , amounting to $\approx 10^{-1}$ to 10^{-2} Å. The intersection of the potential curves can therefore occur only at very high energies, quite far from the energy of the ground vibrational state of the excited electronic term⁸⁾.

These arguments made it necessary to forego the prevalent opinion that the dominant role in the nonradiative transitions is played by the point of intersection of the potential surfaces, and to regard this process as a tunnel transition⁹⁾.

The most convincing is at present the following fundamental scheme of nonradiative transitions in the condensed phase, as proposed first by Robinson and Frosch^[65-67] (see the detailed review^[68]).

After a molecule absorbs a photon, an equilibrium distribution of the energy over the vibrational degrees of freedom is established in the molecule rapidly, in a time on the order of 10^{-12} – 10^{-11} sec.¹⁰⁾ The excess energy dissipates in the medium or goes over to other vibrational degrees of freedom of the large molecule.

The resultant Born-Oppenheimer state is stationary if one stays within the framework of the adiabatic approximation, and a transition from this state to others must be accompanied by photon emission. However, if the Hamiltonian contains the next higher terms in the Born-Oppenheimer parameter κ , which violate the adiabatic approximation, then mixing of the Born-Oppenheimer electronic states sets in and transitions between them become probable. The probability is given by an expression that follows directly from the well-known "Fermi golden rule" of the time-dependent perturbation theory

$$P = \frac{2\pi}{\hbar} L_e^2 F \rho, \quad (85)$$

where L_e is the electronic matrix element of the non-adiabaticity operator, F is the Franck-Condon factor¹¹⁾, and ρ is the density of the vibrational levels of the lower electronic state. We note that a great variety of arguments and approaches were used to obtain the probability P (see, e.g.,^[66-68]), but they led inevitably to a formula of the type (85). In practice one usually considers a transition from the zeroth vibrational level of an upper electronic state to an iso-energetic vibrationally-excited level of a lower electronic state. A formula such as (85) is valid only if it is assumed that dissipation of the vibrational energy takes place very rapidly after the transition to the lower state, for otherwise the molecule could again return to the upper electronic state. A detailed analysis of nonradiative transitions with allowance for dissipation of the vibrational energy is given in^[70-73].

The quantity L_e in (85) can be estimated by adiabatic theory in general form, and its order of magnitude is given by $|L_e/\hbar\omega_e| \sim \kappa$. The value of ρ can also be roughly estimated in general form at $\rho \sim 1/\hbar\Omega$, where $\hbar\Omega$ is the vibrational energy. The most essential multiplier in (85) is the Franck-Condon factor, which depends very strongly on the relative placement of the potential curves of the considered electronic states.

The clarification of the decisive role of the Franck-Condon factor in nonradiative conversion of electronic states was a very important step towards the explanation of the nature of the phenomenon. Calculations of the Franck-Condon factor are made complicated in this case by the fact that approximations that are fully justified in hetanalysis of photon absorption or emission (the principal model, see Chap. 3) cannot be used in this case. The reason is that it is necessary to consider transitions to high-lying vibrational levels of the lower state. In this case one can no longer neglect the differences between the vibration frequencies of the upper and lower states, nor the anharmonicity of the lower well. The first of these effects was considered by Seibrand^[74-76] (see also^[68]), who obtained a general expression for the Franck-Condon factor in the harmonic approximation. The anharmonicity was taken

into account in detail by Makshantsev and Perstnev^[77-79], who succeeded in obtaining an analytic expression for the Franck-Condon factor in the case when the potential wells are approximated by the curves for the Morse oscillator. Estimates show that the probabilities of nonradiative transitions vary by many orders of magnitude, depending on the shapes of the potential curves. This sensitivity to the form of the potential is perfectly understandable, since we are dealing here with a tunnel transition. This leads, on the one hand, to the conclusion that the considered theory makes it possible in principle to explain the experimentally observed probabilities of the nonradiative transitions, but on the other hand this sensitivity to the detailed form of the potential curves hinders, as in many other tunnel processes, the quantitative comparison of theory and experiment. One can speak only of qualitative trends. One of the most important among them is a dependence, clearly, pronounced both in experiment and in theory, of the nonradiative-transition probability on the energy gap between the electronic levels, viz., the transition probability decreases exponentially (or even more strongly) with increasing gap width. This regularity explains, in particular, the rapid relaxation of the upper electronic states (above the first excited state) since the density of the electronic state increases rapidly, as a rule, with increasing energy^[2]. At the same time the lower excited electronic state is as a rule separated from the ground state by a rather wide gap, and therefore the lifetime of this state is frequently comparable with the radiative lifetime.

In addition to the rapid relaxation of the upper electronic states, the strong dependence of the nonradiative-transition probability on the width of the energy gap leads to one more fundamental property typical of most polyatomic molecules. This is a tendency to go over, after electronic excitation to a lower excited singlet level, not to the ground state, but to intermediate metastable levels lying between the first excited singlet and the ground states. A classical example of this tendency is the transition to a triplet level. Another example may be the numerous photochemical transformations, more and more of which are becoming known (see, e.g.,^[82-84]).

Many of the photoproducts can be short-lived, and are exceedingly difficult to register. Photochemical transformation can vary in character—intramolecular restructuring, formation of photodimers^[83-85] containing a pair of dissolved molecules, formation of photoproducts with participation of the solvent (e.g., photohydrates^[83m,84]) or with participation of oxygen molecules dissolved in the solvent^[85], etc. Among the very short-lived photoproducts that exhibit characteristic luminescent attributes are also excimer and exciplexes^[3] (see, e.g.,^[28,82-85]).

On the whole, an impression is gained that a direct nonradiative transition from an excited singlet state to high vibrational levels of the ground state is rather unlikely and the bulk of the molecules that do not radiate photons either go over to a triplet state^[4], or form various photochemical products, and only then do they relax to the ground state.

Many photochemical products can be regarded as metastable excited states of the initial molecule (or a pair of molecules when photodimers and excimers are produced, or else a complex of the considered molecule with the solvent molecules, etc.). The potential curves

of these states are quite strongly shifted from the potential curve of the ground state along several nuclear coordinates ($y_k \gg 1$). This ensures their metastability relative to emission of photons, owing to the smallness of the corresponding Franck-Condon factors. The same excludes the direct photoexcitation of these states. As a result, these states do not manifest themselves in any way in the absorption spectra, but play a very important role in the fate of the electronic excitation.

Although we have dealt here with a concrete case of relaxation of electronic excitation after absorption of a photon, the same reasoning applies equally well to exothermal reactions in condensed media^[86,87]. In fact, in this case we can regard the initial state of the reagents as "excited" and the final as the "ground" state. This approach was used in^[86,87] to consider the reaction of radiative polymerization of formaldehyde at temperatures close to absolute zero. It was shown that the reaction is due to tunneling of the formaldehyde molecule as a unit through a distance of about 0.5 Å towards the end of a growing polymer chain. In general, modern ideas concerning the tunnel mechanism of nonradiative transitions can be of great importance in the understanding of the mechanism of many chemical processes.

8. CONCLUSION

The presented material shows that the theory of vibronic interaction explains quantitatively the main spectral properties of a rather large class of polyatomic molecules. This theory plays the principal role not only in the analysis of such traditional problems as the form of the absorption or luminescence band, but is also essential in the analysis of optical activity and nonradiative transitions. In all cases, the main method of the theoretical analysis is a consistent expansion in terms of a single small parameter, namely the Born-Oppenheimer parameter. During the course of the exposition we have emphasized those conclusions of the theory which are directly based on such an expansion, and are therefore the most rigorous. This approach leads to general formulas of universal significance, and also permits estimates to be made of various expressions. This approach, however, does not permit calculation of individual characteristics of concrete molecules.

To perform calculations of this kind it is necessary to use the methods of quantum chemistry. There are a few attempts at such a calculation, and these studies assure us that the use of modern quantum-chemical calculation methods can yield a rather complete description of vibronic spectra of even sufficiently large molecules. As shown in Chap. 3, in most cases the calculations can be carried out within the framework of the principal model, i.e., without explicitly calculating the potential surfaces of the ground and excited states. This circumstance simplifies the necessary calculations very greatly, and one can hope that work in the field of quantum-chemical calculations of vibronic spectra will develop further in the nearest future.

Perhaps the most rapidly developing theory of recent years is that of nonradiative transitions. As a result, the fundamental aspects of this problem have become much clearer. However, the theoretical papers are in most cases still detached from concrete experimental data. This is due primarily to the difficulty of obtaining quantitative predictions, owing to the exceedingly high

sensitivity of the calculation results to the detailed form and to the relative placement of the potential surfaces.

In this sense, quantum-chemical calculations of the probabilities of nonradiative transitions constitute an incomparably more complicated problem than the calculation of the vibronic spectra. One can therefore hardly hope the theory to be capable of making predictions in the nearest future. Semiquantitative predictions are still possible in those cases when the electronic terms are separated by a narrow energy gap, but the reliability of the estimates decreases rapidly with increasing gap width.

As to further problems in experimental research in this field, notice must first be taken of the need for further research on the nature of the spectral-line broadening. Much progress was made recently in the elucidation of this question, but further more detailed investigations are needed. It would also be desirable to have more accurate data on the intensity distribution in the vibronic spectra, for the purpose of revealing deviations from the principal model and comparing these deviations with theory.

To carry out research of this type it is necessary to choose a system with a well resolved structure. It is possible that the most suitable for this purpose are the spectra obtained by the Shpol'skii method. The vibrational structure of the circular-dichroism and of the circular-polarization-luminescence spectra has been investigated so far quite inadequately.

Further more detailed investigations of nonradiative transitions are indispensable. The main difficulties here are connected with aggravating factors such as the formation of various photochemical products. Therefore the determination of all the channels whereby electron excitation is annihilated is a very complicated task. On the other hand, the important role of the nonradiative tunnel transitions in photochemical processes, as revealed in research of this type, gives grounds for assuming that tunnel processes play an essential role even in various chemical reactions that are not photochemical in nature.

It must be emphasized once more that the theoretical deductions cited in this paper pertain, strictly speaking, only to lower electron-excited states. We have therefore discussed the experimental data for molecule solutions where the research is limited to the visible and near-ultraviolet region. Interest in the shorter-wavelength regions of the spectrum of polyatomic molecules has noticeably increased of late. Research of this type, which has become particularly intensive in connection with the use of synchrotron radiation (see^[88]), yields very interesting information on the properties of absorption at high-lying electronic levels. We can expect here entirely new regularities, connected both with the rapid increase of the density of the electronic states and with the strong change in the properties of the molecules following electronic excitation (the condition that the changes of the force constants be small should be violated in this region). These two circumstances cast strong doubts on the applicability of the principal model to the description of spectra of highly-excited electronic states, and add to the importance of approaches that are not based on this model, similar to the approach used in Chap. 6 for the calculation of the width of the excimer luminescence band.

¹⁾We assume that the wave functions are always real (there is no magnetic field).

²⁾The quantities \mathcal{A}_a and \mathcal{A}_r denote not the absorption and emission intensities I_a and I_r , respectively, but the relative quantities $\mathcal{A}_a = \mathcal{A}_a/\omega$ and $\mathcal{A}_r = I_r/\omega^4$.

³⁾The condition (52) is violated particularly frequently in the case of small molecules and radicals.

⁴⁾We refer here to spectra corresponding to the visible and near-violet regions, to which we confine ourselves in this article. Franck-Condon transitions to electronic levels corresponding to changes in molecular structure are possible, but it appears that they take place at a high energy corresponding to the vacuum ultraviolet region of the spectrum (see Chap. 8).

⁵⁾Calculations of a number of molecules were performed by an analogous procedure by M. A. Kovner and co-workers (see [26]).

⁶⁾The causes of this rule are not quite clear. It may be due to the larger deformation of the surrounding solvent molecules in the polar medium upon electronic excitation of the dissolved molecule. Formally, this explanation corresponds to an increase of the constant γ for the soft vibration on going from an unpolar to a polar solvent.

⁷⁾We emphasize that the values of formulas (83) and (84) go far beyond the scope of the concrete problem of the width of the excimer luminescence spectra. These formulas give, in general form, an estimate of the maximum possible width of the emission band or absorption band for transitions between isolated electronic terms.

⁸⁾A simple estimate shows that at $\gamma \lesssim 1$ the intersection of the electronic terms is possible only at an energy from that of the ground vibrational state of the upper term by an amount exceeding the energy of the electronic excitation.

⁹⁾Incidentally, a detailed analysis based on an expansion in the Born-Oppenheimer parameter shows that in fact no significant changes of the nonradiative-transition probability takes place at the point of intersection of the electronic terms.

¹⁰⁾The cited value of the vibrational relaxation time τ_V follows from the adiabatic theory, according to which this quantity is estimated in terms of the Born-Oppenheimer parameter at $\tau_V \sim 2\pi/\kappa\Omega$.

¹¹⁾Strictly speaking, the formula (85) contains not the Franck-Condon factor $|\langle \varphi_{ng}(q) | \varphi_{n_u}(q) \rangle|^2$, but the expression $|\langle \varphi_{ng}(q) | \Sigma \partial/\partial q | \varphi_{n_u}(q) \rangle|^2$,

however, for large vibrational quantum numbers, these expressions differ only by a numerical factor. In addition, the differentiation can be carried out not with respect to that normal coordinate for which the largest change of the potential curve is observed upon electronic excitation, in which case the expression for the latter will indeed contain only simply the Franck-Condon factor

¹²⁾The universality of this rule, frequently called the Kasha rule, is evidenced by the fact that emission from a second excited electronic state has been reliably observed in only one case (azulene) [80,81]. This is due to the anomalously large gap between the second and first excited states of azulene (see, e.g., [67,82]).

¹³⁾It is particularly important that exciplexes can be formed from an excited molecule of dissolved matter and the solvent molecule (see, e.g., [28]).

¹⁴⁾Of course, all the remarks made above concerning the role of the photochemical processes pertain also to the triplet state.

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