

Vibronic coupling in excited electronic states of complex molecules

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Different aspects of the theoretical interpretation and utilization of the fine-structure vibronic spectra of polyatomic organic molecules in solution for determining characteristics of the electronic excited states of such molecules, such as the orbital type, localization of excitation on fragments, change of nuclear configuration, etc., are presented. The adiabatic approximation with Frank–Condon and Herzberg–Teller coupling is studied. A great deal of attention is devoted to the phenomenon of suppression of most spectral lines in the range corresponding to allowed transitions in vibronic spectra. Some reasons for this phenomenon are discussed.

INTRODUCTION

Experimental investigations of molecular fine-structure vibronic spectra give information about subtle effects in electron-electron and electron-nuclear interactions—spin-orbit and vibronic—in excited electronic states of polyatomic molecules. Vibronic coupling in polyatomic molecules is studied in several reviews.^{1–4} In these reviews, however, the theoretical aspects are emphasized and questions concerning the relation between vibronic coupling and the individual electronic structure of the molecules are not considered. In Refs. 2 and 3 the theoretical description of vibronic spectra and intramolecular interactions in isolated molecules as well as electron-phonon interactions in impurity molecules are studied and in Refs. 1 and 2 interactions in dimers and crystals are studied.

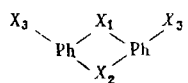
Studies have shown that the concept of nonadiabatic vibronic coupling is very effective in explaining the effects of changes of molecular structure (in the case of chemical reactions and the effect of a catalyst).⁵ In order to describe the vibronic spectra of polyatomic molecules, however, the adiabatic and harmonic approximations are, as a rule, adequate,^{2–4} and in addition in large (complex) molecules the Dushinskii effect (the difference of the system of normal vibrational coordinates in the ground and excited electronic states) can be neglected.⁶ This concept makes it possible to present in a simple analytic form the relation between the intensity of a vibronic line in the vibronic spectrum and the spectroscopic parameters, which reflect the vibronic coupling realized in the normal coordinates of the molecule.^{3,6} The normal coordinate is related with the structure of the molecule through the computed form of the vibration. For this reason, the intensity distribution in fine-structure vibronic spectra of molecules becomes, as a result of theoretical analysis, a valuable source of data on the relation between molecular structure and vibronic coupling; these data in turn contain information about the excited electronic states of complex molecules.⁶

The present review is based on these ideas. The experimental data were obtained by the method of fine-structure vibronic spectroscopy of solid solutions at 4.2 K (in most publications cited above the investigations are based on emission spectra). In this review different approaches to obtaining from the experimental data on vibronic coupling some characteristics of the lowest excited singlet or triplet electronic states of complex molecules (aromatic compounds with heteroatoms) are studied: data on the role of

different heteroatoms in the formation of excited electronic states, the orbital type of the states, the change occurring in the geometry of a molecule as a result of electronic excitation, the most probable mechanisms of spin-orbit interactions, the role of different groups of atoms in a molecule in different types of vibronic coupling, and the potentially possible coordinates of photochemical reactions. A great deal of attention is devoted in this review to the phenomenon of concentration of vibronic coupling in selected vibrational modes of molecules (selectivity of vibronic coupling⁷); this effect is manifested in the vibronic spectra of complex molecules in that their vibrational structure is relatively sparse and there are only a few strong lines.

Heteroatoms introduce great diversity into the electronic structure of molecules of aromatic compounds. For example, with each of the lowest excited electronic states of such compounds there can be associated one of the theoretically possible different orbital types ($\pi\pi^*$, $\pi l\pi^*$, $\pi v^*\pi^*$, $n\pi^*$, etc.).⁸ The principal characteristic of orbital type, which is only scantily reflected in the designation of a state, is associated with the electronic structure of the heteroatom and with the presence in it of, in addition to valence electrons, vacant orbitals (v) or orbitals occupied by an unshared pair of electrons (n , l). For this reason, in order to elucidate the relation between the electronic structure of molecules and vibronic coupling a great deal of attention is devoted in this review to different approaches to determining experimentally the role of the heteroatomic orbitals in the formation of excited electronic states.

The possibility of applying group-theoretical analysis plays a large role in the investigation of vibronic coupling in complex molecules. For this reason, in this review we study data on vibronic coupling which were obtained primarily for molecules having not the lowest symmetry but rather a symmetry axis in addition to a symmetry plane. The general features of the structure of the molecules studied can be conveyed by the diagram



where Ph are benzene moieties and X_1 , X_2 , and X_3 are atomic groupings containing heteroatoms. This scheme combines into a single group molecules of compounds of diverse chemical classes, relating to the most important dyes or their half-

products (derivatives of anthraquinone, acridones, derivatives of fluorene, and indigoids).

On the whole, it can be asserted that the quantitative methods of fine-structure vibronic spectroscopy now constitute a delicate instrument for investigating the lowest excited electronic states of complex polyatomic molecules.

1. STRUCTURE OF THE LUMINESCENCE SPECTRA OF COMPLEX MOLECULES

In the study of the theoretical or experimental spectroscopic data on the excited electronic states of polyatomic molecules with a large number of vibrational degrees of freedom (for example, ≥ 60) the molecules are usually said to be complex (see the proceedings of modern conferences on spectroscopy). This representation is based on the following.⁹ Theoretical analysis of the excited electronic states of complex molecules of different aromatic compounds with heteroatoms shows that the splittings between the energy levels of different excited diabatic states are small. (Diabatic electronic states, i.e., states with fixed positions of the nuclei, are calculated by the methods of modern quantum chemistry.) In each of them the density of vibrational states, which include states of overtones and combination frequencies, is in turn high. The spin-orbit interactions and vibronic coupling, which refine the initial description of the electronic states as diabatic,^{10,11} can lead to non-negligible mixing of the diabatic excited electronic states (Herzberg-Teller effect) or further mixing of such Herzberg-Teller (HT) vibronic states (nonadiabatic interactions and the Jahn-Teller pseudoeffect (JT)). Since the selection rules allow, as a result, almost all vibronic transitions, the overlapping of separate lines can obliterate the structure in the electronic spectra.

1.1. Fine structure of spectra

The electronic spectra of large molecules (solutions at room temperature) consist of wide diffuse bands with little or no structure. Investigations have shown, however, that the main reasons why the structure of electronic bands is obliterated at room temperature are interaction with the solvent,¹ electron-phonon interaction,³ as well as statistical spread of the energy of electronic levels of the impurity mol-

ecule in the field of the solvent (the latter determines the inhomogeneous broadening of the spectrum^{13,14}).

The structure of the electronic spectra of complex molecules is observed under special experimental conditions: investigations at low temperatures (4–77 K) in matrices—solutions in *n*-paraffins (Shpol'skiĭ effect) or in other solvents^{15–17}—or investigations of vapors cooled in a supersonic jet of inert gases.¹⁸ Inhomogeneous broadening of the spectrum can be significantly reduced by using monochromatic light for electronic excitation of the molecules (method of selective spectroscopy^{13,14}).

Figure 1 shows, as an example, the fine-structure luminescence spectra of a complex molecule: fluorescence in solid solutions (b) and fluorescence of vapors in a supersonic jet (a).

The spectra of solutions at 4 K consist of zero-phonon lines with phonon wings. The ratio of the integrated intensity of these components (in the leading-order approximation of the theory of electron-phonon interactions) is preserved in the spectrum.³ In many cases, by choosing a suitable solvent¹⁶ and by selective excitation¹³ the intensity at the maxima of the wide phonon wings can be reduced to less than 10% of the maxima of the corresponding narrow zero-phonon lines. Such spectra are characteristic of a molecule that is subjected to weak intermolecular interactions³ and can be regarded as being "isolated."

Let us examine the typical structure of the vibronic spectra (see Fig. 1). It consists of narrow lines whose width is equal to 1–10 cm^{-1} . To a purely electronic transition between electronic states—the ground state S_0 and an excited singlet state S_1 (or triplet state T_1)—there corresponds a line, which we designate by 00, with a maximum at ν_{00} cm^{-1} . The maxima of the vibronic lines are observed at the frequencies $\nu^{ab} = \nu_{00} + \sum_i \nu_i' \nu_i'$ (in the absorption spectra or the luminescence excitation spectra) and $\nu^j = \nu_{00} - \sum_i \nu_i \nu_i$ (in the luminescence spectra), where ν_i is the vibrational quantum number, ν_i is the frequency of the *i*th vibration, and the prime means that the vibration belongs to the excited electronic state. The index *i* is often assigned a number or an arbitrary (sometimes special) letter: *a*, *b*, *m*, etc. As one can see from Fig. 1, the frequencies of both the fundamental and

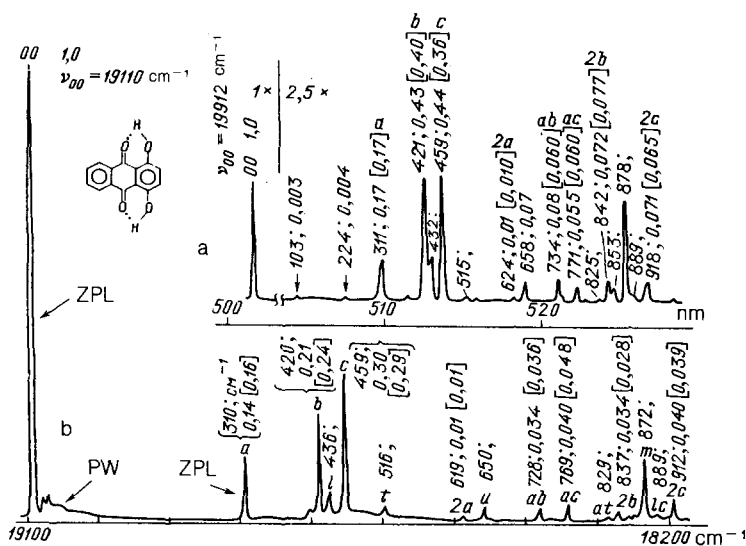


FIG. 1. The fluorescence spectra of 1,4-dihydroxy-9,10-anthraquinone. a) Vapors in a supersonic argon jet, $\nu_{\text{exc}} = \nu_{00}$.¹⁹ b) Solid solution in *n*-octane at 4.2 K; $\nu_{\text{exc}} = 19435 \text{ cm}^{-1}$.²⁰ ZPL and PW are the zero-phonon line and the phonon wing. The following are given at the line peaks: the vibrational frequency, in cm^{-1} (equal to the difference between the maxima ν_{00} and the vibronic line ν^j); the measured intensity I , in relative units; the theoretical value of the intensity (in brackets); and, the same letter designations a and b are assigned to the same vibronic transitions in the spectra.

sum vibrations and overtones are reliably recorded in the fine-structure vibronic spectra. The integral intensity of vibronic lines is also assigned indices corresponding to the vibrational states, for example, $I_{0v}(a)$ or $I(v_a a)$.

1.2. Vibronic coupling and line intensity

The intensity of lines in the fine-structure vibronic spectra reflects the vibronic and spin-orbit couplings. These interactions are described on the basis of perturbation theory. In different approximations the vibronic couplings are expressed in terms of different matrix elements of operators^{1-6,11} which represent the dependence of the Coulomb interaction V of the nuclei and the electrons of the molecule on small displacements of the nuclei from their positions of equilibrium. The electronic functions of the rough adiabatic approximation, i.e., the functions which depend only on the coordinates of the electrons, are the unperturbed (basis) functions. The different types of coupling have been given names. Frank-Condon (FC) coupling gives rise to a displacement of the minimum δQ_i of the electronic potential of the excited electronic state along a totally symmetric normal vibrational coordinates; the symmetry of the molecule does not change. Herzberg-Teller coupling causes the dipole moment of the electronic transition to depend on the coordinates of the nuclei. Jahn-Teller coupling lowers the symmetry of the equilibrium nuclear configuration of the molecule in the excited electronic state below that of the ground state S_0 . Spin-orbit coupling makes transitions between states with different multiplicity (T-S) allowed.

In the FC-coupling approximation transitions to all sublevels of vibrational states of the totally symmetric type are allowed^{1,2} (at 4 K in the above-discussed experiments the initial level is a sublevel of zero-point vibrations). In Fig. 1. the vibrational modes with letter designations (ν_a, ν_c , etc.) correspond to totally symmetric vibrations of the electronic state S_0 .

As a result of HT coupling (or spin-orbit and HT coupling) the transitions S_1-S_0 and T_1-S_0 to the vibrational sublevels of nontotally symmetric normal vibrations are allowed. The selection rules in this case are contained in the symmetry properties of the operators and the combining electronic states (the direct product of representations (Γ) must contain a totally symmetric (TS) representation) and have the following form:¹¹

$$\Gamma(S_1) \times \Gamma(Q_i) \times \Gamma(M_{0k}) \text{ contains } \Gamma(\text{TS}) \quad (1a)$$

$$\Gamma(T_1) \times \Gamma(\hat{H}'_{s0}) \times \Gamma(Q_i) \times \Gamma(M_{0k}) \text{ contains } \Gamma(\text{TS}) \quad (1b)$$

here Q_i is the normal vibrational coordinate, corresponding to the frequency ν_i of the allowed vibration; M_{0k} is the purely electronic dipole moment of the transition between the state S_0 and the state S_k , coupled by the intramolecular interactions with S_1 ($M_{0k} = \langle \varphi_0(r) | r | \varphi_k(r) \rangle$), where $\varphi_n(r)$ are the electronic wave functions of diabatic states, which depend on the coordinates r of the electrons); \hat{H}'_{s0} is the orbital component of the spin-orbit interaction operator \hat{H}_{s0} . It is also necessary to take into account the fact that the triplet state T has three sublevels $T^{(x)}$, $T^{(y)}$, and $T^{(z)}$, whose splitting is $< 1 \text{ cm}^{-1}$ and to which in such spectra there corresponds one line of a purely electronic transition T_1-S_0 (its structure is hidden). As a result of the participation of each

sublevel of the state T_1 in the vibronic transitions, according to the selection rules (1) vibrations of different symmetry from among the nontotally symmetric vibrations are allowed.²

In Fig. 1a the arrows mark vibronic lines in the fluorescence spectrum which correspond to transitions to sublevels of the vibrational states of nontotally symmetric type (according to the selection rules (1a) with $\Gamma(S_1) = A_1$ (Ref. 6) in-plane vibrations with the coordinates $Q_i(b_2)$ and out-of-plane vibrations with the coordinates $Q_i(b_1)$ are allowed). In the spectrum under study the named lines are weak, but this is not a characteristic indicator of such vibronic transitions. Such lines can predominate in the spectra of other molecules (see the next section).

Thus the selection rules theoretically allow all or many of the normal vibrations in the fine-structure electronic spectra of complex molecules which are unsymmetric or belong to point groups of low symmetry (C_s , C_{2h} , C_{2v} , and D_{2h}).

The intensity distribution among the vibronic lines contains more detailed information about vibronic coupling.^{1-3,6} The FC and HT couplings can be characterized, respectively, by the spectroscopic parameters γ_i and L_i , in terms of which the relative integral intensity ${}^v I_{0v}(i)$ of a vibronic line with the maximum $\nu^{ab} = \nu_{00} + \nu_i \nu'_i$ or $\nu^\pi = \nu_{00} - \nu_i \nu_i$ is expressed. (The intensity ${}^v I_{0v}(i)$ with a superscript contains the frequency factor (ν_{00}/ν^{ab}) or (ν_{00}/ν^π)⁴ and is proportional to the squared dipole moment of the vibronic transition.) The expressions (2a) and (2b) given below are valid when only FC coupling and only HT coupling, respectively, operate:³⁾

$${}^v I_{01}(i) = \gamma_i \equiv (\Delta_i/\sqrt{2})^2, \quad (2a)$$

$${}^v I_{01}(\alpha) = 0,5L_\alpha^2. \quad (2b)$$

The significance of the spectroscopic parameters Δ_i and L_i is revealed in the expressions (3) and (4).

The dimensionless parameter Δ_i and the dimensional parameter δQ_i are the displacements of the minimum of the electronic potential of the excited state $\varphi_m(r)$ along the vibrational coordinates $\xi_i(Q_i)$ relative to the potential of the ground electronic state $\varphi_0(r)$:

$$\Delta_i = \delta Q_i(\omega_i/\hbar)^{1/2},$$

where ω_i is the angular frequency of the vibrations.

The displacement of the minimum of the potential is caused by the electronic excitation of the molecule and is determined by the magnitude of the diagonal matrix element of the vibronic-coupling operator:

$$\delta Q_i [r^{1/2} \text{cm}] = \langle \varphi_m(r) | \left(\frac{\partial V}{\partial Q_i} \right)_0 | \varphi_m(r) \rangle \omega_i^{-2}, \quad (3)$$

$$\Delta_i = \langle \varphi_m(r) | \left(\frac{\partial V}{\partial \xi_i} \right)_0 | \varphi_m(r) \rangle (\hbar \omega_i)^{-1}.$$

As follows from Eq. (3), for nontotally symmetric (NTS) coordinates the displacement $\delta Q_{\text{NTS}} = 0$.

The parameter L_i with the index i reflects the dependence of the dipole moment of the electronic transition $P_{0k}(r, Q) = M_{0k} + \sum_i M_{0k}^{(i)} Q_i$ on the coordinates of the nu-

clei: $L_i \sim |\mathbf{M}_{0k}^{(i)}|$. In the approximation of perturbation theory the quantity $\mathbf{M}_{0k}^{(i)}$ can be expressed¹¹ in terms of the vibronic-coupling operators and the function $\varphi(\mathbf{r})$. The parameter L_i is then given by a complicated expression. Thus in the case of the singlet-triplet transition T_1-S_0 , which is allowed with frequency ν_{00} by the orbital symmetry, the parameter $L_\alpha \neq 0$, allowing a transition with frequency $\nu_{00} - \nu_\alpha$ (see the relation (2b), where α is the index of an NTS vibration), is expressed as follows:

$$|L_\alpha| = |\bar{\Phi}_{00}|^{-1} \left| \sum_n \frac{\langle {}^1\varphi_n | \hat{H}_{vs0}^{(\alpha)} | {}^3\varphi_m \rangle \mathbf{M}_{0n}}{3E_m - 1E_n} + \sum_n \sum_k \frac{\langle {}^1\varphi_n | \hat{H}_{s0} | {}^3\varphi_k \rangle \langle {}^3\varphi_k | \hat{H}_{ve}^{(\alpha)} | {}^3\varphi_m \rangle \mathbf{M}_{0n}}{(3E_m - 1E_n)(3E_m - 3E_k)} + \sum_n \sum_{k'} \frac{\langle {}^1\varphi_n | \hat{H}_{ve}^{(\alpha)} | {}^1\varphi_k \rangle \langle {}^1\varphi_k | \hat{H}_{s0} | {}^3\varphi_m \rangle \mathbf{M}_{0n}}{(3E_m - 1E_n)(3E_m - 1E_k)} \right|; \quad (4)$$

Here ${}^1\varphi$ and ${}^3\varphi$ are the wave functions of the singlet and triplet electronic excited states (with indices n, m, k , and k') which do not depend on the coordinates of the nuclei and in which, for brevity, the dependence on the coordinates of the electrons (\mathbf{r}) is not shown; 1E and 3E are the energies of these states; and $(\partial V / \partial \xi_\alpha)_0 \equiv H_{ve}^{(\alpha)}$ and $(\partial \hat{H}_{s0} / \partial \xi_\alpha)_0 \equiv \hat{H}_{vs0}^{(\alpha)}$ are the vibronic-coupling operators. In the expression (4) for different L_α , distinguished by the indices α , the quantity $|\bar{\Phi}_{00}|$ remains constant,⁶ since it is related with the intensity of the line of a purely electronic transition with frequency ν_{00} (see below).

Terms in expressions of the type (4) are often identified with definite intramolecular coupling schemes in which the operators $\hat{H}_{ve}^{(i)}$, $\hat{H}_{vs0}^{(i)}$, \hat{H}_{s0} mix the diabatic states $\varphi(\mathbf{r})$. In the approximation of two-level mixing (for example, the states ${}^1\varphi_1(\mathbf{r})$ with ${}^1\varphi_k(\mathbf{r})$ in the case of the transition S_1-S_0) the expression for L_i has the following simple form:²¹

$$|L_i| = |\bar{\Phi}_{00}|^{-1} \left| \mathbf{M}_{0k} \frac{\langle \varphi_k | \hat{H}_{ve}^{(i)} | \varphi_1 \rangle}{E_1 - E_k} \right| \sim \frac{|\mathbf{M}_{0k}|}{|\mathbf{M}_{01}|} \left| \frac{\langle \varphi_k | \hat{H}_{ve}^{(i)} | \varphi_1 \rangle}{E_1 - E_k} \right|. \quad (5)$$

According to a rough estimate made with the help of the expression (5) the off-diagonal matrix elements of the vibronic-coupling operators are equal to several hundreds of cm^{-1} .²¹

In the approximation of HT coupling in the nontotally symmetric coordinates Q_i and on the basis of the basic model of vibronic coupling ($\nu_i = \nu'_i$, $Q_i = Q'_i$) the intensity $\nu I_{01}(i)$ of vibronic lines with maxima at $\nu_{00} \pm \nu_i$ is the same in the emission and absorption spectra (the spectra are mirror symmetric); this is usually observed. The quantities L_i are found from the intensities νI_{01} in accordance with Eq. (3). The mirror symmetry of the spectra at frequencies associated with NTS vibrations can be destroyed by nondiabatic interactions, which can be neglected in investigations of luminescence spectra.²²

In the spectrum shown in Fig. 1 the intensity of lines with maxima at $\nu_{00} - \nu_\alpha$ (where ν_α are the frequencies of NTS vibrations $\nu_\alpha = 103$ and 224 cm^{-1}) is determined, according to the theoretical ideas described above, by the HT

vibronic couplings, which, leaving $\delta Q_\alpha = 0$, are summed in the spectroscopic parameter L_α (see the formulas (2b) and (4)).

In the FC-coupling approximation, in which the couplings are described in the system of totally symmetric vibrational coordinates, the absorption and emission spectra are mirror symmetric. According to the formula (2a), in this approximation the intensities $\nu I_{01}(i)$ of the vibronic lines a, b , and c in the spectra shown in Fig. 1 can be used to make a rough estimate of the magnitude of the displacement δQ_i of the minimum of the potential in the state S_1 along the corresponding totally symmetric coordinates Q_i . However the mirror symmetry of the spectra at the corresponding frequencies ν^{ab} and ν' can be destroyed even in the adiabatic approximation, since HT coupling can also appear (according to the relations (1)) along the totally symmetric vibrational coordinates.

Thus analysis of the intensity distribution among vibronic lines with maxima at $\nu_{00} \mp \nu \nu_{TS}$ or $\nu_{00} \mp \nu_{NTS} \mp \nu \nu_{TS}$ (where ν is the vibrational quantum number) in the luminescence and absorption spectra of aromatic hydrocarbons²¹⁻²³ and heteroaromatic compounds⁶ showed that, aside from the breakdown of mirror symmetry, in the region of overtones of the totally symmetric vibrations a deviation is observed from the theoretical distribution (6). This deviation is attributable to the purely FC coupling along the totally symmetric coordinates Q_i :^{1,2}

$$\nu I_{0v}(i) = \gamma_i^v / v_i!. \quad (6)$$

This effect could be due to the manifestation of HT and FC couplings simultaneously along the same totally symmetric coordinate Q_i .³

We note that the mechanism of combined FC and HT couplings along totally symmetric coordinates is also reflected in the intensity of the line corresponding to a purely electronic transition.²⁴ Thus, in the FC-coupling approximation the intensity of the line with maximum at ν_{00} in the spectrum of the singlet-singlet transition $S_1 \rightarrow S_0$ is proportional to the quantity $|\mathbf{M}_{01}|^2$, and when the HT coupling is also taken into account it is proportional to the quantity $|\bar{\Phi}_{00}|$:

$$|\bar{\Phi}_{00}| = |\mathbf{M}_{01} - \frac{1}{2} \sum_{TS} \Delta_{TS} \sum_k \mathbf{M}_{0k} \frac{\langle \varphi_k | \hat{H}_{ve}^{(TS)} | \varphi_1 \rangle}{E_1 - E_k}|. \quad (7)$$

For a triplet-singlet transition $|\bar{\Phi}_{00}|$ can be represented by a similar but more complicated expression.

When both FC and HT couplings are realized along the same totally symmetric coordinate Q_i , the corresponding pairs of vibronic-coupling parameters can be extracted by investigating the intensity distribution among lines associated with overtones and the sum frequencies of totally symmetric vibrations. The same data on the parameters Δ_i and L_i can be obtained by studying the deviation from mirror symmetry in absorption and emission spectra. In the approximation $Q_i = Q'_i$ and $\nu_i \approx \nu'_i$ the analysis can be performed using the analytic expressions given in Refs. 3 and 6.

An expression relating the distribution of relative intensity $\nu I_{0v}(i)$ in the luminescence spectrum with the spectroscopic parameters γ_i and L_i in the case when the difference between the frequencies of the totally symmetric vibrations ν_i and ν'_i is small is presented below:^{6,25}

$${}^{\nu}I_{0\nu} = \frac{F_i^{\nu_i-2}}{\nu_i!} \left[F_i + \frac{\nu_i(\nu_i-1)}{2} C_i \right]^2 \left(1 + 2\rho_i \frac{\nu_i G_i}{(2F_i)^{1/2}} \eta_i + \frac{\nu_i^2 G_i^2}{2F_i} \eta_i^2 \right), \quad (8)$$

where

$$F_i = \left(\frac{2\nu_i}{\nu_i + \nu_i'} \right)^2 \gamma_i, \quad G_i = \frac{2(\nu_i \nu_i')^{1/2}}{\nu_i + \nu_i'} L_i,$$

$$C_i = \frac{\nu_i - \nu_i'}{\nu_i + \nu_i'}, \quad \eta_i = \frac{F_i + 2^{-1}(\nu_i - 1)(\nu_i - 2)C_i}{F_i + 2^{-1}(\nu_i - 1)\nu_i C_i}.$$

Another spectroscopic parameter ($|\rho_i| \leq 1$) is employed in the expression (8) in connection with the fact that the directions of the transition dipole moment at the frequencies $\nu_{00}, \nu_{00} - \nu_i, \nu_{00} - 2\nu_i$, etc. (where $i = \text{TS}$) can be different (in molecules without symmetry elements or having C_s, C_2, C_i , or C_{2h} symmetry). In molecules belonging to the symmetry groups C_{2v} and D_{2h} the dipole moments of purely electronic transitions \mathbf{M}_{0k} are collinear, if they belong to the same irreducible representation of the symmetry group; in this case $|\rho_i| = 1$.

The intensity asymmetry appearing in absorption and emission spectra owing to FC and HT couplings along totally symmetric coordinates can be clearly seen at the frequencies ν^j and ν^{ab} , which are related with the fundamental vibrations ($\nu_{00} - \nu_i$ and $\nu_{00} + \nu_i'$). Thus the intensity of the vibronic lines with maxima at $\nu_{00} \mp \nu_i$ is determined in the approximation $\nu_i = \nu_i'$ and $|\rho_i| = 1$ by the following expression

$${}^{\nu}I(i) = (\gamma_i^{1/2} \pm L_i/\sqrt{2})^2. \quad (9)$$

The intensity asymmetry at the frequencies ν^j and ν^{ab} is related with the different signs of the HT parameters ($+ \nu_i L_i$ and $- \nu_i L_i$) in the expressions for the intensity ${}^{\nu}I(\nu_i)$ of vibronic lines.

In order to illustrate the case of combined FC and HT coupling along totally symmetric vibrational coordinates we shall study the data on the intensity of vibronic lines for the molecule shown in Fig. 1b (we designate it briefly as 1,4-OAQ). Intensity asymmetry in the vibronic spectra of its solid solutions was ascertained at 4.2 K.²⁰ Thus, in the fluorescence excitation spectra ($\nu^{ex} = \nu^{ev}$) the intensities of the lines a, c , and $2c$ are equal, respectively, to 0.03, 0.49, and 0.15 ($\nu_a' = 325, \nu_c' = 481, 2\nu_c' = 961 \text{ cm}^{-1}$). These values, especially for the lines a and $2c$, differ significantly from the intensity in the fluorescence spectrum (see Fig. 1b). In accordance with the above theory the collection of parameter pairs ($\Delta_i/\sqrt{2}$ and $L_i/\sqrt{2}$) for each coordinate Q_i ($i = a, b, c$) makes it possible ultimately to describe satisfactorily, on the basis of the approximations $\nu_i = \nu_i'$ and $Q_i = Q_i'$, the intensity of 15 lines at the frequency ν^j and ν^{ex} , which include the overtones and the sum and fundamental frequencies of the vibrations. The theoretical values of the intensity in the fluorescence spectra are presented in Fig. 1b in order to compare them with the experimental values. The intensity at the frequencies ν^{ex} in the spectra of the solid solutions is described by the same small deviation from the experimental value.

It can be expected that in the study of vibronic coupling the spectra of a supersonic jet, which have narrow lines (of width $\sim 1 \text{ cm}^{-1}$), will be an excellent object for revealing nonadiabatic interactions in the excited electronic state for $\nu_i' > 1$ as well as the Dushinskii effect.¹⁹ It should be noted that in the investigation of the intensity distribution and in the subsequent comparison of the spectrum of a supersonic jet with the spectrum of a solid solution it is necessary to pay attention to the difference between the vibrational relaxation processes that precede emission. For example, under the conditions of a supersonic jet the vibronic lines in the short-wavelength part of the absorption and excitation spectra were observed to have significantly different intensities.²⁶ Effects due to saturation of optical transitions are even noted at very moderate excitation energies;²⁰ such effects distort the true intensity distribution at the frequencies ν^{ex} in the spectrum of a jet.

Only a few experiments specially designed for studying vibronic coupling and analysis of the intensity distribution in regions of the spectrum where $\sum_i \nu_i > 1$ under conditions of a supersonic jet have thus far been performed. It has been found that the model of combined FC and HT couplings along the totally symmetric vibrational coordinates with $\nu_i = \nu_i'$ and $Q_i = Q_i'$ makes it possible to describe, within experimental error, the intensity distribution in the fluorescence spectrum and in the fluorescence excitation spectrum, even for vapors cooled in the jet (data on the intensity in the fluorescence spectrum are given in Fig. 1a).

The small difference between the FC-coupling parameters ($\gamma_i^{1/2}$) extracted from the spectra of solid solutions and a supersonic jet makes it possible to conclude²⁰ that the polycrystal field of the paraffin matrix has virtually no effect on the change in the nuclear configuration of the impurity molecule; in an isolated molecule this change is determined by the excitation of the electronic subsystem of the molecule. (For example, for vibronic coupling along the coordinate Q_c of the molecule 1,4-OAQ studied in cooled vapors (j) and solid solutions (m) the following values of the parameters were obtained: $\gamma_c^{1/2} = 0.64 \pm 0.06$ for j and $\gamma_c^{1/2} = 0.63 \pm 0.03$ for m .)

The small absolute values of the HT-coupling parameters, obtained from the spectra of a jet and of solid solutions of the molecules studied²⁰ (for example, for 1,4-OAQ: ($L_c/\sqrt{2} = -0.01 \pm 0.05$) _{j} and ($L_c/\sqrt{2} = -0.07 \pm 0.03$) _{m}), made it impossible, for the time being, to establish experimentally the mechanism of the effect of the medium on the quantity L_i . The theoretical description of the spectroscopic parameter L_i (the formula (4)), however, reveals some reasons for the expected changes in the measured values of this quantity: L_i is expressed in terms of the higher electronic excited (diabatic) states and it depends on the energy splitting between these states. The characteristic absorption bands of the matrix fall into this energy range, and it is here that in the description of the intermolecular interactions the diabatic (or adiabatic) states of the impurity and matrix molecules are most likely to be coupled.

1.3. The characteristics of the structure of the spectra of complex molecules

In concluding this section, which is devoted to description of the structure of the vibronic spectra of complex mole-

cules, we note that immediately after the Shpol'skiĭ effect was discovered the reports²⁷⁻³⁰ of sparse vibrational structure in the luminescence spectra of solid solutions at 77 K of aromatic compounds with a heteroatom appeared very intriguing and unexpected.

For example, a series of maxima split by 1680–1650 cm^{-1} predominates in the luminescence spectra of 9,10-anthraquinone (AQ); this frequency is identified with stretching vibrations of C = O groups.²⁷ Both totally symmetric and nontotally symmetric vibrations of these groups are observed in the spectrum.^{31,32} No frequencies corresponding to vibrations of C = O groups were found in the luminescence spectrum of the molecule TOAQ (1,4,5,8-tetraoxy-9,10-anthraquinone, which is prepared by attaching to AQ four OH groups in the α position).^{29,33} The main maxima in the spectrum are governed by transitions to the vibrational sublevels of other (only four) vibrations. Analogously, the luminescence spectra of thioindigo (TIN) and indigo do not contain frequencies corresponding to stretching vibrations of C = O groups.^{28,34} The predominance of six vibronic lines in the luminescence spectrum of TIN is attributable to the fact that there are only three fundamental totally symmetric vibrations ($\nu = 234, 492, \text{ and } 1534 \text{ cm}^{-1}$). The frequency $\nu = 1534 \text{ cm}^{-1}$ corresponds to the stretching vibration of the central C = C bond in the molecule. In the luminescence spectra of *N*-alkyl derivatives of acridone^{6,7,30} the dominant vibronic line is split from the frequency ν_{00} by 672 cm^{-1} ; this frequency corresponds to out-of-plane vibrations of CH groups in the aromatic fragments of the molecule.

This relatively "simple" vibrational structure of the vibronic spectra does not change much⁶ even with significant narrowing of the vibronic lines in experiments at temperatures below $\sim 10 \text{ K}$ (when the narrow zero-phonon line is separated from the phonon wing).

For example, at 77 K the widths of the three fundamental vibronic lines in the spectrum of TIN (see above) are equal to $\sim 200 \text{ cm}^{-1}$. As the temperature dropped to 4.2 K the widths of the lines decreased to $5\text{--}7 \text{ cm}^{-1}$. Thirteen fundamental vibrational frequencies were recorded under these experimental conditions;^{7,34} eleven frequencies are of class a_g (symmetry group C_{2h}) and two are of class b_g , though according to the selection rules all vibrations of the g -type ($27a_g + 12b_g$) are allowed in the fluorescence spectrum (the transition ${}^1B_u \rightarrow S_0$). Thus fewer than half of the allowed vibrations appear in the fluorescence spectrum. The relative intensity ${}^1I_{01}$ of the corresponding lines falls in the range 0.60–0.01. In addition, as before, at 4.2 K, as also at 77 K, the above-mentioned three lines with intensity in the range 0.60–0.30 predominate in the spectrum. All other lines are weak (their intensities do not exceed 0.06 units).

The "simplicity" of the vibrational structure of the electronic spectra of complex molecules could be attributable (according to the expressions (2) and (8)) to the fact that in a polyatomic molecule relatively large displacements of the minimum of the electronic potential occur only along a small number of coordinates Q_i and the wave function of the excited state depends significantly on only a small number of such coordinates. This effect is termed selectivity of vibronic coupling or concentration of vibronic coupling in selected vibrational modes.⁷ According to the theoretical description of vibronic coupling, the explanation of this phenomenon must

be sought in the special electronic orbital structure of the excited electronic states of complex molecules.

2. SOME RESULTS OF ANALYSIS OF THE VIBRONIC STRUCTURE OF THE LUMINESCENCE SPECTRA OF COMPLEX MOLECULES

The wide-band electronic spectra of heteroaromatic compounds have been used for a long time to determine the orbital type of the corresponding singlet-singlet electronic transition $S_k \leftarrow S_0: \pi \rightarrow \pi^*, \pi l \rightarrow \pi^*, n \rightarrow \pi^*$.³⁰ (In these transitions the charge in the π -system of the molecule changes and charge is transferred from the heteroatom into the π -system. Correspondingly, the symbols $\pi\pi^*, \pi l\pi^*, n\pi^*$, and others are employed⁸ to denote the orbital type of the lowest excited electronic singlet and triplet states S_k and T_k .⁴) The orbital type is identified on the basis of band characteristics, such as the extinction coefficient at maximum and the shift of the band maximum (in the long- or short-wavelength direction) depending on the polarity of the solvent. It is known, however, that these general characteristics of bands cannot always correctly reflect the orbital type of a singlet-singlet transition. The question of determining the orbital type of singlet-triplet transitions from wide-band electronic spectra remains open because the intensity of the absorption bands $T_k \leftarrow S_0$ is low.

The first successes in obtaining structural luminescence spectra of solutions made it possible to employ the vibrational structure of such spectra itself to identify the orbital types of the corresponding electronic transitions of molecules with carbonyl groups (C = O), and this characteristic of the S_1 and T_1 excited electronic states was in turn an important link in the development of the systematics of molecules from the properties of their luminescence spectra.^{8,30} The following empirically established rule is employed to determine the unknown orbital type of an excited state. Strong lines associated with stretching vibrations of C = O groups are observed in vibronic spectra in the case of the transitions ${}^3n\pi^* \rightarrow S_0$. Such lines do not predominate in the transitions ${}^3\pi\pi^* \rightarrow S_0, {}^3\pi l\pi^* \rightarrow S_0, {}^1\pi l\pi^* \rightarrow S_0$. Instead, the vibronic lines associated with vibrations of the hydrocarbon framework stand out. We note that the very fact that the orbital type of an electronic state is reflected in the structure of vibronic spectra does not explain in the general case the sparsity of the vibrational structure of vibronic spectra.

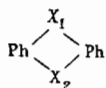
The different approaches based on analysis of vibronic coupling for obtaining more detailed characteristics of the excited electronic states of molecules from the fine-structure luminescence spectra will be studied in the following sections.

The pronounced structure of vibronic spectra of solutions of complex molecules at 4 K makes it possible to measure the integrated intensities of the vibronic lines with acceptable accuracy (from $\sim 10\%$ for $\nu_i = 1$ to $\sim 30\%$ for $\sum_i \nu_i = 3$). This fact has been used to test the theory of vibronic coupling. In Refs. 3 and 6 it was established that in the approximation $Q_i = Q'_i$ and in most cases for $\nu_i = \nu'_i$ also the intensity of the informatively redundant vibronic lines of large molecules of aromatic compounds can, as a rule, be described within experimental error using only two vibronic-coupling parameters for each coordinate Q_i with $|\rho_i| = 1$.

The structure of the vibronic spectra has also been used

to investigate the Dushinskii effect ($Q_i \neq Q'_i$).³⁵⁻⁴⁰ The entanglement of the normal vibrational coordinates is modeled on a computer (J is the entanglement matrix) and the intensities of the vibronic lines are calculated taking into account the diagonal and off-diagonal elements of the matrix J as well as under the assumption $J = E'$, where E' is a diagonal matrix with the elements J_{ii} . In Ref. 35 it is concluded that in the presence of entanglement of coordinates, when the diagonal and off-diagonal elements of the matrix J are of comparable magnitude ($J_{ii} \approx J_{ij} \approx 0.5$), the difference of such computed values of the intensity of the vibronic lines (I_{01}) is equal to 20–30% (for stilbene and diphenylbutadiene molecules). For $(J_{ij}/J_{ii}) \approx 0.3$ this difference is negligible ($\sim 1.5\%$). It should be noted, however, that the error introduced into the purely theoretical calculation of the intensity as a result of the roughness of the model of both the parameters Δ_i and the matrix J (Refs. 38, 41, 42) can apparently nullify the entire gain achieved by taking into account the entanglement of coordinates. For example, the differences between the purely computed values of the intensities of the vibronic lines ($J \neq E'$) and the experimental values in the region of the spectrum where the Dushinskii effect is being modeled can reach 100%.^{35,43}

It is assumed that for large molecules of aromatic compounds, in which the frequencies ν' and ν differ by 10–30 cm^{-1} (1–5%), the Dushinskii effect can be neglected when analyzing vibronic spectra.⁶ In accordance with this assumption, model calculations have shown that the effect of entanglement of coordinates on the intensity of vibronic lines in the fluorescence spectrum (${}^3n\pi^* \rightarrow S_0$) of 9,10-anthraquinone³⁸ and the fluorescence spectrum (${}^1\pi\pi^* \rightarrow S_0$) of anthracene,³⁹ the structure of whose molecules can be characterized by the scheme mentioned above



(see Introduction), is negligible.

The theory of the Dushinskii effect at present has the deficiency that in order to determine the changes δU occurring in the potential field and the changes in the geometric parameters (bond lengths δq), which are necessary for calculating J and Δ_i , of a molecule as a result of electronic excitation quite rough correlations of the quantities δU_{kk} and δq_k with the change in the order of the bonds of the molecule are employed.³⁷ In so doing, the changes in both the off-diagonal force constants U_{cr} and the diagonal elements, associated with the natural vibrational coordinates of the angles between the bonds and planes, in the electronic states are neglected. As a result, the difference between the experimental and computed values of the vibrational frequencies ν' reaches, in many cases, hundreds of cm^{-1} .

We note that the results of experimental investigations of the fine-structure vibronic spectra provide a stimulus for the development of purely theoretical models of vibronic coupling. Thus, initially it was assumed that the changes in the angles $\delta\alpha$ between bonds can be neglected in the excited electronic state of the molecule.³⁷ In subsequent publications^{40,44} approaches for taking the changes $\delta\alpha$ into account theoretically were developed.

We now return to the experimental data on vibronic coupling, which were obtained by analyzing the spectra of

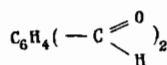
complex molecules neglecting the Dushinskii effect.

Analysis of the fine-structure vibronic spectra of polyatomic molecules (taking into account the intensity distribution in the regions of overtones and the sum frequencies of vibrations) showed that the mechanism of characteristic FC and HT couplings along the totally symmetric coordinates is a common phenomenon.^{3,6,45-50} For example, it has been established that this mechanism is always realized in ${}^3n\pi^*$ -states of compounds containing one or two C = O groups, both in the case when the transitions T_1 - S_0 are forbidden by orbital symmetry and in the case when such transitions are allowed.^{6,49} It has been concluded that HT couplings that not only are linear in the vibrational coordinates Q_{NTS} or Q_{TS} but are also quadratic in $Q_{TS} Q_{NTS}$ play a large role in vibronic coupling.^{45,49,51} The parameters γ_i and L_i obtained from the vibronic spectra characterize the vibronic coupling in the lowest S_1 or T_1 excited electronic state. The investigation of preresonance Raman scattering spectra together with the fine-structure vibronic spectra makes it possible to determine⁵² the parameters of vibronic coupling in higher electronic states.

Nonadiabatic interactions, as a rule, have virtually no effect on the intensity distribution in emission spectra. The parameters γ_i and L_i obtained from such spectra make it possible to estimate, using expressions of the type (5), the effect of nonadiabatic interactions on the absorption spectra.²² Comparison of the vibronic spectrum of an ultrasonic jet with that of a solid solution showed⁵³ that nonadiabatic intramolecular interactions rather than the crystal field of the matrix could be responsible for the lowering of D_{2h} symmetry of the equilibrium nuclear configuration of molecules (with loss of the center of inversion) in the excited electronic state, a phenomenon that is well known for solid solutions.

It has been shown for the example of comparing aromatic and heteroaromatic compounds containing nitrogen that the parameters of the HT coupling along the totally symmetric coordinates in the S_1 state do not, as a rule, become small, while the oscillator strength of the transition S_1 ($\pi\pi^*$)- S_0 increases by an order of magnitude when an N atom is introduced into the benzene ring of hydrocarbons.⁴⁸ For a number of heterocyclic derivatives of fluorene, which contain O, S, and Se atoms in the central five-member fragment of the molecules, it has been established⁵⁴ that the role of the heteroatom in vibronic and spin-orbit couplings in the T_1 state increases (in the same order).⁵⁴

The intensity distribution in vibronic spectra is very sensitive to changes of the conformation of the molecules.^{50,55-57} For example, the intensity distributions differ significantly for the planar and "twisted" forms of diphenyl ($C_6H_5-C_6H_5$) or the cis- and trans-forms of terephthalic aldehyde



in solutions. We note that the observed differences of such spectra could be caused not only by different shifts δQ_i of the minimum of the excited-state electronic potential (relative to the ground state potential) in different conformers,⁵⁷ but also by a change of the selection rules for the corresponding molecules in connection with their different symmetry. In a number of cases it has been found that the changes produced

in the intensity in vibronic spectra by changing the solvent or the conditions under which the impurity molecules are embedded in the solvent matrix are not related with the changes produced in the configuration of the molecule by the solvent. Thus investigations of diphenylene have established that in the case of the transition $T_1(\pi\pi^*)-S_0$ the HT-coupling parameters change significantly while the FC-coupling parameters remain unchanged when the intermolecular interactions change (for example, the hydrocarbon solvent is replaced by CCl_4).⁴⁶ On the other hand, it is precisely the fact that the FC-coupling parameters γ_i for two emission centers are different that has made it possible to prove⁵⁰ the existence of planar and "twisted" forms of diphenyl molecules fluorescing in solid solutions. In some cases, the complex transformations produced in the spectra of impurity molecules embedded in matrices by changing the matrix as well as the conditions of embedding in the matrix are caused by the existence of polyatomic potentials only along the intermolecular nuclear coordinates,⁵⁸⁻⁶⁰ and in this case the effect of the solvent on the form of the electronic potential of the impurity molecule is negligible.

It has been shown that vibronic couplings are selectively concentrated in some vibrational modes.^{6,7} For example, in the case of several Q_{TS} with close frequencies the intensity of one of the corresponding vibronic lines can be determined by purely FC coupling, while the intensity of another vibronic line can be determined by simultaneous FC and HT couplings with the predominant HT-coupling parameter L_{TS} .⁴⁵⁻⁶¹ In the case of purely HT coupling the interaction along one among several coordinates Q_{CH}^\perp , corresponding to out-of-plane vibrations of the CH groups in benzene moieties and belonging to the same irreducible representation of the symmetry group of the molecule, often stands out significantly.⁶

One of the factors responsible for significant weakening of certain lines in the vibronic spectrum has been determined. However this factor, which is manifested in allowed transitions, is not related with the magnitudes of the vibronic-coupling matrix elements. Thus it has been shown^{6,62} that some regularities in the spin-orbit mixing⁶³ of states of orbital type A' and A'' (see footnote 4) as well as the ratio of the oscillator strengths (f) of the transitions $A'-S_0$ and $A''-S_0$, as reflected in the inequalities

$$\langle A'' | \hat{H}_{s0} | A'' \rangle \approx \langle A' | \hat{H}_{s0} | A' \rangle \ll \langle A'' | \hat{H}_{s0} | A' \rangle, \quad (10a)$$

$$f(A'' - S_0) \ll f(A' - S_0), \quad (10b)$$

give rise to a definite rule (Table I) for the appearance of in-

plane and out-of-plane nontotally symmetric vibrations in vibronic spectra. In formulating the rule the fact that the matrix elements of the vibronic coupling operators (HT coupling with the coordinate Q_i) mixing the electronic states of different orbital structure have different magnitudes was neglected. The rule, which has been confirmed experimentally, shows that some vibrations from among those allowed by the selection rules (1a) or (1b) do not appear in the vibronic spectrum, since such lines are suppressed, and they are suppressed not by factors related with vibronic coupling but rather with the relations (10a) and (10b).

Thus, depending on the orbital symmetry A' and A'' (or orbital type $\pi\pi^*$ or $n\pi^*$) of the electronic states and their multiplicities (S, T), all lines with maxima $\nu_{00} - \nu_{NTS}$ from among the allowed lines, where ν_{NTS} belongs to a certain class in the symmetry group of the molecule (see Table I), are suppressed in the spectrum. This effect indeed significantly depletes the vibronic structure of luminescence spectra, but it does not explain completely the selectivity of vibronic coupling, which is manifested also among coordinates Q_i belonging to the same class in the symmetry group (see the discussion in Sec. 6).

The rule explaining the appearance of predominantly in-plane ν_{NTS} or out-of-plane ν_{NTS} vibrations in the vibronic spectra for four types of electronic transitions (see Table I and remarks) can be used for a different purpose: to determine the unknown orbital type of the excited electronic state (see Sec. 4).

3. VIBRONIC COUPLING AND THE ORBITAL STRUCTURE OF EXCITED ELECTRONIC STATES

This section is devoted primarily to FC coupling. In the approximation of diabatic states the electronic excitation $\varphi_0(\mathbf{r}) \rightarrow \varphi_k(\mathbf{r})$ increases the energy of the state by an amount E^0 , if the change in the nuclear configuration of the molecule is neglected. The excited electronic state $\varphi_k(\mathbf{r})$ is customarily characterized, in particular, by changes in the π -conjugation of the bonds (δp_π) or the indices of the bonds ($\delta \zeta$) between atoms as well as by changes in the charge density on the atoms (δe) as compared with the ground electronic state $\varphi_0(\mathbf{r})$. Thus, theoretically, the role of atomic orbitals (A_0) of the atoms in the formation of the orbital structure of the excited electronic states is determined in terms of δp_π and δe as a result of an approximate quantum-chemical calculation.

The next approximation in the determination of the energy of the state $\varphi_k(\mathbf{r})$ —the vibronic coupling linear in Q_i is

TABLE I. The rules for the ratios of the intensities of vibronic lines $I^{(||)}$ and $I^{(\perp)}$ with maxima $\nu_{00} - \nu^{||}$ and $\nu_{00} - \nu^\perp$, respectively, in the spectra of the transitions $S_1 \rightarrow S_0$ and $T_1 \rightarrow S_0$ in planar molecules.

Symmetry and orbital type of the states	$I^{()}$	$I^{(\perp)}$	Symmetry and orbital type of the states	$I^{()}$	$I^{(\perp)}$
$S_1(A''; n\pi^*)$	—	+	$T_1(A''; n\pi^*)$	+ ^a	—
$S_1(A'; \pi\pi^*, \pi\pi^*)$	+	—	$T_1(A'; \pi\pi^*, \pi\pi^*)$	- ^b	+ ^b

$\nu^{||}$ and ν^\perp are the frequencies of the nontotally symmetric in-plane and out-of-plane vibrations; the + and — signs designate relatively strong and weak lines, respectively.^a In molecules with two carbonyl groups.^b Relatively strong lines can appear with out-of-plane distortion of the nuclear configuration.^c The frequencies ν^\perp often correspond to out-of-plane vibrations of CH groups. When formulating the rule, the magnitudes of the matrix elements of the vibronic interactions and the differences of the energies of the mixing diabatic states $\varphi_k(\mathbf{r})$ were neglected.

taken into account to first order in the perturbation theory—results in an additional small decrease of the energy E^0 by an amount δE^{FC} as a result of the change, that was neglected at the first step (see the expression (3)), in the geometric parameters of the molecule. The quantity δE^{FC} can be represented as an expansion in normal vibrational coordinates and expressed in terms of the experimental spectroscopic parameters γ_i :

$$\delta E^{FC} = \sum_i \varepsilon_i^{FC}, \quad \varepsilon_i^{FC} = -\gamma_i \nu_i. \quad (11)$$

Once the distribution ε_i^{FC} has been determined from the relation (11), the coordinates Q_i making the main contribution to the vibronic coupling,⁶⁴ i.e., corresponding to the highest values of ε_i^{FC} , can be found from the set of quantities γ_i and ν_i determined experimentally from the vibronic spectra. The form of the corresponding coordinates Q_i , which is obtained as a result of the calculation of the vibrations, makes it possible to relate the highest values of ε_i^{FC} to the structural elements of the molecule and to determine as a result which groups of atoms in the molecule make the main contribution to the vibronic coupling under study. We shall term these groups of atoms active (AGs).

It is also possible to segregate active groups of atoms in the excited electronic state of a molecule by calculating from the experimental data on γ_i (Refs. 6 and 41) the magnitudes of the changes in the geometric parameters of a molecule—the bond lengths δq (Å) and the bond angles $\delta \alpha$ (rad \times 1 Å)—using the following relation:⁶⁵

$$\left\| \frac{\delta q}{\delta \alpha} \right\| = |D| \cdot \left\| \delta Q \right\| \quad (12)$$

where $\left\| \cdot \right\|$ is a column matrix and $|D|$ is a matrix of the forms of the vibrations.

It is expected that the active groups determined experimentally from the data on γ_i , ν_i , and Q_i will qualitatively correspond to the groups of atoms that in the quantum-chemical calculations correspond to the highest values of δe and δp_π . This follows from the fact that relations between the changes in the geometric parameters δq and the quantum-chemical quantities δp_π (or $\delta \xi$) were determined for the ground electronic state. These relations are also approximately valid for the excited electronic states with energy E^0 .^{37,66}

$$\delta q \approx A(p_\pi) \delta p_\pi, \quad \delta \alpha \approx B(\xi) \delta \xi, \quad (13)$$

where $A(p_\pi)$ and $B(\xi)$ are constants (for example, for aromatic hydrocarbons $A(p_\pi) \approx 0.2$)

3.1. Atomic groups active in vibronic coupling

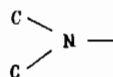
The possibility of segregating a group of atoms on the basis of the experimental data on the spectroscopic parameters γ_i of vibronic coupling (using the expressions (11) and (12) and the computed form of the coordinates Q_i) makes it possible to determine the role of the atomic orbitals of different groups of atoms, in particular, heteroatoms, in the formation of the orbital structure of the excited electronic states of complex molecules.

We shall give some examples of the use of the parameters γ_i , obtained from the fine-structure vibronic spectra, and the expressions (11) and (12) for determining the char-

acteristic features of the electronic states S_1 or T_1 of polyatomic molecules.

Table II gives the results of analysis of experimental data on the distribution ε_i^{FC} in the electronic state S_1 and/or T_1 for a number of complex molecules. The total energy δE^{FC} was determined; it is shown that the number of frequencies of totally symmetric vibrations (N^*) observed in the luminescence spectrum is less than the total number of such frequencies (N_{TS}); the frequencies ν_R of the normal coordinates Q_R , whose contribution to the total vibronic interaction energy ($\varepsilon_i^{FC}/\delta E^{FC}$) exceed some average value ($1/N^*$), are indicated. Examination of the coordinates Q_R singled out in this manner makes it possible to establish the groups of atoms in the molecule that mainly represent the form of these normal coordinates; the corresponding fragments of the molecules are the atomic groups. The last column of Table II gives, for comparison, the orbital type and the symmetry of the electronic state obtained without the help of the data on vibronic coupling. The conclusions regarding symmetry were drawn using the selection rules (1) and the orbital type was determined from quantum-chemical calculations of the diabatic electronic state and from the spectroscopic data on the phosphorescence decay time, the energy (ν_{00}), and the oscillator strength (f) of the transition S_1-S_0 .

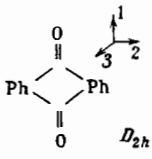
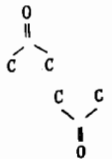
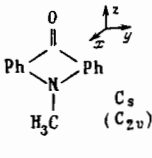
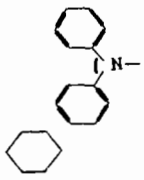
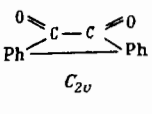
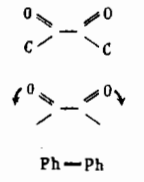
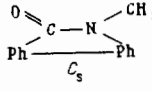
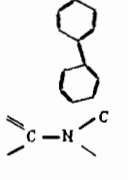
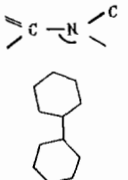
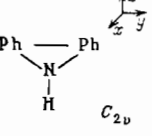
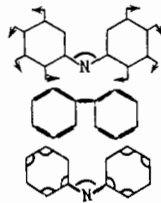
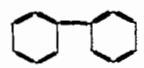
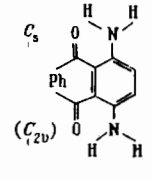
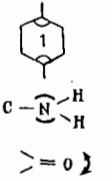
From data on FC coupling (see Table II) it follows that in the molecules I and III, which differ by the relative arrangement of the groups $>C=O$, the main active groups in the state T_1 are groups of atoms containing n -orbitals; this corresponds to defining the state T_1 as a ${}^3n\pi^*$ state. Replacing in such molecules one of the $C=O$ groups by an $N-CH_3$ group (compounds II and IV) increases the duration of phosphorescence, and the state T_1 of these compounds can be referred to a different orbital type. Indeed, according to the data on vibronic coupling in the state T_1 of these molecules the active groups are benzene (terminal) moieties. In the molecule II, however, the active groups also include the group



(the change in the internal angle is associated with this group), and in the molecule IV there is a central biphenyl bond. These data show that l -orbitals centered on the N atom play a larger role in the formation of the state T_1 of the molecule II than of the molecule IV. This result is consistent with quantum-chemical calculations,^{61,73} if one compares, for example, the computational results for the ratios of the changes of the electron density $\delta e_N/\delta e_C$ with the same signs in these molecules, where δe_C corresponds to the maximum change of the electron density on one of the C atoms. Thus this ratio is equal to 2.0 and 0.14 in the molecules II and IV, respectively.

The role of the l -orbitals of a heteroatom can also be seen in the formation of S_1 and T_1 excited electronic states. This is demonstrated in Table II for the example of the molecules IV and V with the six-member and five-member central fragments. While in the state T_1 of these molecules, according to the vibronic-coupling data, the benzene moieties with a biphenyl bond (see ν_i) stand out as the principal active

TABLE II. The distribution of the Frank-Condon energy ϵ_R^{FC} in a complex molecule or the use of the vibronic structure of luminescence spectra for determining the active atomic groups (AG) in which the greatest changes occur in the electronic density accompanying excitation of the molecule into the electronic states S_1 or T_1 .

Molecule		Data on the vibronic structure				Orbital type, symmetry of state	
Designation and structural formula of the molecule	N_{TS} , state, ν_{00} , cm^{-1}	N^* , $(1/N^*)\%$, δE^{FC}	ν_R , cm^{-1}	$\epsilon_R^{FC}/\delta E^{FC}$, %	AG		
AQ (I)		$12a_{1g}$, T_1 , 21768	4^* , 25%, 3400 (1500) ^a	$\nu_\theta = -1653$	96 90 ^a		$\pi\pi^*$, ${}^3B_{1g}$ (Refs. 38 and 67)
NMA (II)		$40a'$ ($25a_1$), T_1 , 22260	7^* , 14%, 830	$\nu_l = -1611$ $\nu_m = -1460$	60 16		$\pi\pi^*$, ${}^3A'$ (3A_1) (Refs. 7 and 45)
PQ (III)		$23a_1$, T_1 , 17014	13^* , 8%, 1210	$\nu_\theta = 1684$ $\nu_\psi = 360$ $\nu_z = 1285$	60 16 11		$\pi\pi^*$, 3B_1 (Ref. 68)
MPD (IV)		$50a'$, T_1 , 23246	18^* , 6%, 1710	$\nu_l = 1612$ $\nu_q = 1338$	33 12		$\pi\pi^*$, ${}^3A'$ (Ref. 64)
		$50a'$, S_1 , 29107	9^* , 11%, 1045	$\nu_g = 1340$ $\nu_z = 1278$ $\nu_0 = 1313$	33 17 14		$\pi\pi^*$, ${}^1A'$ (Ref. 69)
CBZ (V)		$21a_1$, S_1 , 29978	11^* , 9%, 1780	$\nu_c = 1311$ $\nu_l = 1631$ $\nu_z = 1277$ $\nu_s = 645$	24 15 14 12		$\pi\pi^*$, 1A_1 (Ref. 70)
CBZ (V)		$21a_1$, T_1 , 24421	7^* , 14%, 2480	$\nu_l = -1629$	66		$\pi\pi^*$, 3B_2 (Ref. 70)
AAQ (VI)		$39a'$, ($27a_1$), S_1 , 17049	18^* , 6%, 1360	$\nu_n = 1408$ $\nu_0 = 1298$ $\nu_l = 448$ $\nu_{CN} = 1272$ $\nu_x = 1005$ $\nu_\psi = 405$	30 14 11 13 10 11		$\pi\pi^*$, ${}^1A'$ (1A_1) (Ref. 71)

Ph denotes the benzene moiety C_6H_5 ; ν_{00} is the frequency of a purely electronic transition; N_{TS} is the number of totally symmetric (TS) vibrations; numbers enclosed in parentheses are also the number of totally symmetric vibrations but for an approximate higher symmetry group, where only in-plane

TABLE II. (continued)

vibrations are included; N^* is the number of totally symmetric (in-plane) vibrations, observed in the luminescence spectra; R is the designation adopted in Ref. 72 for the form of the normal vibrations; ν_R are the frequencies of the normal vibrations with the highest amplitude (indicated when necessary) on active groups to which the values ϵ_R^{FC} correspond (see expression (11)) and distinguished by their contribution to the total value of the Frank-Condon (FC) energy

$$\delta E^{FC} = \sum_R^{N^*} \epsilon_R^{FC}$$

*Quantities obtained on the basis of the model of purely FC coupling, neglecting Herzberg-Teller coupling.

groups, in the states S_1 the fragments containing a nitrogen heteroatom with an l -orbital (see ν_q in the molecule IV and ν_e, ν_q , and ν_s in the molecule V) start to become more significant as active groups. Indeed, according to the quantum-chemical calculations^{73,74} the ratio $\delta e_N/\delta e_C$ increases from the state T_1 to S_1 : for the molecule IV it varies from 0.14 to 0.48, respectively, and for the molecule V it varies from 1.0 to 3.8.

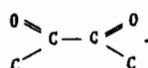
A very interesting feature of FC coupling is presented for the example of the state S_1 of the molecule VI (this molecule is similar to the molecule I, but it has two substituents, designated by the number 1, in the aromatic fragment). Thus in the electronic state S_1 ($\pi l\pi^*$) of the molecule VI the main active group consists of half the molecule: the benzene moiety 1, the substituents NH_2 , and (see ν_ψ) the group $C=O$; these groups make a contribution of 89% to δE^{FC} . In the other half of the molecule (in the benzene moiety designated as Ph) the vibronic couplings were found to be very weak. The same effect was found in the molecule having a similar structure but containing two OH groups instead of two NH_2 groups.⁷¹

It has been found that the vibronic couplings in the state S_1 are approximately equivalent for molecules with the substituents OH and NH_2 in the fragment 1.⁷⁵ Thus the result of different substitution in it—one OH group and one NH_2 group—is manifested for molecules with this structure in vibronic coupling of higher than C_s symmetry in the benzene moiety 1 (approximately C_{2v}), in spite of the difference of the electron-donor capability of O and N atoms and the ener-

gy of the intramolecular hydrogen bond between $C=O$ and the groups OH and NH_2 .

The role of l -orbitals of X-atoms (N or O) in the formation of the orbital structure of the states S_1 ($\pi l\pi^*$) in molecules of the type VI is reflected in the vibronic coupling, namely, in the dominant values of the energies ϵ_x^{FC} associated with the coordinates of the change in the angle CXH (Table II). According to the quantum-chemical calculations^{76,77} the ratio $\delta e_N/\delta e_C = 2.2$ in the diabatic state S_1 of the molecule VI, i.e., the electronic state is indeed of the orbital type $\pi l\pi^*$ and not $\pi\pi^*$.

Examples of the segregation of active groups on the basis of the changes in the geometric parameters of molecules in the states T_1 or S_1 relative to the ground state S_0 as a result of using the relation (12) are presented in Figs. 2a and b. The active group in the molecule a (or III in Table II) in the state T_1 is the fragment⁶⁸



Thus the basic changes in bond lengths and bond angles are observed precisely in this separate fragment. It is interesting that not only the interior but also the exterior angles of the molecules change: in the state T_1 the bonds $C=O$ rotate symmetrically in the direction of the long axis of the molecule. The changes of the bond lengths in the benzene moieties of molecule III in the electron state T_1 ($n\pi^*$) are an order of magnitude smaller than, for example, in the state T_1 ($\pi\pi^*$) of benzene.⁶

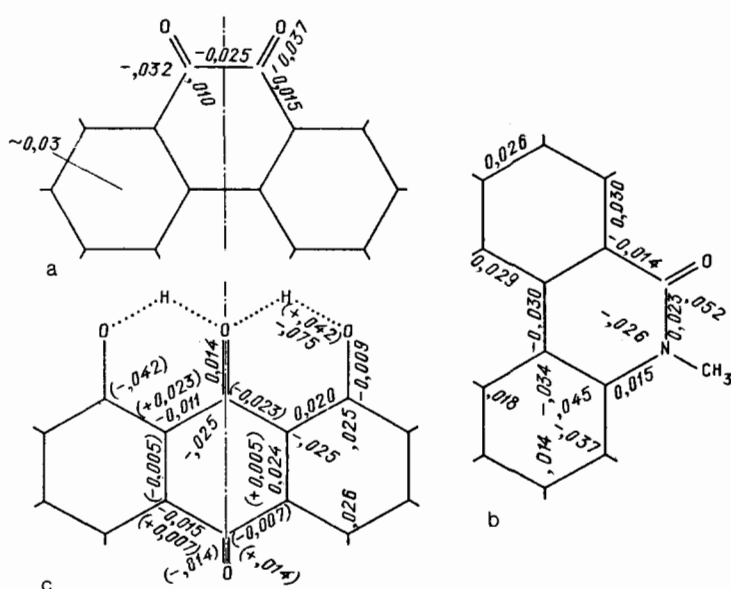


FIG. 2. The change in the equilibrium nuclear configuration of molecules in an excited electronic state according to data obtained from vibronic spectroscopy (changes of the bond lengths δq (Å) and bond angles $\delta\alpha$ (rad); in the angles the integer value of the number (0) is dropped). a) Phenanthrenequinone in the $^3n\pi^*$ state (the magnitudes of one of the symmetrically equivalent elements are indicated).⁶⁸ b) N-methyl-phenanthridone in the $^1\pi l\pi^*$ state.⁷⁸ c) 1,8-dihydroxy-9,10-anthraquinone in the state S_1 ($\pi l\pi^*$) with proton transfer⁷⁹ (see text); the change in the position of the hydrogen atom was not estimated; the magnitudes of one of the symmetrically equivalent elements are given and the symmetry-destroying corrections are indicated in parentheses. *—values of δq and $\delta\alpha < 25\%$ of the maximum value are not presented.

In the molecule *b* the role of the lactam fragment in FC coupling (it corresponds to the characteristic, with respect to form, vibration ν_q ; see the molecule IV in Table II) is not as pronounced in the map of changes of the geometric parameters of the molecule in the state S_1 as in the distribution of the quantities $\varepsilon_R^{\text{FC}}$. (Although both methods for determining the active groups are based on the intensity distribution in the vibronic spectrum, in one method the quantities $(2\gamma_R)^{1/2}$ are employed while in the other method the quantities γ_R are employed.) In Ref. 78 it is suggested that the active groups be determined from data on the change in the geometric parameters of molecules by searching for the approximate local C_2 -symmetry axis from data on δq or/and $\delta\alpha$. The direction C_2 indicates the position of the active group. As one can see from Fig. 2b, in the state S_1 of the molecule IV such an inclined axis with an *N* atom on it can be found in one of the benzene moieties of the molecule. We note that for the state T_1 of the same molecule the principal C_2 axis in the map of changes of the geometric parameters is different and is coincident with the biphenyl bond.⁷⁸

3.2. Intramolecular hydrogen bond

Figure 2c shows an example of the use of vibronic spectra and the expression (12) not for searching for active groups but rather for obtaining data on the configuration of a molecule which can be realized in one of special forms: in a form with a transferred hydrogen atom or proton in the excited electronic state S'_1 . According to the theory (Fig. 3) molecules with an intramolecular hydrogen bond $O\cdots HN <$ or $O\cdots HO$ (in the ground electronic state S_0 ; see Fig. 3a) can be found in an excited state S'_1 either in the quinoid form (b) or in the bipolar form (c).^{80,81}

Correspondingly, transfer of H or H^+ is usually represented in the form of a four-level scheme of energy levels of the system in the states S_0 , S_1 , S'_1 , and S'_0 , where the primed symbols designate another minimum of the corresponding electronic potential. The transition $S'_1 \rightarrow S'_0$ is taken to be associated with a wide structureless fluorescence band with an anomalously large Stokes shift (greater than 2000 cm^{-1}) relative to the absorption spectrum $S_1 \leftarrow S_0$.^{80,82} In several cases (for OH-substituted AQ molecules) it was possible to record⁸³⁻⁸⁶ simultaneously with $S'_1 \rightarrow S'_0$ the shorter-wavelength transition $S'_1 \leftrightarrow S_0$, to which there corresponds a weak fine-structure spectrum. Such a spectrum was employed for estimating the change in the configuration of the molecule (see Fig. 2c) in the state S'_1 as compared with the state S_0 .

Numerical estimates of the changes in the bond lengths and angles showed that the configuration of molecules in the state S'_1 should be referred more to the bipolar form (c) than the quinoid form (b) with a different arrangement of the single C–O and double C=O bonds (the lengths of these bonds differ, as a rule, by more than 0.1 \AA). The conclusion that the bipolar form is realized⁷⁹ agrees with investigations

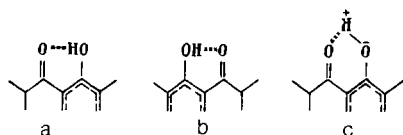


FIG. 3.

of chemical shifts by the NMR methods in the ground electronic state (S_0 and S'_0) and with spectral investigations of the energies of the transitions $S'_1 \rightarrow S'_0$ and $S_1 \leftarrow S_0$ of some molecules when the solvent is changed.^{81,82,87}

It should be noted that a characteristic feature of the change in the geometric parameters of a molecule in the form with proton transfer—namely, a change in certain bond angles and a tendency toward equalization of bond lengths in the benzene (side) moieties and the central fragment (sesquialteral and single bonds)—reflected in the symmetric component (see Fig. 2c) is not exclusively a feature of the bipolar form. The same feature of configurational change is characteristic for another molecule having a similar structure (for the molecule 1,8-diamino-9,10-anthraquinone), but which has single-well potentials in the states S_0 and S_1 and the standard structural fluorescence.⁷⁹ Thus the symmetric component of the changes δq and $\delta\alpha$ (Fig. 2c) reflects primarily the orbital nature of the standard excited electronic state (π/π^* -orbital type) in molecules with substituent groups OH or NH_2 in the positions 1,8 of anthraquinone-9,10.

An important result of the segregation of active groups and numerical estimates of the change in the geometry parameters of molecules on the basis of analysis of vibronic spectra are data (see Table II and Fig. 2) showing significant changes in the angles $\delta\alpha$ (whose relative change is not less than that of the bond lengths) not only in the electronic states of the $n\pi^*$ -orbital type but also of the $\pi\pi^*$ or π/π^* type. In many cases the following behavior is observed: According to data from vibronic spectroscopy, the relatively large changes in the π -electron density on atoms (with π - or l -orbitals of the valence or unshared electron pairs), as obtained from quantum-chemical calculations of the diabatic $\pi\pi^*$ or π/π^* states, are accompanied by appreciable changes, occurring in the excited state, in the angles with the corresponding central atoms.

The intramolecular hydrogen bond (IMHB) is not unimportant in excited electronic states of complex molecules. A striking manifestation of IMHB is proton transfer. However this is not such a frequent case. Nonetheless the position of the H atom forming the IMHB also changes as a result of electronic excitation in states without proton transfer. Thus the change in the angle COH in the state S_1 is equal to $\sim 3^\circ$ (Refs. 6 and 41) in derivatives of anthraquinone-9,10; this follows from data on vibronic couplings (γ_x) that are linear in the coordinate of bending vibrations.

3.3. Deuteron-substitution effect at the frequency ν_{00}

The richest information about IMHB in the state S_1 is contained in vibronic couplings that are linear in the coordinates Q_{OH} (or Q_{NH}) of the stretching vibrations of the groups OH or NH. However the corresponding vibronic transitions, as a rule, cannot be recorded. Investigations have shown^{88,89} that vibronic couplings which are quadratic or linear in the coordinates Q_{OH} (or Q_{NH}), giving rise to changes in the force constants, i.e., the form of the electronic potential in a given section, make the main contribution to the quantity $\Delta_{00} = \nu_{00} - \nu_{00}^D$ —the change produced in the frequency of a purely electronic transition by substituting D atoms for H atoms in groups with IMHB. It has been shown that Δ_{00} can be used to estimate the change in IMHB energy

(δE_{HB}) in the state S_1 . Thus for a molecule of α -tetra-substituted anthraquinone-9,10 the increase δE_{HB} per bond $\text{O}^{***}\text{H}-\text{O}$ is equal to ~ 1.8 kcal/mole.

The quantity Δ_{00} in molecules with IMHB can also serve as a delicate indicator of the effect of changes of molecular structure (caused, for example, by attachment of different substituents) on the change occurring in the form of the potential in the section of the potential along the coordinate Q_{XH} (where X is an O or N atom) as a result of a transition of the molecule into an excited electronic state.⁸⁹ An extreme case of a change in the form of the electronic potential in the state S_1 is the formation of a second minimum (S_1') and transfer of a proton. The results of investigations of the deuteron effect at the frequency of a purely electronic transition (data on Δ_{00}) have made it possible to draw the following conclusion. In the state S_1 ($\pi 1\pi^*$) the form of the electronic potential in the section along the coordinate Q_{XH} undergoes increasingly smaller changes (compared with the state S_0) as the electron-donor properties of the Y group located in the para-position with respect to X (in the order $Y = \text{H}, \text{Ph}, \text{OH}, \text{and } \text{NH}_2$) increase.

4. CHARACTERISTICS OF THE EXCITED ELECTRONIC STATES OF MOLECULES AND VIBRONIC COUPLING IN THE HERZBERG-TELLER APPROXIMATION

In this section some results as well as possible ways to utilize the experimental data on HT coupling in order to investigate excited electronic states of complex molecules are presented.

When the HT and spin-orbit couplings are taken into account the wave function of the adiabatic excited state $\Psi_m^{\text{HT}}(\mathbf{r}, Q)$ can be represented as a linear combination of the electronic wave functions of the upper diabatic states $\varphi_k(\mathbf{r})$. For example, the triplet-state function has the following form:

$$\begin{aligned} {}^3\Psi_m^{\text{HT}}(\mathbf{r}, Q) &= {}^3\varphi_m(\mathbf{r}) + \sum_k b_k^1 \varphi_k(\mathbf{r}) + \sum_{k'} \sum_s \eta_k^{(s)} Q_s \left(\frac{\omega_s}{\hbar}\right)^{1/2} {}^1\varphi_{k'}(\mathbf{r}) \\ &+ \sum_n \sum_\alpha \mu_n^{(\alpha)} Q_\alpha \left(\frac{\omega_\alpha}{\hbar}\right)^{1/2} {}^1\varphi_n(\mathbf{r}) \\ &+ \sum_{n'} \sum_{\alpha, s} \lambda_{n'}^{(\alpha, s)} Q_s Q_\alpha \frac{(\omega_s \omega_\alpha)^{1/2}}{\hbar} {}^1\varphi_{n'}(\mathbf{r}), \end{aligned} \quad (14)$$

where $b, \eta, \mu,$ and λ are constants; α and s are indices of the vibrational coordinates of nontotally symmetric and totally symmetric states, respectively; $m, k, k', n,$ and n' are indices of the electronic wave functions. The coefficients $\eta_k^{(s)}, \mu_n^{(\alpha)}, \lambda_{n'}^{(\alpha, s)}$, enter into the expression of the corresponding spectroscopic parameters L_i (if the coefficients are equal to zero, then L_i are also equal to zero; $i = \alpha$ or s). As an example, consider the expression (4) for the parameter L_α . Comparing the corresponding term in the expression (14) and the form of the expression (4) in the approximation in which only three levels are mixed (neglecting, in order to simplify the presentation, the summation over the index n) shows that the coefficient $\mu^{(\alpha)}$ (or the parameter L_α) can be determined by different mechanisms of the intramolecular interactions. One mechanism is combined spin-orbit and vibronic

couplings (first term in Eq. (4)). The second term represents the vibronic mixing of the triplet states $\langle H_{\text{ev}}^{(\alpha)} \rangle_{\text{TT}}$. The last term represents vibronic mixing of the singlet states $\langle H_{\text{ev}}^{(\alpha)} \rangle_{\text{SS}}$. We also note that the orbital component of the spin-orbit coupling operator \hat{H}'_{s0} corresponds to three irreducible representations of the rotation group (for example, $b_{1g}, b_{2g},$ and b_{3g} for the symmetry group D_{2h}).

The utilization of the selection rules (1) and other rules and relations (see the relation (10) and Table I) for analyzing fine-structure vibronic spectra permits determining in each specific case the most probable schemes of mixing of the diabatic electronic states or the unknown symmetry of the states. In so doing, it is also helpful to draw upon the most general information from theoretical calculations of interactions in the LCAO approximation:⁹⁰

- the electronic diabatic states mixed by the intramolecular interaction operators must have general molecular orbitals (MO) ψ occupied by one electron;
- single-center integrals make the main contribution to the spin-orbit interactions; and
- the action of an operator should lead to the best overlapping of the atomic orbitals which correspond to the two mixing MOs.

We shall give an example of the analysis of intramolecular interactions based on the vibronic spectrum. The position of the group X, containing a heteroatom, on the C_2 -symmetry axis of the molecule makes it possible to limit on the basis of the symmetry properties the types of MOs ψ to be considered in the investigation of the interactions. For example, for the state $T_1(n\pi^*)$ of the molecule AX, where X denotes C = O groups (see I in Table II), on the basis of spatial considerations the main types of orbitals can be the π -type MOs $\psi(b_{3u})$ or $\psi(b_{2g})$ and σn -type MOs $\psi(b_{2u})$ or $\psi(b_{3g})$ with resulting orbital symmetry B_{1g} or A_{1u} of the state; the operator is $\hat{H}'_{s0}(b_{1g})$. According to data from fine-structure vibronic spectroscopy the transition T_1-S_0 with frequency ν_{00} is forbidden; transitions to the vibrational sublevels of symmetry b_{1u} are allowed with the highest probability (i.e., the operator $\hat{H}_{\text{ve}}^{(\alpha)}(b_{1u})$ is the main operator of the set $\hat{H}_{\text{ve}}^{(\alpha)31,32,91}$). On the basis of such data it is possible to construct the following schemes of intramolecular interactions which allow transitions with frequencies $\nu_{00} - \nu_\alpha(b_{1u})$ in the phosphorescence spectrum of $n\pi^*$ -type:

$$[{}^3B_{1g}(n\pi^*) \xrightarrow{\hat{H}_{\text{vs0}}(b_{1g} \times b_{1u} = a_{1u})} {}^1B_{1u}(\pi\pi^*)] \rightarrow S_0, \quad (15a)$$

$$[{}^3B_{1g}(n\pi^*) \xrightarrow{\hat{H}_{\text{ve}}(b_{1u})} {}^3A_{1u}(n\pi^*) \xrightarrow{\hat{H}'_{s0}(b_{1g})} {}^1B_{1u}(\pi\pi^*)] \rightarrow S_0, \quad (15b)$$

$$[{}^3B_{1g}(n\pi^*) \xrightarrow{\hat{H}'_{s0}(b_{1g})} {}^1A_{1g}(\pi\pi^*) \xrightarrow{\hat{H}_{\text{ve}}(b_{1u})} {}^1B_{1u}(\pi\pi^*)] \rightarrow S_0, \quad (15c)$$

where the designation (symmetry, orbital type) of the diabatic lower ($m = 1$) excited state ${}^3\varphi_m(\mathbf{r})$ is given in brackets on the left and the designation of the higher excited diabatic electronic state ${}^1\varphi_n(\mathbf{r})$ from which, as it is said, the intensity of the vibronic transition is "taken," is given on the right.

Three mechanisms of vibronic and spin-orbit couplings are reflected in schemes of the type (15). They are also presented in the expression for the spectroscopic parameter L_α .

The scheme (15b) corresponds to the vibronic mechanism $\langle H_{ve}^{(\alpha)} \rangle_{TT}$ and the scheme (15c) corresponds to the mechanism $\langle H_{ve}^{(\alpha)} \rangle_{SS}$. Group-theoretical analysis alone cannot give preference to either mechanism. However some additional data (on the MOs, Q_i , and L_i) make it possible, in some cases, to indicate the most probable mechanism of the intramolecular interactions. We shall present such data in Secs. 4.1.1-4, where the results are designated by the numbers 1*-4*.

4.1. Mechanism of interactions

4.1.1. Intramolecular interactions in the state $T_1(n\pi^*)$ of molecules containing C=O groups with a purely electronic transition, both forbidden and allowed on the basis of orbital symmetry, and with different energy splitting between the states that are important in the scheme $\langle H_{ve}^{(\alpha)} \rangle_{TT}$ were studied. The fact that the strongest lines (maximum L_α) observed in the spectrum correspond to vibronic coupling in the vibrational coordinates Q_θ and the form of the latter is in turn characterized by localization of high amplitudes on the groups

$$\begin{matrix} c \\ \diagdown \\ c \end{matrix} c = 0.$$

is taken into account. The following conclusion was drawn:⁶¹ 1*. In molecules with two C=O groups the mechanism of vibronic mixing of triplet diabatic states ${}^3\varphi(\mathbf{r})$ of the $n\pi^*$ orbital type is more likely to be responsible for the formation of the triplet adiabatic state ${}^3\psi^{HT}(\mathbf{r}, Q)$ of the $n\pi^*$ orbital type than the mechanism in which the singlet diabatic states of the $\pi\pi^*$ orbital type are mixed (i.e.,

$$\langle H_{ve}^{(\alpha)} \rangle_{TT} > \langle H_{ve}^{(\alpha)} \rangle_{SS}.$$

4.1.2. Conclusions about coupling mechanisms were also drawn from analysis of vibronic spectra corresponding to the transitions $T_1(\pi l\pi^*) \rightarrow S_0$ in molecules containing on the C_2 -symmetry axis both heteroatoms N or O with an l -orbital and a C=O group.^{45,61,92} Examples of such molecules are the molecules of NMA (see II in Table II) and xanthone (in the latter molecule the group $>N-CH_3$ is replaced by an $>O$ atom).

The lowest excited electronic state ${}^3\varphi_1(\pi l\pi^*)$ of these molecules is totally symmetric (3A_1 in the approximation of the symmetry group C_{2v}) and corresponds to charge transfer from the l -orbital. The triplet state ${}^3n\pi^*$ lies higher. On the basis of vibronic spectroscopy the electronic transition with the frequency ν_{00} is allowed, and among vibronic transitions the most probable allowed transitions are transitions to the vibrational sublevels of out-of-plane vibrations of symmetry b_1 .

The coupling schemes constructed on the basis of the experimental data for the molecules of NMA and xanthone and using the different rules given at the beginning of this section showed the following (see 2 and 3):

2*. There are cases when vibronic mixing of triplet diabatic states of different orbital type ${}^3\pi l\pi^*$ and ${}^3n\pi^*$ ($\langle H_{ve}^{(\alpha)} \rangle_{TT} \approx 0$) separated by a small energy gap ($\sim 2000 \text{ cm}^{-1}$) is negligible.

We note, as a refinement, that these interactions are allowed according to the selection rules

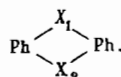
$${}^3A_1(\pi l\pi^*), \quad H_{ve}^{(\alpha)}(a_2), \quad {}^3A_2(n\pi^*).$$

However the vibronic-coupling operator in this case has symmetry such that it cannot contain displacements of atoms lying on a C_2 -symmetry axis from their positions of equilibrium. For this reason, vibronic coupling of singlet states of different orbital type ($\pi l\pi^*$ and $\sigma\pi^*$) is manifested in the spectra (the main mechanism is $\langle H_{ve}^{(\alpha)} \rangle_{SS}$):

$${}^1A_1(\pi l\pi^*), \quad H_{ve}^{(\alpha)}(b_1), \quad {}^1B_1(\sigma\pi^*).$$

The coupling schemes, supplemented by the results of the determination of L_θ and $L_\theta^{(\alpha)}$ from vibronic spectra⁴⁵ (where θ and α are the indices of the totally symmetric (a_1) and nontotally symmetric (b_1) coordinates, respectively) also showed the following.

3*. In the triplet states of the type $\pi l\pi^*$ of molecules with the structure



where the heteroatom of the group X_2 , having an l AO, lies on a two-fold symmetry axis (C_2), the $T^{(Y)}$ sublevel of the state T_1 plays the main role in spin-orbit interactions allowing optical vibronic transitions. This means that the most effective component of the operator \hat{H}_{s0} for the state ${}^3\pi l\pi^*$ is the component of symmetry b_1 (in the point group C_{2v}) or b_{2g} (in the point group D_{2h}). This result is also confirmed by analysis of the HT component of the phosphorescence spectra of molecules of heterocyclic derivatives of fluorene (see below).

4.1.3. Using only the conditions a-c at the beginning of Sec. 4 it is possible to draw another important conclusion concerning the spin-orbit mixing of states of the $\pi\pi^*$ - and $n\pi^*$ -orbital types. As follows from the relations (10a), such interactions are usually relatively strong ($\sim 10 \text{ cm}^{-1}$ (Ref. 63)). This, however, is not always so. Suppose that in the molecule the group C=O with an n -orbital lies on a C_2 symmetry axis; the $n\pi^*$ -type state has symmetry A_2 (which corresponds to the principal configurations $\psi_{n\sigma}(b_2) \times \psi_\pi(b_1)$) and the $\pi\pi^*$ -type state has symmetry B_2 with the principal configurations $\psi_\pi(a_2) \times \psi_\pi(b_1)$. In this case the orbital component $\hat{H}'_{s0}(b_1)$ mixes $\psi_{n\sigma}(b_2)$ and $\psi_\pi(a_2)$, where in the first MO only the coefficients of atomic orbitals in the group

$$\begin{matrix} c \\ \diagdown \\ c \end{matrix} c = 0$$

are large (especially in C=O) and in the second MO the coefficients for all atoms lying on the C_2 axis are equal to zero. As a result, atomic orbitals of the two-atom C=O group itself do not participate in the single-center approximation.

4*. Thus it can be expected that in molecules with a definite nuclear configuration and a definite orbital symmetry of states of the type $\pi\pi^*$ and $n\pi^*$ the energy of spin-orbit mixing of these states will be sharply smaller than 10 cm^{-1} (the matrix element $\langle {}^3A_2(n\pi^*) | \hat{H}_{s0} | {}^1B_2(\pi\pi^*) \rangle$ is small). Since the relations (10a) play an important role in the development of the systematics of molecules from the properties of the luminescence spectra,^{30,63,91} the conclusion 4 indi-

cates one reason for possible deviations from the established regularities in these states.

4.1.4. We shall give an example of the application of the rules presented in Table I for studying triplet excited electronic states of molecules not containing a carbonyl group and having a five-member central fragment with a heteroatom X lying on a C_2 symmetry axis⁵⁴ (an example of such a molecule is V (or carbazole) in Table II).

According to the rule (see Table I) the spectra of the transition $T_1 (\pi\pi^*) \rightarrow S_1$ should contain out-of-plane vibrations (a_2 or b_1). Such vibrations, namely b_1 , are indeed observed in the phosphorescence spectra (${}^3B_2 (\pi\pi^*) \rightarrow S_0$) of molecules of heterocyclic derivatives of fluorene, where X is a N, O, S, or Se atom (we designate the molecules as CBZ, DBF, DBT, and DBS). In the spectra of the first two molecules, however, the corresponding lines are weak ($I_{01} \sim 0.2$ and 0.04), while in the spectra of the molecules DBT and DBS such lines are very strong ($I_{01} \sim 1.7$ and 14.0, respectively). Since the values of the HT-coupling parameters L_α depend on the ratios of the oscillator strengths of the electronic transitions, the reasons for this difference of intensity can be sought, on the basis of the rule employed, in the magnitudes of the dipole moments $|M_{0n}|$ of transitions from the highest final states (see expression (4)). It is precisely for heterocyclic derivatives of fluorene that the oscillator strengths of the transitions ${}^1A_1-S_0$ and ${}^1B_2-S_0$ are known to be substantially different. Taking this fact into consideration and concentrating here, for simplicity, on vibronic coupling of the type $\langle H_{ve}^{(\alpha)} \rangle_{SS}$ the following schemes can be given for the interactions allowing transitions with frequencies $\nu_{00} - \nu(b_1)$ in these molecules:

$$[{}^3B_2(\pi\pi^*) \xrightarrow{\hat{H}_{ve}^{(a_2)}} {}^1B_1(\sigma\pi^*) \xleftarrow{\hat{H}_{ve}^{(b_1)}} {}^1A_1(\pi\pi^*)] \rightarrow S_0, \quad (16)$$

$$[{}^3B_2(\pi\pi^*) \xrightarrow{\hat{H}_{ve}^{(b_1)}} {}^1A_2(\sigma\pi^*) \xleftarrow{\hat{H}_{ve}^{(b_1)}} {}^1B_2(\pi\pi^*)] \rightarrow S_0. \quad (17)$$

The scheme (16) explains the weakness of the corresponding vibronic lines in the spectra of carbazole and DBF, while the scheme (17) explains the significant increase in the intensity of such lines in the phosphorescence spectra of DBT and DBS. Comparing these schemes we can conclude that the replacement of O and N atoms by the multielectronic atoms S and Se, which have d -orbitals, makes the intramolecular spin-orbit interactions with the operator $\hat{H}'_{so}(b_1)$ more efficient than interactions with the operator $\hat{H}'_{so}(a_2)$. Such a change in the coupling mechanism could be caused by an increase in the contribution of single-center integrals localized on the heteroatom to the spin-orbit interaction.⁵⁴

An investigation of FC coupling according to the vibronic structure of the same phosphorescence spectra showed⁵⁴ that the contribution of orbitals of the heteroatoms S and Se to the formation of the diabatic state ${}^3\varphi_1(\mathbf{r})$ is larger in the corresponding molecules than that observed for molecules with the heteroatoms O or N (see carbazole in Table II). Thus the results of analysis of FC and HT coupling in heterocyclic derivatives of fluorene confirms the conclusion 3*.

Aside from data on the vibronic spectra, independent data on the direction of the dipole moments M_{0n} of vibronic transitions and data obtained by the method of magnetic

resonance with optical detection (ODMR) on the sublevels $T^{(x)}$, $T^{(y)}$, and $T^{(z)}$ of the state T_1 are useful for determining intramolecular-coupling schemes representing the state $\Psi^{HT}(\mathbf{r}, Q)$. We note that such results, which in a number of cases have been published in the literature, provide independent confirmation of the coupling schemes chosen above (see references to the corresponding literature in Refs. 6 and 54).

4.2. Identification of the orbital type of electronic states

In conclusion we shall discuss the use of HT-coupling data, obtained from the vibronic structure of electronic spectra, for determining the orbital type (see footnote 4) of the states S_1 or T_1 . The orbital characteristic of the state is attributed to $\varphi_1(\mathbf{r})$, the diabatic component appearing in the expression for the adiabatic function $\Psi_1^{HT}(\mathbf{r}, Q)$. Nonetheless, the data on the spectroscopic parameters L_i , which are determined by the more accurate description (14) of the state, can also serve as an indicator of the orbital type. The data presented in Table I should be used for this purpose; with their help the unknown orbital type of the state S_1 or T_1 can be determined from the ratio of the intensities of the lines associated with the vibrations ν_j^{\parallel} and ν_j^{\perp} .

We note that the presence of frequencies ν_θ , associated with the stretching vibrations of the C = O groups, in the vibronic spectra is in itself not a reliable indicator of the $n\pi^*$ orbital type of the electronic state. First, the lowering of the symmetry of the molecule in the state $T_1 (\pi\pi^*)$ as a result of even weak configuration mixing of the states ${}^3\varphi(\pi\pi^*)$ with ${}^3\varphi(n\pi^*)$ in the initially planar molecule results in the appearance of strong lines with frequencies ν_θ in the vibronic spectrum, it reduces the decay time of phosphorescence, and it changes the polarization of the luminescence (this was observed, for example, for benzaldehyde⁹³). Second, vibrations with frequency ν_θ could be present in the vibronic spectra primarily because of HT and not FC coupling. In other words, the totally symmetric vibration ν_θ can be observed in the spectrum for $\gamma_\theta \approx 0$, i.e., when the change, for example, of the bond length of the C = O group is small in accordance with the small change of the electron density on this bond; the state $\varphi_1(\mathbf{r})$ is then of the $\pi\pi^*$ - and not $n\pi^*$ -orbital type. This feature was observed, for example, in the phosphorescence spectra of NMA and xanthone molecules.^{61,92} Another difficult case is the possible inversion, caused by intermolecular interactions⁹² or conformational changes in the molecule owing to internal rotations,⁹⁴ of the relative position of the energy levels of the two lowest electronic states of different orbital type in molecules in different solvents.

A frequency analysis of spectra in regions where nontotally symmetric vibrations appear, which can also give information about the orbital type of the state S_1 or T_1 , is preferable to a meticulous analysis of line intensities for the purpose of determining the parameters γ_i associated with $\varphi_1(\mathbf{r})$. Thus according to the rule for the appearance of nontotally symmetric vibrations in luminescence spectra (see Table I) the spectrum of the transition $T_1 (\pi\pi^*) \rightarrow S_0$ should contain strong lines with maxima at $\nu_{00} - \nu_1$, which are associated with out-of-plane vibrations ν_1 of the molecule. Experiments show that out-of-plane vibrations of C-H groups with characteristic frequencies are often observed among them. Conversely, in the spectra of the transitions $T_1 (n\pi^*) \rightarrow S_0$

lines with maxima at $\nu_{00} - \nu_i$ should be relatively weak. The effectiveness of this "rule" (see Table I) has been checked experimentally on a large number of molecules containing C = O groups, groups with heteroatoms N, O, and S, and benzene moieties.⁶

We especially emphasize the fact that when nontotally symmetric vibrations, observed in vibronic spectra, are employed as indicators of the orbital type of the states S_1 or T_1 the form of the vibrational normal coordinates along which HT coupling is realized does not play any special role (in contrast to the case when data on FC coupling are employed).

5. REFLECTION OF THE PHOTOCHEMICAL PROPERTIES OF COMPLEX MOLECULES IN THE SPECTROSCOPIC PARAMETERS OF VIBRONIC COUPLING

According to the hypothesis recently stated in Ref. 95 the spectroscopic parameters L_i associated with intramolecular HT coupling contain information about the potential capability of molecules to undergo phototransformations as a result of photochemical reactions (PCRs). In this case, the collection of normal vibrational coordinates along which HT coupling occurs indicates the active group of atoms in a complex molecule. Thus the form of the corresponding normal coordinates Q_i of the intramolecular HT coupling becomes very significant in this special role of the parameters L_i .

The form of the electronic potential is studied in theoretical investigations of PCRs.⁹⁶ In the case at hand, however, we focus our attention on the wave function of the electronic state. It follows from the representation of the wave function in the form (14) that the relation between the displacements of atoms from their positions of equilibrium (more accurately, between the dimensionless normal vibrational coordinates ξ) and the concomitant change of the electronic wave function is reflected in the coefficients $\eta^{(s)}$, $\mu^{(\alpha)}$, and $\lambda^{(\alpha s)}$. Conversely, in the presence of external perturbations the change produced in the wave function of the state of the molecule as a result of intermolecular interactions should give rise to displacements of atoms out of the position of equilibrium, if the coefficients mentioned above (or one of them) are not equal to zero. The magnitude of the coefficients is a measure of this relation.

It is usually supposed⁹⁵ that the collection of displacements of atoms caused by external perturbations, which is called the initial coordinate of the reaction in the excited electronic state of the molecule (Q^{PCR}), can be represented as a linear combination of the coordinates $Q_i (\omega_i/\hbar)^{1/2}$ and the squares of the corresponding coefficients $\eta^{(s)}$, $\mu^{(\alpha)}$, and $\lambda^{(\alpha s)}$. These coefficients are expressed in terms of the matrix elements of the HT coupling operator (see the expression (4)). For the example of $\mu^{(\alpha)}$ the following relation is valid in the approximation of two- or three-level mixing of states:

$$L_\alpha : L_{\alpha+1} : L_{\alpha+2} \dots \approx \mu^{(\alpha)} : \mu^{(\alpha+1)} : \mu^{(\alpha+2)} \dots, \quad (18)$$

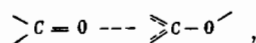
where $\alpha, \alpha + 1$, etc. correspond to the indices of the vibrational coordinates Q , corresponding to the same irreducible representation (Γ) of the symmetry group of the molecule in the state S_0 . The ratio of the quantities L_α belonging to different representations Γ does not reflect the ratio of the quantities $\mu^{(\alpha)}$. Using L_i the coordinate Q^{PCR} can be ex-

pressed in the following form:

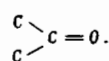
$$Q^{\text{PCR}} = \sum_{\Gamma} a_{\Gamma} \sum_i (\tilde{L}_i^2 Q_i (\omega_i/\hbar)^{1/2})_{\Gamma}, \quad (19)$$

where a_{Γ} are constants and $(\tilde{L}_i)_{\Gamma}$ is the value of the spectroscopic parameter L_i normalized to the maximum value $(L_i)_{\Gamma}^{\text{max}}$ for each Γ .

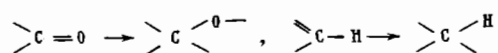
The following correlations and simplifications have been proposed for practical applications of the relation (19), i.e., for predicting the coordinates Q^{PCR} from data on \tilde{L}_i and the form of the coordinates Q , as well as for subsequent comparison with experimental data on the PCR itself. Thus the results of the photoreduction reaction on the carbonyl group, in which the hybridization of the atomic orbitals of oxygen changes significantly



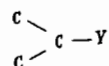
are associated with the coordinate $Q^{\text{PCR}}(\text{PR})$, for which the normal coordinate Q_{θ} of the stretching vibrations of the groups



is taken as the principal coordinate in the expression (19). The results of photoattachment reaction, in which the hybridization of the orbitals of the central atom in the group changes significantly ($sp^2 \rightarrow sp^3$), for example,



are associated with the coordinate $Q^{\text{PCR}}(\text{PD})$, for which the out-of-plane normal coordinates associated with out-of-plane motion of the terminal atoms are taken as the principal coordinates in the expression (19). For the $>C=O$ and $>C-H$ groups these coordinates are Q_{γ} and Q_{CH}^{\perp} , respectively.⁵ The reaction accompanied by breaking of some bond in the group of atoms



(substitution reactions) is associated with the coordinate $Q^{\text{PCR}}(\text{PS})$, for which the coordinate $Q_{\text{CCY}}^{\parallel}$ of in-plane bending vibrations of the group CCY is taken as the principal coordinate; the normal coordinates $Q_{\text{CCY}}^{\parallel}$, just as Q_{CH}^{\perp} , have their own letter designations of form.

The following relations are used to predict the probability of photochemical reactions in excited electronic states of molecules:

$$\begin{aligned} Q^{\text{PCR}}(\text{PR}) &\approx \tilde{L}_{\theta}^2 Q_{\theta}, & Q^{\text{PCR}}(\text{PA}) &\approx \tilde{L}_{\gamma}^2 Q_{\gamma}, \\ Q^{\text{PCR}}(\text{PA}) &\approx \tilde{L}_{\text{CH}}^2 Q_{\text{CH}}^{\perp}, & Q^{\text{PCR}}(\text{PS}) &\approx \tilde{L}_{\text{CCY}}^2 Q_{\text{CCY}}^{\parallel}. \end{aligned} \quad (20)$$

According to these relations the photoreduction or photoattachment or photosubstitution reaction is probable if according to analysis of the vibronic spectra of the "isolated" molecules the corresponding parameter $\tilde{L}_{\theta}^2, \tilde{L}_{\gamma}^2, \tilde{L}_{\text{CH}(\perp)}^2$ or \tilde{L}_{CCY}^2 is close in magnitude to unity. It is considered that to the "isolated" molecule there corresponds a fine-structure vibronic spectrum of solid solutions in *n*-paraffins at 4.2 K or a vapor spectrum. However solutions in saturated and unsaturated hydrocarbon, alcohol, and other solvents at room

temperatures with photoexcitation at frequencies in the energy range of several lowest singlet-singlet electronic transitions of the molecule are usually employed in order to study the PCR's themselves.⁹⁷

It should be noted that in order to predict PCR's from data on the parameters L_i not only strong vibronic lines of the spectrum but also very weak lines, for example, the ones designated by the minus sign in Table I, must be used. This is because when the relations (20) are used the \tilde{L}_i^2 must necessarily be normalized. The collection of normalized quanti-

ties $(\tilde{L}_i^2)_\Gamma$, in contrast to $(L_i)_\Gamma$, does not contain information about the orbital type of the states S_1 or T_1 ; moreover, the vibronic coupling of the higher electronic diabatic states can play the main role in the expression for L_i . For this reason, the prediction of PCR's on the basis of data on the parameters \tilde{L}_i can refer not to the lowest S_1 or T_1 state but rather to higher lying excited electronic states. The reaction can be described in both the adiabatic and nonadiabatic approximations.

On the basis of the ideas regarding the role of vibronic

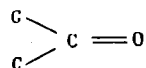
TABLE III. Prediction of the capability of molecules to enter into photoreactions $Q^{\text{PCR}}(\text{PT})$ in excited electronic states according to the HT-coupling spectroscopic parameters compared with data on the photochemical reactions themselves (PCR's).

Molecule	$N(N^*)$	Γ	R	ν_R	$\tilde{L}_R^2(\text{B})$	$Q^{\text{PCR}}(\text{PT})$	PCR	References		
PQ	5(4 [*])	b_{1u}	θ	1665	1(90%)	$\text{PR}_{\text{C=O}}$	Yes	[6] ^s ,		
T_1	3(2 [*])	b_{3u}	f	903	1(77%)	PA_{CH}	Yes	[98] ^s ,		
$(n\pi^*)$	5(2 [*])	b_{2u}	ψ	414	1(67%)	$\text{PS}_{\text{C=O}}$	No	[97, 102] _p		
AQ	10(9 [*])	b_{1u}	θ	1676	1(75%)	$\text{PR}_{\text{C=O}}$	Yes	[6] ^s ,		
T_1	6(3 [*])	b_{3u}	γ	175	1(50%)	$\text{PA}_{\text{C=O}}$	Yes	[62] _p ^s ,		
$(n\pi^*)$	10(3 [*])	b_{2u}	ψ	390	1(60%)	$\text{PS}_{\text{C=O}}$	Yes	[103] _p		
NMA	25(1 [*])	a_1	θ	1655	1(100%)	$\text{PR}_{\text{C=O}}$	Yes	[99] _p ^s ,		
T_1	12(8 [*])	b_1	g	671	1(65%)	$\text{PA}_{\text{C=O}}$	Yes	[100] ^s		
$(\pi\pi^*)$						PA_{CH}	No?			
PQ	23(2 [*])	a_1	θ	1684	0,9(47%)	$\text{PR}_{\text{C=O}}$	Yes	[99] _p ^s ,		
T_1			ψ	360	1(53%)			[100] _p ^s		
$(n\pi^*)$	22(7 [*])		θ	1700	1(73%)		$\text{PA}_{\text{C=O}}$	Yes		
	10(1 [*])		ν	534	1(100%)			PA_{CH}	No	
	11(2 [*])		g	700	1(62%)			$\text{PS}_{\text{C=O}}$	Yes	
MPD	45(3 [*])	a'	θ	1660	0,0(0%)	No $\text{PR}_{\text{C=O}}$	No	[100] _p ^s		
T_1	21(7 [*])	a''	γ_{NC}	161	1(31%)	RCF	Yes			
$(\pi\pi^*)$			x	131	1(31%)					
CBZ	10(3 [*])	b_1	i	887	1(50%)	PA_{CH}	No	[70] ^s ,		
T_1	20(1 [*])	b_2	φ_{NH}	1230	1(100%)	PS_{NH}	Yes	[104] _p		
$(\pi\pi^*)$										

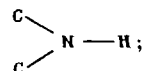
PQ designates the molecule *p*-quinone



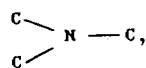
The structural formulas for the other molecules are given in Table II; N and N^* are the total number of vibrations of class Γ of the corresponding symmetry group and the number of such vibrations observed in the phosphorescence spectra; R is the letter designation adopted for the form of the vibrations;⁷² ν_R is the vibrational frequency corresponding to the maximum normalized value of the parameter $(L_R^2)_\Gamma = (L_R^2)_\Gamma / (L_R^{\text{max}})^2$; B is the relative quantity $(L_R^2)_\Gamma / (\sum_R L_R^2)_\Gamma$, $Q^{\text{PCR}}(\text{PT})$ is the predicted type (PT) of photoreaction: $(\text{PR})_{\text{C=O}}$ or $(\text{PS})_{\text{C=O}}$ denotes photoreduction or photosubstitution on the group $>\text{C}=\text{O}$, $(\text{PA})_{\text{C=O}}$ or $(\text{PA})_{\text{CH}}$ denotes photoattachment on the group $>\text{C}=\text{O}$ or $>\text{C}-\text{H}$; RCF denotes rupture of bonds in the central fragment. In the column PCR the word "yes" or "no" indicates that the corresponding reaction product is or is not observed experimentally; in the reference column the symbols p or s indicate whether the work contains data on the PCR or the spectroscopic parameters L_R . R ($= \theta, \psi$, and γ) designates stretching, in-plane bending, and out-of-plane vibrations of the group



φ_{NH} designates in-plane deformations of the group



γ_{NC} , x , and ν designate out-of-plane deformations of the group,



the central fragment, and the benzene moiety; see also the footnote 5 at the end of the paper.

coupling in the capability of electronically excited molecules to enter into photochemical reactions, it is usually supposed that under the appropriate experimental conditions a photochemical reaction can be stimulated by additional irradiation at the frequency ν_R of the vibrations of the molecule which correspond to the maximum values of \tilde{L}_R^2 .⁹⁸

Up to now, the prediction of Q^{PCR} based on complete spectroscopic data on the parameters L_i and comparison of the results with existing published data on the PCRs themselves have been made for a small number of complex molecules: AQ, PQ, NMA, MPD (see the formulas in Table II), xanthone, *p*-quinone, and 1,4-naphthoquinone.^{62,98-101} The predictions agree satisfactorily with experiment. Some data are presented in Table III.

We call attention to some interesting aspects of the agreement between the conclusions regarding Q^{PCR} and the data on PCRs. Thus, in the molecule AQ the C = O group is reactive, while in the PQ molecule (and 1,4-naphthoquinone) the >C-H group also becomes reactive. The NMA molecule and its isomer MPD, which also contain the heteroatom >N-, have markedly different capability of photoreduction on the C = O group. The heteroatom O of the >C = O group and the heteroatom N of the >NH group in the NMA and carbazole molecules, respectively, do not make an appreciable contribution to the formation of the excited diabatic electronic triplet state (see Table II). However in agreement with data on the parameters \tilde{L}_R , indicating that the wave function of the state must be described more accurately, the C = O and >NH atomic groups in the excited electronic states of these molecules are reactive.

Thus, as a result of the experimental investigation of HT coupling, which is reflected in the spectroscopic parameters \tilde{L}_R^2 , a small number of normal vibrational modes, corresponding to large values of \tilde{L}_R^2 , can be singled out in an "isolated" complex molecule (having ≈ 60 vibrational degrees of freedom). Comparison of the prediction of the probable coordinates Q^{PCR} made with the help of \tilde{L}_R^2 , with independent experimental data on the PCRs themselves in solution showed that the capability of molecules to enter into photochemical reactions in the excited electronic state is indeed reflected in the experimental values of the spectroscopic parameters \tilde{L}_R^2 .

6. LOCALIZATION OF VIBRONIC COUPLING AND THE ELECTRONIC STRUCTURE OF MOLECULES

In complex molecules, both FC and HT couplings are realized along a small number of coordinates, associated with the displacement of atoms from their position of equilibrium—the normal vibrational modes Q_R . This phenomenon of concentration of vibronic coupling in only selected modes (in other words, the selectivity of vibronic coupling⁷) is presented in Table II for the case of FC coupling and in Table III for the case of HT coupling. Thus for each representation Γ of the symmetry group of the molecule, first, the number of fundamental vibrations $(N^*)_\Gamma$ observed in the vibronic spectrum (according to the selection rules) is usually less than their total number $(N)_\Gamma$. Second, as a rule, the contribution of the vibronic coupling only along some modes Q_R to the total vibronic coupling, realized for each Γ along the observed modes strongly predominates. The spectroscopic parameters γ_R and \tilde{L}_R^2 are employed in this char-

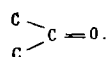
acteristic of vibronic coupling, presented in the column $\epsilon_R^{\text{FC}}/\delta E^{\text{FC}}$ in Table II and in the column B of Table III, respectively.

Thus analysis of vibronic coupling by the methods of fine-structure vibronic spectroscopy has shown that the selectivity of vibronic coupling could be connected with both FC and HT couplings along the coordinates Q_R . Selectivity is observed in the case of the coordinates Q_R relative to both the localized form (for example, Q_θ) and the delocalized form (for example, Q_l and Q_g). The selectivity of vibronic coupling in complex polyatomic molecules plays a key role in the theoretical investigation of nonradiative conversion processes.⁶³

We note that the relative sparsity of the vibrational structure of vibronic spectra (see Sec. 1) that has been pointed out in many publications is caused—still on the basis of the selection rules (1)—not only by the concentration of vibronic coupling in modes but also some other factors, which are not related with the vibronic coupling (see the relation (10) and Table I). These additional factors, which deplete the vibrational structure of the vibronic spectra, are related, in particular, with the spatial characteristic of the atomic orbitals— σ , π , l , and n —in molecules.

In addition to concentration of vibronic coupling in some modes, localization of vibronic coupling in separate fragments, in other words, subsystems of complex molecules (the molecules AQ, PQ, and AAQ in Table II and Fig. 2a), is also of great interest. In Fig. 4 the subsystems of some molecules, determined by FC coupling in excited electronic states, are encircled by dotted lines (Ph is a benzene moiety).

Comparing such data on vibronic coupling⁶ with quantum-mechanical calculations of diabatic electronic states of the corresponding molecules showed that one reason why vibronic couplings are localized in separate fragments could be that the electronic excitation in the corresponding states of complex molecules is of an approximately local character. Thus the main changes in the electronic density on atoms (δe) and in the bond orders (δp_π) in ${}^3n\pi^*$ states of anthranone (as in the $n\pi^*$ state of other carbonyl-containing molecules) are concentrated primarily in the group¹⁶



In the dibenzofuran (DBF) molecule or 1,4-dihydroxy-9,10-anthraquinone (1,4-OAQ) the changes δe and δp_π are small in the >O group or the Ph fragment, free of a substituent, respectively.^{105,106} In the thioindigo (TIN) molecule the principal chromophoric group is the central fragment:

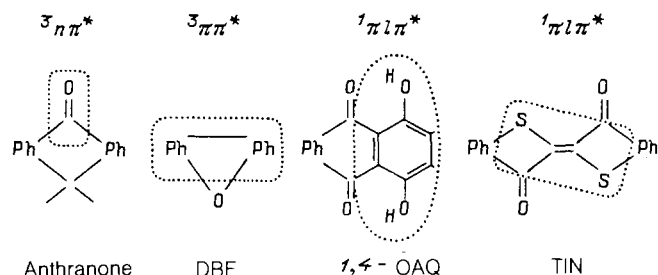


FIG. 4.

five-member rings connected by a C = C bond.^{107,108}

The established fact that vibronic coupling in polyatomic molecules segregates separate subsystems suggests that the basic characteristics of luminescence of luminophor molecules remain the same in even more complex molecular structures (for example, structured polymers). Such properties of polyatomic molecules are the basis for a promising direction in the search for new materials.¹⁰⁹

We note that in the case when electronic excitation in complex molecules is approximately localized the phenomenon of localization of vibronic coupling in some fragments of the molecules can be manifested in the vibronic spectra if the normal vibrational coordinates Q_R have a special form. Specifically, for some group of atoms the natural vibrational coordinates corresponding to the form of some coordinates Q_R must predominate in amplitude over other forms. This property (localization of form) of some coordinates Q_R is well known.⁷² It was established, for example, for the above-mentioned molecules of anthranone, 1,4-OAQ, and TIN. The localization of the form of the coordinate Q_β is widely employed in the analysis of experimental data (see, for example, the conclusions 1* and 4* in Sec. 4 regarding the special features of vibronic and spin-orbit coupling).

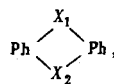
In order to explain the phenomenon of localization of vibronic coupling in vibrational modes (and not localization in fragments of molecules) it is necessary, in the general case, to study in detail the structure of both the electronic configurations and the coordinates Q_R . It can be shown¹¹⁰ that the selectivity of vibronic coupling is a consequence of approximately high local symmetry of intramolecular interactions in complex polyatomic molecules.

An expression for the FC-coupling matrix elements $H_{mm}^{(R)}$ (see also Eq. (3)) in the excited electronic state $\varphi_m(\mathbf{r})$ is presented below (the state is expanded in molecular orbitals (MOs) and the indices i and j refer to the vacant and occupied MOs (ψ_i and ψ_j) from the main configuration representing $\varphi_m(\mathbf{r})$):

$$\{H_{mm}^{(r)} H_{mm}^{(k)} H_{mm}^{(l)} \dots\} = \{ \{ \langle \vec{\delta}_1 \rangle_{ii} \langle \vec{\delta}_2 \rangle_{ii} \dots \} - \{ \langle \vec{\delta}_1 \rangle_{jj} \langle \vec{\delta}_2 \rangle_{jj} \dots \} \} \times \begin{vmatrix} \vec{\gamma}_{1r} & \vec{\gamma}_{1k} & \vec{\gamma}_{1l} & \dots \\ \vec{\gamma}_{2r} & \vec{\gamma}_{2k} & \vec{\gamma}_{2l} & \dots \\ \dots & \dots & \dots & \dots \end{vmatrix} \quad (21)$$

here $\{H_{mm}^{(R)}\}_R$, $\{\langle \vec{\delta}_\beta \rangle_{ii}\}_\beta$, and $\{\langle \vec{\delta}_\beta \rangle_{jj}\}_\beta$, are row matrices of dimension R' and β' , where R is the letter designation of the normal vibrational modes and β enumerates the atoms in the molecule; in the square matrix $|\vec{\gamma}|$ each column corresponds to displacement of atoms from their positions of equilibrium, each vibrational mode being represented by R . The matrices $\{\langle \vec{\delta}_\beta \rangle_{ii}\}$ and $\{\langle \vec{\delta}_\beta \rangle_{jj}\}$ can be regarded as representing the forces¹¹¹ acting on the atoms of the molecule in the state $\varphi_m(\mathbf{r})$, as a result of which the nuclear configuration of the molecule changes. In order to simplify the presentation, all configuration-mixing coefficients $C^{(m)}$ representing the diabatic state $\varphi_m(\mathbf{r})$ are taken to be negligibly small, except for one, which is equal to unity in the principal electronic configuration.

Without loss of generality we can study molecules with a structure of the type



having C_{2v} symmetry, and we can focus our attention on the vibrational modes of the molecule that are primarily coupled with benzene moieties (Ph). In the FC-coupling approximation all nine totally symmetric vibrations (of class A_1), referring to these fragments, are allowed in the vibronic spectrum. In this case the symmetry of the displacements of the atoms from their positions of equilibrium in each fragment Ph corresponds to the class a' of the group C_s .

The vibrational modes of molecules with benzene moieties have, however, a significant feature.^{72,101} As analysis of the form of the normal coordinates Q_R of complex molecules has shown, the vibrations of a molecule that are associated with the fragments Ph can be classified approximately, on the basis of the signs of the amplitudes of displacement of the atoms from their positions of equilibrium, according to the irreducible representations (Γ) of a symmetry group of higher symmetry than C_s , for example, D_{2h} . It has been proposed that special letter designations R be assigned, on the basis of this indicator, to each pair of vibrational frequencies ν_R and corresponding coordinates Q_R of the entire molecule. Then the totally symmetric vibrations of the molecule that are associated with the fragments Ph, can be approximately classified as follows:

$$9A_1(C_{2v}) \approx [9a'(C_s) = \{3a_{1g}\nu_R(R=r, k, l) + 2b_{3g}\nu_R(R=l, s) + 2b_{1u}\nu_R(R=m, p) + 2b_{2u}\nu_R(R=o, n)\}(D_{2h})]_{locally} \quad (22)$$

The nine nontotally symmetric in-plane vibrations $B_2(C_{2v})$ are classified analogously. We note that vibrations of the classes A_1 and B_2 , whose forms in the fragments Ph are close, have the same letter designations (but they correspond to different vibrational frequencies). In this approximation the form of the coordinate Q_R can be studied locally in a fragment.

The displacements of the atoms from their positions of equilibrium in each normal vibration $\vec{\gamma}_\beta^{(R)}$ appear in the expression for vibronic coupling (21). For this reason, an important aspect of the classification of vibrations of complex molecules is that in each fragment Ph all independent variants of the displacement of six atoms from their positions of equilibrium in the plane (with the center of gravity remaining stationary) are represented by nine sets of the form $\vec{\gamma}_1^{(R)} \dots \vec{\gamma}_6^{(R)}$ which are not only approximately mutually orthogonal but which are also approximately classified according to the irreducible representations of the groups D_{2h} or D_{6h} . (A similar classification is also possible in complex polyatomic molecules for out-of-plane displacements of the atoms.) For this reason the columns of the matrix $|\vec{\gamma}|$ are a kind of "grid" which always exists and locally analyzes in the fragments Ph the symmetry of the representations $\{\langle \vec{\delta}_\beta \rangle_{ii}\}$ and $\{\langle \vec{\delta}_\beta \rangle_{jj}\}$. The symmetry properties of the latter (if the geometric factor is neglected) are determined by the symmetry properties of the MOs ψ_i and ψ_j :

$$\Gamma(\{\langle \vec{\delta}_\beta \rangle_{ii}\}) = \Gamma(\psi_i) \times \Gamma(\psi_j).$$

In molecules of aromatic compounds with or without

heteroatoms the lowest excited electronic states of orbital type $\pi l\pi^*$ or $\pi\pi^*$ contain the MOs ψ_i and ψ_j , represented in the form of LCAOs primarily of the type $p_x(\pi)$. Locally, in the fragments Ph, the functions ψ_i and ψ_j belong in the general case to the representation a'' of the symmetry group C_s . The individual structure of these MOs can be approximately described by a linear combination of six MOs of the benzene molecule. The well-known MOs ψ_N^0 of benzene have a standard enumeration ($N = 1, 2, \dots, 6$) and belong to the irreducible representations of the symmetry group D_{6h} : a_{2u} ($N = 1$), e_{1g} ($N = 2, 3$), e_{2u} ($N = 4, 5$), b_{2g} ($N = 6$).

If locally in the fragment Ph both the MO ψ_i and the MO ψ_j in a complex molecule are each similar to some one basis function ψ_N^0 , then $\{\langle \delta_\beta \rangle_{ii}\}$ and $\{\langle \delta_\beta \rangle_{ij}\}$ can belong only to the totally symmetric representation (a_{1g}) of the symmetry group D_{2h} (in the matrix $|\gamma|$ the columns with $R = r, k, t$ correspond to this representation). If locally in the Ph fragment the MO ψ_i is expressed in terms of the basis functions of benzene $\psi_i \sim \psi_N^0 + \psi_{N'}^0 + \dots$, then the representations of the group D_{2h} , into which the representation of $\{\langle \delta_\beta \rangle_{ii}\}$ can be expanded, can be obtained from the following expression:

$$\Gamma(\{\langle \delta_\beta \rangle_{ii}\}) = \Gamma(\psi_N^0) \times \Gamma(\psi_N^0) + \Gamma(\psi_{N'}^0) \times \Gamma(\psi_{N'}^0) + \Gamma(\psi_N^0) \times \Gamma(\psi_{N'}^0) + \dots \quad (23)$$

In this case also the representation of $\{\langle \delta_\beta \rangle_{ij}\}$ will not contain the complete representation of the group D_{2h} for many of the possible structures of the MOs ψ (see below). (In accordance with the formula (21) the same procedure of expanding in ψ_N^0 must be performed for the MO ψ_j .)

Many quantum-chemical calculations of the wave functions of the lowest excited electronic states $\varphi_m(\mathbf{r})$ of the types $\pi\pi^*$ or $\pi l\pi^*$ of different molecules have shown that the MOs ψ_i and ψ_j studied here are indeed very similar to the benzene wave functions ψ_N^0 . Different possible distributions of the plus and minus signs among the AOs which represent the individual MOs ψ_i or ψ_j locally in the fragment Ph of the complex molecule can be described by different combinations. There can be 26 such different cases of MOs, for example, with an even number (6 or 4) of nonzero coefficients of the AOs (if all six ψ_N^0 are also included in their number); in addition, in the representation of these MOs the number of ψ_N^0 comprising them fluctuates from one to four. Most of these MOs, 22 to be precise (we denote them as ψ_i^* or ψ_j^*), have the following important features. The representation $\Gamma(\psi_i^*) \times \Gamma(\psi_j^*)$, expanded in representations of the symmetry group D_{2h} , contains, in addition to a_{1g} , only one of the nontotally symmetric representations: b_{1u} or b_{2u} or b_{3g} (Fig. 5). Thus the vibronic selectivity with respect to the totally symmetric coordinates of the molecule can be realized for many of the possible types of structures of the MOs ψ_i (and ψ_j).

In the case of HT coupling, which mixes the excited electronic states $\varphi_m(\mathbf{r})$ and $\varphi_n(\mathbf{r})$, the expression for the corresponding matrix elements $H_{nm}^{(R)}$ has the following form:

$$\{H_{nm}^{(r)} H_{nm}^{(k)} \dots H_{nm}^{(n)}\} = \{\langle \delta_\beta \rangle_{ij} \dots \langle \delta_\beta \rangle_{ij}\} |\vec{\gamma}|, \quad (24)$$

where the indices i and j refer to the MOs, chosen in a definite manner, of the states $\varphi_m(\mathbf{r})$ and $\varphi_n(\mathbf{r})$.

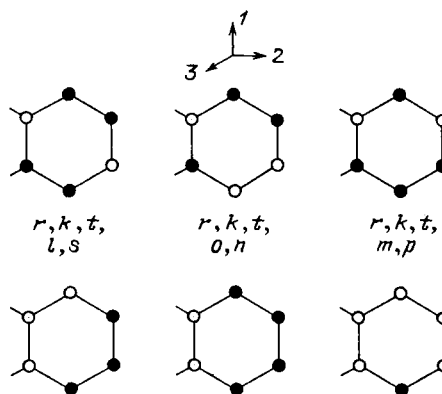


FIG. 5. Some variants of the structure of the π -MO ψ_i or ψ_j on the fragments of molecules and the vibrational modes Q_R which correspond to this structure and to which selective vibronic coupling is related. The different signs of the coefficients of the AO in the MO are indicated by the different shading of the circles. The relation between ψ and the distinguished modes Q_R ($R = m, p$ or $0, n$ or l, s) is reflected in the expressions (21) and (22).

The selectivity of HT coupling is realized for a smaller type of MO from among the ψ_i^* and ψ_j^* , namely, in the case when the MOs entering into the expression (24) satisfy the following additional condition: $\Gamma(\psi_i^*) \times \Gamma(\psi_j^*)$ and $\Gamma(\psi_i^*) \times \Gamma(\psi_j^*)$ contain the same nontotally symmetric representation of the group D_{2h} . When this condition is satisfied the expression $\Gamma(\psi_i^*) \times \Gamma(\psi_j^*)$ contains two other nontotally symmetric representations of this group.

In addition to Fig. 5, Table IV could also be useful for practical applications of the representation with approximately high local symmetry of vibronic coupling in polyatomic molecules. Table IV gives the results of a symmetry analysis of the force matrices— $\{\langle \delta_\beta \rangle_{ii}\}$ or $\{\langle \delta_\beta \rangle_{ij}\}$ —using only any two basis functions (ψ_N^0 and $\psi_{N'}^0$) in the expressions for the MOs ψ_i or ψ_j . The obtained irreducible representations of the group D_{2h} are given in R -letter designations of the vibrational modes (in accordance with Eq. (21)). A nonzero result is obtained only by multiplication by columns of the matrix $|\gamma|$ which have the corresponding R . The table has the form of a matrix in which ψ^0 labelled with the numbers N and N' occur in the columns and rows. Vibrations of class A_1 with designations R , which are allowed in the vibronic spectrum in the FC approximation, can be found in accordance with the expressions (23) along the diagonal of the matrix (two elements) and at the intersection with the index NN' . For example, if the components of the MO ψ_i are ψ_3^0 and ψ_6^0 , then the vibrations t, r, l , and s are allowed. Table IV can also be used in the case of HT coupling, when the vibronic interaction forces are represented, according to the expression (24), by the off-diagonal matrix element.

Thus the selectivity of vibronic coupling in complex molecules is governed simultaneously by two factors. One factor is the approximately high symmetry of the group (D_{2h} , D_{6h}) to which the representations describing the displacements of atoms from their positions of equilibrium $|\gamma|$ locally in the fragments Ph in the corresponding vibrational modes of the large molecule belong. The second factor is the approximate symmetry D_{2h} or C_{2v} (with a $C_2(z)$ or $C_2(y)$ axis) or C_{2h} (with a $C_2(x)$ axis), to which groups belong the

TABLE IV. Decomposition of the representation of intramolecular vibronic coupling forces according to the vibrational modes of the benzene moieties (Ph) of molecules as a function of the combinations of the benzene orbitals ψ_N^0 and $\psi_{N'}^0$, describing the MO ψ of the excited state of the molecule.

D_{2h}	$\psi_{N'}^0 = \psi_{N'}^0$	ψ_1^0	ψ_2^0	ψ_3^0	ψ_4^0	ψ_5^0	ψ_6^0
b_{3u}	ψ_1^0	r	m, p	o, n	l, s	k, t	m, p
b_{2g}	ψ_2^0	m, p	k	l, s	o, n	m, p	k, t
b_{1g}	ψ_3^0	o, n	l, s	t	m, p	o, n	l, s
a_{1u}	ψ_4^0	l, s	o, n	m, p	t	l, s	o, n
b_{3u}	ψ_5^0	k, t	m, p	o, n	l, s	k	m, p
b_{2g}	ψ_6^0	m, p	k, t	l, s	o, n	m, p	r

The vibrational modes with letter designations are classified in terms of the representations of the symmetry group D_{2h} according to the expression (22); the intramolecular vibronic coupling forces are represented by the matrices $\{\langle\delta_\beta\rangle_{ii}\}$, $\{\langle\delta_\beta\rangle_{ij}\}$ and $\{\langle\delta_\beta\rangle_{ij}\}$ in the expressions (21) and (24); the MOs ψ_i and ψ_j , occupied by one electron, are selected according to known rules (see text). The table makes it possible to predict (depending on the structure of the MOs) the vibronic lines (of the corresponding modes R) that are allowed in the local-symmetry approximation.

representations describing the forces acting on the atoms— $\{\langle\delta_\beta\rangle_{ii}\}$ and $\{\langle\delta_\beta\rangle_{ij}\}$ (they can be called Coulomb and exchange forces, respectively)—once again locally in the Ph fragments with a change of the electronic state of the molecule.

The matrix of displacements of atoms $|\vec{\gamma}|$ is determined by all MOs of the molecule (of both σ and π types) which are occupied by at least one electron. (For example, the anthracene molecule $C_{14}H_{10}$ has three doubly occupied MOs.) For this reason, the presence of a small number of atomic groups—substituents with heteroatoms (O, N, S,...)—in complex molecules having two or more Ph fragments does not, as a rule, radically change the local symmetry properties of the representation of $|\vec{\gamma}|$ in the Ph fragments. (For this reason, for example, in semiempirical calculations of the vibrations a good initial approximation is obtained by transferring fragments of the potential field from one molecule to another. For this reason, in such molecules the change in the system of normal vibrational coordinates in the lowest excited electronic states relative to the ground electronic state can be neglected.)

In contrast to $|\vec{\gamma}|$, the matrices of the intramolecular forces $\{\langle\delta_\beta\rangle_{ii}\}$ and $\{\langle\delta_\beta\rangle_{ij}\}$ in complex molecules can be determined in the limit by only two MOs (with $C^{(m)}$ and $C^{(n)}$ equal to 1) from among the highest occupied and lowest vacant orbitals. The structure of these MOs changes significantly when different atomic substituent groups are introduced into the molecule. It is this factor that is mainly responsible for the radical differences in the fine-structure vibronic spectra of complex molecules. In this sense a vibronic spectrum, that is to say, the intensity distribution in the spectrum over all vibrational modes on the basis of the selection rules, reflects the orbital nature of the excited electronic states of molecules. The symmetry of the representation of vibronic-coupling forces, which is not too low locally in separate fragments of the molecule, can, however, lead to (see the condition on the representation of $|\vec{\gamma}|$) additional selectivity of vibronic coupling—strong suppression and even vanishing of some vibronic lines, even though their presence in the spectrum is consistent with the selection rules for the molecule of interest.

CONCLUSIONS

The vibrational structure of the vibronic spectra of solid solutions at the temperature of liquid helium can be used for more than identification of compounds (in the usual standpoint of applied spectroscopy). Vibronic spectra also contain rich information about the excited electronic states of polyatomic molecules.

The fine structure of vibronic spectra is an excellent object for testing different theoretical approximations employed for describing the excited electronic states of complex molecules. Thus the study of the fine structure has shown, in particular, that the Condon approximation is inadequate for describing the intensity distribution of vibronic lines in the spectra of molecules of aromatic compounds with heteroatoms. In order to describe satisfactorily the intensity (including the region of the spectrum where overtones of vibrations are observed) it is necessary to use the adiabatic approximation, taking into account at least the linear (and sometimes quadratic) dependence of the dipole moment of the electronic transition on the coordinates of the nuclei.

Fine-structure vibronic spectra can also be employed together with theoretical models in order to determine some general features of the formation of excited electronic singlet and triplet states of molecules, and in addition these features can be correlated with the electronic structure of the constituent atoms of a molecule. The discrimination of separate vibrational modes in vibronic coupling, an effect observed in vibronic spectra, is very important. It is manifested in the fact that some lines corresponding to transitions allowed by the selection rules are anomalously weak. This feature is explained primarily by the symmetry properties of intramolecular interactions, when the symmetry of vibronic coupling of higher order than the symmetry of the entire molecule as a whole is realized in separate (for example, aromatic) fragments of complex molecules.

The characteristics of the spatial structure of the atomic orbitals of heteroatoms (for example, O, N, and S), which make a significant contribution to the electronic configurations of the excited electronic states of molecules of heteroaromatic compounds, are manifested in the vibronic spectrum.

Experimental investigations of the intensity distribution in the vibronic structure of the spectra, together with analysis of the normal vibrational coordinates, make it possible to determine the orbital type of the electronic state as well as to determine the molecular fragments in which the greatest changes of the electronic density occur as a result of a transition of molecules from the ground electronic state into an excited electronic state. Such spectra are the source for quantitative data on the changes occurring in the bond lengths and bond angles in polyatomic molecules accompanying electronic excitation. The same data are also utilized to improve theoretical quantum-chemical models of Frank-Condon coupling.

It can be expected that the potentially possible photochemical properties of compounds are reflected in the vibronic coupling in "isolated" molecules. A number of experiments has shown that the luminescence spectra of solutions in "inert" solvents at 4.2 K make it possible to determine the atomic groups with which the photochemical instability of a complex molecule in an excited electronic state accompanying a change of the intermolecular interactions can be associated. In this respect, the study of vibronic coupling in solutions where specific intermolecular interactions are realized is promising.

The method of vibronic spectroscopy of molecules in vapors cooled in a supersonic jet of inert gases opens up new possibilities in the investigation of the excited electronic states of complex molecules. Significant new types of investigations here (as compared with the spectra of solid solutions) are investigations of relaxation processes on vibrational sublevels of the excited electronic state in connection with the different activity of the corresponding vibrational modes in different types of vibronic coupling.

An attractive feature of a spectrum of vapors in a supersonic medium as compared with a solid solution is its higher degree of structure as a result of the narrowing of vibronic lines and vanishing of phonon wings. Such structure makes unnecessary the approximation of the theory of electron-phonon interactions and it enables attention to be focused on checking approximations in the description of intramolecular interactions in isolated molecules using more accurate values of the spectroscopic parameters (frequencies and intensities). Under these conditions additional possibilities open up for investigating the Dushinskii effect, anharmonicity of vibrations, and nonadiabatic interactions.

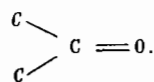
Investigations in vapors are also of interest for clarifying the question of the distorting effect of an "inert" matrix on the nuclear configuration of the molecules embedded in it. Although the first experiments showed that this effect of a matrix is negligibly small, this question requires a more detailed analysis, especially with respect to investigations of the Herzberg-Teller coupling. Here it is of interest to establish the mechanisms of intermolecular interactions that result in changes of the spectroscopic parameters of vibronic coupling which correspond to different approximations of their theoretical description and also to determine the relation between the changes occurring in these parameters and the presence of different structural groups with heteroatoms in complex molecules.

¹⁾ We shall not study molecules which B. S. Neporent classifies as complex¹² and which have homogeneously broadened vibronic spectra devoid of structure.

- ²⁾ Jahn-Teller coupling makes the spectrum even more complicated. However the Jahn-Teller pseudo effect is rarely observed in the luminescence spectra of complex molecules whose nuclear configuration has a low symmetry and we shall not study it further in this review.
- ³⁾ It is assumed that the difference of the frequencies ν and ν' in the ground and excited electronic states as well as the Dushinskii effect ("entanglement" of the normal vibrational coordinates Q and Q') can be neglected. See the remark concerning this in Sec. 2.
- ⁴⁾ The use of the symbols n , l , and v in the designations of the orbital type of electronic states indicates that the corresponding orbitals of the heteroatoms make an appreciable contribution to the structure of the bonding and nonbonding molecular orbitals (MOs) forming the excited electronic state of the molecule. We note that the orbital component of the diabatic wave function of the excited electronic $n\pi^*$ -state (and also the $\sigma\pi^*$ -state) belongs to the irreducible representation A'' of the symmetry group C_s . However the states of orbital types $\pi\pi^*$, $\pi l\pi^*$, and $\pi l v \pi^*$ belong, according to their symmetry properties, to a different irreducible representation (A') of the same group.
- ⁵⁾ Special letter designations R (Chapter II in Ref. 72) have been adopted to designate the form of the normal coordinates Q_R . In particular, the designations $R = j, f, i$, and g have been adopted for Q_{CH}^1 . These designations denote the phase relations of the displacements of the H atoms in the benzene moieties.



of molecules. We note that in many cases the normal coordinate Q_g also includes the large amplitude of the out-of-plane natural coordinate of the change of the angle in the group.



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