Translated from *Uspekhi Khimii*, **49**, 327-361 (1980) U.D.C. 541.14,541.65,535.37

Theoretical Foundations of the Classification of Molecules by Luminescence Spectra

V.G.Plotnikov

The relationship between the luminescence spectra and the structure of aromatic molecules is discussed theoretically. Various semi-empirical methods of calculating the electronic states of polyatomic molecules are briefly described. The orbitals involved in the electronic transitions and states and the effect of molecular structure and other factors on the energy of the states are considered. The spin-orbit interaction of molecular states is discussed, and radiative transitions in molecules are examined in relation to the nature of the molecule. Modern views on the nature of the conversion processes are outlined, and the variation of their rate with the type of transition and with the energy spectrum and structure of the molecule is analysed. Molecules are classified into five types according to their luminescence spectra, and a justification of this classification is given.
The bibliography includes 154 references.

CONTENTS

I.	Introduction	172
II.	The adiabatic approximation	173
III.	Types of molecular orbital, electronic transition, and electronic state	174
IV.	Effect of structure on the position of the lower electronically excited states of molecules	176
V.	Spin-orbit interaction in electronic states of molecules	178
VI.	Radiative transitions in aromatic molecules	179
VII.	Non-radiative conversion processes	181
VIII.	Classification of molecules by luminescence spectra	185

I. INTRODUCTION

Many problems in photochemistry, radiation chemistry, the chemistry of organic phosphors and scintillators, chemiluminescence, and photobiology are difficult (or impossible) to solve without a knowledge of the relationship between the luminescence-spectral properties of molecular systems and their structure. This is because of the widespread use of luminescence as a method of investigation in those fields of science, and also because the light emission process (luminescence) is one of the most important paths for the dissociation of electronically excited molecules, and must be included in the overall scheme of possible reaction mechanisms.

The study of the luminescence spectra of molecules as a function of molecular structure is a fundamental aspect of molecular spectroscopy: it is one part of the more general problem of the relationship between properties and structure in molecules, first formulated and investigated by Butlerov. The practical importance of this problem was suddenly magnified by the increasing use of organic molecules (especially aromatic molecules, including dyes) in laser technology[1]. A rational search for compounds offering good generation properties (i.e. efficient phosphors and scintillators) presupposes an understanding of the dependence of the luminescence properties on the structural parameters of the molecules.

In the last 5–10 years important advances have been made towards the solution of this problem as a result of the widespread application of theoretical ideas on the structure of molecules and on the nature of their electronic states to the large number of experimental results stimulated by the discovery of the Shpol'skii effect. The experimental aspects of this work have been discussed[2,3] and reviewed[4], but the theoretical side has not yet been reviewed in detail. This article aims to fill this gap. The discussion will be limited mainly to aromatic and hetero-aromatic molecules (all of which will be termed aromatic in the interest of brevity) in the condensed phase. These are the systems of greatest practical interest, both because of their widespread application in different fields of technology and because of the multiplicity of their luminescence properties. The vast majority of the published work, both experimental and theoretical, relates to molecules of this type.

Our decision to confine the discussion to the condensed phase stems not only from the overwhelmingly greater practical importance of condensed systems. No less relevant is the fact that the fast ($\lesssim 10^{-11}$ s) vibrational relaxation processes which are possible in the condensed phase introduce a considerable simplification of the theoretical treatment, since both radiative and non-radiative processes normally take place from an electronically excited state in vibrational equilibrium. This is not always true in the case of luminescence from vapours at low pressures[5,6], and the theoretical treatment of this case is less well developed than its experimental study[7]. Discussions of molecules in the condensed phase are usually confined to the low-temperature region, where the vibrational energy of the molecules (active vibrations, see Section VII) would be greater than the thermal energy. Under these conditions the problem is simplified still further, because the initial state of the radiative and conversion processes is the zeroth vibrational state of the excited energy level.

Throughout most of the discussion we shall assume that the molecules are photochemically stable, as is the case in practice for most aromatic compounds in rigid solvents[8]. Only in the concluding section will the effect of possible photochemical reactions be considered (briefly). Most of the formulae use a system of atomic units in which the charge and mass of the electron and Planck's constant $\hbar$ are taken to be unity.

II. THE ADIABATIC APPROXIMATION

The Hamiltonian of a molecular system can be expressed as the sum of the electronic kinetic energy operator T_r, the nuclear kinetic energy operator T_R, terms describing the interactions of electrons ($U(r, r')$), nuclei ($U(R, R')$), and electrons and nuclei ($U(r, R)$), and the spin–orbit interaction operator H_{so}:

$$H = T_r + U(r, r') + U(r, R) + T_R + U(R, R') + H_{so}, \quad (1)$$

where r denotes the set of electron coordinates $\{r_i\}$ and R the set of nuclear coordinates $\{R_q\}$. The eigenfunctions of the Hamiltonian (1) cannot be found in the general case, and we must resort to approximate methods.

In molecules which contain no heavy atoms the effect of spin–orbit interaction on the position of the electronic states is not very important. Therefore in the first stage of our discussion we can ignore the operator H_{so}, but we shall allow for it (by using perturbation theory) in the subsequent treatment (see Sections VI and VII). The eigenfunction ($H - H_{so}$) of the Hamiltonian can be chosen to be also the eigenfunction of the operator of the square of the total electronic spin moment of the molecule ($\hat{S}^2$) and of the operator of one of its projections ($\hat{S}_z$). The states described by these wave functions are called pure spin states and can be classified in terms of the quantum numbers S and S_z. In most molecules the ground state is a singlet ($S = 0$, $S_z = 0$). Excited states can be either singlet or triplet ($S = 1$, $S_z = 0, \pm 1$). Under the influence of spin–orbit and spin–spin interaction and of an external magnetic field the triplet state splits into three sublevels corresponding to the three possible values of S_z.

The second approximation, known as the adiabatic or Born–Oppenheimer approximation[9–14], relies on the fact that the mass of the nuclei is several orders of magnitude greater than the mass of the electrons, and therefore the velocity of the electrons is much greater than that of the nuclei. The full wave function of the system in the adiabatic approximation is expressed as the product $\Phi_j(r, R)\Omega_j^n(R)$. The electronic part of the wave function $\Phi_j(r, R)$, which is parametrically dependent on the coordinates of the nuclei, is determined by a wave equation with fixed values of R:

$$[T_r + U(r, r') + U(r, R) + U(R, R') - E_j(R)]\,\Phi_j(r, R) = 0, \quad (2)$$

where $E_j(R)$ is the electronic energy of the system for fixed values of the nuclear coordinates. The subscript j denotes the set of electronic quantum numbers; $E_j(R)$ defines the potential energy surface of the electronic state of the system (energy level). The wave function describing the motion of the nuclei, $\Omega_j^n(R)$, is found from the equation

$$[T_R + E_j(R) + \langle \Phi_j(r, R) | T_R | \Phi_j(r, R) \rangle - W_{jn}]\,\Omega_j^n(R) = 0, \quad (3)$$

where the index n denotes the set of vibrational quantum numbers and W_{jn} is the vibronic energy of the system. The term $\langle \Phi_j(r, R) | T_R | \Phi_j(r, R) \rangle$, in which the angle brackets indicate integration with respect to the coordinates of the electrons, is usually small.

The states described by the wave function $\Phi_j(r, R)\Omega_j^n(R)$ are called adiabatic pure spin states. We shall also use the symbol $|j\{n\}\rangle$ for these states. The methods of evaluating the wave functions $\Phi_j(r, R)$ are described in Section III. The problem of evaluating the wave functions $\Omega_j^n(R)$ reduces to solving the classical problem of small vibrations in a system of particles[11]. The potential surface is determined from the condition of correspondence between calculated and experimental vibration frequencies. The Morse potential is commonly used[12] when allowance for the anharmonicity of the vibrations is needed.

Let us briefly examine the conditions under which the adiabatic approximation is valid†. We shall define the non-adiabaticity operator $\hat{V}$ through its effect on the adiabatic wave functions:

$$\hat{V}(\Phi_j\Omega_j^n) = \Omega_j^n T_R \Phi_j - \sum_q M_q^{-1} \frac{\partial \Phi_j}{\partial R_q} \cdot \frac{\partial \Omega_j^n}{\partial R_q}, \quad (4)$$

where M_q is the mass of the nucleus q, and the operator T_R takes the form

$$T_R = \frac{1}{2} \sum_q M_q^{-1} \frac{\partial^2}{\partial R_q^2}. \quad (5)$$

A detailed analysis[9,10,13] has shown that the adiabatic approximation is valid when the $\langle j\{n\}|\hat{V}|j'\{n'\}\rangle$ matrix elements with $j \neq j'$ are small compared to the difference in energy between the corresponding states. A sufficient condition is low molecular vibration frequencies (as compared to the electronic transition energies[10,13]). Similarly, the approximation in which the operator H_{so} is ignored is valid if the $\langle j\{n\}|H_{so}|j'\{n'\}\rangle$ matrix elements are small in comparison to the energy of the transitions. In molecules which do not contain heavy atoms these matric elements are usually smaller than ~100 cm^{-1} (see Section V). Both conditions are easily met by the lower vibrational levels of the ground state of most molecules. On the other hand in electronically excited states neither of these criteria applies, and as a result we have long-lived after-effects. Nevertheless, for the non-trivial reasons discussed in Section VII, we are forced to use adiabatic pure spin functions in any discussion of the luminescence, photochemical, and other spectral properties of molecules.

The most widely used (and often quite satisfactory) model is the "coarse" adiabatic approximation, which ignores the dependence of Φ_j on the coordinates of the nuclei and assumes equilibrium values of R_0 (for a given electronic state) in the expression for Φ_j.[14] The expressions for the H_{so} and $\hat{V}$ matrix operators become

$$\langle j\{n\}|\hat{V}|j'\{n'\}\rangle = \langle \Omega_j^n | \Omega_{j'}^{n'} \rangle \langle \Phi_j^0 | T_R | \Phi_{j'}^0 \rangle - \sum_q M_q^{-1} \left\langle \Omega_j^n \left| \frac{\partial}{\partial R_q} \right| \Omega_{j'}^{n'} \right\rangle \left\langle \Phi_j^0 \left| \frac{\partial}{\partial R_q} \right| \Phi_{j'}^0 \right\rangle, \quad (6)$$

$$\langle j\{n\}|H_{so}|j'\{n'\}\rangle = \langle \Phi_j^0 | H_{so} | \Phi_{j'}^0 \rangle \langle \Omega_j^n | \Omega_{j'}^{n'} \rangle; \quad (7)$$

where the differentials with respect to nuclear coordinates, the Φ_j^0 and $\Phi_{j'}^0$ wave functions, and the H_{so} operator are taken for equilibrium geometry. This approximation is also known as the Condon approximation. The Franck–Condon factors $\langle \Omega_j^n | \Omega_{j'}^{n'} \rangle$ do not vanish, in general, for $n \neq n'$. The following formula is also useful for calculating (from Eqn.(2)) the matrix elements of the operator $\hat{V}$:

$$\left\langle \Phi_j \left| \frac{\partial}{\partial R_q} \right| \Phi_{j'} \right\rangle = \left\langle \Phi_j \left| \frac{\partial U(r, R)}{\partial R_q} \right| \Phi_{j'} \right\rangle [E_{j'}(R) - E_j(R)]^{-1}. \quad (8)$$

When allowance for the variation of Φ_j with R is unavoidable (for example, when the matric elements vanish in the Condon approximation) we use the Herzberg–Teller expansion[15] in which the dependence of the electronic wave functions on the nuclear coordinates is allowed for by an expansion with respect to electronic wave functions of the different electronic states (with an equilibrium configuration), using coefficients depending on the deviation (δR_q) of the coordinate R_q from its equilibrium value:

$$\Phi_j(r, R) = \Phi_j^0 + \sum_q \sum_{j' \neq j} a_{j'j}^q \delta R_q \Phi_{j'}^0. \quad (9)$$

†The terminology used in recent publications often fails to distinguish between the adiabatic approximation and the approximation in which the H_{so} operator also is ignored.

Under conditions for which the first-order perturbation theory is applicable the quantity $a^q_{j'j}$ is given by

$$a^q_{j'j} = \left\langle \Phi^0_{j'} \left| \left(\frac{\partial U(r, R)}{\partial R_q} \right)_{R=R_0} \right| \Phi^0_j \right\rangle [E_j(R_0) - E_{j'}(R_0)]. \quad (10)$$

III. TYPES OF MOLECULAR ORBITAL, ELECTRONIC TRANSITION, AND ELECTRONIC STATE

The molecular orbital (MO) method is the most widely used and effective approach to the study of the electronic structure of molecules, but the localised orbital (LO) method is also commonly used to describe the spectroscopic characteristics of molecules. The former method can be used to describe directly the one-electron properties of molecules (e.g. in photo-electron spectroscopy). The latter method often offers a fairly clear interpretation of the nature and properties of electronically excited states of molecules. In their most developed form (allowing for configurational interaction) the two methods give the same results for identical sets of basic functions.

The MO method is discussed extensively in the literature[16-20], and therefore we shall limit our own discussion to a few general remarks. In the simplest case the electronic wave function of the system (Φ_j) is expressed as a Slater determinant, assembled from one-electron spin orbitals in which the spatial part is an expansion with respect to fixed basic functions

$$\psi_i = \sum_\nu \chi_\nu c_{\nu i}. \quad (11)$$

In the case of a singlet ground state the equations for the coefficients $c_{\nu i}$ and for the orbital energies ε_i have the form[16]

$$\sum_{\nu'} (F_{\nu\nu'} - \varepsilon_i S_{\nu\nu'}) c_{\nu' i} = 0, \quad (12)$$

where $F_{\nu\nu'}$ are the matrix elements of the Hartree–Fock operator F, and $S_{\nu\nu'} = \langle \chi_\nu | \chi_{\nu'} \rangle$ are the overlap integrals of the basic function. The system (12) is solved by an iterative method.

In calculations for complex polyatomic systems the functions χ_ν are usually represented by Slater atomic orbitals, which for the atoms of the first two periods can be written

$$\begin{gathered} 1s = (\xi^3/\pi)^{1/2} e^{-\xi r}, \quad 2s = (\xi^5/3\pi)^{1/2} r e^{-\xi r}, \\ 2p_x = (\xi^5/\pi)^{1/2} e^{-\xi r} x, \quad 2p_y = (\xi^5/\pi)^{1/2} e^{-\xi r} y, \\ 2p_z = (\xi^5/\pi)^{1/2} e^{-\xi r} z, \end{gathered} \quad (13)$$

where ξ are the Slater parameters[9]. The functions (13) are defined in a system of Cartesian coordinates with its origin at the nucleus of the appropriate atom.

In planar molecules (which include most aromatic and hetero-aromatic molecules) we can distinguish two types of molecular orbital: π and σ. If the z axis of the coordinate system is chosen at right angles to the plane of the molecule the π orbitals will contain only p_z functions in their expansion, whereas the σ orbitals will contain (in general) p_x, p_y, and s atomic functions.

Semi-empirical methods of studying π-electron systems rely on the principle of zero differential overlap[17-20]. The expressions for the $F_{\nu\nu'}$ matrix elements in this approximation (the Pariser–Parr–Pople or PPP approximation) are

$$\begin{gathered} F_{\nu\nu} = H_{\nu\nu} + N_\nu \gamma_{\nu\nu} - \frac{1}{2} p_{\nu\nu} \gamma_{\nu\nu} + \sum_{\nu'} (p_{\nu'\nu'} - N_{\nu'}) \gamma_{\nu\nu'}, \\ F_{\nu\nu'} = H_{\nu\nu'} - \frac{1}{2} p_{\nu\nu'} \gamma_{\nu\nu'}. \end{gathered} \quad (14)$$

In these expressions $H_{\nu\nu} = -I_\nu$ if the ν atom contributes one electron to the π system ($N_\nu = 1$), and $H_{\nu\nu} = -I_\nu - \gamma_{\nu\nu}$ if $N_\nu = 2$; I_ν is the ionisation potential of the p electrons of the ν atom; $\gamma_{\nu\nu}$ and $\gamma_{\nu\nu'}$ are the one-centre and the two-centre Coulomb integrals of the electronic interaction respectively; $p_{\nu\nu}$ is the electron density on the ν atom; $p_{\nu\nu'}$ is the bond order of the ν and ν' atoms; $H_{\nu\nu'} = \beta_{\nu\nu'}$ is the resonance integral. The integrals $\gamma_{\nu\nu}$, $\gamma_{\nu\nu'}$, and $\beta_{\nu\nu'}$ are determined empirically[17-20]. In spite of the large number of different ways of defining the quantities $\gamma_{\nu\nu}$, $\gamma_{\nu\nu'}$, and $\beta_{\nu\nu'}$ most of the results discussed below are independent of the method of parametrisation. Of course, in studies of specific classes of molecules the integrals must be defined uniquely#.

Various semi-empirical methods of calculating the electronic structure of molecules in the valence approximation have been proposed. In molecules containing hetero-atoms whose valence is lower than the number of electrons in the valence shell we can distinguish some σ orbitals for which the coefficients of the expansion are large only on the hetero-atom or on several equivalent hetero-atoms in the molecule. These orbitals (whose energy is greater than ~−10 eV) are doubly occupied in the electronic ground state and correspond to the antibonding orbitals of the LO method (n orbitals). Assuming full localisation of the n orbitals on the hetero-atom (as in the LO method, see below), the energy ε_n for these orbitals is determined only by the diagonal matrix element $\langle n|F|n\rangle$, where $|n\rangle$ denotes the atomic wave functions of the n electrons. If the number of π electrons of a hetero-atom with n electrons is one, the energy ε_n is given by the expression[21-23]

$$\varepsilon_n = -I_n - \sum_\nu (p_{\nu\nu} - N_\nu) \gamma_{\nu n} - \frac{1}{2} p^\pi_n \varkappa, \quad (15)$$

where I_n is the ionisation potential of the unshared pair of the hetero-atom in the valence state, $\gamma_{\nu n}$ are the integrals of the Coulomb interaction of the n electrons with the $p\pi$ electrons of the ν atom, p^π_n is the density of π electrons on the hetero-atom with n electrons, and $\varkappa$ is the one-centre exchange interaction integral of the n and $p\pi$ electrons.

The parameters which appear in Eqn.(15) can be evaluated semi-empirically[20-24]. In carbonyl, nitro, and thiocarbonyl compounds the n electrons of the O (or S) atoms are described by a p atomic orbital whose axis of symmetry is perpendicular to the bond between the carbon atom and the hetero-atom. In aza-heterocyclic compounds the wave function of the n orbitals takes the form of an sp^2 hybrid orbital. In compounds containing several equivalent pairs of n electrons (for example, in nitro compounds) the wave function of the n electrons should be expressed, strictly speaking, as a linear combination of the orbitals of the individual atoms even in the localised model: this leads to some change in the energy values and to splitting of the energy levels of the excited states[24]. This splitting is usually small, but it can be important in the interpretation of the luminescence spectra of molecules[4].

Another method frequently used for qualitative conclusions at present is the Hückel method, in which the parameters are the matrix elements of the Hartree–Fock operator $F_{\nu\nu} = \alpha_\nu$ and $F_{\nu\nu'} = \beta_{\nu\nu'}$.[18,20]

The π and σ orbitals can be bonding or antibonding: in the latter case they are denoted as π^* and σ^*. In the electronic ground state the bonding orbitals and the n orbitals are doubly occupied by electrons (see Fig.1). Knowing ε_i and $c_{\nu i}$ we can calculate the energy of the ground state

---

#Typical values are $\gamma_{\nu\nu} \cong 10$ eV, $\gamma_{\nu\nu'} \leqslant 5$–$7$ eV, $\beta_{\nu\nu} \leqslant 2$ eV, and $\varkappa \cong 1$ eV (see also formula (15)).[17-20,23,24]

(Φ_0) by the formula

$$E_0 = 2\sum_i \varepsilon_i - \sum_{i,i'} (2J_{ii'} - A_{ii'}), \qquad (16)$$

where the summation extends only over the occupied orbitals, $J_{ii'}$ is the Coulomb interaction integral, and $A_{ii'}$ is the exchange interaction integral of the electrons on the i and i' MO.

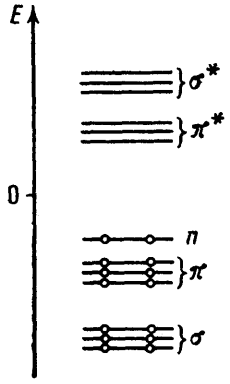


Figure 1. Relative position of one-electron levels in molecules.

In complex molecules the wave functions of the excited states and their energies are usually defined as follows. Using π^* and σ^* virtual orbitals we construct the $|i \to k>$ excited configurations, corresponding to the transition of an electron from the i orbital (filled in the ground state) to the vacant k orbital. These configurations can be singlet (S) or triplet (T), and their energies are given by the formulae

$$^S E_{ik} = \varepsilon_k - \varepsilon_i - J_{ik} + 2A_{ik}, \qquad (17)$$

$$^T E_{ik} = \varepsilon_k - \varepsilon_i - J_{ik}, \qquad (18)$$

where the integrals J_{ik} and A_{ik} have the same significance as in Eqn.(16). The wave function of the excited state is assembled as a superposition of excited configurations with coefficients given by the variational principle. We note that since $A_{ik} > 0$ the energies of the triplet configurations (and of the triplet states) are lower than the energies of the corresponding singlets. The parameters used in the calculation of $F_{\nu\nu'}$ are also used to evaluate the integrals J_{ik} and A_{ik}. In the Hückel method the energy of a transition is equal to the difference between the corresponding orbital energies§.

Thus, the following types of electronic transition are possible in aromatic molecules: $\pi \to \pi^*$, $n \to \pi^*$, $\sigma \to \sigma^*$, $n \to \sigma^*$, $\pi \to \sigma^*$, and $\sigma \to \pi^*$, as well as the following electronic states: $S_{\pi\pi^*}$, $T_{\pi\pi^*}$, $S_{n\pi^*}$, $T_{n\pi^*}$, $S_{\pi\sigma^*}$, $T_{\pi\sigma^*}$, $S_{\sigma\sigma^*}$, $T_{\sigma\sigma^*}$, etc. We should remember that these designations apply only in the absence of quasi-degeneracy of the states.

The designations of the $\pi\pi^*$ states are unnecessarily general, because they contain no detailed information on the nature of the electronic transition. Yet it is experimentally well established[4,25-27] that the luminescence spectra of π-electron molecules are strongly influenced by the presence of electron-donor (OH, NH_2, OCH_3, Hal, etc.) or electron-acceptor (BH_2) substituents. Hence we must distinguish different types of $\pi\pi^*$ state while retaining as far as possible the generality of the designation. This is most conveniently (and most clearly) done in the language of the LO method[28].

Let us examine the most characteristic features of the LO method by considering aromatic molecules containing electron-donor substituents. In addition to the σ (and n) electrons the hetero-atoms of the donor substituents (O, N, Hal) have an unshared pair of electrons which can take part in π-conjugation (unlike the n-electrons). The orbitals of these electrons are conventionally designated by the index l.[25]

In the zeroth approximation we can ignore the interaction of the electrons in the aromatic part of the molecule with the l-electrons of the substituent. The configuration which contributes most to the ground state is obtained from the doubly occupied π orbitals and the atomic l orbital. In addition to this configuration we can construct other configurations corresponding to the excitation of π electrons and configurations with an electronic transition from an l orbital to a π^* orbital. The latter configurations (involving charge transfer) can be designated $l\pi^*$ (or la_π configurations in Kasha's nomenclature[25]). These make some contribution to the wave function of the ground state. The wave functions of the excited states are constructed by superimposing $\pi\pi^*$ and $l\pi^*$ configurations. In molecules containing relatively few π-electrons these configurations have comparable weight[29]. Electronically excited states in molecules with l-electrons have therefore been designated[29] as $\pi l, \pi^*$. The only difference between the $\pi l, \pi^*$ states of planar molecules and $\pi\pi^*$ states is a substantial redistribution of the electron density during the transition from the S_0 to the $\pi l, \pi^*$ state. Nevertheless the difference in the corresponding luminescence spectra is very marked (see below). The designation is widely used at present, though it is somewhat artificial, since as the number of π-electrons increases the contribution of $l\pi^*$ configurations to the excited states decreases and the $\pi l, \pi^*$ states are continuously transformed into $\pi\pi^*$ states[29].

The situation is very similar in the case of molecules containing atoms (or electron-acceptor groups) with low-lying empty atomic orbitals (ν orbitals). The charge-transfer configurations are now those in which an electron has been transferred from a π orbital to a ν orbital: $\pi\nu$ configurations, which can interact with the $\pi\pi^*$ configurations of the aromatic part of the molecule. Therefore we have suggested[30] the designation $\pi,\nu\pi^*$ for the $\pi\pi^*$ excited states in the special case of boron-aromatic molecules. This designation has not yet been extended to include compounds with electron-acceptor groups (H–C=O, NO_2, etc.), in which the vacant π^* orbitals of the groups act as ν orbitals. We therefore retain the conventional designation $\pi\pi^*$ of these states. In molecules containing l and ν orbitals the excited states can, of course, be termed $\pi l, \nu\pi^*$. In the case of molecules with n-electrons and ν-orbitals we can use the designation $n,\nu\pi^*$ for the $n\pi^*$ states. We should stress that the LO method is often applied to aromatic molecules which do not contain l and ν orbitals, but consist of weakly bound fragments. In this case the π and π^* orbitals of the fragments play the role of localised orbitals.

As stated above, the concept of π-electrons localised on a hetero-atom is more characteristic of the LO than of the MO method. Indeed, calculations by the MO method show some delocalisation (often substantial) of the n-electrons on the σ-orbitals[31-34]. Experimental data[35], mainly on vibronic spectra (see Section VI), indicate a large degree of localisa-

§ The exchange interaction A_{ik} of the electrons should not be confused with the exchange interaction of the Heitler–London theory, which in most cases (in the S-state) leads to bonding and therefore has a negative sign.

tion of n-electrons and $n \rightarrow \pi^*$ transitions. The slight inconsistency between MO results and experiment can be avoided by allowing for the interaction of the $\sigma\pi^*$ configurations, which leads to marked localisation of the excitation. It follows that in order to calculate the energy of $n\pi^*$ states allowing for the interaction of the $n\pi^*$ configurations but not of the $\sigma\pi^*$ configurations we must use a localised model of the n-electrons with partial allowance for electron correlations.

Only very brief mention of non-planar molecules can be made here. If the deviation from planarity is small, and the energies of the π orbitals are significantly different from those of the σ orbitals, the unavoidable mixing of the π and σ orbitals is also not very great[36]. This mixing has little effect on the position of the lower electronically excited states of the molecules, and therefore on the probability of singlet–singlet optical transitions. However one of the parameters of the electronic structure of molecules is very sensitive to deviations from planarity: the spin–orbital interaction (see Section V). We must therefore allow for this effect when considering $S-T$ conversion and the properties of triplet states. Throughout this paper the lower excited states of this type of molecule will be interpreted as $\pi\pi^*$, πl, π^*, etc.

IV. EFFECT OF STRUCTURE ON THE POSITION OF THE LOWER ELECTRONICALLY EXCITED STATES IN MOLECULES

Calculations of the energies of $\pi\pi^*$ states are described in many recent publications[17,18,20–24,37–41]. In spite of the variety of the methods used, two important conclusions can be drawn from these measurements. 1) The energy of the $\pi\pi^*$ states decreases as the length of the chain of conjugated bonds in the molecule increases, the magnitude of this effect increasing with the conjugation energy. 2) The difference in energy between the lower $S_{\pi\pi^*}$ and the lower $T_{\pi\pi^*}$ states is relatively high ($\geq$1 eV or 10^4 cm^{-1}, see below)[21–24,29,37–41]. The first of these conclusions can be obtained by the simple Hückel method. Thus, for a polyene chain containing $N\pi$-electrons (where N is even) the energy of the long-wave transition (between the $(N/2)$ and $(N/2)+1$ orbitals) is given by the expression[28]

$$E_{\pi\pi^*} = 4|\beta| \sin \frac{\pi}{2(N+1)}, \qquad (19)$$

where β is the resonance integral. We can see from this equation that the energy of the transition decreases as N increases, and vanishes in the limit of $N \rightarrow \infty$. However formula (19) is not applicable at high values of N, since experimental values of $E_{\pi\pi^*}$ tend towards a finite limit. It has been shown[42] that allowance for electron correlation makes the asymptotic value of $E_{\pi\pi^*}$ finite at high values of N. The energies of $\pi\pi^*$ states in aromatic molecules span the range 5–1 eV. The general rules describing the change in the energy of $\pi\pi^*$ states with the size and the topology of the conjugated bond system in aromatic hydrocarbons are discussed in Refs.4 and 41.

The second conclusion, which is fully consistent with experiment, stems from the presence of large (~10 eV) $\gamma_{\nu\nu}$ one-centre Coulomb integrals in the expression for the exchange integral A_{ik} of Eqn.(17): the coefficients in front of $\gamma_{\nu\nu}$ are not small, since the π and π^* orbitals are not spatially separated.

The energy of the $n\pi^*$ states depends on several characteristics of the molecules, the most important of which are the nature of the atom with n-electrons, the length and topology of the chain of conjugated bonds, and the presence of electron-donor substituents (l-orbitals) in the system.

According to formula (15) the energy of the $n\pi^*$ states decreases as the ionisation potential of the atom with n-electrons decreases. It follows, for example, that the energy of the $n\pi^*$ states should decrease on going from the carbonyl to the analogous thiocarbonyl compounds. This conclusion is confirmed by the experimental $S_{\pi\pi^*}$ energies[4] of the $S_{\pi\pi^*}$ states for benzophenone (~3.3 eV) and thiobenzophenone (1.8 eV) molecules.

Let us discuss the dependence of the energy of the $n\pi^*$ states on the length of the conjugated chain. The simplest treatment, based on the Hückel method, leads to the conclusion that the energy of the $n\pi^*$ states should decrease with increase in the length of the chain of conjugated bonds. Thus, if we assume that the energy of the n-orbital ε_n is independent of the length of the conjugated chain (a valid assumption, since the ionisation potential for the n-electrons is only weakly affected by the number of π-electrons[43]) we can express the energy of the $n \rightarrow \pi^*$ transition as $E_{n\pi^*} = \varepsilon_{\pi^*} - \varepsilon_n$, where ε_{π^*} is the energy of the lower vacant π-orbital. For a polyene molecule with a substituent containing n-electrons (e.g. O=CH–(CH=CH)$_{(N/2)-1}$–H) we have $\varepsilon_{\pi^*} = \alpha + 2\beta \cos[j\pi/(N+1)]$ with $j = (N/2)+1$ if we ignore the effect of the hetero-atom on the π-system[28]. Therefore[44]

$$E_{n\pi^*} = 2\beta \cos \frac{(N+2)\pi}{2(N+1)} + \alpha - \varepsilon_n = \Delta I_n + 2|\beta| \sin \frac{\pi}{2(N+1)}, \qquad (20)$$

where ΔI_n is a parameter of the same order of magnitude as the difference in ionisation potential between the p-electrons of the C atom and the n-electrons. It follows from (19) and (20) that the energy of the $n\pi^*$ states increases more slowly than the energy of the $\pi\pi^*$ states (by a factor of two, on average) when N increases. Since for small N the energy of the $n\pi^*$ states is lower than that of the $\pi\pi^*$ states[4,41] the levels should become inverted as N increases. This result[44] was one of the basic propositions used to construct a systematic classification of the molecules.

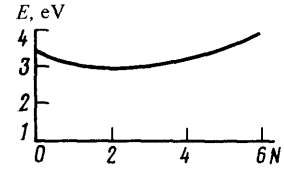


Figure 2. Energy of the $S_{n\pi^*}$ states of H–(CH=CH)$_N$–HC=O molecules as a function of N.

A stricter analysis[23], allowing for electron interaction and configurational interaction, confirmed this conclusion but revealed additional complications. It is clear from formulae (17) and (18) that the energy of the transition is determined by two terms, since the quantity A_{ik} is small for $n\pi^*$ states (see below). The first term, $\varepsilon_{\pi^*} - \varepsilon_n$, varies with N as described by formula (20). The Coulomb interaction integral $J_{n\pi^*}$ also decreases as N increases, since the π-electrons are becoming more delocalised. These two terms appear in the expressions with different signs, and therefore different variants of the change in the $n \rightarrow \pi^*$ transition energy with N are possible: the energy can decrease, remain unchanged, or increase as N increases. All these possibilities are realised in the polyene ketone molecules (Fig.2) with different values of N. The conclusion that the $n\pi^*$ and $\pi\pi^*$ states can become inverted as N increases remains valid, but the value of N for which inversion takes place is defined more exactly.

The singlet–triplet splitting of the $n\pi^*$ states is much smaller than the splitting of the $\pi\pi^*$ states. This is because the expression for the $A_{n\pi^*}$ exchange integral contains only the κ exchange integrals, the largest of which (one-centre integral) is ~1 eV. Furthermore the spatial separation of the n- and π-electrons makes $A_{n\pi^*}$ smaller than $A_{\pi\pi^*}$. Calculations[22–24,45–52], supported by experiment[4,41], give values between 0.2 and 0.5 eV for the $S-T$ splitting of the $n\pi^*$ states.

Calculated values of the energies of the $S_{\pi\pi^*}$, $T_{\pi\pi^*}$, $S_{n\pi^*}$, and $T_{n\pi^*}$ states for H–(CH=CH)$_N$–CH=O molecules[23] are shown in Fig.3. We can distinguish five different variants (or types) of relative position of the electronic states. Similar results have been obtained for aromatic ketones (Fig.4), and also (both theoretically[23,24,52] and experimentally[2–4]) for aza-aromatic and nitro compounds, quinones, and thioketones. All these results indicate the existence of five different types of relative position of $n\pi^*$ and $\pi\pi^*$ S and T state. Classification of molecules into five types according to the relative position of these energy states was suggested for the first time[53] in 1966.

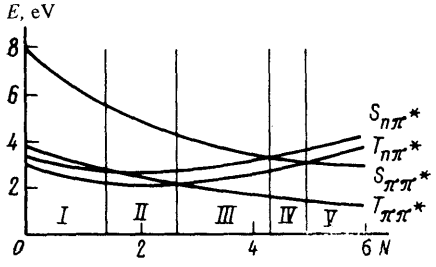


Figure 3. Five types of relative position of the electronic states of H–(CH=CH)$_N$–HC=O molecules.

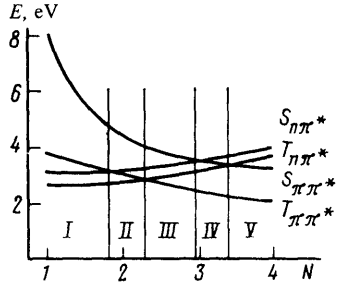


Figure 4. Relative position of the electronic states of Ph–(CH=CH)$_N$–HCO molecules.

The change in relative position of the $n\pi^*$ and $\pi\pi^*$ states caused by electron-donor substituents is due to the change in energy of both the $n\pi^*$ and $\pi\pi^*$ states attending the transformation of the latter into $\pi l, \pi^*$ states. Many theoretical studies of the position of the $\pi l, \pi^*$ states with respect to the $\pi\pi^*$ states of the unsubstituted hydrocarbons have been published[24,28,29,52,54]: the conclusion in every case is that the introduction of l-orbitals into a system of π-conjugated bonds decreases the energy of the lower $\pi\pi^*$ (or, more accurately, $\pi l, \pi^*$) states. This effect is most marked when the ionisation potential of the l-electrons is low and the chain of conjugated bonds is short[29,52]. The influence of the substituent decreases as the length of the conjugated chain of the hydrocarbon part of the molecule increases. This is a consequence of the lack of a sharp boundary between $\pi\pi^*$ and $\pi l, \pi^*$ states (in contrast to the $\pi\pi^*$ and $n\pi^*$ states).

An important spectroscopic property of the $\pi l, \pi^*$ states is their relatively low $S-T$ interval (0.7–0.8 eV [25–29]), which is lower than that of the $\pi\pi^*$ states of aromatic hydrocarbons though it is greater than that of $n\pi^*$ states. This lowering is due to the contribution of $l\pi^*$ configurations to the wave functions of the excited states and to the spatial separation of the l and π orbitals, which lowers the value of A_{ik} in Eqn.(17).[29,54,55] All these statements apply also to the $\pi, \nu\pi^*$ states[30].

The introduction of electron-donor groups into the molecule increases the energy of the $n\pi^*$ states. The simplest explanation of this effect[46,56] postulates an increase in the energy level of the π^* orbital on introducing l-orbitals into a π-conjugation system. Calculations by the PPP method[24] indicate a substantial contribution to the increase in energy of the $n\pi^*$ states from the change in Coulomb interaction of the electrons. The electronic states of the nitrobenzene molecule and its amino derivatives, calculated[24] by that method, are shown in Fig.5: it is clear that the introduction of l-electrons does indeed raise the energy of the $n\pi^*$ states, the magnitude of the effect depending on the position of the substituent. Many examples of the effect of electron-donor substituents on the relative position of the $n\pi^*$ and $\pi\pi^*$ (or $\pi l, \pi^*$) states are given in Ref.4. Substituents with ν-orbitals should lower the energy of the $n\pi^*$ states[52], but this effect has not been adequately studied.

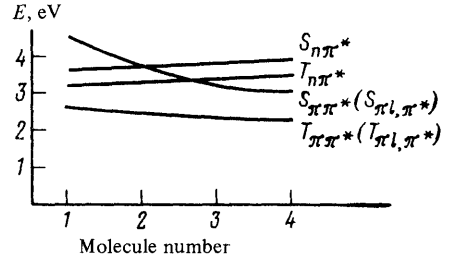


Figure 5. Electronic states of the following molecules: 1) nitrobenzene, 2) *p*-nitroaniline, 3) *m*-nitroaniline, 4) *o*-nitroaniline.

Another factor which influences the relative position of the $n\pi^*$ and $\pi\pi^*$ states is the hydrogen bond, or the formation of complexes with protonic solvents (in the limit, the protonation of the molecule). Hydrogen bond formation (or protonation) leads to bonding of the n-electrons, increases I_n in Eqn.(15), and hence causes a sharp increase in the energy of the $n\pi^*$ states, which can invert the relative position of the levels corresponding to $\pi\pi^*$ and $n\pi^*$ states[57,58].

In conclusion we shall summarise the properties of $n\pi^*$ and $\pi\pi^*$ states which can be used to distinguish these states experimentally. The energy of the $\pi\pi^*$ states decreases steeply as the length of the conjugation chain increases. At the same time the energy of the $n\pi^*$ states can decrease (though less markedly), it can remain unchanged, or it can even increase. The $S-T$ splitting of the $\pi\pi^*$ states is $\geq$1 eV, and substantially greater than the $S-T$ splitting of the $n\pi^*$ states (~0.2–0.5 eV). The $S-T$ splitting of the $\pi l, \pi^*$ (or $\pi\nu, \pi^*$) states lies between these two extremes. The introduction of l-electrons into the molecule produces a large increase in the energy of the $n\pi^*$ states and a decrease

in the energy of the $\pi\pi^*$ states (accompanied by their transformation into $\pi l, \pi^*$ states). Hydrogen bond formation (or protonation) produces a large increase in the energy of the $n\pi^*$ states and can lead to inversion of the levels. The most fundamental of these results is the conclusion that five types of relative position of the S, T, $n\pi^*$, and $\pi\pi^*$ states are possible. The factors listed above determine which of these five types is realised in practice.

V. SPIN–ORBIT INTERACTION IN ELECTRONIC STATES OF MOLECULES

The spin–orbit interaction (spin–orbit bond) of electronic states is characterised by the matrix element $\langle i|H_{so}|f\rangle$, where $|i\rangle$ and $|f\rangle$ are electronic wave functions of states of different multiplicity. The spin–orbit interaction operator is written[59]

$$H_{so}=\frac{1}{2c^2}\sum_q\sum_i\frac{Z_q}{r_{qi}^3}(\hat{l}_{iq}\cdot\hat{S}_i), \tag{21}$$

where c is the velocity of light, Z_q is the effective charge of the nucleus q, r_q is the distance between this nucleus and the electron i, and $\hat{l}_{iq}$ and $\hat{S}_i$ are the operators of the orbital and spin moment of the electrons. The brackets in Eqn.(21) contain the scalar product of the vector operators $\hat{l}_{iq}$ and $\hat{S}_i$. According to this approximation (whose justification is discussed in Ref.60) the H_{so} operator is a one-electron operator. Hence the matrix elements of the configurations included in $|i\rangle$ and $|f\rangle$, which differ only by one spin orbital, are non-zero[61]. This is one of the selection rules which the matrix elements of the H_{so} operator must satisfy: it implies, for example, that the $\pi\pi^*$ states are not bound to $\sigma\sigma^*$ states by spin–orbit interaction, though $\pi\pi^*$ states may be bound to $n\pi^*$ states.

Allowing for the effect of the spin moment projection operators on the spin functions[62] and considering the interaction of a singlet S_{ik} excited configuration (transition of an electron from the i-th orbital of the ground state configuration to the k-th vacant orbital) and of the three triplet configurations $T_{ik'}^0$, $T_{ik'}^{+1}$, and $T_{ik'}^{-1}$ (with projections of the spin moment on the z axis of 0 and ±1 respectively) we can write, after integration of the spin variables[63,64],

$$\begin{aligned}
\langle S_{ik}|H_{so}|T_{ik'}^0\rangle &= -\langle k|H_{so}^z|k'\rangle,\\
\langle S_{ik}|H_{so}|T_{ik'}^{+1}\rangle &= \frac{1}{\sqrt{2}}\langle k|H_{so}^x|k'\rangle+\frac{i}{\sqrt{2}}\langle k|H_{so}^y|k'\rangle,\\
\langle S_{ik}|H_{so}|T_{ik'}^{-1}\rangle &= -\frac{1}{\sqrt{2}}\langle k|H_{so}^x|k'\rangle+\frac{i}{\sqrt{2}}\langle k|H_{so}^y|k'\rangle,
\end{aligned} \tag{22}$$

where, for example,

$$H_{so}^z=\frac{1}{4c^2}\sum_q\frac{Z_q}{r_{iq}^3}\hat{l}_{iqz},$$

and $\hat{l}_{iqz}$ is the operator of the projection of the orbital moment on the z axis. Integration of Eqn.(22) is carried out with respect to the coordinates of one electron.

Similar formulae can be written for the matrix elements in the case of the integration of S_{ik} configurations with T_{jk} configurations, or of the interaction of ground state configurations with triplet configurations. If the multi-configuration approximation is used for the wave functions the expression for $\langle i|H_{so}|f\rangle$ contains a sum of matrix elements in the form of (22) with coefficients which define the contribution of each configuration to $|i\rangle$ and $|f\rangle$.

If the $|k\rangle$ and $|k'\rangle$ molecular orbitals are in LCAO form the matrix elements of (22) are evaluated by finding the effect of the $\hat{l}_x$, $\hat{l}_y$, and $\hat{l}_z$ operators on the atomic orbitals and calculating the one-, two-, and three-centre integrals for electron–nucleus interaction. We note that the one-centre integrals (when not identically equal to zero) are usually greater in absolute value than the two-centre integrals, and the latter are usually greater than the three-centre integrals.

In many important cases the coordinate system can be defined so that one of the matrix elements in (22) is non-zero: for example, the matrix element of the H_{so}^z operator. The effect of the $\hat{l}_x$, $\hat{l}_y$, and $\hat{l}_z$ operators on the p-functions is easily found from the explicit form of these operators[13] and of the atomic orbitals (Eqn.(13)):

$$\hat{l}_z p_z=0,\ \hat{l}_z p_x=ip_y,\ \hat{l}_z p_y=-ip_x. \tag{23}$$

In these expressions the $\hat{l}_z$ operator and the p-functions are given for the same centre. The action of the $\hat{l}_x$, $\hat{l}_y$, and $\hat{l}_z$ operators on the s-functions is to make these functions vanish, since they are eigenfunctions of the $\hat{l}_x$, $\hat{l}_y$, $\hat{l}_z$ operators with eigenvalues of zero. If the operators and the functions are given for different centres appropriate formulae can be obtained[64].

We shall now turn to specific cases. For the interaction of the $S_{\pi\pi^*}$ and $T_{\pi\pi^*}$ states of planar molecules the $\langle\pi_k^*|H_{so}^z|\pi_k^*\rangle$ matrix element (the only non-zero one if the z axis is perpendicular to the plane of the molecule) is expressed in terms of one-, two-, and three-centre integrals containing only p_z atomic functions (or $2p_z$ in the case of aromatic hydrocarbons). One-centre integrals are identically equal to zero as a consequence of the first of formulae (23). The two-centre integrals are also zero[59,64]. In this case only the three-centre integrals are finite[59], and even these are small in absolute value because the overlap of the $2p_z$-functions of the different atoms is not very marked and the interaction energy falls off very rapidly ($\propto r^{-3}$) with increasing interatomic distance. Calculations allowing for the terms of the spin–orbit interaction operator not included in (21) give ~0.3 cm^{-1} for the spin–orbit bond energy of the $\pi\pi^*$ states[65]. The matrix elements of the spin–orbit interaction of the $n\pi^*$ states also have approximately this value, since π^* orbitals appear as the k and k' orbitals in this case. A spin–orbit interaction of ~0.3 cm^{-1} should be interpreted as small.

However even this level of spin–orbit interaction is not always realised in the $\pi\pi^*$ states. The matrix elements of the H_{so} operator for molecules possessing symmetry elements must obey the selection rules (which are fully discussed in Ref.41). For the present discussion it is important to note that as a consequence of the symmetry properties the lower triplet state of many aromatic hydrocarbons is not connected by spin–orbit interaction to the electronic ground state[41]. This conclusion is highly relevant to the mechanism of $T-S$ conversion in aromatic hydrocarbons.

In the case of $n\pi^*$ and $\pi\pi^*$ states of different multiplicity the $\langle k|H_{so}^z|k'\rangle$ matrix element will include (for $|k\rangle$) the wave function of the n-electron orbital, and for $|k'\rangle$ the wave function of the π-electron orbital. We choose a coordinate system such that the x axis is perpendicular to the plane of the molecule and the axis of symmetry of the wave function of the n-orbital (in the one-centre approximation) coincides with the y axis. From the second formula (23) we can easily obtain

$$\langle S_{n\pi^*}|\hat{H}_{so}|T_{\pi\pi^*}\rangle\cong -ic_{k'n}b\,\frac{1}{4c^2}\left[np_y np_y\left|\frac{Z_n}{r^3}\right|\right], \tag{24}$$

where $c_{k'n}$ is the expansion coefficient of the k' π-orbital for an atom containing n-electrons. The one-centre integral $\left[np_y np_y\left|\frac{Z}{r^3}\right|\right]$ describes the interaction of the electron density $|np_y(r)|^2$ with the nucleus of the atom containing n-electrons, which has an effective charge Z. The other integrals in (24) are ignored (see below). An identical expression (but with

the opposite sign) can be obtained for the $\langle S_{\pi\pi^*}|H_{SO}|T_{n\pi^*}\rangle$ matrix element.

The integral in formula (24) can be evaluated analytically: the result is $1/3Z^4n^{-3}$, where n is the principal quantum number of the p-orbital. Equating Z to the Slater charges on the nuclei, and taking the $c_{k'n}$ values obtained in any of the π-MO approximations, we can find the value of (24). Calculations of this type[24,60,63,66-70] show that the spin–orbit interaction energy of the $n\pi^*$ and $\pi\pi^*$ states of different multiplicity is greater than ~10 cm^{-1} in the case of molecules containing N, O, and S atoms, and greater than ~100 cm^{-1} in molecules with heavy atoms (Br, I).

The one-centre integral $\left[np_y np_y \left|\frac{Z}{r^3}\right.\right]$ is used in the theory of atomic spectra to express the multiplet splitting constant ζ (given[71] as $1/6c^{-2}Z^4n^{-3}$). Hence the matrix element (24) can be written

$$\langle S_{n\pi^*}|H_{so}|T_{\pi\pi^*}\rangle = -ic_{k'n}b\frac{\xi}{2}. \qquad (25)$$

Calculations by formula (25) with experimental values of ζ give values of the spin–orbit bond of $n\pi^*$ and $\pi\pi^*$ states in good agreement with those given by formula (24). Allowance for the delocalisation of n-electrons and for the two-centre integrals in the expression for the matrix elements, and the use of multi-configuration wave functions[24], have very little effect on the result of the calculation.

The order of magnitude of the matrix element in formula (24) can be determined (with low precision, and with some *ad-hoc* assumptions) from data on the life time of the $T_{n\pi^*}$ states[72]. These "experimental" values of the spin–orbit coupling of $T_{n\pi^*}$ and $S_{\pi\pi^*}$ states are consistent with calculated values[73].

Formula (24) was obtained by assuming that the molecule contains only one pair of n-electrons. In more complicated cases the expression for the $\langle S_{n\pi^*}|H_{SO}|T_{\pi\pi^*}\rangle$ matrix element contains a summation over the different (equivalent) atoms with n-electrons. In these circumstances the one-centre integrals could mutually cancel out, making the matrix element small. In practice this does not happen. Because of the small splitting of the $n\pi^*$ states (in this case, $S_{n\pi^*}$) the vibronic interaction with non-fully-symmetrical vibrations leads to almost complete mixing[33]. The order of magnitude of the matrix element is found to be independent of the symmetry of the wave functions of the n-electrons.

These considerations lead to the very important conclusion that the spin–orbit interaction of states of different orbital type ($n\pi^*$ and $\pi\pi^*$) exceeds more than 30-fold the spin–orbit interaction of states of the same orbital type. The ratio of the square of their moduli, which appears in all calculations, is 10^3–10^4 for molecules containing N, O, and S atoms and over 10^4 for molecules containing halogen and other heavy atoms. This conclusion was reached[72] for molecules of aromatic azines from measurements of the life-time of $T_{n\pi^*}$ and $T_{\pi\pi^*}$ states, and from a theoretical study[63] of azines and of the carbonyl derivatives of thiocarbonyl compounds and nitro compounds. This large difference between the spin–orbit coupling between the different states is not surprising, since in the case of $n\pi^*$ and $\pi\pi^*$ interactions the matrix element contains one-centre integrals, whereas in the interaction of states of the same orbital type the matrix element contains only three-centre integrals.

The following general statement appears to be valid: if the $|k\rangle$ and $|k'\rangle$ orbitals (or one of them) contain different p-functions in their expansion with respect to atomic orbitals we can expect to find non-zero one-centre integrals in the expression (22) for one of the matrix elements. In general this matrix element is quite large, and increases rapidly with the charge on the nucleus of the atoms present in the molecule.

Other electronic states may be mentioned briefly. The matrix elements of the spin–orbit interaction operator for $\pi\pi^*$ and $\sigma\pi^*$ (or $\pi\sigma^*$) states of aromatic molecules contain non-zero one-centre integrals, leading to large interaction energies. The spin–orbit interaction amounts to 2–5 cm^{-1} for molecules of aromatic hydrocarbons[64,65,74], and exceeds 10 cm^{-1} for their derivatives containing atoms with a nuclear charge greater than that of carbon atoms. The spin–orbit interaction of $\sigma\sigma^*$ states is also large, which explains the low quantum yield of fluorescence in aliphatic molecules[64].

Non-planar molecules containing π-electrons are especially interesting. Typical of these are many aromatic and unsaturated amines in which the nitrogen atom is in an sp^3 hybrid state. As was pointed out in Section III, in these molecules the orbitals corresponding to the π-orbitals of the planar configuration include a small contribution from σ-orbitals, and their expansion in general contains not only p_z functions but also other p-functions (with a small statistical weight). Accordingly, the matrix elements of the spin–orbit interaction operator for the S_0, $S_{\pi l}, \pi^*$, and $T_{\pi l}, \pi^*$ states contain one-centre integrals, and their value is estimated[36] to be of the order of 1 cm^{-1}, i.e. intermediate between the corresponding quantities for the $\pi\pi^*$ states and the $n\pi^*$ and $\pi\pi^*$ states. When the amines form complexes with electron-acceptor systems (protons) the contribution of $l\pi^*$ configurations to the excited states decreases, and the spin–orbit interaction decreases at the same time[75]. These effects are manifest in the luminescent properties of the amines[76].

All the above statements apply equally to non-planar molecules with ν-orbitals, but so far no calculations of spin–orbit interactions have been reported for these molecules.

The spin–orbit interaction of $\pi l, \pi^*$ and $n\pi^*$ states is slightly smaller than that of $\pi\pi^*$ and $n\pi^*$ states in molecules which do not contain l-electrons. This is due to the spatial separation of the n- and l-orbitals[24].

The fundamental conclusion from this discussion is the statement[63,72] that the spin–orbit interaction of S and T states of different orbital type in planar molecules is over 30 times greater than the spin–orbit interaction of states of the same orbital type. This conclusion is crucially important to an understanding of the luminescence-spectral properties of molecules.

VI. RADIATIVE TRANSITIONS IN AROMATIC MOLECULES

The term radiative transition denotes transitions between vibronic states of molecules accompanied by the absorption or emission of photons. The photon emission process (luminescence) may or may not involve a change in the multiplicity of the states. In the latter case it is termed fluorescence, in the former case phosphorescence.

The probability of a transition from the state $|i\{n\}\rangle$ to the state $|f\{n'\}\rangle$ is proportional to the square of the matrix element $\langle i\{n\}|\mathbf{r}|f\{n'\}\rangle$, where integration is carried out over the variables r and R, and $\mathbf{r} = \sum_i \mathbf{r}_i$ is the sum of the radius vectors which define the position of the electrons in the molecule[13].

The probability of transitions which are allowed by symmetry and multiplicity can usually be calculated quite satisfactorily by the Condon approximation

$$\langle i\{n\}|\mathbf{r}|f\{n'\}\rangle = d_{if}\langle\{n\}|\{n'\}\rangle, \qquad (26)$$

where $\mathbf{d}_{if} = \langle i|\mathbf{r}|f\rangle$. The second multiplier in Eqn. (26) is the Franck–Condon factor, which defines the intensity of the individual spectral lines of the vibronic band. In the case of transitions allowed by multiplicity but forbidden by

symmetry the Condon approximation becomes invalid because the quantity d_{if} vanishes. If the transition is from the ground state to an electronically excited state we only need to allow for the dependence on R of the electronic wave function of the excited state. If the Herzberg–Teller expansion (9) is applicable we can write the following expression for the matrix element (26):

$$\langle i\{n\}|\mathbf{r}|f\{n'\}\rangle = \sum_{f'\neq f,q} \mathbf{d}_{if'} a^q_{f'f} \langle\{n\}|\delta R_q|\{n'\}\rangle = \\ = \sum_q \tilde{\mathbf{d}}^q_{if} \langle\{n\}|\delta R_q|\{n'\}\rangle, \quad (27)$$

where the subscript f' denotes the number of the electronically excited state, $a^q_{f'f}$ is defined by Eqn.(10), and δR_q is the deviation of the coordinate of the oscillator (q) from the equilibrium position. The matrix elements $\langle i\{n\}|\mathbf{r}|f\{n'\}\rangle$ for pure spin functions of different multiplicity are zero because of the orthogonality of the spin functions. The probability of transitions between states of different multiplicity can be made finite only by allowing for spin–orbit interaction. In this case, by analogy with (27) we obtain

$$\langle i\{n\}|\mathbf{r}|f\{n'\}\rangle = \sum_{f'\neq f} \mathbf{d}_{if'} b_{f'f} \langle\{n\}|\{n'\}\rangle = \tilde{\mathbf{d}}_{if}\langle\{n\}|\{n'\}\rangle, \quad (28)$$

where $b_{f'f} = \langle f'|H_{SO}|f\rangle (E_f - E_{f'})^{-1}$ and the multiplicity of the state $|f'\rangle$ is different from that of the state $|f\rangle$ but equal to that of the state $|i\rangle$. If necessary we can allow for the mixing of the wave function of the ground state $|i\rangle$ with the wave functions of the excited states in the derivation of formulae (27) and (28). By comparing the expressions (26), (27), and (28) we can understand the origin of the matrix element of a transition forbidden by multiplicity and symmetry[77] but which is allowed in the second-order perturbation theory for the vibronic interaction operators (10) and H_{SO}.

Transitions involving the absorption of a photon are usually characterised by their oscillator strength f, and the reverse transitions with emission of a photon by the rate constant for the radiative dissociation of the state (k_r) or by the radiative life time $\tau = 1/k_r$. In most cases the quantities f and k_r denote summations over all values of $\{n'\}$ in the last term with averaging (using the Boltzmann factor) over the vibrational states of the first term. Allowing for normalisation and for the full set of vibrational wave functions in the Condon approximation we have[13]

$$f = \frac{2\omega}{3}|\mathbf{d}_{if}|^2 = \frac{2\omega}{3}(x^2_{if} + y^2_{if} + z^2_{if}), \quad (29)$$

$$k_r = \frac{4\omega^3}{3c^3}|\mathbf{d}_{if}|^2 = \frac{4\omega^3}{3c^3}(x^2_{if} + y^2_{if} + z^2_{if}), \quad (30)$$

where ω is the frequency corresponding to the maximum of the vibronic band, c is the velocity of light, $x_{if} = \langle i|x|f\rangle$, etc. Eqns.(29) and (30) apply to non-degenerate states. In the case of a multiplicity-forbidden transition the value of $\mathbf{d}_{if}$ given by formula (28) must be used in formulae (29) and (30). From (29) and (30) we obtain the useful relationship $k_r = (\omega^2/1.5)f\ s^{-1}$ (if ω is expressed in cm^{-1}). In the case of symmetry-forbidden transitions, and assuming that the equilibrium position of the oscillators (q) involved in the transition is the same in states $|i\rangle$ and $|f\rangle$, we obtain (for low temperatures)

$$f = \frac{2\omega}{3}\sum_q |\mathbf{d}^q_{if}|^2 (2\mu_q\omega_q)^{-1}, \quad (31)$$

$$k_r = \frac{4\omega^3}{3c^3}\sum_q |\mathbf{d}^q_{if}|^2 (2\mu_q\omega_q)^{-1}, \quad (32)$$

where μ_q and ω_q are the reduced mass and frequency of the oscillator q. We note that the f and k_r values for symmetry-forbidden transitions are a function of temperature.

Let us examine the characteristic quantities f and k_r. We shall begin with the symmetry-allowed singlet–singlet transitions. In the case of $\pi \to \pi^*$ transitions the matrix element $\mathbf{d}_{ij}$ equals $\sqrt{2}\langle\pi_i|\mathbf{r}|\pi^*_f\rangle$, where π_i and π^*_f are the molecular orbitals between which the electronic transition takes place. From symmetry considerations the matrix components of the vector $\mathbf{r}$ lying in the plane of the molecule are non-zero. It follows that the $\pi \to \pi^*$ transitions are polarised in the plane of the molecule. The matrix elements $|\langle\pi_i|\mathbf{r}|\pi^*_f\rangle|$ are relatively large (~2 a.u.). According to formula (29) the value of f is approximately 0.1.[37–39,78–80]. For large conjugated molecules (e.g. dyes) f could approach or even exceed unity. From formula (30) we find that k_r for $S_{\pi\pi^*}$ states is $\sim 10^8$–$10^7\ s^{-1}$, and the radiative life time is $\sim 10^{-8}$–10^{-7} s. In dye molecules the k_r value can be as high as $10^9\ s^{-1}$.[41] Singlet–singlet $n \to \pi^*$ transitions are allowed in many aza-aromatic molecules, in which the n-orbital includes a contribution from the 2s atomic function. The matrix element of the transition contains the non-zero one-centre integrals $[2s2p_z|z]$, which can be evaluated[9] and found to be ~1 a.u. Calculations of f in azines[80–82] give $\sim 5\times10^{-3}$–10^{-2}, and $\sim 10^6\ s^{-1}$ for k_r in $S_{n\pi^*}$ states. These values agree with experiment[41]. The allowed $n \to \pi^*$ transitions are polarised perpendicular to the plane of the molecule. The mechanism of $\sigma \to \pi^*$ and $\pi \to \sigma^*$ transitions in aromatic hydrocarbons is entirely analogous: these transitions have f values of the same order and they are polarised perpendicular to the plane of the molecule[78].

In the molecules of carbonyl, thiocarbonyl, and nitro compounds, in which the n-orbitals have some p-character, and also in some azines, singlet–singlet $n \to \pi^*$ transitions are symmetry-forbidden in the Condon approximation. In order to calculate their probability we must allow for the vibronic interaction. Since we can put $(2\mu_q\omega_q)^{-1} \cong 10^{-1}$ in Eqn.(28), and $a_{f'f}$ has a similar value[70], we obtain $\sim 5\times10^{-4}$ and $\sim 10^5\ s^{-1}$ for f and k_r respectively in the case of symmetry-forbidden $n \to \pi^*$ transitions[81,83,84]. The polarisation of these transitions is determined by the polarisation of the transitions which limit the intensity, and it can therefore vary[83,85]. The probability of the symmetry-forbidden $\pi \to \pi^*$ transitions is similar to that of allowed $n \to \pi^*$ transitions in azines[41,86,87].

Singlet–triplet $\pi \to \pi^*$ transitions are allowed because of the spin–orbit interaction of the $T_{\pi\pi^*}$ states with $S_{\pi\pi^*}$, $S_{\sigma\pi^*}$, $S_{\pi\sigma^*}$, and $S_{n\pi^*}$ states (if n-electrons are present in the molecule), and of the interaction of the S_0 state with the $T_{\pi\pi^*}$, $T_{\sigma\pi^*}$, $T_{\pi\sigma^*}$, and $T_{n\pi^*}$ states. The spin–orbit coupling between the $T_{\pi\pi^*}$ state and the $S_{\sigma\pi^*}$, $S_{\pi\sigma^*}$, and $S_{n\pi^*}$ states is fairly strong (see Section V), but the oscillator strengths of the $S_0 \to S_{\sigma\pi^*}$, $S_0 \to S_{\pi\sigma^*}$, and $S_0 \to S_{n\pi^*}$ transitions are small. The oscillator strengths of the $S_0 \to S_{\pi\pi^*}$ transitions are large, but the spin–orbit coupling between $T_{\pi\pi^*}$ and $S_{\pi\pi^*}$ states is weak. It follows that the terms of the summation in Eqn.(28) contain a small multiplier for these transitions, and $\tilde{\mathbf{d}}_{if}$ is small. The situation is unchanged if allowance is made for the interaction of the S_0 state with the T states. The values of f and k_r for S–T transitions are calculated[88,89] to be $\sim 10^{-7}$–10^{-8} and ~10–1 s^{-1} respectively. Hence the radiative life time of the $T_{\pi\pi^*}$ states is ~0.1–1 s, i.e. these states are relatively long-lived (see below). In the case of symmetry-forbidden S–T transitions the life time of the $T_{\pi\pi^*}$ states is an order of magnitude greater[41,77]. It was shown experimentally[90,91,96] that $T_{\pi\pi^*} \to S_0$ transitions in aromatic hydrocarbons are polarised almost perpendicular to the plane of the molecule, and therefore k_r is determined by the spin–orbit interaction of $\pi\pi^*$ states with $\sigma\pi^*$ and $\pi\sigma^*$ states.

Singlet–triplet $n \to \pi^*$ transitions are allowed because of the spin–orbit interaction of the $T_{n\pi^*}$ states with the $S_{\pi\pi^*}$ and S_0 states: their energy is greater than ~10 cm^{-1}. Since the

f value for $\pi \rightarrow \pi^*$ singlet–singlet transitions is also large, the life time of the $T_{n\pi^*}$ states should be small. Calculation[66-68,89] gives $f \cong 10^{-5}$ for the $S_0 \rightarrow T_{n\pi^*}$ transitions, and $k_r \cong 10^3-10^2$ s^{-1} for the $T_{n\pi^*}$ states. Thus the $T_{n\pi^*}$ states are relatively short-lived. Since the $S_0 \rightarrow T_{n\pi^*}$ transitions determine the intensity of the $S_0 \rightarrow S_{\pi\pi^*}$ transitions they are polarised in the plane of the molecule. These results are consistent with experiment[41,72].

The probability of $S_0 \rightarrow S_{\pi l, \pi^*}$ and $S_0 \rightarrow T_{\pi l, \pi^*}$ transitions in substituted hydrocarbons is usually greater than the probability of long-wave $\pi \rightarrow \pi^*$ transitions in unsubstituted aromatic hydrocarbons. In the case of $S_0 \rightarrow S$ transitions this is because the presence of the substituent often leads to removal of the symmetry prohibition[29]. In the case of $S-T$ transitions the increase in probability arises from the decrease in the energy of the $\sigma\pi^*$ and $\pi\sigma^*$ states (decrease in the quantity $E_j - E_{j'}$ in Eqn.(28)), from the increase in the energy of the spin–orbit bond between the states (since the charge of the nuclei in the substituent is greater than the charge of the carbon nucleus, see Section V), and also from the non-planar structure of the molecule (for example, in the case of many amine molecules)[36]. The increase in probability is specially marked in the case of $S-T$ transitions in halogen-substituted molecules, for which the k_r value of the $T_{\pi l, \pi^*}$ states is ~$10-10^2$ s^{-1}. All these statements apply also to molecules with ν-orbitals, but this case has not been discussed theoretically (with one exception[30]), though it has been studied experimentally[92].

Let us examine briefly the problem of the vibrational structure of the absorption and luminescence bands, which has attracted much experimental[93-105] and theoretical[106-108] work. In the harmonic and in the Condon approximation the probability of a transition from the zero vibrational state $|0\rangle$ with excitation of the n-vibrational state of a normal oscillator in the molecule is proportional to the square of the Franck–Condon factor

$$|\langle 0|n\rangle|^2 = e^{-\gamma}\gamma^n (n!)^{-1}, \qquad (33)$$

where $\gamma = 0.5\Delta^2\mu\omega$, Δ is the change in the equilibrium position of the normal coordinate of this oscillator, and ω and μ are the frequency and mass of the oscillator. Formula (33) often describes the distribution of line intensities in vibrational progressions quite satisfactorily[98,106,108]. However in many cases we must go beyond the Condon approximation[99,100].

The following two observations are specially relevant to this discussion. Firstly, the vibrational structures of fluorescence and phosphorescence bands due to transitions of the same orbital type are approximately the same[41,95,106]. This means that the geometric characteristics of a molecule in the $S_{\pi\pi^*}$ and $T_{\pi\pi^*}$ (or $S_{n\pi^*}$ and $T_{n\pi^*}$) states are not very different. The γ parameter has been shown[95] to differ by less than 30% between the fluorescence and the phosphorescence spectra of aromatic molecules. Secondly, the vibrational structure of bands arising from $\pi \rightarrow \pi^*$ transitions is very different from that of bands arising from $n \rightarrow \pi^*$ transitions. This means that molecules in the $\pi\pi^*$ and $n\pi^*$ states have very different geometrical structures. Thus the most active vibrations (with $\gamma \cong 1$) in the bands of $\pi \rightarrow \pi^*$ transitions in carbonyl compounds are those of the aromatic rings, whereas in the bands of $n \rightarrow \pi^*$ transitions the stretching vibrations of the C=O group are the most active, with $\gamma \geq 1$.[93,94,99-101]. In thiocarbonyl compounds the vibrations of the C=O group are replaced by those of the C=S group[102], and in nitro compounds by the symmetrical stretching vibrations of the NO_2 group[105]. In aza-aromatic compounds the vibrations of the aromatic ring are active in the $\pi \rightarrow \pi^*$ bands, and those of the  corner are active in the $n \rightarrow \pi^*$ bands[96,97,103,104]. This difference in the vibrational structure of the bands is due to the nature of the transitions and is consistent, in particular, with localisation of the $n \rightarrow \pi^*$ transitions.

The vibrational structure of the absorption and luminescence bands associated with $\pi l, \pi^*$ and $\pi, \nu\pi^*$ states is usually much more diffuse than the vibrational structure of $\pi \rightarrow \pi^*$ bands[26,27]. This is due to the contribution of the $l\pi^*$ (or $\pi\nu$) configurations to the wave functions of the excited states, and to the consequent change in bond length and in bond angle in the group with l- or ν-orbitals[29,30]. The contribution from these configurations decreases as the length of the chain of conjugated bonds increases, and also on going from singlet to triplet states. Therefore the vibrational structure is less diffuse in the phosphorescence spectra, and in molecules with a large number of π-electrons[26].

We note that even in very complex molecules the parameter γ is significantly different from zero for a small number (1–3) of oscillators[93-108]. In most aromatic molecules the highest-frequency vibrations of the C–H bonds are inactive, and therefore the γ value for these vibrations is close to zero. All these results are highly relevant to the mechanism of non-radiative conversion processes (see Section VII).

Thus the radiative life time of $S_{\pi\pi^*}$ states is typically ~$10^{-7}-10^{-8}$ s, i.e. one or two orders of magnitude smaller than the radiative life time of $S_{n\pi^*}$ states. The radiative life times of triplet states show the opposite relationship: the life time of $T_{n\pi^*}$ states is ~$10^{-2}-10^{-3}$ s, and is two or three orders of magnitude shorter than the life time of $T_{\pi\pi^*}$ states. The radiative life time of the $T_{\pi l, \pi^*}$ states is intermediate between the life time of the $T_{\pi\pi^*}$ states in aromatic hydrocarbons and that of the $T_{n\pi^*}$ states. The vibrational structures of the bands due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions differ very substantially as a result of the difference in geometric structure of the molecule in the $\pi\pi^*$ and $n\pi^*$ states, and of the localised nature of the $n \rightarrow \pi^*$ transitions. The bands associated with transitions into (or from) the $\pi l, \pi^*$ (or $\pi, \nu\pi^*$) states are usually more diffuse than bands due to $\pi \rightarrow \pi^*$ transitions.

Early measurements of luminescence quantum yields have shown[109] that the yield is almost invariably less than unity, even in the absence of photochemical reactions. This effect is due to the non-radiative conversion processes discussed in the next Section.

VII. NON-RADIATIVE CONVERSION PROCESSES

The term non-radiative conversion denotes transitions between electronic states in molecules for which the electronic excitation energy is fully or partly converted into vibrational energy of the system as a whole. Conversion processes are a special case of intramolecular non-radiative transitions, which include various photochemical molecular transformation or pre-ionisation processes. Non-radiative transitions have been discussed in detail[110-114]: for our present purpose we only need to consider the dependence of the rate constant of the conversion upon the type of transition, the energy spectrum of the molecule, and the structure of the molecule.

One of the basic problems in the theory of non-radiative transitions concerns the nature of the interaction giving rise to the transition. This problem is directly associated with the problem of defining the state into which a molecule is converted upon electronic excitation. The problem was solved relatively recently[115-117] when it was shown that excitation by a broad-band source of light brings the molecule to a state whose wave function is not an eigenfunction of the full Hamiltonian of the system. (The case of monochromatic or quasi-monochromatic excitation is discussed in Refs.118 and

119.) This result, assumed without proof¶ until recently[115-117], is valid provided that (as is usually the case) the excitation region includes one pure spin adiabatic state into which an optical transition from the ground state is allowed. The pure spin adiabatic state is not a stationary state because its wave function is not an eigenfunction of the full Hamiltonian of the system, and such a state can dissociate non-radiatively under the influence of the operators V and H_{SO}. The dissociation is irreversible only if the system in its final state has a continuous (or quasi-continuous) spectrum of energy levels[13,115-117]. In the case of molecules in a condensed phase this condition is invariably satisfied.

Since only some of the intramolecular oscillators undergo a marked change in equilibrium position (and in frequency) during electronic transitions in substituted hydrocarbon molecules (see Section VI), sometimes accompanied by similar changes in some of the local vibrations of the solvent, the matrix elements of the non-adiabaticity and of the spin–orbit interaction operators will differ from zero, with a small number of oscillators excited in the final electronic state (see Section II). These oscillators (active in non-radiative conversion) are directly involved in the conversion process, accepting electronic energy and subsequently transferring it to other (inactive) vibrational modes of the molecule and of the solvent. In addition to the oscillators whose characteristics are different in the combined electronic states, the most anharmonic (and high-frequency) oscillators in the immediate vicinity of the part of the molecule where the electronic transition is localised are also active. All these conditions limit the number of modes which can be active in non-radiative transitions, and make it possible to calculate the rate constants of the conversion processes even in complex molecules.

At low temperatures ($kT < \omega$, where ω is the frequency of the active oscillators, $\omega \geq 500$ cm^{-1}), and if the vibrational relaxation rate constant (Γ) is greater than the conversion rate constant, we can write the following expression for the rate constant of the conversion between the levels i and f:[121,122]

$$k_{nr} = \sum_{\{n\}} \Gamma \left| \langle i\{0\}| \hat{R} | f\{n\} \right\rangle|^2 \cdot \left(\Delta^2_{\{n\}} + \frac{\Gamma^2}{4}\right)^{-1}, \qquad (34)$$

where the summation is taken over the vibrational states of the level f, for which $\Delta_{\{n\}} = E_{i(0)} - Ef\{n\} \leq 100$ cm^{-1}, and $\hat{R}$ is the level shift operator, defined by the expression

$$\hat{R} = V + H_{so} + (V + H_{so})\, g_1 \hat{R} + V + H_{so} + (V + H_{so})\, g_1 (V + H_{so}) + \ldots, \qquad (35)$$

and g_1 is given by

$$g_1 = \sum_{f'\{n'\}} \frac{|f'\{n'\}\rangle \langle f'\{n'\}|}{E_i - E_{f'\{n'\}}}.$$

The summation in this expression is taken over the states not included in Eqn.(34). If the value of k_{nr} given by (34) is greater than Γ the conversion rate constant is $\Gamma/2$.[118]

We can define different types of non-radiative conversion. If the multiplicity of the state is unaffected by the transition the process is termed internal conversion. If there is a change in the multiplicity of the state the process is called intercombinations ($S-T$ or $T-S$) conversion. For a transition of the system to the ground state the term "conversion" is sometimes replaced by "degradation" (internal, $S_1 \rightsquigarrow S_0$, or intercombinational, $T \rightsquigarrow S_0$).

Two rules on the rate of internal conversion processes have been formulated empirically: Kasha's rule[25] and Ermolaev and Sveshnikova's rule[123-125]. The first states that in most molecules internal conversion processes between electronically excited states (of the same resultant spin) take place in times shorter than ~10^{-11} s, and a significant quantum yield ($\geq 10^{-3}$) can be expected only for transitions from the lower excited state of the given multiplicity. The Ermolaev–Sveshnikova rule states that in many light-stable molecules in a condensed phase the conversion between S_1 and S_0 states can be ignored in comparison to fluorescence processes.

The theory of internal conversion processes in aromatic molecules containing additives has been developed in the writer's laboratory[126]. The expression for the internal conversion rate constant is

$$k_{IC} = \sum_{\{n\}} |V^{if}_{\{n\}}|^2 \Gamma (\Delta^2_{\{n\}} + \Gamma^2/4)^{-1}, \qquad (36)$$

where $V^{if}_{\{n\}}$ is a matrix element of the non-adiabaticity operator, calculated from the vibronic functions $|i\{0\}\rangle$ and $|f\{n\}\rangle$.

The main contribution to k_{IC} in the case of transitions between $\pi\pi^*$ (or $\sigma\sigma^*$) states, or between an $S_{\pi\pi^*}$ state and the ground state, comes from the matrix elements containing differentials with respect to the coordinates of the stretching vibrations of the C–H bonds (promoting modes[113]). This is because these vibrations have the greatest anharmonicity and the highest frequency of all the vibrations in the molecule. Ignoring the dispersion of the C–H stretching vibration frequencies, which is small even for small n [11] and decreases rapidly as n increases[127], we can re-write the expression for k_{IC} as[126]

$$k_{IC} \cong 10^{15} E^2_{if} \sum_{\nu,\{n\}} |c_{\nu i} c_{\nu f}|^2 \left| \left\langle 0 \left| \frac{\partial}{\partial x_\nu} \right| n \right\rangle \right|^2 \prod_{\nu' \neq \nu} |\langle 0 | n_{\nu'} \rangle|^2 \ (s^{-1}), \qquad (37)$$

where E_{if} is the difference in electronic energy of the i and f levels (in eV), the summation over ν includes all the C–H bonds in the molecule, $c_{\nu i}$ and $c_{\nu f}$ are the coefficients of the expansion of the π-orbitals, whose population is different in the $|i\rangle$ and $|f\rangle$ states, and x_ν is the coordinate of the C–H stretching vibrations. The ν' product in Eqn.(37) is taken for all the vibrations of the molecule whose characteristics are different in the $|i\rangle$ and $|f\rangle$ states (acceptor modes).

Using the Morse potential to describe the vibrations of the C–H bonds we can convert the formula for $|\langle 0|\frac{\partial}{\partial x}|\rangle|^2$ into

$$\left| \left\langle 0 \left| \frac{\partial}{\partial x} \right| n \right\rangle \right|^2 = \frac{\alpha^2 \Gamma^2 (2s - n + 1)}{n! \, \Gamma(2s - 2n) \, \Gamma(2s - 2n + 1) \, \Gamma(2s)} \cdot \eta^{2s} \rho^{-4s+2n} \times$$
$$\times \left[\frac{\eta}{2\rho} F\left(-n, 2s - n + 1; 2s - 2n + 1; \frac{1}{\rho}\right) - \right. \qquad (38)$$
$$\left. - \frac{s}{2s - n} F\left(-n, 2s - n; 2s - 2n + 1; \frac{1}{\rho}\right) \right]^2,$$

where α is the parameter of the Morse potential (~1 a.u.), $\eta = e^{\alpha\Delta}$, $\rho = \frac{1}{2} + \eta/2$, $\Gamma(x)$ is the gamma-function, $F(\alpha, \beta; \gamma; x)$ is a hypergeometric function, $s = 2D/\omega - \frac{1}{2}$, D is the dissociation energy of the C–H bond, ω is its vibration frequency, and Δ is the difference in length of the C–H bond between states $|i\rangle$ and $|f\rangle$. The Franck–Condon factors $\langle 0|n_{\nu'}\rangle$ are easily calculated because the $n_{\nu'}$ values are small and we can use the harmonic approximation in which $|\langle 0|n_{\nu'}\rangle|^2$ is given by Eqn.(33).

As was pointed out in Section VI electronic transitions in polyatomic molecules do not give rise to significant changes in the length of the C–H bonds. The γ parameter (formula (33)) for the stretching vibrations of the C–H bonds of the benzene molecule is ~10^{-2} ($\Delta = -0.014$ Å [128]). As the number of aromatic rings in the molecule increases the value of γ falls off rapidly to ~10^{-3} or less for a molecule containing two or more rings[99]. It follows that the most characteristic case is when $\Delta = 0$.

¶ The need for a proof was first stated in Ref. 120.

In Fig.6 the logarithm of the function $\theta = k_{IC} E_{if}^2 [\Sigma_\nu |c_{\nu i} c_{\nu f}|^2]^{-1}$ is plotted against the energy of the electronic transition for different values of Δ for C–H bonds, assuming typical values of $\gamma = 1$ for stretching vibrations of the aromatic nuclei at a frequency of ~1400 cm^{-1} and $\gamma = 0.5$ for bending vibrations at a frequency of ~400 cm^{-1}. The summation with respect to ν is easily evaluated because the $c_{\nu i}$ and $c_{\nu f}$ values are known for many molecules[37–40]. It is of the same order of magnitude as N_{C-H}/N^2, where N_{C-H} is the number of C–H bonds and N is the number of π-electrons in the molecule.

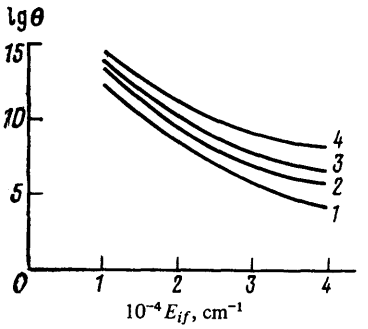


Figure 6. Variation of the factor θ with the energy of the transition: *1)* $\Delta = 0$, *2)* $\Delta = -0.01$ a.u., *3)* $\Delta = -0.02$ a.u., *4)* $\Delta = -0.03$ a.u.

These calculations lead to a number of conclusions. The internal conversion rate constant for $E_{if} \lesssim 10^4$ cm^{-1} is $\gtrsim 10^{11}$ s^{-1}, irrespectively of the value of Δ, and this is the main dissociation process available to the state $|i\rangle$. A similar (or smaller) value of E_{if} is characteristic of transitions between electronically excited states, and this calculation of k_{IC} is a theoretical justification of Kasha's rule. For E_{if} values lying between 10^4 and 2×10^4 cm^{-1} the internal conversion rate constant is of the same order as the rate constants for allowed radiative transitions. This is observed, for example, for the $S_2 \rightsquigarrow S_1$ transition in the azulene molecule, with an E_{if} value of 1.4×10^4 cm^{-1}. Formula (37) gives $\lesssim 10^9$ s^{-1} for the k_{IC} value of this transition, confirming that the luminescence properties of this molecule infringe Kasha's rule[129].

For $E_{if} \gtrsim 2 \times 10^4$ cm^{-1} (as found in the transitions between S_1 and S_0 states in many aromatic molecules) the parameter k_{IC} depends not only on E_{if} but also on the Δ value of the C–H bonds. For many molecules we can write $\Delta = 0$: in this case (see Fig.6) k_{IC} is smaller than the radiative dissociation constant (k_r) of the S_1 states. It is also smaller than the rate constants for the $S-T$ conversion (see below). This result is a theoretical verification of the Ermolaev–Sveshnikova rule. It can also apply, with acceptable precision, for slightly smaller values of E_{if} if one of the following conditions obtains: 1) fast (~10^{-11} s) $S-T$ conversion processes between $n\pi^*$ and $\pi\pi^*$ states are possible; 2) the molecules have narrow luminescence bands and the γ parameter for their skeletal vibrations is $\gamma \leq 0.5$; 3) the radiative life time of the S_1 states is small (~10^{-9} s). The last two conditions are obeyed by many dye molecules, which can show strong fluorescence corresponding to transitions between S_1 and S_0 states even for $E_{if} < 2 \times 10^4$ cm^{-1} (but nevertheless $E_{if} > 10^4$ cm^{-1}).

In small aromatic molecules the Δ value of the C–H bonds can be relatively large in absolute value, so that $\pi \rightarrow \pi^*$ excitation may produce a decrease in length of the C–H bonds: for example, in benzene[128] and phenol[130] $\Delta \cong -0.03$ a.u. As a result the k_{IC} values can be close to the k_r values for the S_1 states even for $E_{if} \cong 4 \times 10^4$ cm^{-1}. This is an example of deviation from the Ermolaev–Sveshnikova rule. A similar behaviour may be discovered in other small molecules (for example, azabenzene), for which we can expect $|\Delta| \cong 0.03$ a.u. However in most aromatic molecules $|\Delta| < 10^{-2}$ a.u.[99], and the Ermolaev–Sveshnikova rule is accurately obeyed.

Internal conversion processes between $n\pi^*$ and $\pi\pi^*$ states have also been studied[126], as well as conversion between $S_{n\pi^*}$ and S_0 states. For $E_{if} > 5000$ cm^{-1} these processes are found to be slower than the conversion between $\pi\pi^*$ states, because the stretching vibrations of the C–H bonds in planar molecules do not act as promoting vibrations in this case. This result has been confirmed experimentally for the thioxanthone and thioxanthione molecules[102].

The probability of singlet–triplet conversion is very sensitive to the spin–orbit interaction of the states involved in the conversion. Using the calculations of spin–orbit interaction given in Section V we obtain the following expression[89,131] for the rate constant of the $S-T$ conversion between $\pi\pi^*$ (or $n\pi^*$) states in planar molecules in the Condon approximation and in first-order perturbation theory for the H_{SO} operator:

$$k_{ST} \cong 10^9 \sum_{\{n\}} \prod_q |\langle 0 | n_q \rangle|^2 \ (s^{-1}), \qquad (39)$$

and the following expression for the rate constant of the $S-T$ conversion between $S_{n\pi^*}$ and $T_{n\pi^*}$ (or between $S_{\pi\pi^*}$ and $T_{\pi\pi^*}$) states:

$$k_{ST} \cong 10^{12} \sum_{\{n\}} \prod_q |\langle 0 | n_q \rangle|^2 \ (s^{-1}). \qquad (40)$$

In Eqns.(39) and (40) the summation extends over the vibrational quantum numbers of the high-frequency ($\omega > 500$ cm^{-1}) oscillators whose characteristics differ in the S and T states and for which the squares of the Franck–Condon factor are a maximum. The n_q values must satisfy the condition of minimum $|E_{if} - \sum_q n_q \omega_q|$. Thus the calculation of k_{ST} reduces to a calculation of the Franck–Condon factors.

An estimate of $|\langle 0|n_q\rangle|^2$ can easily be obtained by using the Robinson–Frosch semi-empirical formula[132]. This approach gave the following results[89]. The rate constants for the $S-T$ conversion between states of the same orbital type lie between 10^6 and 10^8 s^{-1}, which is of the same order as the rate constants for the radiative dissociation of singlet states. The characteristic rate constants for $S-T$ conversion between states of different orbital type are ~10^{10}–10^{11} s^{-1}, i.e. more than two or three orders of magnitude greater than the rate constants for the radiative dissociation of singlet states. These calculations have led to the classification of molecules into five types according to their luminescence spectra[53,89].

In recent years a great deal of experimental information has been obtained on the spatial structure of aromatic molecules in different electronic states (see Section VI). Therefore we can now evaluate k_{ST} more reliably by using expressions of the type of (33). This was done in Ref.131 for molecules of carbonyl, thiocarbonyl, aza-heterocyclic, and nitro compounds, and the results were consistent with the estimates of k_{ST} given in Ref.89. It was shown that the spin–orbit coupling of combining states is not the only reason for the large difference (three orders of magnitude) between the k_{ST} values for transitions between states of different orbital type and states of the same orbital type, or the k_r values for singlet states. As pointed out in Section VI, the spatial structure of the molecules is different in the $n\pi^*$ and $\pi\pi^*$ states. As a result, the Franck–Condon factor for the

$S \rightsquigarrow T$ transition between $n\pi^*$ and $\pi\pi^*$ states is significantly higher than the factor for transitions between states of the same orbital nature.

These considerations lead to the important conclusion that if $S-T$ conversion can occur between states of different orbital nature it has a rate constant of $10^{10}-10^{11}$ s^{-1}, and it gives rise to fluorescence quenching. Recent experimental measurements[133-135] on transitions between $n\pi^*$ and $\pi\pi^*$ states have given $k_{ST} \cong 10^{11}$ s^{-1}.

By using data on the spatial structure of molecules in electronically excited states and on the structure of their energy spectrum we can calculate not only the most probable range of k_{ST} values but also the dependence of k_{ST} on the structure of the molecule. Thus it has been shown[131,136] that the probability of $S-T$ conversion between $\pi\pi^*$ states increases sharply in the presence of a $T_{\pi\pi^*}$ state. But even in this case the k_{ST} value does not exceed ~10^9 s^{-1}. Other conditions being equal the k_{ST} value for a transition between $\pi\pi^*$ states is lower, the lower the value of γ in formula (33). However γ decreases as the length of the chain of conjugated bonds increases[98], and this is why many dye molecules have a high fluorescence quantum yield.

The effect of highly excited $n\pi^*$ states on the probability of $S-T$ conversion between $\pi\pi^*$ states has been studied[70]. In molecules containing N, O, and S atoms and having spin–orbit coupling between $n\pi^*$ and $\pi\pi^*$ states of intermediate magnitude the vibronic mixing effects do not substantially increase k_{ST} for transitions between $\pi\pi^*$ states. As before, k_{ST} is of the same order of magnitude as k_r for $S_{\pi\pi^*}$ states. However this parameter decreases quite markedly as the energy difference between the $\pi\pi^*$ and $n\pi^*$ states increases (for example, as the length of the conjugation chain increases, in the presence of electron-donor substituents, or when proton-donor substituents are used, see Section IV). All these factors tend to increase the fluorescence yield of the molecules in which the lower S and T states are of the $\pi\pi^*$ type ($\pi l, \pi^*$ and $\pi, \nu\pi^*$).

In molecules containing atoms with a large nuclear charge (Br, I, Cl) the vibronic mixing effects affecting $n\pi^*$ and $\pi\pi^*$ states can make k_{ST} take a value of ~10^{10} s^{-1} for conversion between $\pi\pi^*$ states in molecules with a small ($\leqslant$10) number of electrons; as the number of electrons increases this value rapidly decreases[70]. Thus in molecules containing heavy atoms fluorescence is possible if the number of π-electrons is large. Deviations of k_{ST} from the usual behaviour can occur in small molecules, and are related to the weakening of the LS coupling in heavy atoms.

In molecules with $S_{\pi\pi^*}$ and $T_{\pi\pi^*}$ states lying above the lower $S_{n\pi^*}$ state (see Figs.3 and 4) the vibronic interaction effects can cause quenching of the fluorescence from $S_{n\pi^*}$ states. This is due to the smallness of k_r for $S_{n\pi^*}$ states and also to the fact that the difference in energy between $T_{n\pi^*}$ and $T_{\pi\pi^*}$ states can be small (2000–3000 cm^{-1}). This explains the absence of fluorescence in many aromatic carbonyl compounds such as benzophenone and anthrone[137]. However the situation is made more complicated by the lack of planarity of these molecules.

Deviation from planarity in molecules leads to mixing of the π and σ orbitals, to an increase in the spin–orbit interaction of states of the same orbital type (Section V), and to an increase in k_{ST}. The $\pi l, \pi^*$ states of non-planar aromatic molecules can be taken as an example[96]. Another example is provided by aliphatic hydrocarbon molecules[64], and by the non-planar aromatic carbonyl molecules mentioned above.

We can now turn to a discussion of the role of internal conversion processes in the dissociation of excited states. The variation of the internal conversion constant k_{IC} with E_{if} is shown diagrammatically in Fig.7 for $\Delta_{C-H} = 0$. The cross-hatched region shows the most characteristic values of the rate constant for the dissociation of an S state by the radiative mechanism and by the $S-T$ conversion mechanism (k) on the assumption that $\pi\pi^*-n\pi^*$ conversion is not involved. Three energy regions can be defined: the Kasha region, in which $k_{IC} > k$, an intermediate region ($k_{IC} \cong k$), and the Ermolaev–Sveshnikova region ($k_{IC} < k$). When $S-T$ conversion processes between $\pi\pi^*$ and $n\pi^*$ states are possible the k value increases sharply and the Ermolaev–Sveshnikova region expands. We shall examine the case of molecules which obey the Ermolaev–Sveshnikova rule, even if only approximately, i.e. molecules in which the first singlet excited state has an energy in excess of ~1.5 eV.

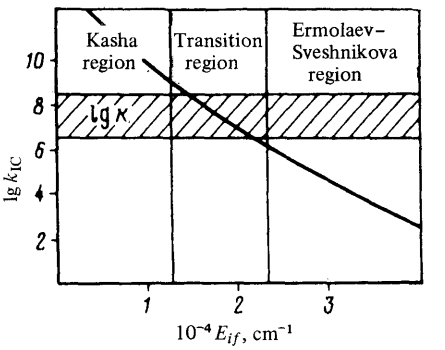


Figure 7. Relative values of k_{IC} and k as a function of the energy of the transition.

We have to consider processes of intercombination conversion from the lower triplet state to the ground state, which compete with the phosphorescence process. These processes have been studied in depth, both experimentally and theoretically, and they are discussed in the monograph literature[8,41] and in reviews[111,112]. In spite of their different approaches, all the theoretical studies conclude that the rate constant for conversion between S_0 states (k_{TS}) increases rapidly as the difference in energy between the states decreases[132,138,139]. This result, which follows directly from the simple formula (33) for the Franck–Condon factor, is consistent with experiment. However order-of-magnitude quantitative agreement between experimental and theoretical values of the constant has not yet been obtained, or has been obtained by postulating unrealistic potential energy surfaces for the molecules in excited states[111].

The difficulty of calculating the constant k_{TS} arises from the fact that, since E_{if} is large ($\geqslant$1 eV), the Franck–Condon factors for the $T \rightsquigarrow S_0$ transitions are small, and therefore the second- and higher-order terms in formula (35) cannot be ignored. (This is the difference between $T-S_0$ conversion and $S-T$ conversion.) The situation is made even more complex by the fact that in many aromatic molecules the matrix element of the operators of the spin–orbit interaction between the lower T state and the S_0 state is identically equal to zero in the Condon approximation (see Section V). In this case the transition is forbidden in the first-order (and in the Condon approximation) for the operator H_{SO}, and agreement between calculated values of k_{TS} and experiment cannot be obtained simply by improving the precision of the calculated Franck–Condon factor.

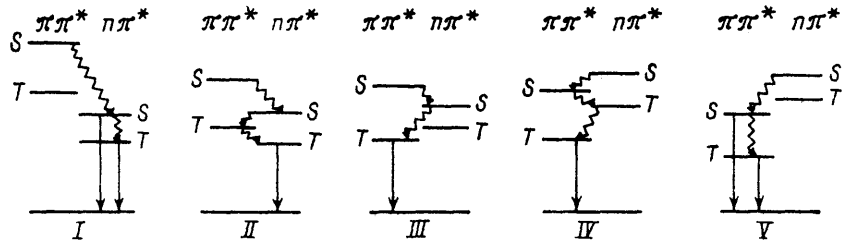


Figure 8. Most probable conversion processes between excited states, and radiative processes, involving molecules of the five luminescence-spectral types.

An important contribution[140] to our understanding of the mechanism of $T-S$ conversion in aromatic molecules points out that the constant k_{TS} is proportional to the constant k_r of the triplet state and to the overlap integral of the phosphorescence spectrum and of the infrared absorption spectrum of the molecule corresponding to the upper vibrational states of the C–H bonds, into which transitions are allowed as a result of the anharmonicity of the vibrations. This means[141,142] that k_{TS} is determined by a non-adiabatic interaction, and it should be calculated with allowance for second- and higher-order terms in the operators V and H_{SO}. It follows that k_{TS} should be proportional to the spin–orbit coupling of the T states with the S states, and to the constant k_{IC} for the conversion between these S states and the S_0 state (calculated for an E_{if} value equal to the energy of the T state[136]). Since the vibrational factor in the calculation of k_{IC} contains differentials with respect to the coordinates of the C–H bonds, and allowance for the anharmonicity of the vibrations is essential, the vibrational factor cannot be reduced to a Franck–Condon factor. In particular, the quantity $\langle 0|n\rangle$ for $n \neq 0$ and $\Delta = 0$ vanishes, and the quantity $\langle 0|\frac{\partial}{\partial x}|n\rangle$ for the anharmonic oscillator under these conditions cannot vanish for any value of n.

Conversion between $T_{\pi\pi^*}$ and the S_0 state can be achieved by mixing $S_{\pi\pi^*}$, $S_{n\pi^*}$, $S_{\sigma\pi^*}$, and $S_{\pi\sigma^*}$ states with the $T_{\pi\pi^*}$ state, and by mixing the appropriate triplet states with the S_0 state. In this case both the spin–orbit interaction and k_{IC} are small, since internal conversion between an $n\pi^*$ (or $\sigma\pi^*$, or $\pi\sigma^*$) state and the S_0 state cannot be promoted by stretching vibrations of the C–H bonds (see above, and Ref. 126). Therefore the conversion rate constants (k_{TS}) in the solid phase and at low temperatures are relatively small: in most molecules these constants differ by less than an order of magnitude from the k_r value for the $T_{\pi\pi^*}$ states[41,143]†. Under these conditions the dependence of the rate constant for the $T-S$ conversion on E_{if} is determined by the dependence of the matrix elements of (38) upon n, and is not very different from the dependence of k_{IC} on E_{if}. Theoretical calculations of k_{TS} as a function of E_{if} agree satisfactorily with experiment[140,136]. For $E_{if} \leq 1.5$ eV the constant k_{TS} becomes greater than k_r: in these molecules phosphorescence is impossible. At these energies the predominant contribution to k_{TS} can be obtained by the first-order perturbation theory if $\langle T_S|H_{SO}|S_0\rangle \neq 0$.[136]

The $T_{n\pi^*} \rightsquigarrow S_0$ intercombination conversion is much faster than conversion from a $T_{\pi\pi^*}$ state. This is because the spin–orbit interaction of $T_{n\pi^*}$ states with both S_0 and $S_{\pi\pi^*}$ states is large. In the condensed phase at low temperatures the constant k_{TS} for conversion from $T_{n\pi^*}$ states is similar in value to k_r for $T_{n\pi^*}$ states in many molecules[41,143]. The theory of $T-S_0$ conversion processes is still far from being fully developed.

To conclude this Section we shall list the main features of the conversion processes. Internal conversion between electronically excited states occur in ~10^{-11} s. In photochemically-stable molecules in a condensed phase we can usually ignore the $S_1 \rightsquigarrow S_0$ internal conversion (degradation) process. The rate constant for $S-T$ conversion between $n\pi^*$ and $\pi\pi^*$ states is ~10^{10}–10^{11} s^{-1}. The rate constant for $S-T$ conversion between states of the same orbital type in planar molecules is ~10^6–10^8 s^{-1}. The only exception are molecules containing heavy atoms (e.g. halogen) and having a small number (≤ 10) of π-electrons, for which the constant k_{ST} can be as high as 10^{10} s^{-1}. In the case of transitions between $\pi\pi^*$ states k_{ST} decreases as the energy difference between the $\pi\pi^*$ and $n\pi^*$ states increases and as the length of the conjugated bond chain increases. In non-planar molecules k_{ST} is higher than in planar molecules. The rate constants for $T \rightsquigarrow S_0$ conversion in the solid phase are similar in magnitude to the k_r values for triplet states. As the energy of the T state decreases the constant k_{TS} increases, lowering the phosphorescence yield.

VIII. CLASSIFICATION OF MOLECULES BY LUMINESCENCE SPECTRA

Let us now consider the luminescence-spectral properties of molecules in relation to the relative position of their electronically excited states#. We shall show that each of the five types of relative position of the $\pi\pi^*$ and $n\pi^*$ states (see Section IV) has its own set of luminescence-spectral characteristics, i.e. it corresponds to a type of molecule[53,89]. We shall assume that the molecules obey the Kasha and the Ermolaev–Sveshnikova rules, that they do not contain heavy atoms, and that their structure is planar.

Type I. The sequence of states is: S_0, $T_{n\pi^*}$, $S_{n\pi^*}$, $T_{\pi\pi^*}$, $S_{\pi\pi^*}$. Since the rate constants k_r (for $S_{n\pi^*}$ states) and k_{ST} (for the $S_{n\pi^*} \rightsquigarrow T_{n\pi^*}$ conversion) are similar in value (see Sections VI and VII), both fluorescence and (in the solid

†With rare exceptions, phosphorescence is not observed in the liquid phase because of the possibility of quenching of the T states by bimolecular processes.

#In this discussion the electronically excited states are arranged in order of increasing energy.

phase) phosphorescence are possible in these molecules. The fluorescence yield cannot be large because the constant k_r is relatively small. These molecules have a long-lived fluorescence and a short-lived phosphorescence. In the absorption spectra of molecules of the first luminescence-spectral type the bands corresponding to $n \to \pi^*$ and $\pi \to \pi^*$ transitions are separated by a relatively large ($\geq$1 eV) energy difference. Examples of this type of molecule are acetone, diacetyl, thiobenzophenone, and other molecules[4,53].

Type II. The sequence of states is: S_0, $T_{n\pi^*}$, $T_{\pi\pi^*}$, $S_{n\pi^*}$, $S_{\pi\pi^*}$. Because of the possibility of fast (~10^{-11} s) $S_{n\pi^*} \rightsquigarrow T_{\pi\pi^*}$ interconversion this type of molecule has a short-lived phosphorescence from the $T_{n\pi^*}$ state, and the fluorescence yield cannot exceed 10^{-3}. The $n \to \pi^*$ and $\pi \to \pi^*$ absorption bands are also well resolved in molecules of type II. Typical type II molecules are acetophenone, naphthoquinone, anthraquinone, and others[2-4].

Type III. The sequence of states is: S_0, $T_{\pi\pi^*}$, $T_{n\pi^*}$, $S_{n\pi^*}$, $S_{\pi\pi^*}$, Fast $S_{n\pi\pi^*} \rightsquigarrow T_{\pi\pi^*}$ interconversion is possible also in molecules of this type. Therefore these molecules can have only long-lived phosphorescence from the $T_{n\pi^*}$ states; the fluorescence yield cannot be greater than 10^{-3}. In the absorption spectra the $n \to \pi^*$ band is close to the $\pi \to \pi^*$ band, with the possibility of partial overlap. Examples of this type of molecule are benzoic acid, phthalic anhydride, etc.[4].

Type IV. The sequence of states is: S_0, $T_{\pi\pi^*}$, $T_{n\pi^*}$, $S_{\pi\pi^*}$, $S_{n\pi^*}$. Because of the possibility of $S_{\pi\pi^*} \rightsquigarrow T_{\pi\pi^*}$ interconversion processes in times of the order of 10^{-11} s the long-lived phosphorescence from $T_{\pi\pi^*}$ states is predominant in the radiation from these molecules. The fluorescence yield is small, but it can exceed the fluorescence yield of type-III molecules because the k_r values for $S_{\pi\pi^*}$ states are substantially higher than those for $S_{n\pi^*}$ states. An important difference between the luminescence properties of type IV and type III molecules is the ability of the former to be converted into type-V molecules (see below) under the influence of solvents giving rise to hydrogen bonds, since the energy difference between the $S_{\pi\pi^*}$ and $T_{n\pi^*}$ states is ~1000 cm^{-1}. Activation of the fluorescence of type II and type III molecules requires a much greater increase in the energy of the $n\pi^*$ states, which can be realised by dissolving the molecules in acids[144]. The bands corresponding to $n \to \pi^*$ transitions in the absorption spectra of type-IV molecules show complete overlap with the much stronger $\pi \to \pi^*$ bands, and they are not observed in poorly resolved spectra. Typical molecules of this type are acridine and quinoline in non-polar solvents.

Type V. The sequence of states is: S_0, $T_{\pi\pi^*}$, $S_{\pi\pi^*}$, $T_{n\pi^*}$, $S_{n\pi^*}$. Since the relatively slow ($\geq 10^{-9}$ s) $S_{\pi\pi^*} \rightsquigarrow T_{\pi\pi^*}$ processes are the only interconversion processes possible in this type of molecule we can expect both fluorescence and phosphorescence, with comparable yields. The ratio of the yields is determined by the relative values of k_r for the $S_{\pi\pi^*}$ states and k_{TS} for the $S_{\pi\pi^*} \to T_{\pi\pi^*}$ conversion, and of k_r for the $T_{\pi\pi^*}$ states and k_{TS} for the $T_{\pi\pi^*} \rightsquigarrow S_0$ conversion, which were discussed in the last two Sections. The $n \to \pi^*$ bands in the absorption spectra of type-V molecules are usually overlapped by the stronger bands due to $\pi \to \pi^*$ transitions, and they can be observed only when they lie between two of these bands. Dye molecules are typical of the luminescence-spectral type V.

The most probable conversion processes between electronically excited states and radiation processes involving molecules of the five luminescence-spectral types are illustrated in Fig.8. The diagram corresponds to k_{ST} values obtained in the Condon approximation. By going beyond this approximation[70] we can, on the one hand, describe differences between molecules in the same spectral type, and on the other hand we can demonstrate the absence of sharp boundaries between the five spectral types. We shall justify the latter statement by considering the transition from type I to type II. As the $T_{\pi\pi^*}$ state approaches the $T_{n\pi^*}$ state the extent of mixing of these states due to vibronic interaction increases, and the constant k_{ST} for the $S_{n\pi^*} \rightsquigarrow T_{n\pi^*}$ transition also increases very markedly. The energy of the $T_{\pi\pi^*}$ state can be higher than that of the $S_{n\pi^*}$ state, but since the $S-T$ splitting of the $n\pi^*$ states and the constant k_r for the $S_{n\pi^*}$ state are both small the fluorescence may be suppressed. Similar arguments can be applied in the other cases.

In other words, great care is needed to describe the luminescence-spectral properties of molecules whose electronic states lie in the transition region between two of the types defined above. This conclusion is entirely consistent with the well known increase in complexity of the spectral properties of systems with degenerate or quasi-degenerate states (the Jahn–Teller effect or pseudo-effect)[145]. The criterion for the validity of the scheme shown in Fig.8 is that the vibronic interaction of $n\pi^*$ and $\pi\pi^*$ states must be small compared with the energy difference between these states. In most cases this criterion is obeyed and the scheme of Fig.8 is applicable[79].

In the light of these considerations, the differences in properties between $\pi\pi^*$ (or $n\pi^*$) states arising from differences in orbital nature, from the presence or absence of quasi-degeneracy of the lower $S_{\pi\pi^*}$ state with the upper $T_{\pi\pi^*}$ state, from the differences in the vibronic bond with the upper states, etc. are only second-order differences and can be allowed for in the scheme proposed here. This is because none of the rate constants for $S-T$ conversion suffers a catastrophic change (by several orders of magnitude) as a result of these effects. The scheme outlined in Fig.8 remains valid, though there may be a change in the designation of the states and (or) a limited change in the rate constants for the dissociation of the states leading to luminescence.

Possible luminescence-spectral types of molecules of different orbital classes*.

Class	Type I	II	III	IV	V	Class	Type I	II	III	IV	V
$(\sigma\pi)$	–	–	–	–	+	$(\sigma\pi n)$	+	+	+	+	+
$(\sigma\pi l)$	–	–	–	–	+	$(\sigma\pi ln)$	+	+	+	+	+
$(\sigma\pi v)$	–	–	–	–	+	$(\sigma\pi vn)$	+	+	+	+	+
$(\sigma\pi lv)$	–	–	–	–	+	$(\sigma\pi lvn)$	+	+	+	+	+

*The plus sign denotes that this type of molecule can exist, the minus sign that it cannot.

The luminescence-spectral type to be expected in molecules of various types can therefore be stated without difficulty. Aromatic (unsaturated) molecules can be divided into the following classes[146], depending on the set of orbitals which characterise their electronic structure: $(\sigma\pi)$, $(\sigma\pi l)$, $(\sigma\pi v)$, $(\sigma\pi lv)$, $(\sigma\pi n)$, $(\sigma\pi ln)$, $(\sigma\pi vn)$, and $(\sigma\pi lvn)$. These designations hardly need to be explained: for example, the $(\sigma\pi)$ class includes the aromatic hydrocarbon molecules, the $(\sigma\pi l)$ class the aromatic hydrocarbon molecules with donor substituents, etc. The possibilities of observing the various luminescence-spectral types are summarised in the Table[146].

A set of molecules of different classes but of the same luminescence-spectral type is termed a luminescence-spectral series. Molecules of one series have similar (but numerically different) properties owing to the differences in orbital nature of their states and to the other factors discussed above. Transitions between molecules of different types or classes can be brought about by changes in chemical structure and by external factors (see Section IV).

All the above statements apply to molecules which do not contain heavy atoms, i.e. atoms with a multiplet splitting constant ξ greater than ~500 cm^{-1}.[70] Infringement of this condition causes k_{ST} for transitions between $\pi\pi^*$ states in molecules formally classified as type V to reach values of the order of 10^{11} s^{-1}: these molecules will have a low ($\leqslant 10^{-3}$) fluorescence quantum yield. The effect is clearly shown by molecules with a small ($\leqslant 10$) number of π-electrons.

The agreement between the luminescence-spectral classification of molecules and experimental data has been demonstrated by many workers[2-4,53,58,92,99,100,147-150].

This method of classification offers a unified description of the properties of a large number of molecular systems. It has been applied in the chemistry of phosphors and scintillators[147], in biophysics[148], and in photochemistry[114], and it has helped in the selection of materials with good light-emitting properties (for the active regions of lasers operating in the visible and the u.v. region)[144,149,150]. It has also been valuable in molecular spectroscopy[4].

The validity of our classification is limited by the possibility of photochemical processes. The problem is by no means trivial, because conversion processes can be initiated by photochemical processes whose yield is immeasurably low. A special case is met in systems with two or more minima in the potential surface of one electronic state[151].

Since this paper was submitted for publication the following relevant papers have appeared: a discussion[152] of the general problems in systematising the luminescence-spectral properties of molecules, a study[153] of the initiation mechanisms of conversion by photochemical reactions, and an analysis[154] of the mechanism of triplet–singlet conversion processes.

REFERENCES

1. B.I.Stepanov and A.N.Rubinov, Uspekhi Fiz.Nauk, **95**, 45 (1968).
2. R.N.Nurmukhametov, Uspekhi Khim., **34**. 1629 (1967) [Russ.Chem.Rev., No.9 (1967)].
3. D.N.Shigorin, Zhur.Vses.Khim.Obshch.imeni Mendeleeva, **20**, 32 (1975).
4. R.N.Nurmukhametov, "Pogloshchenie i Lyuminestsentsiya Aromaticheskikh Soedinenii" (Absorption and Luminescence in Aromatic Compounds), Izd.Khimiya, Moscow, 1971.
5. K.G.Spears and S.A.Rice, J.Chem.Phys., **55**, 5561 (1971).
6. U.Boesl, H.J.Neusser, and E.W.Schlag, Chem.Phys. Letters, **31**, 17 (1975).
7. N.A.Borisevich, "Vozbuzhdennye Sostoyaniya Slozhnykh Molekul v Gazovoi Faze" (Excited States of Complex Molecules in the Gas Phase), Izd.Nauka i Tekhnika, Minsk, 1967.
8. J.G.Calvert and J.N.Pitts, "Photochemistry" (Translated into Russian), Izd.Mir, Moscow, 1968.
9. G.G.Gelman, "Quantum Chemistry" (Translated into Russian), Izd.ONTI, Moscow, 1937.
10. M.Born and J.R.Oppenheimer, Ann.Physik, **84**, 457 (1927).
11. M.V.Vol'kenshtein, L.A.Gribov, M.A.El'yashevich, and B.I.Stepanov, "Kolebaniya Molekul" (Molecular Vibrations), Izd.Nauka, Moscow, 1972.
12. P.M.Morse, Phys.Rev., **34**, 57 (1929).
13. A.S.Davydov, "Kvantovaya Mekhanika" (Quantum Mechanics), Fizmatgiz, Moscow, 1963.
14. A.Nitzan and J.Jortner, Chem.Phys.Letters, **11**, 458 (1971).
15. G.Herzberg and E.Teller, Z.phys.Chem., **B21**, 410 (1933).
16. C.C.J.Roothaan, Rev.Mod.Phys., **23**, 69 (1951).
17. R.Parr, "Quantum Theory of Molecular Electronic Structure", Benjamin Press, New York, 1963.
18. T.E.Peacock, "Electronic Properties of Aromatic and Heterocyclic Molecules" (Translated into Russian), Izd.Mir, Moscow, 1969.
19. V.A.Gubanov, V.P.Zhukov, and A.O.Litinskii, "Poluempiricheskie Metody Molekulyarnykh Orbitalei v Kvantovoi Khimii" (Semi-empirical Molecular Orbital Methods in Quantum Chemistry), Izd.Nauka, Moscow, 1976.
20. I.A.Misurkin and A.A.Ovchinnikov, Uspekhi Khim., **43**, 2195 (1974); **44**, 393 (1975) [Russ.Chem.Rev., No.12 (1974); No.3 (1975)].
21. V.G.Plotnikov, Optika i Spektrosk., **20**, 394 (1966).
22. T.R.Grinter and T.Edvards, Mol.Phys., **15**, 357 (1968).
23. V.M.Komarov and V.G.Plotnikov, Spectr.Letters, **8**, 363 (1975).
24. V.G.Plotnikov and V.M.Komarov, Spectr.Letters, **9**, 265 (1976).
25. M.Kasha, Discuss.Faraday Soc., **9**, 14 (1950).
26. V.L.Ermolaev, Optika i Spektrosk., **11**, 492 (1961).
27. R.N.Nurmukhametov and G.V.Gobov, Optika i Spektrosk., **18**, 227 (1965).
28. J.N.Murrel, "The Theory of the Electronic Spectra of Organic Molecules", Wiley, New York, 1963.
29. V.M.Komarov and V.G.Plotnikov, Teor.i Eksper. Khim., **10**, 62 (1974).
30. V.M.Komarov, K.L.Rogozhin, A.N.Rodionov, V.G.Plotnikov, and D.N.Shigorin, Zhur.Prikl. Spektrosk., **23**, 348 (1976).
31. J.M.Foster and S.F.Boys, Rev.Mod.Phys., **32**, 303 (1960).
32. J.M.Hollas, E.Gregorek, and L.Goodman, J.Chem. Phys., **49**, 1745 (1968).
33. M.F.Merienne-Lafore and H.P.Trommsdorf, J.Chem. Phys., **64**, 3790 (1976).
34. L.V.Orlovskaya and A.F.Terpugova, Izv.Vys.Ucheb. Zaved., Fizika, 134 (1974).
35. J.H.Lichtenbelt et al., J.Chem.Phys., **22**, 297 (1977).
36. V.M.Komarov, V.G.Plotnikov, and L.G.Belousova, Optika i Spektrosk., **29**, 1006 (1970).
37. R.Pariser, J.Chem.Phys., **24**, 250 (1956).
38. G.Favini, J.Vandoni, and N.Simoneta, Theor.Chim. Acta, **3**, 45 (1965).
39. M.M.Mestechkin, L.S.Gutyrya, and V.N.Poltavets, Optika i Spektrosk., **27**, 454 (1970); **30**, 1022 (1971).
40. Yu.B.Malykhanov, Optika i Spektrosk., **43**, 431 (1977).
41. S.P.McGlynn, T.Azumi, and M.Kinosita, "Molecular Spectroscopy of the Triplet State" (Translated into Russian), Izd.Mir, Moscow, 1972.
42. I.A.Misurkin and A.A.Ovchinnikov, Teor.i Eksper. Khim., **3**, 431 (1967).

43. V.N.Kondrat'ev (Editor), "Energii Razryva Khimicheskikh Svyazei. Potentsialy Ionizatsii i Srodstva k Elektronu" (Dissociation Energies of Chemical Bonds. Ionisation Potentials and Electron Affinities), Izd.Nauka, Moscow, 1974.
44. V.G.Plotnikov, Optika i Spektrosk., **20**, 589 (1966).
45. T.Anno and A.Sado, J.Chem.Phys., **26**, 1759 (1957).
46. L.Goodman and R.W.Harrel, J.Chem.Phys., **30**, 1131 (1959).
47. D.R.Kearns and M.A.El-Bayoumi, J.Chem.Phys., **38**, 1508 (1963).
48. L.V.Orlovskaya, I.V.Sokolova, and A.F.Terpugova, Optika i Spektrosk., **36**, 1508 (1963).
49. J.L.Whitten and M.Hackmeyer, J.Chem.Phys., **51**, 5584 (1969).
50. K.Yamaguchi and T.Fueno, Bull.Chem.Soc.Japan, **44**, 43 (1971).
51. K.Inuzuka and R.S.Becker, Bull.Chem.Soc.Japan, **45**, 1557 (1972).
52. V.M.Komarov, Thesis, Moscow, 1978.
53. R.N.Nurmukhametov, V.G.Plotnikov, and D.N.Shigorin, Zhur.Fiz.Khim., **40**, 1154 (1966)[Russ. J.Phys.Chem., No.7 (1966)].
54. M.Kasha and M.R.Rawls, Photochem.Photobiol., **7**, 561 (1968).
55. R.N.Nurmukhametov and I.A.Misurkin, Zhur.Fiz. Khim., **42**, 217 (1968).
56. S.F.Mason, J.Chem.Soc., 494 (1960).
57. R.N.Nurmukhametov et al., Optika i Spektrosk., **22**, 740 (1967).
58. D.N.Shigorin, N.A.Sheglova, and Yu.I.Kozlov, "Proceedings of the International Conference on Luminescence", Budapest, 1966, p.528.
59. D.S.McClure, J.Chem.Phys., **20**, 682 (1952).
60. J.L.Ginsburg and L.Goodman, Molec.Phys., **15**, 441 (1968).
61. I.G.Kaplan, "Simmetriya Mnogoelektronnykh Sistem" (Symmetry of Many-electron Systems), Izd.Nauka, Moscow, 1969.
62. N.F.Mott and I.Sneddon, "Wave Mechanics and Its Applications" (Translated into Russian), Izd.Nauka, Moscow, 1966, p.119.
63. V.G.Plotnikov, Optika i Spektrosk., **22**, 735 (1967).
64. V.G.Plotnikov, Optika i Spektrosk., **27**, 928 (1969).
65. E.Clement, J.Mol.Spectroscopy, **6**, 497 (1961).
66. J.W.Sidman, J.Chem.Phys., **29**, 644 (1958).
67. E.Clement and M.Kasha, J.Mol.Spectroscopy, **2**, 297 (1958).
68. L.Goodman and V.G.Krishan, Rev.Mod.Phys., **35**, 541 (1963).
69. Pill-Soon Song and W.H.Gardon III, J.Phys.Chem., **74**, 4234 (1970).
70. V.G.Plotnikov and B.A.Dolgikh, Optika i Spektrosk., **44**, 450 (1978).
71. I.I.Sobel'man, "Vvedenie v Teoriya Atomnykh Spektrov" (Introduction to the Theory of Atomic Spectra), Fizmatgiz, Moscow, 1963.
72. M.A.El-Sayed, J.Chem.Phys., **38**, 2834 (1963).
73. D.N.Shigorin and N.A.Shcheglova, Optika i Spektrosk., **36**, 740 (1974).
74. B.R.Henry and W.Siebrand, J.Chem.Phys., **54**, 1072 (1971).
75. V.M.Komarov and V.G.Plotnikov, Zhur.Prikl. Spektrosk., **20**, 256 (1974).
76. V.A.Smirnov, V.A.Sapozhnikov, O.M.Andreev, and M.V.Alfimov, Khimiya Vys.Energii, **5**, 121 (1971).
77. A.C.Albrecht, J.Chem.Phys., **38**, 354 (1963).
78. L.Burnelle and M.Kranepool, J.Mol.Spectroscopy, **37**, 383 (1971).
79. C.P.Yue and D.P.Chong, Mol.Phys., **14**, 487 (1968).
80. A.Kaito, M.Hatano, and A.Tajiri, J.Amer.Chem.Soc., **99**, 5241 (1977).
81. J.W.Sidman, Chem.Rev., **58**, 689 (1958).
82. L.Goodman, J.Mol.Spectroscopy, **6**, 109 (1961).
83. J.A.Pople and J.W.Sidman, J.Chem.Phys., **27**, 1270 (1957).
84. V.A.Kilin, A.F.Terpugova, and E.I.Cheglokov, Optika i Spektrosk., **41**, 770 (1976).
85. R.Shimada and L.Goodman, J.Chem.Phys., **43**, 2027 (1965).
86. J.N.Murrel and J.A.Pople, Proc.Phys.Soc.(London), **A69**, 245 (1956).
87. M.J.Robey et al., Chem.Phys., **23**, 207 (1977).
88. B.R.Henry and W.Siebrand, J.Chem.Phys., **51**, 2396 (1969).
89. V.G.Plotnikov, Optika i Spektrosk., **23**, 39 (1967).
90. T.Azumi and S.P.McGlynn, J.Chem.Phys., **37**, 2413 (1962).
91. M.A.El-Sayed, Nature, **197**, 481 (1963).
92. A.N.Rodionov, Thesis, Moscow, 1976.
93. R.N.Nurmukhametov and D.N.Shigorin, Zhur.Fiz. Khim., **35**, 72 (1961)[Russ.J.Phys.Chem., No.1 (1961)].
94. V.L.Ermolaev and A.N.Terenin, Uspekhi Fiz.Nauk, **71**, 137 (1960).
95. V.L.Ermolaev, Optika i Spektrosk., **16**, 704 (1964).
96. F.Dörr and H.Gropper, Z.Elektrochem., **67**, 193 (1967).
97. K.K.Innes, J.P.Byrne, and I.G.Ross, J.Mol. Spectroscopy, **22**, 125 (1967).
98. V.P.Kochkov and V.L.Bogdanov, Optika i Spektrosk., **34**, 70 (1973).
99. N.S.Strokach, E.A.Gastilovich, and D.N.Shigorin, Optika i Spektrosk., **35**, 239 (1973).
100. E.A.Gastilovich, G.T.Kryuchkova, et al., **39**, 235 (1975).
101. M.A.Souto and C.T.Lin, Chem.Phys., **17**, 129 (1976).
102. M.Mahaney and J.R.Huber, Chem.Phys., **9**, 371 (1975).
103. N.Kanamuru and E.C.Lim, J.Chem.Phys., **61**, 1582 (1974).
104. A.E.W.Knight, G.M.Lamburgh, and C.S.Parmenter, J.Chem.Phys., **63**, 4336 (1975).
105. O.S.Khalil and S.P.McGlynn, J.Luminescence, **11**, 185 (1975).
106. E.F.McCoy and I.G.Ross, Austral.J.Chem., **15**, 573 (1962).
107. K.K.Rebane, "Elementarnaya Teoriya Kolebatel'noi Struktury Spektrov Primesnykh Tsentrov Kristallov" (Elementary Theory of the Vibrational Structure of the Spectra of Impurity Centres in Crystals), Izd. Nauka, Moscow, 1968.
108. M.D.Frank-Kamenetskii and A.V.Lukashin, Uspekhi Fiz.Nauk, **116**, 193 (1975).
109. S.I.Vavilov, Z.Physik, **42**, 311 (1927).
110. S.Lower and M.A.El-Sayed, Uspekhi Fiz.Nauk, **94**, 289 (1968).
111. B.R.Henry and M.Kasha, Uspekhi Fiz.Nauk, **108**, 113 (1972).
112. J.Jortner, S.A.Rise, and R.M.Hochstrasser, Adv. Photochem., **7**, 149 (1969).
113. K.F.Freed, Fortschr.Chem.Forsch., **31**, 105 (1972).
114. V.G.Plotnikov and A.A.Ovchinnikov, Uspekhi Khim., **47**, 444 (1978)[Russ.Chem.Rev., No.3 (1978)].
115. M.Bixon and J.Jortner, J.Chem.Phys., **48**, 715 (1968).

116. W.Rhodes, B.R.Henry, and M.Kasha, Proc.Nat.Acad. Sci.USA, **63**, 31 (1969).
117. V.G.Plotnikov and G.G.Konoplev, Optika i Spektrosk., **34**, 1101 (1973).
118. E.D.Trifonov and V.L.Shekhtman, Fiz.Tverdogo Tela, **11**, 2984 (1969).
119. V.G.Plotnikov and G.G.Konoplev, Zhur.Eksper.Teor. Fiz., **65**, 960 (1973).
120. K.K.Rebane, Trudy Inst.Fiz.Akad.Nauk EstSSR, No.7, 62 (1958).
121. V.G.Plotnikov and G.G.Konoplev, Fiz.Tverdogo Tela, **15**, 680 (1973).
122. V.G.Plotnikov and G.G.Konoplev, Pre-print of the Institute of Theoretical Physics of the UkrSSR Academy of Sciences ITF-74-55R, Kiev, 1974.
123. V.L.Ermolaev, Optika i Spektrosk., **13**, 90 (1962).
124. V.L.Ermolaev and E.B.Sveshnikova, Optika i Spektrosk., **16**, 587 (1964).
125. V.L.Ermolaev and E.B.Sveshnikova, Acta.Phys. Polon., **34**, 771 (1968).
126. V.G.Plotnikov and B.A.Dolgikh, Optika i Spektrosk., **43**, 882 (1977).
127. A.A.Ovchinnikov and N.S.Erikhman, Optika i Spektrosk., **34**, 690, 887 (1973).
128. G.Herzberg, "Electronic Spectra and Structure of Polyatomic Molecules" (Translated into Russian), Izd. Mir, Moscow, 1969.
129. H.C.Longuet-Higgins and M.Beer, J.Chem.Phys., **23**, 1390 (1955).
130. K.D.Bist and J.S.Brand, J.Mol.Spectroscopy, **24**, 413 (1967).
131. V.G.Plotnikov, B.A.Dolgikh, and V.M.Komarov, Optika i Spektrosk., **43**, 1072 (1977).
132. G.W.Robinson and R.P.Frosch, J.Chem.Phys., **37**, 1962 (1962); **38**, 1187 (1963).
133. R.M.Hochstrasser, H.Lutz, and G.W.Scott, Chem. Phys.Letters, **24**, 162 (1974).
134. R.W.Anderson, R.M.Hochstrasser, H.Lutz, and G.W.Scott, Chem.Phys.Letters, **28**, 153 (1974).
135. Y.Hirata and I.Tanaka, Chem.Phys.Letters, **41**, 336 (1971); **43**, 568 (1976).
136. R.N.Nurmukhametov and V.G.Plotnikov, Izv.Akad. Nauk SSSR, Ser.Fiz., **39**, 2259 (1975).
137. T.Kobayashi and S.Nagakura, Chem.Phys.Letters, **43**, 429 (1976).
138. W.Siebrand, J.Chem.Phys., **44**, 4055 (1966).
139. R.Engelman and J.Jortner, Mol.Phys., **18**, 145 (1970).
140. V.L.Ermolaev and E.B.Sveshnikova, Chem.Phys. Letters, **23**, 349 (1973).
141. E.N.Bodunov and E.B.Sveshnikova, Optika i Spektrosk., **36**, 340 (1974).
142. E.N.Bodunov, Optika i Spektrosk., **40**, 942 (1976).
143. V.L.Ermolaev, Uspekhi Fiz.Nauk, **80**, 3 (1963).
144. V.V.Gruzinskii, L.A.Barkova, and N.M.Poltarak, Zhur.Prikl.Spektrosk., **20**, 619 (1974).
145. Yu.E.Perlin and B.S.Tsukerblat, "Effekty Elektronno-kolebatel'nogo Vzaimodeistviya v Optich-eskikh Spektrakh Primesnykh Paramagnitnykh Ionov" (Vibronic Interaction Effects in the Optical Spectra of Paramagnetic Impurity Ions), Izd. Shtiintsa, Kishinev, 1974.
146. D.N.Shigorin and V.G.Plotnikov, Dokl.Akad.Nauk SSSR, **234**, 121 (1977).
147. B.M.Krasovskii and B.M.Bolotin, "Organicheskie Lyuminofory" (Organic Phosphors), Izd.Khimiya, Leningrad, 1976.
148. V.M.Komarov and L.P.Kayshin, Stud.Biophys., **52**, 107 (1975).
149. N.A.Borisevich and V.V.Gruzinskii, Symposium "Kvantovaya Elektronika i Lazernaya Spektroskopiya" (Quantum Electronics and Laser Spectroscopy), Izd. Inst.Fiz.Akad.Nauk BelorussSSR, Minsk, 1971, p.81.
150. A.N.Simonov, Thesis, Moscow, 1975.
151. B.S.Neporent, Optika i Spektrosk., **32**, 38 (1972).
152. D.N.Shigorin, Zhur.Fiz.Khim., **51**, 1894 (1977)[Russ. J.Phys.Chem., No.8 (1977)].
153. V.G.Plotnikov and G.V.Maier, Optika i Spektrosk., **47**, 113 (1979).
154. B.A.Dolgikh and V.G.Plotnikov, Optika i Spektrosk., **47**, 231 (1979).

Obninsk Branch of the Karpov
Physicochemical Research Institute