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Association of Dye Molecules and Its Spectroscopic Manifestation

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Theoretical data for the influence of the association of the molecules of complex organic compounds (dyes) in solutions on their electronic spectra and other optical characteristics are examined and surveyed. The conditions for the formation of associated species and the influence of solvents, concentration, and temperature on this process are described. Methods for the determination of the association constants and the structure and compositions of the associated molecules are examined. The results of studies undertaken to investigate the luminescent associated dye species, their triplet states, and pathways leading to the deactivation of the electronic excitation are described. The nature of the forces which lead to the binding of the dye molecules in associated species is discussed and studies on the concentration-induced quenching of the luminescence of dye solutions are analysed.
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I. INTRODUCTION

Numerous studies have been carried out during recent decades on the association of the molecules of complex organic compounds in view of both scientific interest in the nature of excited electronic states and their role in chemical and biological processes and photochemical reactions, and the extensive use of organic dyes in laser technology, in cine-phototechniques, and in other fields. For example, in the course of photosynthesis chlorophyll functions in an associated state and haemoglobin consists of four subunits, the haem groups being involved in a close interaction. Nitrogen-containing bases, forming part of nucleic acids and interacting with one another, give rise to a molecular aggregate. The study of various properties of complex molecules which exist in the monomeric state in solution is complicated by different types of intermolecular interaction and this is the reason why studies on association permit a deeper understanding of their intramolecular energetics.

One of the most important classes of compounds with a complex molecular structure, which are widely used in technology, are organic dyes. Dyes are unique agents capable of transforming light energy. Their extensive technical applications are in fact due to their photophysical properties–their ability to absorb light and transform it into radiation at other frequencies. These properties depend on many factors, including intermolecular interaction. The association of dye molecules has a significant influence on their photophysical properties, resulting either in a loss of capacity for luminescence or in an appreciable redistribution of the emitted energy.

The association of molecules of complex organic compounds has been studied in numerous investigations. Nevertheless, there is not yet a unanimous view in the literature on many problems, such as, for example, the quantitative relation between the migration of the excitation energy in dye solutions and quenching of the luminescence, which are closely related to problems of association. All the aspects of the spectroscopic manifestation of association have not been ultimately elucidated either.

The aim of the present review is to give an account of the association of dye molecules from the standpoint of the influence of this process on their photonics and the spectroscopic changes occurring in their aggregation. Associated dye molecules, which are stable in the ground state and which are formed in weak and intermediate interactions, are examined; aggregates produced by covalent bonding (the so-called intramolecular associated species) and problems associated with formation of excimers and and charge-transfer complexes are not considered.

II. EXPERIMENTAL STUDY OF ASSOCIATION. CONDITIONS FOR THE FORMATION OF ASSOCIATED SPECIES AND THEIR STRUCTURE

The procedures used to investigate the aggregation of complex organic molecules are extremely varied: methods based on the study of diffusion[1], conductivity[2], light scattering[3], polarography[4,5], and electron paramagnetic resonance[6]. Spectroscopic methods (spectrophotometric and luminescence methods) are most widely used and yield the most fruitful results. This review presents the results of spectroscopic studies of association.

The association of dye molecules has been observed in various solvents and its nature (degree and order of association and the structure of aggregates) depend significantly on the nature of the solvent. Dye molecules are very effectively associated in water[7-11] and in mixtures of polar and non-polar solvents[12-15]. In polar solvents, where dye molecules are strongly solvated, their aggregation occurs at high concentrations[16,17]. In non-polar solvents chlorophyll molecules associated even at low concentrations[18,19], but dyes do not usually dissolve in such solvents. A decrease of the temperature of the solution intensifies association[20-27].

In the majority of studies of the association of the molecules of complex organic compounds the authors observed the occurrence of aggregation in different solvents, calculated the monomer–dimer equilibrium constants and the

heat of association (the binding energy of the molecules), isolated the spectrum of the associated species, and determined the degree (fraction of associated molecules) and order (number of molecules in the associated species) of association.

The most typical three kinds of changes in the absorption spectra of dyes occurring when their molecules are associated are as follows: (1) the formation of a narrow band (cyanine dyes); (2) decrease of absorbance (thiazine dyes); (3) the splitting of the absorption band into two and more components (xanthene dyes, acridine compounds, etc.).

Fig. 1 presents the absorption spectra of solutions of rhodamine 6G for different concentrations in an ethanol–carbon tetrachloride mixture. The changes in the spectra with increasing dye concentration indicate the formation of associated rhodamine species.

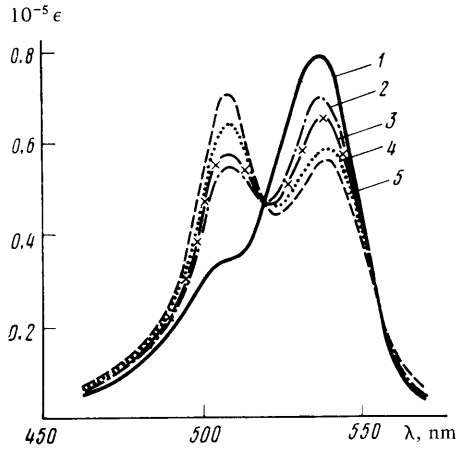


Figure 1. The absorption spectra of solutions of rhodamine 6G in a mixture of ethanol and carbon tetrachloride as a function of concentration (M): 1) 1.0×10^{-4}; 2) 6.4×10^{-4}; 3) 1.0×10^{-3}; 4) 2.5×10^{-3}; 5) 4.0×10^{-3}.

Association is most pronounced in aqueous solutions. Scheibe and coworkers[28,29] observed the formation in water of involved complexes of cyanine dyes, which have come to be called "Scheibe polymers". An increase of the concentration of these compounds leads to the appearance of a new very intense absorption band with $\lambda_{max} =$ 574 nm in the absorption spectra at $c = 4 \times 10^{-3}$ g ml^{-1}. The half-width of this band proved to be approximately six times smaller than that in the absorption spectrum of the dilute solution. The viscosities of such concentrated solutions are greatly increased; these phenomena are fully reversible on dilution or on heating of the solution. Förster[30] proposed a model for the Scheibe polymers, according to which the planar dye molecules are arranged in a row at equal distances from one another and have translational symmetry. If the oscillators of the individual molecules forming the polymer have the same amplitudes and vibration phases, the latter are added together, which gives rise to a resultant transition moment differing from the moment of each component oscillator; according to Förster, this should result in the appearance of a new absorption and luminescence band. The small width of this band is due to the fact that translational symmetry obtains only along the polymer axis. In this case the width is determined by the corresponding transitions allowed by selection rules. The formation of associated cyanine molecules has been observed not only in water but also in many organic solvents[31], for which narrow absorption bands appeared gradually with increased concentration of cyanine solutions and not abruptly; with increase of concentration, the association process is merely strongly accelerated. Aggregates of cyanine dyes, which are formed in aqueous ethanol solutions[32,33] also have an ordered layer structure with a definite distribution of anions between individual layers. This conclusion was based on a study of the concentration-induced changes in circular dichroism spectra and ultraviolet absorption spectra.

The concentration and temperature effects in aqueous solutions of rhodamines 3B and 6G have been investigated by Levshin and Baranova[7], who studied the influence of pH on the state of the dye and described a method for the determination of the degree of association in its solutions. The association of Congo Red, Methylene Blue, Crystal Violet, and other dyes in water and aqueous alcoholic solution has been studied[5,34,35] by both spectroscopic and polarographic methods. The authors of these investigations obtained conflicting results for the compositions of the associated species. Thus, according to their data, associated Crystal Violet species consist of 5–6 molecules. However, it has been noted[9] that this dye forms a mixture of associated species and the number of molecules in such association complexes increases with concentration. An estimate of this number based on diffusion measurements[1] yielded 18 molecules, while for substances analogous to those investigated by Hiroshi et al.[32] an association order of 2–3 was obtained.

With increase of dye concentration and with decrease of temperature, the equilibrium between monomeric dye molecules and associated molecules shifts towards the latter. A number of studies have been made on these problems for xanthene dyes in aqueous solutions[17,36-42]. On the assumption that the associated species of these dyes are dimers, methods have been developed for the isolation of their absorption spectra, the monomer–dimer equilibrium constants have been calculated, and chemical relaxations have been studied.

The influence of the solvent on aggregation processes is determined by the extent to which it promotes or hinders the combination of dye molecules by surrounding them with a solvation shell. The addition of organic solvents to aqueous solutions has a significant influence on the association of dye molecules[8,43-45], suppressing the latter. Absorption bands due to dimers and trimers have been observed in the absorption spectra of aqueous glycerol solutions and pyronine and fuchsine as a function of concentration ($5 \times 10^{-2} - 5 \times 10^{-6}$ M) at room temperature and at 80 K;[43] these spectroscopic changes can be satisfactorily accounted for within the framework of exciton theory.

The formation of associated species in aqueous solutions has been observed for thiazine dyes[46] (dimers), Acridine Orange, and Methylene Blue[47] (complex polymers), and for Bonadur Red[48] (dimerisation via hydrogen bonding with a heat of dimerisation of approximately 6 kcal mole^{-1}).

Associated species can also be formed from unlike molecules. However, the problem of association of unlike molecules of complex organic compounds has been inadequately investigated. There have been a few studies devoted to this subject[40,49-51]. It has been established[51]

that, with increase of the concentration of Acridine Orange and rhodamine 6G in aqueous solution of Methylene Blue, the absorbance falls both in the band of Methylene Blue (λ_{max} = 664 nm) and in the bands of Acridine Orange (λ_{max} = 492 nm) and rhodamine 6G (λ_{max} = 526 nm); in the first case new absorption bands do not arise. Such behaviour of the absorption spectra of the above systems indicates association of unlike species (their bond energy is 12 kcal mole^{-1} in the first case and 7 kcal mole^{-1} in the second). The study of such aggregates is the significant interest for the further development of the theory of the association of complex organic molecules.

The problem of whether or not dye molecules associate in solutions with a polar organic solvent remained unsolved for a long time. The difficulty was that the electronic absorption spectra of such solutions do not vary over a wide concentration range[52]. However, by measuring the concentration dependence of the average molecular weight of rhodamine dyes in alcoholic solutions, it was established[16] that in this case association takes place also. This was demonstrated indirectly in another study[53]. The degree of association in such highly concentrated solutions reaches 16%.[16] Associated species in alcoholic solutions of rhodamine dyes were detected also by EPR.[6] Nevertheless, studies where it is concluded that there is no aggregation of dye molecules in alcoholic solutions in view of the lack of any changes in the absorption spectra are still being continued[37,54]. The reason for this is that the degree of association of dye molecules in polar organic solvents is insignificant[16] and the absorption spectrum of the resulting associated species is similar to that of the monomer.

The study of the role of the anion in the association process[55,56] in various solvents showed that it does not have a significant influence on the aggregation of dye molecules. On the other hand, the structure of dye molecules has a strong influence on the development of association[57-59], which will be discussed below. The influence of temperature on the association of xanthene dye molecules has been studied[26,60-62]. Investigation of the ultraviolet absorption spectra of acridines in the range from 20° to −140°C [63] led to the conclusion that on cooling dimerisation takes place with participation of the hydrogen bonds in the NH groups.

The study of the association of dye molecules usually reduces to the determination of a number of constants, among which the number of molecules in the associated species n and the aggregation constant K_n are important. These constants are difficult to determine from spectroscopic data, since the number of unknowns is greater than the number of equations which can be set up. These difficulties have been overcome[20] with the aid of the equation

$$\lg [C_0(\varepsilon - \varepsilon_1)] = n \lg [C_0(\varepsilon - \varepsilon_n/n)] + \lg [K_n n (\varepsilon_1 - \varepsilon_n/n)^{1-n}], \quad (1)$$

where ϵ is the observed absorbance at a specified wavelength, ϵ_1 and ϵ_n are the absorbances of the monomer and the associated species, and C_0 is the overall concentration of the dye in solution. By plotting $\lg C_0(\epsilon - \epsilon_1)$ against $\lg C_0(\epsilon - \epsilon_n/n)$, it is possible to determine the order of the aggregation n from the slope of the resulting straight line and K_n can be found from the intercept on the ordinate axis. The difficulty of this method lies in the fact that one must know exactly the values of ϵ_1 and ϵ_n/n.

Other graphical methods have been proposed[64]. The authors call these procedures the "method of maximum slope" and the "method of optimum deviation". These methods make it possible to determine the molar extinction coefficient and the number of molecules in the dye aggregates provided that there is equilibrium between the monomers and associated species, and the absorption spectrum of the monomers is known. Comparison of the two methods[65] showed that they yield concordant results. A method for the determination of the order of association of dyes involving the study of the deviation from Beer's law has been described[66].

The knowledge of the geometrical structure of aggregates is of great interest for the theory of the association of complex molecules. In particular, it can help in the elucidation of the nature of the forces binding dye molecules into associated species. Although the geometry of such species can apparently be extremely varied in different instances, in theoretical calculations it is usually assumed that they have an ordered structure[67-70]. The spectra of solutions of dyes in which their molecules are associated also very often indicate the existence of such order. For a "sandwich" structure of the aggregates, the angle between the planes of the associated molecules φ is calculated from the formula[67,71-76]

$$\mu_s/\mu_d = (1 + \cos\varphi)/(1 - \cos\varphi), \quad (2)$$

where μ_S and μ_d are the electronic transition moments for the short- and long-wavelength absorption bands of the dimer, which are calculated with the aid of the relation $\mu^2 = 1.09 \times 10^{-19} \int \alpha(\nu) d\nu$ [$\alpha\nu$ is the absorption spectrum of the corresponding band]. The transition moments are related to the oscillator strength f by the expression

$$f = 8\pi^2 m_e c g \nu \mu^2 / 3he^2 \quad (3)$$

where ν is the frequency (cm^{-1}), m_e and e are the electronic mass and charge, g is the degeneracy of the excited state, and $\alpha(\nu)$ is the absorption spectrum of the corresponding band. The resolution of the spectrum of the dimer into the long-wavelength and short-wavelength bands presents a definite difficulty. Methods for such resolution in specific but practically important instances have been developed[77,78].

In order to solve the above problems, it is also necessary to know the concentration of the associated species in solution. This can be determined from absorption spectra[79] and by measuring the number-average molecular weight[16]. A method has been proposed[80] for the determination of the concentration of dimers and the equilibrium constants for their formation based on the measurement of the concentration dependence of the degree of polarisation and the luminescence quantum yield. A satisfactory agreement of the results obtained by this method and spectrophotometrically has been demonstrated for water–glycerol mixtures. The method is convenient when the dependence of the absorption spectra on concentration is insignificant.

The aggregates formed are very often treated as dimers in studies of association. However, when the order of the association is determined, experiments shows that this is by no means always the case. For example, in the study of concentrated solutions of 1,1-diethyl-2,2-cyanine bromide at low temperatures[81] it was possible to resolve the individual absorption bands referring to dimers (483 nm), trimers (465 nm), and tetramers (458 nm). On the basis of spectroscopic data, it was then concluded that several forms of aggregates exist: aggregates with a perpendicular disposition of the interacting molecules relative to the long axis of the aggregate and aggregates consisting of left- and right-hand helicoidal structures with eight monomers per turn of the helix. The study of the absorption and luminescence spectra of fluorescein, eosin, erythrosin, pyronine, and fuchsin at

different concentrations and temperatures[43,82] showed that, with increase of the concentration of dyes, characteristic changes occur in the spectra due to the formation of dimers and more complex aggregates. Electronic spectra for aggregates acquire partial exciton character.

The study of the association of rhodamines C, 3B, and 6G and of unsubstituted rhodamine in various solvents at 9° and 22°C [17,83,84] made it possible to obtain the aggregation constants and to reach a conclusion about the geometrical disposition of the molecules in the dimers ("in a stack" in water and "end to end" in ethanol). The study of azulenes in isopentane–methylcyclohexane glasses at 77 K and $c \simeq 10^{-3}$ M showed[85] that dimers are formed and their energy levels were calculated. The luminescence of such dimers was not detected. It has been established[16,26] that, in concentrated alcoholic solutions of rhodamine dyes at room temperatures, and on cooling, involved associated species comprising six dye molecules are formed on cooling. The molecules are arranged "end to end" and the angle between them decreases with decrease of the solution temperature. The geometrical structure of the aggregates of cyanine dyes has been studied[86] in various solvents by electron microscopy, optical microscopy, X-ray diffraction, and absorption spectroscopy. The results suggest that the planes of the molecules in the associated species are parallel, i.e. the aggregates have a "sandwich" structure. The authors separated the absorption bands for small aggregates up to pentamers.

On the basis of a study of the electronic spectra of a number of compounds in EPA (a mixture of ether, pentane, and ethanol), an interesting hypothesis has been put forward[87], namely that the spectroscopic changes on passing to dimers are due mainly to a change in the geometry of the monomer itself and that the splitting of the levels plays a secondary role. However, this hypothesis can be hardly regarded as sufficiently well founded.

The knowledge of the geometrical structure of the associated species may prove to be important for the elucidation of the nature of the forces responsible for the association of dye molecules. Quite inadequate attention has been devoted to this problem in the literature, evidently owing to the great complexity of the inter-molecular interactions in solutions of organic compounds. It has been concluded[88] that thionine and Methylene Blue dimers are formed as a result of van der Waals forces. The free energy of the dimerisation of Methylene Blue in water at 26.7°C was found to be 4.9 kcal mole^{-1}.

According to the theory of intermolecular interactions[89,90], the attraction energy of two identical molecules with a long-wavelength absorption band having a maximum at λ_0 is proportional to $f^2\lambda_0^3$, where f is the oscillator strength. Since f and λ_0 are large for dyes, the attraction forces between their molecules should also be greater when the latter approach one another sufficiently closely than for the corresponding colourless forms. These forces combine dye molecules into dimers or more complex associated species. Terms taking into account dipole–quadrupole and quadrupole-quadrupole interactions, evaluated by Margenau[90], may be added to those for the London dipole–dipole interaction[89] in the case of dyes.

Calculations by Davies and Coulson[91] showed that, for large molecules with extensive π-electron clouds, the dispersion forces, which make the greatest contribution to the van der Waals molecular interaction energy, may reach large values (tens of kcal mole^{-1}) for short intermolecular distances. These calculations were carried out for molecules which were simple compared with dyes.

The theory of van der Waals forces was constructed on the assumption that the distances between the interacting molecules are greater than their transverse dimensions[92,93].

For small intermolecular distances, characteristic of highly concentrated solutions, forces which decrease faster than as $1/R^6$, for example, forces associated with the quadrupole interaction, may become important also. It is usually believed that the energy of the van der Waals interaction does not exceed 2 kcal mole^{-1} for dye molecules[10,11]. However, this cannot apparently be regarded as a firmly established theoretical fact (for large molecules of the type of dyes, the bond energy has not been calculated rigorously) or as an accurate experimental result (the attempts at a quantitative test of the theory of universal molecular forces failed to yield sufficiently convincing results, since they were based on the measurement of integral effects which depend on the interaction of many molecules at different distances[94]). The view according to which dye molecules associate via van der Waals forces is shared also by many other workers[30,31,95-99], who investigated the association of the molecules of various compounds in different solvents.

Another view is that the association of dyes takes place via hydrogen bonding. It has been shown for a large number of dyes that the hypothesis of the major role of dispersion forces in the formation of associated species conflicts with many experimental facts. These are in the first place the strong dependence of the efficiency of the association process on the nature of the solvents employed and the structure of the dye molecules[13,93,100-102]. Concentration-induced changes in the absorption spectra, indicating the association of dye molecules in solutions, have been observed for compounds whose molecules have active N–H groups. The spectra of solutions of dyes whose molecules have no such groups do not change in the same solvents with increase of their concentration, which indicates the absence of association according to the authors of the above investigations.

Hydrogen bonds can be formed either directly between dye molecules or the latter may be combined with the aid of water molecules, which play the role of intervening bridges. The presence of intermolecular hydrogen bonds $\rangle$N–H...O=C$\langle$ and $\rangle$N–H...O$\langle$ has been established for rhodamine 6G also on the basis of infrared absorption spectra[103-105]. In chloroform–carbon tetrachloride mixtures the intensity of the absorption band due to free N–H vibrations (ν_{max} = 3445 cm^{-1}) decreases appreciably and the intensity of the broad band, which is appreciably displaced towards longer wavelengths (ν_{max} = 3200 cm^{-1}), increases in the spectrum of this dye with increased content of the non-polar component. This indicates the appearance of N–H vibrations perturbed by hydrogen bonding. Analogous changes occur in the infrared spectra of the solutions with increase of the dye concentration and with decrease of solution temperature[106].

Analysis of numerous experimental data obtained for solutions of xanthene and triphenylmethane dyes[105] showed that their associated species are formed on combination of two ion pairs via hydrogen bonds between the N–H group of the cation in one pair and the anion of another:

$$RN^+—H \ldots A^-RN^+—R.$$

The fundamental role of hydrogen bonds in the association of dye molecules in aqueous and aqueous alcoholic solutions as well as in binary mixtures of a polar and

non-polar solvent has also been indicated in other studies[60,107,108].

However, one should note that in the above studies it has been suggested that the polar organic solvents there is no association of dye molecules[109-111] because the active N–H groups of dyes are "occupied" by solvent molecules. Further study of this problem showed[16] that molecular associated species containing active N–H groups (rhodamine G, 6G, and others) and without active groups (rhodamine C, 3B, S, and others) are formed at high dye concentrations, the association in the former case beginning at lower concentrations. This apparently shows that association via hydrogen bonding takes place to a definite extent also in alcoholic solutions. In the second case associated species are evidently formed via van der Waals forces. This is indicated also by the finding that the associated species in such solutions are involved (approximately 6 molecules in a single aggregate). The energy of the bond between two molecules in such associated species is approximately 4 kcal mole^{-1} in all rhodamines[26], i.e. approaches the energy of the hydrogen bond.

In some studies it has been suggested that hydrophobic forces[107] and the interaction of dye molecules with the accompanying anions[56,112] are responsible for their association. The study of rhodamine dyes showed that the tendency towards association increases with increasing number and size of alkyl substituents[54].

The problem of the nature of the forces responsible for the association of dyes must apparently be solved in each specific instance in its own way. There is no point in extending the results for several examples to all cases. On the other hand, van der Waals forces, being universal, always act between dye molecules at a sufficiently short distance.

However, theories attempting to explain the spectroscopic changes occurring in the association of dye molecules do not take into account the nature of the intermolecular interactions.

III. THEORY OF THE SPECTRA OF ASSOCIATED MOLECULES

Förster's theory[30,113], describing the molecular properties of aggregates has been developed solely for dimers. It is assumed that the associated species consist of monomeric dye molecules whose planes are parallel to one another. Such dimeric molecules should possess an additional twofold symmetry axis apart from the symmetry elements of the monomer. The transition moments (oscillators) of these molecules are also parallel for the visible part of the spectrum. In consequence of thermal vibrations or structural assymmetry, the parallel arrangement may break down. For such a model, the oscillators of both molecules can be represented by two normal vibrations at different frequencies, each involving separate oscillators with the same amplitudes. However, the vibrations of one set of oscillators have the same phase, while those of the other set differ by 180°, i.e. the vibrations can be both symmetric and antisymmetric.

The vibrations of individual oscillators can be represented schematically as follows:

$$\rightleftarrows \quad \rightleftarrows \quad .$$

Symmetric vibrations give rise to a resultant non-zero dipole moment; for antisymmetric vibrations, the changes in the moments of individual oscillators cancel out. On absorption and emission of light, only symmetrical vibrations of the dipole are therefore excited, while the antisymmetrical vibrations are inactive. The two types of vibrations have different intrinsic frequencies due to the electric coupling of the two oscillators. Such coupling enhances in the case of the symmetric vibrations and weakens in the case of the antisymmetric vibration the force which restores the oscillators to the equilibrium position. As a result, compared with the vibration of the monomeric oscillator, the symmetric coupled vibration has a higher intrinsic frequency and the antisymmetric vibration has a lower frequency.

Thus, when two molecules approach one another, the electronic transition band is split. However, for the antisymmetric vibration the overall dipole moment of the dimer is unchanged and the absorption spectrum manifests only the transition associated with the symmetric vibrations of the oscillators, i.e. vibrations having a higher frequency. This leads to the experimentally observed hypsochromic shift of the absorption band on dimerisation of dye molecules. Since the transition corresponding to the antisymmetric vibrations, i.e. the transiton from the lowest excited level, is forbidden, the dimers do not luminesce.

This hypothesis cannot explain the finding that the spectra of the dye dimers frequently consist of two bands. According to Förster's theory the observation of such dimers would be impossible in view of the metastability of the excited state with the lower energy. Förster therefore suggests that in such cases the bond energy in the associated species is low and the oscillators of both molecules fail to attain a parallel arrangement in the ground state.

By applying the free electron model to a system consisting of two monomers, each of which has two electronic levels in the free state, Nikitin[114] obtained identical splittings of the energy levels of the ground and excited states, between which four electronic transitions are possible. Two of these have the same energy, equal to the transition energy in the monomer. The other two transitions are displaced–the frequency of one is smaller and that of the other greater than the frequency of the transitions in the monomer. The probabilities of the last two transitions proved to be much greater than the sum of the probabilities with identical frequencies. Thus Nikitin's calculation predicts qualitatively the splitting of the absorption band of the monomers into two components on formation of dimers. Förster's and Nikitin's theories explain only the displacement and splitting of the absorption spectrum on association of dye molecules. They do not yield quantitative relations for the calculation of the splittings.

Simpson and coworkers[115,116] carried out a quantum-mechanical calculation on dye dimers assuming that the molecular planes of their cations in the dimer are parallel ("sandwich" structure) and neglecting the interaction between the components corresponding to the monomers of the electronic wave functions for the ground state and the doubly degenerate first excited state. Thus it is suggested that the wave function of the ground state of the dimer has the form $\Psi_1\Psi_2$ and that of the excited state is $\Psi_1^*\Psi_2$ and $\Psi_1\Psi_2^*$, where Ψ_1 and Ψ_2 are the wave functions of individual molecules *1* and *2* forming the dimer and the asterisk denotes electronic excitation.

In their calculations Simpson and coworkers used the following expression for the molecular interaction potential:

$$V = (-2\Sigma z_1 \Sigma z_2 + \Sigma x_1 \Sigma x_2 + \Sigma y_1 \Sigma y_2)\, e^2/R^2, \qquad (4)$$

where e is the electronic charge, R the distance between the molecules, and x, y, and z are the coordinates of the electrons of the corresponding molecules. The exact wave function for the excited state is

$$\Psi_{\pm} = 2^{-1/2}(\psi_1^*\psi_2 \pm \psi_1\psi_2^*). \quad (5)$$

Simpson and coworkers[115,116] showed that, in the case of a strong interaction of the molecules of dyes *1* and *2*, the interaction energy in the dimer is given by the following expression in terms of the dipole approximation:

$$W_{\pm} = \pm \bar{m}_1\bar{m}_2/R^3, \quad (6)$$

where, for example, the x component of the dipole moment of the transition $\bar{m}_1$ can be written as follows:

$$(m_1)_x = e\int \psi_1 \Sigma x_1 \psi_1^* d\tau_1. \quad (7)$$

The transition moment for absorption by the dimer is given by the expression

$$\bar{m}_{\pm} = 2^{-1/2}(\bar{m}_1 \pm \bar{m}_2). \quad (8)$$

If the disposition of molecules in such that $\bar{m}_1 = -\bar{m}_2$, then the transition moment (on absorption of a light quantum) to the lower of the excited split levels with an energy W_+ is zero and the moment of the transition to the higher of the levels with an energy W_- is $2^{1/2}m_1$, which corresponds to an increase of the absorption intensity by a factor of two compared with a monomeric molecule.

Simpson and coworkers[115,116] explained the agreement between their model and experiment by the fact that the short-wavelength absorption band in the spectrum of the dimer is usually more intense than the long-wavelength band: on the other hand, the appearance of the latter can be accounted for by the fact that the molecular planes of dyes in the aggregate are not rigorously parallel. In their model the distance between identical molecules in the dimer is expressed in terms of the energy of the splitting of the levels by the formula

$$\Delta W = W_- - W_+ = 2|\bar{m}_1|2/R^3. \quad (9)$$

De Voe[117,118] developed a semiclassical theory of the electronic absorption spectra of associated species with weak bonding, where the Born–Oppenheimer approximation was used in the electronic and vibrational components as the zeroth approximation to the wave function for each monomer. Using the first-order perturbation theory, De Voe derived equations relating the extinction coefficient of the band due to the associated species to the parameters of the spectra of its constituent monomers.

De Voe's fundamental hypothesis is that the optical properties of each monomer can be described by one or several one-dimensional complex polarisabilities with different directions of polarisation and different frequency dependences. The associated species is characterised by M different polarisabilities $\alpha_i^0(\nu)$ of N monomers ($M \geqslant N$) and the directions of their polarisations are specified by unit vectors $\mathbf{e}_i$, where i varies from 1 to M. In quantum theory polarisability corresponds to the dipole moment of the transition from the ground to the excited electronic state. The vector $\mathbf{e}_i$ has the same direction as the electronic moment of the transition $\boldsymbol{\mu}_i^0$.

It is assumed that the associated species consists of N monomers and that it is small compared with the wavelength of the incident light. On can therefore neglect the lag effect and can assume that the electric field of the incident light is the same within the limits of the associated species. The polarisability of each monomer is determined by the strength of the local field in which the monomer is located (the field of the incident light plus the field due to other monomers). The real component of the polarisability describes the polarisation in phase with the electric field of the incident light and the imaginary component describes the out of phase polarisation causing the absorption of light.

If $\epsilon_i(\nu)$ is the molar extinction coefficient of an isolated monomer, then the real and imaginary components of $\alpha_i^0(\nu)$ are given by the following equations:

$$\mathrm{Re}\,\alpha_i^0(\nu) = \frac{6\cdot 2303c}{8\pi^3 N_0}\int \frac{\varepsilon_i(x)\,dx}{x^2-\nu^2} \equiv R_i(\nu), \quad (10)$$

$$\mathrm{Im}\,\alpha_i^0(\nu) = -\frac{3\cdot 2303c}{8\pi^2 N_0}\cdot\frac{\varepsilon_i(\nu)}{\nu} \equiv I_i(\nu), \quad (11)$$

where c is the velocity of light and N_0 the Avogadro number. The principal value of the integral is used.

If the aggregate is in the field $\mathbf{E}$ of plane-polarised light at a frequency ν, then each of the N monomers undergoes polarisation, which depends on the incident field and the field of the other monomers. The complex amplitude of the induced moment of the polarisability of an individual monomer can be formulated as follows:

$$m_i(\nu) = \alpha_i^0(\nu)\left[\mathbf{e}_i\mathbf{E} - \sum_{j=1}^{M} G_{ij}m_j(\nu)\right]. \quad (12)$$

The expression in brackets represents the amplitude of the local field along $\mathbf{e}_i$. The above equation expresses the induced moment of the polarisability of the ith monomer as a linear function of the induced moments of all other monomers in the aggregate. The interaction coefficient G_{ij} is interpreted as the energy of the Coulombic interaction between two point dipoles with dipole moments oriented along $\mathbf{e}_i$ and $\mathbf{e}_j$. In terms of the point dipole approximation, these coefficients are given by the expressions

$$G_{ij} = r_{ij}^{-3}[\mathbf{e}_i\mathbf{e}_j - 3(\mathbf{e}_i\mathbf{e}_{ij})\mathbf{e}_j\mathbf{e}_{ij})], \quad (13)$$

where $\mathbf{e}_{ij}$ is the unit vector along the line connecting the ith and jth monomers and r_{ij} is the distance between them.

For aggregates with an appreciable interaction between the monomers, De Voe[117,118] used the following expression for the density of the transition:

$$G_{ij} = V_{ij}/|\mu_i|\,|\mu_j|, \quad (14)$$

where V_{ij} is the energy of the Coulombic interaction between the charge densities of two molecules.

On solving M equations of type (12) written in matrix form, it is possible to calculate the optical properties of the aggregate. For a dimer with the same polarisability of each monomer ($N = M = 2$), the extinction coefficient is

$$\epsilon_d(\nu) = \sum_i\sum_{j\neq i}\varepsilon_i(\nu)\frac{1 - 2G_{12}R_i e_1 e_2 + G_{12}^2(I_1I_2 + R_j^2)}{[1 - G_{12}^2(R_1R_2 - I_1I_2)]^2 + [G_{12}^2(R_2I_1 + R_1I_2)]^2}. \quad (15)$$

De Voe[118] obtained a formula whereby G_{ij} can be expressed in terms of experimental quantities. For a dimer, G_{12} can be determined from the equation

$$\varepsilon(\nu) = \varepsilon^0(\nu)[1 - 2R(\nu)G_{12}(\mathbf{e}_1\mathbf{e}_2)],$$

where $\epsilon^0(\nu)$ and $\epsilon(\nu)$ are the extinction coefficients of the monomer and the dimer. Knowing the extinction coefficient of the monomer and the dimer for a specified value of ν and having calculated $R(\nu)$, it is possible to determine G_{12}.

The experimental study of the optical characteristics of the monomers, dimers, and more involved associated species of dyes[119-121] showed that there is only a qualitative agreement between De Voe's theory and experiment.

At the present time the main theory used to explain the spectroscopic features arising on aggregation of dye molecules is the exciton theory. The exciton model, developed by Davydov[122] for molecular crystals, has been used by a number of workers[67-70] to develop a theoretical method for the investigation of the spectra of associated species. For an aggregate comprising N molecules, the exciton band consists of N discrete levels. The dipole transitons in this system are allowed only for one or several (a small number equal to the number of molecules in the associated species) exciton states. The energy and wave function of the ground state of the aggregate are the same as for the monomers.

The wave function of the ground state of the dimer is

$$\Psi_0 = \psi_1 \cdot \psi_2, \tag{16}$$

where Ψ_1 and Ψ_2 are the wave functions of the ground state of the free monomer. The Hamiltonian of the dimer is

$$H = H_1 + H_2 + V_{12}, \tag{17}$$

where H_1 and H_2 are the Hamiltonians of the isolated molecules 1 and 2 and V_{12} is the intermolecular interaction potential (the Coulombic potential represented approximately by point dipole terms in the point-multipole expansion). The energy of the ground state of the dimer is obtained from the Schrödinger equation

$$E_0 = \int\int \psi_1\psi_2 H \psi_1\psi_2 \, d\tau_1 \, d\tau_2 \tag{18}$$

or

$$E_0 = E_1^0 + E_2^0 + \int\int \psi_1\psi_2 (V_{12}) \, \psi_1\psi_2 \, d\tau_1 \, d\tau_2. \tag{19}$$

The last term corresponds to the van der Waals interaction energy between the ground states of molecules *1* and *2* and E_1^0 and E_2^0 are the energies of the ground states of the isolated molecules.

The wave functions of the excited state of the dimer are written in the following form:

$$\Psi_E = r\psi_1^*\psi_2 + s\psi_1\psi_2^*, \tag{20}$$

where Ψ_1^* and Ψ_2^* are the wave functions of the excited state (with the energies E_1^* and E_2^*) and r and s are coefficients which must be determined. The Schrödinger equation for the excited state is

$$H(r\psi_1^*\psi_2 + s\psi_1\psi_2^*) = E_E(r\psi_1^*\psi_2 + s\psi_1\psi_2^*). \tag{21}$$

On multiplying the two sides of this equation by $\Psi_1^*\Psi_2$, integrating with respect to the coordinates of molecules *1* and *2*, and repeating this process for $\Psi_1\Psi_2^*$, we arrive at two equations containing terms which are symmetrical with respect to sub-scripts *1* and *2*:

$$\begin{aligned} H_{11}(=H_{22}) &= \int\int \psi_1^*\psi_2 H \psi_1^*\psi_2 \, d\tau_1 \, d\tau_2, \\ H_{12}(=H_{21}) &= \int\int \psi_1^*\psi_2 H \psi_1\psi_2^* \, d\tau_1 \, d\tau_2. \end{aligned} \tag{22}$$

The determinant of the coefficients r and s in these equations is zero for non-trivial solutions:

$$\begin{vmatrix} H_{11} - E_E & H_{12} \\ H_{21} & H_{22} - E_E \end{vmatrix} = 0. \tag{23}$$

The roots E_E are given by the following expressions in view of the equivalence of the terms of Eqns. (22):

$$\begin{aligned} E_E' &= H_{11} + H_{12} \text{ for } \Psi_E' = 2^{-1/2}(\psi_1^*\psi_2 + \psi_1\psi_2^*), \\ E_E'' &= H_{11} - H_{12} \text{ for } \Psi_E'' = 2^{-1/2}(\psi_1^*\psi_2 - \psi_1\psi_2^*). \end{aligned} \tag{24}$$

Having calculated E_E' and E_E'', we have, by virtue of the orthogonality condition for the wave functions of each molecule,

$$\begin{aligned} E_E' &= E_1^* + E_2 + \int\int \psi_1^*\psi_2 (V_{12}) \, \psi_1^*\psi_2 \, d\tau_1 \, d\tau_2 + \int\int \psi_1^*\psi_2 (V_{12}) \, \psi_1\psi_2^* \, d\tau_1 \, d\tau_2, \\ E_E'' &= E_1^* + E_2 + \int\int \psi_1^*\psi_2 (V_{12}) \, \psi_1^*\psi_2 \, d\tau_1 \, d\tau_2 - \int\int \psi_1^*\psi_2 (V_{12}) \, \psi_1\psi_2^* \, d\tau_1 \, d\tau_2. \end{aligned} \tag{25}$$

The last term in Eqns. (25) describes the exciton splitting:

$$\mathscr{E} = \int\int \psi_1^*\psi_2 (V_{12}) \, \psi_1\psi_2^* \, d\tau_1 \, d\tau_2, \tag{26}$$

It becomes, in terms of the point dipole approximation

$$\mathscr{E} = \mathbf{M}_1\mathbf{M}_2/r^3 - 3(\mathbf{M}_1 \cdot \mathbf{r})(\mathbf{M}_2 \cdot \mathbf{r})/r^5 \tag{27}$$

and represents the energy of the interaction due to the exchange of the excitation energy between molecules *1* and *2* at a distance r. The third term in Eqns(25) is analogous to the corresponding term in Eqn. (19) and corresponds to the van der Waals interaction between the excited molecule *1* and the ground state of molecule *2*. $\mathbf{M}_1$ and $\mathbf{M}_2$ are the transition moments in molecules *1* and *2* and $\mathbf{r}$ is the vector directed from molecule *1* to molecule *2*.

The exciton model describes the resonance splitting of the excited states of complex molecules. The ground state is displaced relative to the ground state of the initial molecules solely due to the van der Waals interaction.

Here one considers different limiting cases of the intermolecular bond. The ratio of the force of the intermolecular electronic interaction between excited states and the force of the intramolecular vibronic coupling serves in practice as a criterion for the assessment of the intermolecular bond[116]. For a strong bond, the following ratio is used as a criterion:

$$2U/\Delta\varepsilon \gg 1, \tag{28}$$

where $2U$ is the width of the exciton band and $\Delta\epsilon$ is the width of the Franck–Condon band of the corresponding molecular electronic transition in the monomer. The opposite inequality has been suggested as a criterion for a weak bond:

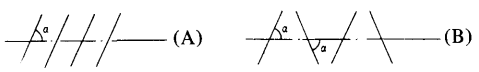
$$2U/\Delta\varepsilon \ll 1. \tag{29}$$

In the case of a strong bond, the electronic and vibrational wave functions are separated by the Born–Oppenheimer method. The absorption spectra of the dimer will be split if even one of the components of the electronic transitions is prohibited and is not shown in the spectrum. For a linear polymer of N molecules, the interaction of the latter leads to an exciton band consisting of N discrete exciton states. The selection rules for linear polymers have been developed by McRae and Kasha[67]. The bands of the resolved components then become very narrow, since excitation is in this case "smeared" over many molecules and each molecule has approximately the same electronic structure as the molecule in the ground state, i.e. the Franck-Condon principle allows in this case only the non-vibration 0–0 electronic transition.

A weak bond corresponds to the nonresolvability of the molecular wave functions by the Born–Oppenheimer method. In the limiting case of a weak bond no change in the spectral band is observed, but effects such as hypochromism or hyperchromism may be manifested.

The case of an intermediate bond constitutes an unsolved problem in exciton theory. Here one can observe a general distortion of the band contour.

McRae and Kasha[67] examined associated dye molecules having the following structures:



The theoretical calculation presented by the authors predicts the splitting of the energy levels of the excited states of associated species comprising N molecules into N levles. The splittings are

$$\mathscr{E} = 4\,[(N-1)/N\,](m^2/r^3)\,(1-3\cos^2\alpha), \tag{30}$$

for structure (A) and

$$\mathscr{E} = 4\,[(N-1)/N]\,(m^2/r^3)\,(1+\cos^2\alpha) \tag{31}$$

for structure (B), where m is the transition moment for the monomer. An increase of the probability of intercombination transitions in the association of dye molecules has been predicted[67].

In later studies the exciton theory was refined and tested experimentally. Thus, theoretical calculations of the spectroscopic characteristics of stable anthracene dimers were made and a satisfactory agreement with experiment was demonstrated[123,124]. An asymptotic expression for the shape of the dimer absorption bands has been obtained[125] by the method of exciton theory for the case of strong interaction of complex molecules. Allowance for intermolecular vibrations in dimers[126] made it possible to introduce certain refinements into the form of their absorption spectra. The vibrational states of the monomers constituting the molecular aggregates were also taken into account in the exciton theory[127]. The vibronic interactions in aggregates have been examined[128-131]. In this case the theory includes a parameter taking into account the intramolecular vibrations of the monomers and a parameter characterising the extent of the interaction between them. The theory taking into account such interactions has been tested in detail in experimental studies[132-134] whose results have been surveyed[135]. An experimental test showed that the predictions of the theory hold rigorously only for certain values of its parameters, which do not alway correspond to real systems.

Using the molecular exciton theroy, the vibronic interactions in helical aggregates were investigated theoretically[136] and a study was made of the influence of intramolecular vibrations of the monomers on their electronic absorption spectra.

More refined experiments[137], designed to investigate the absorption and polarisation spectra of luminescent dimeric forms of rhodamine C at room temperature and 77 K (in this case LiCl was added to improve the vitrification of the solutions), showed that the exciton theory cannot account for the measured polarisation characteristics of the dimers, whose interpretation requires allowance for the vibronic interactions in the molecules of the test compound. These ideas were subsequently developed[138] and confirmed experimentally for associated rhodamine and acridine dyes.

Thus the existing theories explain qualitatively many features arising in the electronic spectra of complex organic compounds when their molecules undergo association and also describe many quantitative effects. However, they apply only to dimers and more complex aggregates with a specific configuration. Complex associated species with an arbitrary structure, which can be formed in concentrated solutions, are not described by these theories.

One should note that the overall Hamiltonian (17) used in the exciton theory for the dimer does not take into account the perturbing effect of the field due to solvent molecules on the associated dye molecules.

Furthermore, it has been shown[139] that the stability of the associated species depends on the solvation shell consisting of solvent molecules, i.e. the theory must take into account also this form of intermolecular interaction.

IV. LUMINESCENT ASSOCIATED SPECIES

Association of dye molecules leads as a rule to the loss of their luminescent properties. However, under certain conditions the associated species fluoresce. The study of luminescent associated species is of both scientific and spectroscopic interest. Thus elucidation of the causes of the radiationless degradation of the electronic excitation energy of associated molecules can lead to the solution of a more complex problem, which Vavilov formulated as follows[140]: "The main problem of the photoluminescence of solutions, which has still not been solved even in broad outline, involves the question why some molecules luminescence while others do not". A study of the conditions governing the formation of luminescent associated species may help to elucidate the pathways whereby their electronic excitation energy is exchanged and the nature of their electronic spectra.

When non-luminescent associated species are formed, the absorption spectra of the dye solutions change, while their luminescence spectra do not undergo any alteration in form. Variable luminescence spectra and invariant absorption spectra would indicate the formation of excimers[141]. The formation of luminescent associated species in dye solutions is accompanied by the deformation of both their absorption spectra and their luminescence spectra.

In his study of the influence of concentration on electronic spectra, Levshin observed[142] that an increase of the concentration of fluorescein and Rhoduline Orange in rock candy leads to appreciable changes in their luminescence spectra. He also showed that Acridine Orange in rock candy forms luminescent associated species at 20° and −183°C.[143] At 20°C, starting from $c = 10^{-3}$ g g^{-1}, the luminescence spectra of rock candy activated with acridine show a gradual weakening of the green emission band ($\lambda_{max} = 534$ nm) due to the luminescence of monomers and the simultaneous increase in the intensity of the emission band of the associated species ($\lambda_{max} = 575$ nm). The influence of the concentration of this compound on the electronic spectra and the duration and yield of luminescence in frozen alcoholic solutions has been studied[144] and it has been shown that, with increase of the concentration of acridine from 1.6×10^{-6} to 1.3×10^{-2} M, the maximum in the overall luminescence spectrum shifts by 110 nm to the red region and the form of the spectrum change markedly. The fact that the association of Acridine Orange molecules leads to a marked weakening of the intensity of the long-wavelength absorption band and to the intensification of the short-wavelength band suggested that the transition to the upper electronic state is prohibited to some extent in associated molecules, i.e. that the associated molecules have a higher symmetry than the monomer.

In contrast to the spectra of aqueous solutions of Acridine Orange, the formation of a new band in the luminescence spectrum of rock candy is extremely slow, although the deformation of the absorption spectra begins to appear in both cases at approximately the same concentrations[143] and the positions of the maxima in the luminescence spectra are the same. However, it follows from the deformation of the absorption and luminescence spectra of Acridine Orange in rock candy that the amount of associated species in such solid solutions is smaller than in aqueous solutions at the same concentrations.

Measurement of the dependence of the pH of the solutions on the concentration of acridines showed that the changes in the spectra are not associated with the ionisation of their molecules in solution, as observed by Levshin[145]. The concentration-induced changes in the spectra of acridines occurred in the region corresponding to the existence of their molecules in the form of singly charged ions and must be attributed to their association. At the same time, it has been shown[20,143,144] that the associated Acridine Orange species exhibit an appreciable phosphorescence. This is caused by the higher probability of the transition of dimers to the triplet state as compared with the monomers.

With increase of the concentration of Acridine Orange above 10^{-3} M in ethanol, bands at 600 and 629 nm arise in the luminescence spectrum and their intensity increases[146]. They have been attributed to the luminescence of the associated Acridine Orange species. Eosin, whose monomeric form has a luminescence maximum at 568 nm, fluoresces with λ_{max} = 603 nm when associated species are formed in alcohols[147].

The study of the fluorescence of associated acriflavins and rhodamine 3B species in various solvents[148] showed that, when dimers, trimers, and more complex aggregates are formed, their luminescence maximum is displaced further towards the red region. Analysis of the spectroscopic data showed that the luminescence spectra of associated species are broader and the degree of polarisation of their luminescence is smaller than for the monomers[62,149].

As noted above, Scheibe polymers belong to the class of luminescent associated species. The luminescence of polymerised solutions of cyanine dyes proved to be very sensitive to the presence of various luminescence quenching agents. Thus the addition of approximately 10^{-5} M catechol to a solution containing 0.2% of pseudoisocyanine chloride[150,151] leads to a sharp decrease of the intensity of the luminescence of the dye. This implies that the emission of light by the entire complex is affected when even one of the dye molecules forming the chain comes into contact with a molecule of the quenching agent. It has been established[152] that, by virtue of the migration of excitation energy along the entire polymer chain, one molecule of the quenching agent per 10^3–10^6 dye molecules is sufficient for appreciable quenching. This suggested that the electrons of individual molecules in such polymers form a single electron cloud.

Another form of luminescent species made up of dye molecules has been observed[153,154] and investigated in detail by Morozov and coworkers[21,22]. When aqueous and aqueous alcoholic solutions are cooled to approximately −30°C, the luminescence of rhodamines virtually vanishes. Further cooling leads to the appearance of a new luminescence band displaced towards longer wavelengths. The intensity of this "red" luminescence band increases on successive cooling of the solutions. The addition of glucose, thiamine hydrochloride, etc. to the solution increase the intensity of the "red" band, but the "yellow" does not vanish completely. The addition of polar solvents to the solution (alcohol, pyridine, acetone, etc.) greatly weakens the above effects. In this case the intensity of the "yellow" band changes only slightly when the temperature of the solution is reduced and a weak "red" luminescence band appears only at approximately −100°C.

The above results have been explained[152] on the basis that freezing aqueous solutions removes the prohibition on singlet–triplet transitions and the "red" band is due to the phosphorescence of the associated dye molecules. The introduction of various additives into the solution alters, according to the author[152], the probabilities of the $S^* \rightarrow T_1$ and $T_1 \rightarrow S_0$ transitions. However, the marked dependence of the observed effects on the dye concentration in solution[22] indicates their relation with intermolecular processes. Furthermore, the durations of luminescence are the same order of magnitude for both rhodamine C bands: $\tau_L \simeq 10^{-8}$ s; $\tau_{Cr} \simeq 4.5 \times 10^{-9}$ s.

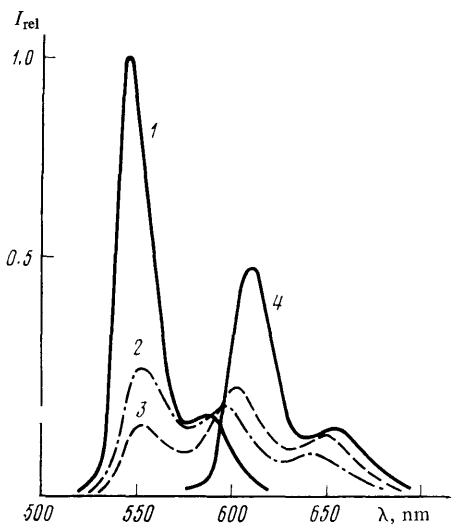


Figure 2. The luminescence spectra of solutions of rhodamine 6G in ethanol at −180°C as a function of concentration (M): 1) 1×10^{-5} (the I_{rel} scale has been reduced by a factor of 2); 2) 5×10^{-3}; 3) 1×10^{-2}; 4) 5×10^{-2}.

On the other hand, the difference between τ_L and τ_{Cr} for frozen solutions shows that different luminescence centres are responsible for the appearance of these bands.

The observed phenomenon has been explained[21,22] by the fact that the crystallisation of the solvent on freezing leads to the breakdown of the homogeneity of the solution, which decomposes into a solid phase consisting of the frozen solvent, not containing dye molecules, and a liquid phase to which virtually the entire dye is transferred together with the polar solvents added to the solution. The composition of the liquid phase differs from that of the initial solution by the markedly higher concentration of the dye. Cooling of such solutions leads to a gradual freezing out of water from the liquid phase and an

increase of the concentration of the dye in the latter, which creates favourable conditions for the formation of luminescent associated dye species. The authors[21,22] believe that the associated species formed under these conditions are dimers and that the "red" luminescence band is due to their fluorescence.

It was shown subsequently[6,24-26,62] that luminescent associated rhodamine dye species are formed also in purely polar solvents wihout breakdown of the homogeneity of the solutions on freezing. Not only dimers but also more complex associated species consisting of six molecules are formed in such solutions. Apparently in the instances described in the literature[21,22] the associated species are complex. The luminescence spectrum of such associated rhodamine 6G species in ethanol at −180°C is illustrated in Fig. 2. It consists of two luminescence maxima: the main maximum at $\lambda_{max} = 620$ nm and a lateral maximum at $\lambda_{max} = 670$ nm, which may constitute the manifestation of a vibrational structure. In the spectra of mixtures of polar and non-polar solvents at room temperature the luminescence maximum at $\lambda =$ 620 nm was attributed[155] to the phosphorescence of associated rhodamine dye molecules.

Luminescent associated rhodamine dye species have been detected at room temperature in mixtures of polar and non-polar solvents[156-161]. In this case the luminescence band of the associated molecules is displaced towards either shorter or longer wavelengths relative to the luminescence spectra of their monomeric molecules. The "red" luminescence of the associated species ($\lambda_{max} =$ 610 nm) has been observed for rhodamines in a mixture of chloroform (10%) and carbon tetrachloride (90%) at concentrations of approximately 5×10^{-4} M. The "blue" luminescence of the associated species of these dyes arises when the dyes are transferred to a non-polar medium by extraction from aqueous solutions with non-polar solvents (carbon tetrachloride). In the former case a long-wavelength maximum arises in the absorption spectra of the solutions, while in the latter case a short-wavelength maximum is generated. The formation of associated species comprising dye molecules in the above instances, which luminesce at room temperature, takes place as a rule in solutions whose homogeneity has been affected. Their structure and photoenergetics require further investigation.

V. TRIPLET STATES OF ASSOCIATED SPECIES

For many organic compounds, the triplet states of their molecules play the main role in radiationless electronic excitation energy exchange and in various photochemical reactions. The interest in the study of the triplet states of complex molecules is therefore understandable. However, the triplet states of associated molecules have been studied quite inadequately.

It is known from the theory of the electronic states of molecular aggregates[67,115,116,122] that, on molecular association, the singlet excited levels undergo appreciable changes, while the triplet levels change only slightly as a result of the spin-intercombination prohibitions.

The first experimental studies on the triplet state of associated dye molecules[162,163] confirmed these theoretical conclusions. A detailed study of the phosphorescence of associated Acridine Orange and rhodamine C species, dissolved in water and in a mixture of glucose and water, showed[162] that the maximum in the phosphorescence spectrum of acridine dimers is displaced towards longer wavelengths by approximately 100 Å relative to the phosphorescence line of its monomeric form. The values of τ for the phosphorescence of monomers and dimers then differ only slightly. For example, at room temperature $\tau_{phosph} = 10^{-2}$ s for the monomers and 6.3×10^{-2} s for the dimers of Acridine Orange, the ratio of these quantities remaining virtually unchanged on cooling the solutions. This shows that the probabilities of emission from the triplet levels and of the quenching of these levels are similar for the monomers and dimers. The phosphorescence yield for Acridine Orange dimers is much higher than for its monomeric form and depends on temperature to a greater extent. This can be explained by the mutual approach of the S_1^* and T_1 levels and the consequent increase of the probability of the $S_1^* \rightarrow T$ transition.

The phosphorescence spectrum of rhodamine C dimers in water with added glucose consists of two bands with maxima at approximately 620 and 690 nm. With decrease of temperature, the intensity of the short-wavelength band falls and that of the long-wavelength band increases. Since the maximum of the former band is close to that in the fluorescence spectrum of the dimers, the author[162] believes that it refers to α-phosphorescence, while the second band refers to the β-phosphorescence of the dimers.

Experimental evidence for the phosphorescence of the dimers of three organic compounds has been obtained[163]. The shape of the phosphorescence spectra of eosin, rhodamine C, and Acridine Orange in water at 77 K proved to be the same, but the phosphorescence spectrum of the dimers is displaced towards the red by 100–200 Å, relative to the phosphorescence spectrum of the monomers. The authors[163] concluded that both in the ground state of the associated species and in the triplet state the intermolecular distance is the same and that the decrease of energy by 300–500 cm^{-1} accompanying dimerisation is greater for the triplet state than for the ground state.

Spectroscopic methods make it possible to establish the probabilities of various transitions and the rate constants for many processes–emission and quenching of luminescence as well as intercombination transitions in organic molecules. Very few such measurements have so far been made for associated dye molecules and yet they are important not only for many practical tasks but also for the theory of association. The study of the redistribution of the probabilities of radiative and radiationless transitions, occurring when the dye molecules associate, is therefore of special interest. Such redistribution is caused particularly by a change in the relative disposition of the excited singlet and triplet levels when molecules associate.

Thus the influence of the association of eosin and erythrosin molecules at 80 K on processes involving the population and deactivation of the triplet state leads to an increase of the phosphorescence quantum yield relative to the fluorescence yield and a decrease of τ_{phosph} for solutions[164]. An increase of the concentration of solutions of these dyes in polar media results in a change of the probability of the intercombination transition and of the quenching of phosphorescence and has almost no influence on the probability of the radiative process.

New possibilities for the study of the triplet states of associated molecules of organic compounds arose following the discovery of the method of flash photolysis[165]. However, in contrast to the numerous studies of monomeric molecules by this procedure, the study of associated species is only beginning. Thus the triplet states and electronic excitation energy degradation processes in

associated rhodamine 6G–the dye most widely used in lasers†–have been investigated[166-168].

Associated rhodamine 6G species were obtained in two ways: (I)–concentrated solutions of the dye in a polar medium (aliphatic alcohols, acetonitrile, dimethyl sulphoxide, etc.) where diluted with a non-polar solvent (CCl_4, toluene, cyclohexane, etc.) so that the polar component did not exceed 0.2% of the volume of the solution; (II)–an aqueous solution of the dye was treated with polymethacrylic acid at the optimum concentration for the formation of associated species[169].

The results of the study of associated rhodamine 6G molecules reduce to the following findings. In binary mixtures dimers and complex associated dye species containing 15–20 molecules are formed. The associated species obtained by the second method consist of approximately 10 monomeric rhodamine molecules. The S_1^*-T splitting then depends on the order of the association. For example, the triplet level of rhodamine 6G dimers is higher ($14\,930\ cm^{-1} < E_T < 18\,400\ cm^{-1}$) than in more complex associated species ($14\,930\ cm^{-1} < E_T < 16\,800\ cm^{-1}$), while the positions of the triplet levels of the monomers and complex associated species are virtually the same[166]. The S_1^*-T splitting is directly related to the efficiency of the various pathways involved in electronic excitation exchange. For dimers, which are formed in solutions containing up to 80% of the non-polar component, there is a direct population of their triplet levels on pulse excitation. The luminescence quantum yield for the dimers is close to zero and the degradation of their singlet excitation energy takes place by a radiationless pathway as a result of an internal transition, which has a quantum yield $B_{it} \simeq 0.7$ and an intercombination transition whose quantum yield $B_T \simeq 0.3$.

In contrast to dimers, more complex associated rhodamine 6G species of both types luminesce with a fluorescence quantum yield of approximately 0.02.[167] The quantum yield of the intercombination transitions into the triplet state B_T is ≤ 0.2 for associated species of type (I) and 0.5 for those of type (II). Under pulsed illumination of deoxygenated solutions, complex associated species of type (I) are capable of a direct transition to the triplet state and in the spectra of such solutions the T–T absorption appears in the red region with $\lambda_{max} = 620$ nm. Fig. 3*a* illustrates the complete $T-T$ absorption spectrum of associated species of type (I). There is a great similarity between this spectrum and the $T-T$ absorption spectrum of rhodamine 6G monomers (fig. 3*b*). The study of the triplet states of associated rhodamine 6G species shows that they are characterised by a number of properties typical for the monomers of the dye: a long lifetime of the triplet state, the occurrence of bimolecular processes involving the deactivation of this state, and electron transfer reactions. The hypothesis of a high reactivity of the triplet states of monomeric molecules can therefore be applied to the triplet states of the associated species.

Measurements of the rate of deactivation of the triplet states of associated rhodamine 6G species showed, firstly, that their formation in solutions leads to an increase of the efficiency of the $T \rightarrow S_0$ intercombination degradation (this is consistent with the hypothesis of the intensification of the spin–orbital interaction in the associated dye), and, secondly, that the lifetime of the triplet states of the associated species is almost independent of the dye concentration, i.e. that the concentration-induced quenching of the triplet states, characteristic of rhodamine 6G monomers[168], hardly takes place with associated species. The latter finding conflicts with the conclusions reached in a study[164] where associated eosin and erythrosin species were investigated at a low temperature.

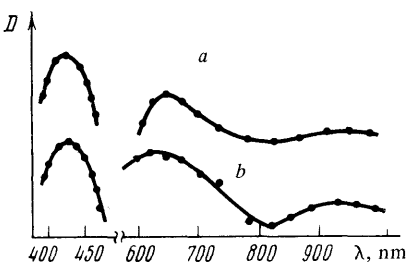


Figure 3. Triplet–triplet absorption spectra: *a*) of associated rhodamine 6G in carbon tetrachloride–butanol mixtures; *b*) of rhodamine 6G monomers in water (at pH 6).

In recent years the photonics of dye molecules have been studied in multicomponent solutions. Investigation of associated derivatives of biphenyl at different temperatures in three-component solutions showed[170] that the radiationless deactivation of their excited singlet state takes place without any appreciable involvement of the triplet level. The intramolecular radiationless deactivation of the fluorescent associated molecules takes place preferentially via the transition to the ground state.

The study of the triplet states and the pathways leading to the deactivation of the electronic excitation energy of associated dye molecules can lead to the elucidation of the causes of the loss of their capacity for luminescence.

VI. ASSOCIATION AND CONCENTRATION-INDUCED QUENCHING OF LUMINESCENCE

The phenomenon of the concentration-induced quenching of luminescence (CQL) consists in the fact that, starting from a threshold concentration of the dye solution, the luminescence yield falls. The concentration-induced quenching of luminescence is usually accompanied by a decrease of the lifetime of the excited state of the dye molecules and by depolarisation of the luminescence. The CQL for solutions of xanthene dyes has been studied quantitatively by Vavilov[171] and Levshin[172-174] and later by Dushinskii[175,176] and Pekerman[177,178]. A characteristic feature of the CQL is a distinct dependence of the nature of the luminescent substances–the CQL has not been observed for many organic compounds over a wide range of concentrations[177].

Physicochemical and physical hypotheses of second-order collisions[171], inductive quenching[179], etc. have been put forward to account for the CQL. Subsequently two approaches to the explanation of the nature of the CQL were outlined. The first is based on the possibility of

† See also A.K.Chibisov and T.D.Slavnova, J.Photochem., 8, 285 (1978).

the inductive resonance migration of the electronic excitation energy between monomeric dye molecules[180]. These ideas subsequently served as a basis of the migration theory of the CQL developed by a number or workers[181-183]. According to this theory, the quenching of the luminescence at high concentrations of the luminescent substances takes place as a result of the resonance transfer of electronic excitation from one dye molecule, in the monomeric form, to another similar molecule. Some of these transitions are accompanied by quenching. However, the cause of the development of radiationless transitions in the migration of excitation has not been specified more precisely. It has been suggested that quenching may occur also in the energy transfer between molecules separated by considerable distances, but the probability of the quenching of excitation in the course of migration increases faster with decrease of the distance than the probability of transfer without quenching. However, there are neither theoretical nor experimental data showing that the fluorescence lifetime and hence the luminescence yield should then decrease. This theory describes quantitatively the changes in the luminescence yield, in the lifetime of the excited state of dye molecules, and in the polarisation of their luminescence as a function of concentration.

Studies of alcoholic solutions of dyes whose electronic absorption spectra do not vary over a wide concentration range but where CQL develops served as an experimental justification of the migration theory of the CQL.[177,178] The absence of concentration-dependent changes in the absorption spectra indicated, according to the authors of the migration theory of the CQL, the absence of physicochemical interactions in solutions, i.e. of the association of dye molecules.

In order to account for the fact that the depolarisation of luminescence occurs appreciably before quenching, it was arbitrarily assumed that there exist two sorts of molecules in solutions: the transfer of excitation to molecules of one sort takes place without quenching, while that to the other involves quenching. The additional hypothesis of the sphere of instantaneous quenching around the excited molecule made it possible[52] to explain the experimental non-parallel concentration variation of the luminescence yield and τ.

Another approach to the explanation of the CQL emphasised the importance of the reversible association of the molecules of luminescent substances. In the first studies on the CQL this phenomenon was accounted for by the inactive absorption of the non-luminescent associated species. A theory of the quenching of luminescence as a result of the migration of excitation energy from monomers to associated species has been developed[184], but in this investigation no account was taken of the inactive absorption by associated species and a number of simplifications were made in the calculations; it was therefore not possible to obtain the correct concentration variation of the effects. The association theory of the CQL created by Levshin[185,186] provides for the intrinsic inactive absorption by the associated species and the migration of excitation from the monomers to these species. The postulates of this theory were subjected to a comprehensive experimental test. Thus, the study of the nature of the CQL in solutions of rhodamines 6G and 3B in various solvents[79,187] made it possible to separate various types of quenching of the luminescence. The associative nature of the CQL in aqueous and glycerol solutions of Na-fluorescein has been demonstrated[61]. In these and in a number of other studies[60,109] it was shown that, even if the migration of the electronic excitation between monomeric molecules does lead to radiationless processes in the latter, this plays a very insignificant role in the overall CQL.

The study of concentration effects in alcoholic solutions of rhodamine dyes[16], whose absorption spectra do not change appreciably even in the case of concentrated solutions, showed that the CQL observed in such spectra if related to the association of the dye molecules. This was established by measuring the number-average molecular weight. Fig. 4 presents the concentration variation of the luminescence yield (curve *1*) and of the relative number-average molecular weight of rhodamine 6G (curve *2*) in ethanol. The resolution of the CQL into migration quenching (curve *3*) and quenching due to the inactive absorption by associated species (curve *4*) showed that the variation of the migration quenching of luminescence and of τ with concentration is the same. This demonstrates that the discrepancy between the variation of the yield and τ with concentration is associated with the inactive absorption by the associated species and that the so-called sphere of instaneous quenching does not exist.

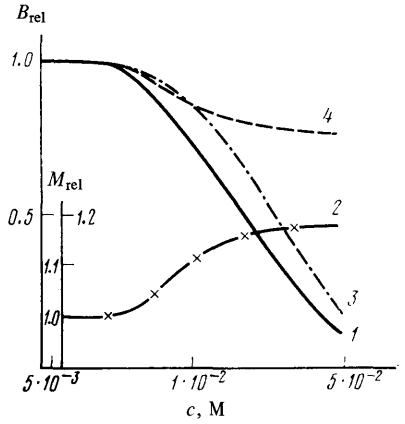


Figure 4. Dependence of the luminescence yield (curve *1*) and the number-average molecular weight (curve *2*) of rhodamine 6G in ethanol on concentration; 3) quenching due to the migration of energy; 4) quenching consequent upon the inactive absorption by the associated species.

Measurement of the differential spectra of alcoholic solutions of rhodamine dyes[188] also showed that associated species are formed at high concentrations.

In recent years both theoretical and experimental problems of the CQL in solutions of organic dyes have been considered by Bojarski and coworkers and other investigators[189-193], who based their treatment on association hypotheses. They take into account the possibility of multistage excitation energy transfer to associated species, involving several molecules, as a result of which the electronic excitation energy is converted into heat[194]. This more general theory of the CQL leads to the following dependence of the relative luminescence quantum yield B on concentration:

$$B/B_0 = [1 - f(\gamma)]/[1 - \alpha f(\gamma)], \quad (32)$$

where

$$f(\gamma) = \pi^{1/2}\gamma e^{\gamma^2}\left[1 - 2\pi^{-\frac{1}{2}}\int_0^{\gamma} e^{-t^2}dt\right],$$

$$\gamma = \gamma_м + \gamma_a = (c_м/c_{0м} + c_a/c_{0a})(\pi B_0)^{1/2}/2,$$

$$\alpha = \gamma_м/(\gamma_м + \gamma_a),$$

c_m and c_a are the concentrations of the monomers and associated species, c_{0m} and c_{0a} are the critical concentrations for the radiationless excitation energy transfer between monomers and between monomers and associated species, and B_0 is the luminescence quantum yield for the dye solution in the absence of quenching. For $\gamma_m \ll \gamma_a$, this expression becomes identical with that obtained by Förster[195]. An experimental test carried out on aqueous and aqueous glycerol solutions of xanthene dyes[191], including the anti-Stokes region[196], indicated a satisfactory agreement with theory. The parameter taking into account the quenching of the luminescence in the transfer of electronic excitation between monomers then has a value such that the above process hardly leads to CQL. It has been shown theoretically[197] that, in the dipole–dipole interaction between luminescent molecules, there is a change in the angular dependence of the probability of the absorption and emission of light with increase of their concentration. In the migration theory of the CQL [52] this change is taken into account with the aid of the hypothesis of an instantaneous transfer. An estimate[197] of the size of the "sphere of instantaneous transfer" showed that the angular effect can influence the anisotropy of the emission only in the presence of associated species in solution.

Thus theoretical and experimental studies fully confirm that the concentration-induced quenching of luminescence in solutions of organic dyes involves the formation of associated molecules in the latter.

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