===== PHOTONICS =====

Formation of Triplet Molecular States in Molecular Photonics and Radiation Chemistry

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Abstract—The mechanism of formation of triplet excited states of molecular systems in photonics and radiation chemistry has been considered. Intersystem crossing processes, two-photon excitation of high triplet states, and their evolution are discussed. The specific features of the formation of triplet states in radiation chemistry have been considered. Examples of using the concepts of triplet states in various fields, such as molecular luminescence, photochemistry, radiation chemistry, photodynamic therapy, design of organic light-emitting diodes, and information recording, are presented.

Keywords: formation of triplet states, highly excited triplet states, practical application of triplet states

The discovery of triplet molecular states by Terenin [1] and Lewis and Kasha [2] marked the beginning of a new stage of development of spectroscopy, especially luminescence, and photochemistry of molecular systems. These two research lines combined under the new term "molecular photonics", introduced by Terenin [3], received the conceptual basis for their development. The introduction of the concept of multiplicity of electronic states of polyatomic molecules along with the development of ideas about their orbital nature [4] determined to a great extent the further progress of molecular photonics. The photonics concepts introduced into radiation chemistry and photobiology have become an integral theoretical part of these disciplines.

Intensive development of a number of applied areas, such as photodynamic therapy [5, 6], radiation processing [7, 8] including nanomaterial fabrication technologies [9], designing of new phosphors and scintillators [10], and development of molecular optical sensor systems [11] is impossible without the knowledge about the pathways of formation of triplet states. It is in this context that we consider the problem in the present paper.

In the case of optical excitation of a molecular system, the initial electronically excited state is a singlet state, the optical transition into which from the ground state is allowed because the latter is also singlet S_0 for the overwhelming majority of substances. (A notable exception is oxygen, whose molecule has the triplet ground state). The formation of triplet states by direct optical excitation of the ground state is unlikely except for molecules containing heavy atoms (see below). However, there are several pathways, both intra- and intermolecular, of the formation of triplet states, which will be considered below. Furthermore, in the case of irradiation of a molecular system with ionizing radiation, there are additional channels of the formation of triplet states. They also will be briefly discussed below. In this consideration, we confine ourselves to the condensed phase, since most of the experimental data and application areas relate to this case.

In accordance with the title, attention in this paper is focused on the principles of the formation of triplet states. Therefore, we will consider only those properties which are important for the description of these processes. The comprehensive description of spectroscopic manifestations and properties of triplet molecular states can be found in monographs and reviews listed in the References section.

1. INTERSYSTEM CROSSING PROCESSES

After the transition of a molecular system into a singlet excited state, the latter undergoes a number of evolution processes. If the lower singlet state S_1 is excited, the most likely process is vibrational relaxation resulting in that the system goes into the equilibrium state of a vibrational subsystem (Fig. 1).

If the initial state is a highly excited singlet state S_n, in addition to the above process, internal conversion occurs within $\sim 10^{-11}-10^{-12}$ s resulting in the transition

to the lower electronically excited state, suppressing the processes of fluorescence from the upper states (Kasha's rule [5]). Although there are exceptions from this scheme [12], it is the most typical for most molecules. Occurring in the electronically excited state S_1 at vibrational equilibrium, the molecular system can undergo evolution via three pathways: fluorescence, intersystem crossing (transition to the triplet state), and internal conversion (transition to the ground state). Systems in which the latter process is negligible are quite common [13]. However, in molecules with a developed chain of conjugated bonds (dye molecules), internal conversion processes involving the transition from state S_1 to the ground state are also possible when the energy of the S_1 state is less than 2 eV [14]. This behavior is due to the dependence of the internal conversion rate constant on the energy of the transition and the orbital nature of the combining states [15]. In accordance with the objective of this paper, it is important to us to discuss the features of intersystem crossing processes occurring as a result of the spin−orbit interaction, which is relativistic in nature.

Spin−orbit coupling has been the subject matter of a wealth of studies [14−18]. The main results of these studies concerning the probability of the intersystem crossing processes are as follows. The spin−orbit coupling operator has the following form in the central field approximation [16]:

$$\hat{H}_{SO} = \frac{\alpha^2}{2} \sum_{\nu,i} \frac{Z_\nu}{r_{\nu i}^3} \left(\hat{l}_{\nu i} \hat{s}_i \right), \qquad (1)$$

where α is the fine structure constant ($\alpha = \frac{1}{137.3}$ a. u.), $\hat{l}_{\nu i}$ is the orbital momentum operator of the ith electron relative to the νth nucleus, $\hat{s}_i$ is the spin momentum operator of the ith electron, Z_ν is the effective (Slater) charge of the νth nucleus, and $r_{\nu i}$ is the distance between the νth nucleus and the ith electron. Except for the cases of $\pi\pi^*$ or $n\pi^*$ interaction of singlet and triplet states of planar molecules, one-center integrals make the main contribution to the matrix elements of the spin−orbit coupling of singlet and triplet states. In the most common case of interaction of $S_{\pi\pi^*}$ and $T_{n\pi^*}$ or $S_{n\pi^*}$ and $T_{\pi\pi^*}$ states, the expression for the modulus of the coupling matrix element in the single-configuration approximation is:

$$\beta_{SO} = c_\pi b \frac{\alpha^2}{4} \left[np_x np_x \left| \frac{Z}{r^3} \right| \right], \qquad (2)$$

where c_π is the coefficient of expansion of the π-orbital of an atom with n electrons, b is the factor for the np_x orbital in the expansion of the orbital of n electrons in the atomic orbitals (assuming that the z axis of the coordinate system is normal to the plane of the molecule), and Z is the effective charge of the atomic nucleus with n electrons. The one-center integral in Eq. (2) can be calculated analytically using the Slater
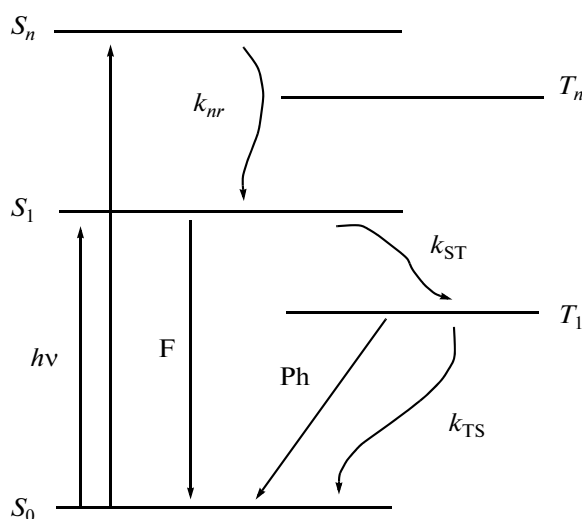

Fig. 1. Scheme of electronic states of molecules and the most probable radiative (fluorescence (F) and phosphorescence (Ph)) processes and nonradiative conversion processes.

functions for the p orbitals to give $\frac{1}{3} Z^4 n^{-3}$, where n is the principal quantum number of the p orbital. From this expression it is clear that the spin−orbit interaction of the states under consideration sharply increases with increasing Z. This is the cause of the heavy atom effect in molecular luminescence. In the case of heteroaromatic molecules containing N, O, or S atoms, a class to which the majority of organic molecules belong, calculations using the Slater values of Z give ~10 cm^{-1} for β_{SO} and ≥100 cm^{-1} for molecules with heavier atoms (Cl, Br, J) [17]. Close values for β can be obtained using an experimentally found fine splitting constant for atoms with n electrons, whose expression contains the integral from Eq. (2). From Eq. (2) it can be seen that β_{SO} decreases as $\sim N^{-\frac{1}{2}}$ with the increasing number N of π electrons in the molecule if the molecule contains one heteroatom with n electrons. (This follows from the normalization condition of the π orbitals, which delocalized over the entire molecule).

In the case of interaction between the $S_{\pi\pi^*}$ and $T_{\pi\pi^*}$ states or $S_{n\pi^*}$ and $T_{n\pi^*}$ states of planar molecules, three-center integrals will be different from zero in the expression for the matrix element [16−18] and the values of these integrals will be low because of smallness of the overlap of atomic orbitals in different centers and a rapid decrease in the integrand with increasing r. Calculation gives the most characteristic value of ~0.3 cm^{-1} for the magnitude of spin−orbital coupling in this case.

Such a large difference between the values of the matrix element of spin−orbit coupling in these two cases leads to a substantial difference in value between the intersystem crossing rate constants as they are pro-

portional to the square β_{SO}. In the case of the $S_{\pi\pi*}-T_{\pi\pi*}$ or $S_{n\pi*}-T_{n\pi*}$ crossing processes, the characteristic value of k_{ST} is ~10^7-10^9 s^{-1} and coincides in the order of magnitude with the rate constant of radiative transitions from singlet states. In the case of the $S_{\pi\pi*}-T_{n\pi*}$ or $S_{n\pi*}-T_{\pi\pi*}$ intersystem crossing processes, the value of k_{ST} is ~$10^{10}-10^{11}$ s^{-1}, which is significantly higher than the values of the rate constants of emission from singlet states. In other words, molecular systems in which conversion processes of only the first two types are possible can exhibit fluorescence whereas the fluorescence is suppressed and the yield of triplet states is close to unity in systems in which processes of the second type are possible. The likelihood of conversion processes of a certain type is determined by the relative positions of the $S_{\pi\pi*}$, $T_{\pi\pi*}$, $S_{n\pi*}$, and $T_{\pi\pi*}$ states. These concepts form the basis of spectral–luminescent systematization of molecules [15, 17, 19, 20]. Examples of molecules of carbonyl, azaheterocyclic, nitro, azo, etc. compounds to illustrate this feature can be found in [10, 19].

In the case of molecules containing halogen atoms, the effects of vibronic mixing of $n\pi*$ and $\pi\pi*$ states due to Herzberg–Teller coupling with out-of-plane C–H vibrations can lead to the k_{ST} value for the transition between $\pi\pi*$ states to be as high as ~$10^{10}-10^{11}$ s^{-1} [21]. This is especially frequent in molecules with a small number ($N \leq 10$) of π electrons. Thus, the yield of triplet states will be ~1 for these molecules if their size is not large. For chlorinated molecules, k_{ST} will be <10^9 s^{-1} if $N > 1$, and that for Br- or J-containing molecules will be less than 10^9 s^{-1} if $N > 20-30$, for example, in the case of dye molecules. An increase in the magnitude of spin–orbit coupling in molecules with heavy atoms leads to an increase in the probability of not only nonradiative, but also radiative transitions. This increase is manifested as a decrease in the lifetime of triplet states and a substantial increase in the probability of the S_0-T optical transitions in absorption, thereby allowing for both the experimental observation and direct excitation of the triplet states. Even greater values of spin–orbit coupling can be observed in complexes of organic molecules with metals. Their properties and applications are briefly discussed in Section 4.

The deviation of the spatial arrangement of a molecule from the planar structure leads to enhancement of spin–orbit coupling of $\pi\pi*$ states. This is caused by the fact that all molecular π orbitals have an admixture (sometimes substantial) of σ orbitals. Consequently, one-center integrals appear in the expressions for matrix element β, which lead to an increase in its value [22]. The same effects are observed when deviation from the planar structure of the molecule occurs only in the excited state [18]. For the same reason, the value of spin–orbit coupling of the $\sigma\sigma*$ states of the nonplanar molecules of saturated hydrocarbons is 5–10 cm^{-1} [23], ensuring a high probability of intersystem cross-

ing. This is important in describing the photochemical properties of these molecules [20].

In addition to the intramolecular factors, the intersystem crossing probability is affected by intermolecular interactions. The effect of an external heavy atom is especially noticeable, which consists in a significant enhancement of the probability in solvents with heavy atoms (for example, halogenated hydrocarbons). The increase in the spin–orbit coupling due to the intermolecular heavy-atom effect also leads to an increase in the probability of optical singlet–triplet transitions. A detailed description of these effects can be found in [14]. The effect of polarity of the medium on the spatial structure of aminochalcones and, as a consequence, the value of the spin–orbit coupling and the yields of triplets and fluorescence in such systems [24] should also be noted.

Molecules with a high yield of triplet states are effective energy donors. This method for obtaining triplet excited molecules is based on the use of triplet–triplet energy transfer. The phenomenon of intermolecular triplet–triplet energy transfer was discovered by Terenin and Ermolaev [25, 26]. It was found that energy can be transferred from the lower triplet state of an energy donor molecule to the triplet state of an acceptor molecule. The theory of triplet–triplet energy transfer was developed by Dexter [27]. He showed that the process occurs as a result of electron exchange coupling (exchange-resonance mechanism). In accordance with this mechanism, the transfer probability decreases exponentially with increasing distance R between the donor and acceptor molecules, in contrast to the mechanism of inductive resonance energy transfer between singlet states, which is due to dipole–dipole interaction and has the probability decreasing as R^{-6}. The radius of singlet–singlet energy transfer exceeds 50 Å, and that of triplet–triplet transfer is 12–15 Å. The features of triplet–triplet transfer have been comprehensively investigated, and the process itself has found numerous applications in molecular luminescence and photochemistry. In particular, it forms the basis of photodynamic therapy for generating reactive oxygen molecules in the singlet excited state and is used for sensitizing many photochemical reactions. A fairly complete description of the features of triplet–triplet energy transfer involving the lower triplet states can be found in the book by Ermolaev et al. [28].

2. HIGHLY EXCITED TRIPLET STATES

The most common method of generating high triplet states is triplet–triplet absorption from the lower triplet state. Photoinduced absorption was first observed by Lewis et al. [29] for fluorescein molecules in solid boric acid before the discovery of triplet states. This absorption occurs at longer wavelengths compared with the singlet–singlet absorption of the fluorescein molecule, and it was interpreted as triplet–
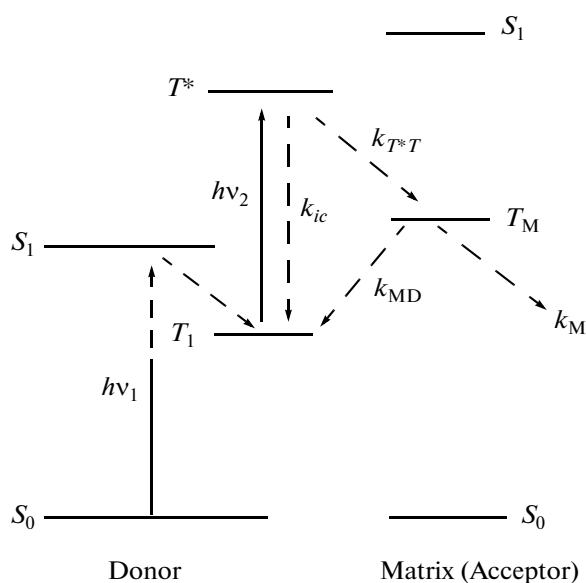
Fig. 2. Scheme of electron states and main transitions during energy transfer from higher triplet levels.

The energy level diagram of the system and the most likely processes are shown in Fig. 2.

Spectroscopic evidence for triplet–triplet energy transfer from highly excited triplet states was first obtained in [32]. It was demonstrated that the phosphorescence yield of carbazole in frozen toluene solutions dropped when the system was excited with two sources so that the radiation of one of them was absorbed by a carbazole molecule in the lower triplet state to be excited to a high triplet state followed by energy transfer to a toluene molecule. Investigation of mixed biphenyl and chrysene solutions in toluene with excitation by two sources made it possible to detect not only the transfer of energy from higher triplet states of chrysene to toluene, but also its migration in the toluene matrix to be accepted by the triplet states of biphenyl followed by its phosphorescence. The direct energy transfer between chrysene and biphenyl can be ruled out, since the phosphorescence of biphenyl was not observed in ethyl alcohol or diethyl ether used as solvents with no low-lying triplet states. A schematic of the energy transfer and migration process is shown in Fig. 3.

The efficiency of energy transfer from the upper triplet states of a donor molecule to acceptor molecules, which are usually solvent (matrix) molecules, is characterized by coefficient β of irreversible energy transfer from the state T^*, taking into account possible partial back energy transfer from the solvent molecules to the T_1 state [34]. The coefficient is defined as the product of the efficiency of energy transfer from the state T* and the efficiency of energy migration along solvent molecules and is related to the kinetic parameters of the system as follows (see Fig. 2):

$$\beta = \frac{k_{T^*T}}{k_{T^*T} + k_{ic}} \frac{k_M}{k_M + k_{MD}}, \tag{3}$$

where k_{T^*T} is the rate constant of triplet–triplet energy transfer from the donor to the solvent molecule, k_{ic} is

triplet absorption later. To date, the measurement of triplet–triplet absorption spectra has become a standard method for studying excited molecular states. In contrast to other techniques (see Section 4), this method makes it possible to selectively excite high triplet states. The main decay process of these states is internal conversion with the transition to the lower triplet state, which leads to their short lifetime ($\sim 10^{-11}$–10^{-12} s) as in the case of high singlet states. Nonetheless, a large number of processes occurring in highly excited triplet states have been discovered [30, 31]. Of the photophysical processes, intermolecular triplet–triplet energy transfer from highly excited molecules, discovered and studied in detail in [32–36], is the most common.
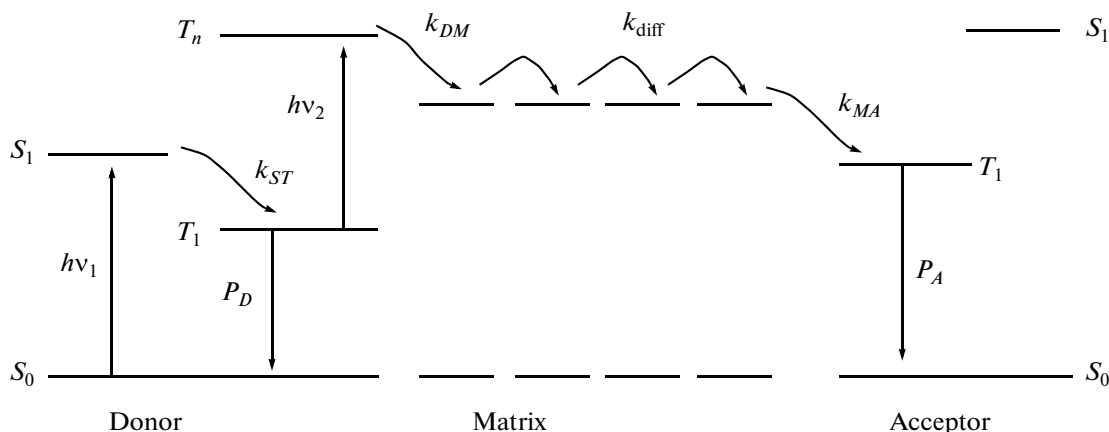

Fig. 3. Schematic of energy transfer and migration from a highly excited chrysene to a biphenyl molecule.

Table 1. Energy of triplet levels of some saturated compounds

Matrix	T_m, cm^{-1}	S_m, cm^{-1}	$S_m - T_m$, cm^{-1}	β
MCH	47800–48450	55679	7600	0.004
ECH	47800–48450	–	–	0.004
ICH	47320–47800	55249	7700	0.008
trans-Decalin	47320–47800	53650	–	0.03
Ethanol	47800–48450	–	–	0.0015
Ether	47800–48450	–	–	0.018
Isooctane	48450–50000	–	–	–

the decay rate constant of the T* state in the internal conversion process, k_M is the sum of the rate constants of energy migration and relaxation in the solvent, and k_{MD} is the rate constant of return of electronic excitation energy to the donor molecule. From Eq. (3) it is clear that the value of β is the most critically dependent on k_{T*T}, which decreases exponentially with an increase in the distance between the molecules and growth in the resonance defect of the transition E_{if}, reducing the value of β.

Consider the dependence of the probability for energy transfer from highly excited triplet states upon the electronic structure of energy acceptor molecules. It is reasonable to start with saturated hydrocarbons, whose interaction with aromatic hydrocarbons is minimal. Energy transfer from higher triplet states to saturated hydrocarbon molecules was first proved in [35, 36]. In those studies, we practiced the same kinetic method using two excitation sources as for the unsaturated solvents mentioned above. Energy transfer occurred from various aromatic molecules (biphenyl,

Table 2. Shifts of triplet–triplet absorption spectra (ΔE_{TT}) in toluene relative to ethanol. E_{T*} is the energy of a highly excited triplet level

Entry no.	Compound	E_{T*}, cm^{-1}	ΔE_{TT}, cm^{-1}
1	Triphenylene	46530	575
1'	Triphenylene	37100	190
2	Naphthalene	45590	600
3	2,3-Dimethylnaphthalene	45090	490
4	2,7-Dimethylnaphthalene	44420	475
5	Phenanthrene	42160	430
6	Anthracene	38430	510
7	1,2-Benzanthracene	37010	370
8	Picene	36105	255
9	1,2-Benzopyrene	36515	335
10	1,12-Benzoperilene	37640	500
11	Pyrene	41040	570
11'	Pyrene	36030	330

fluorene, triphenylbenzene) and was detected as a reduction in the phosphorescence yield of the donor upon two-photon excitation and accumulation of a certain amount of energy by an aromatic molecule in the higher triplet state, which was over 47800 cm^{-1} for methylcyclohexane (MCH), ethylcyclohexane (ECH), ethanol, and ether or more than 47320 cm^{-1} for isopropylcyclohexane (ICH) and decalin (Table 1). In this way, the position of the triplet state of some saturated compounds undetectable by other means was determined.

In [36] the transfer radii were estimated at 5.1 Å for decalin and 5–7 Å for toluene from the concentration dependence of the efficiency of energy transfer. The smallness of the radius of energy transfer from higher triplet states as compared with that from lower triplet states (12–15 Å) was supposed to be due to a high rate constant of internal conversion from the higher triplet levels of the donor molecule. It was shown that the migration of energy in saturated compounds is unlikely in contrast to the toluene molecule. The lack of migration is associated with both their low photochemical stability in triplet states and the fact that the lower excited states are generated from the excited states of the C–C bonds [37] localized and screened from each other by hydrogen atoms.

Increased values of β are observed in systems in which the formation of donor–acceptor complexes between energy donor and acceptor molecules is possible [36]. An even greater increase in β was revealed in the case of solutions of aromatic compounds, for example, toluene [36, 38, 39]. In addition to the increase in β, a bathochromic shift of the triplet–triplet absorption band relative to its position in alcoholic solutions and broadening of its vibronic structure occur. These effects are substantially dependent on the excitation energy of the donor molecule, as follows from the data in Table 2 and Fig. 4.

The data show a downward trend of the magnitude of the shift with decreasing energy of the triplet state. This trend is particularly evident when the data for the same molecule (triphenylene and pyrene) are compared. However, it should be borne in mind that there are several causes of the shift in absorption bands. In particular, the influence of dispersion and dynamic

polarization interactions with the solvent is essential for molecules of nonpolar aromatic hydrocarbons. The magnitude of the band shift depends on the difference in polarizability between molecules in the combining states in the former case and the electronic-transition oscillator strength in the latter case. Our measurements for the first singlet–singlet transitions gave the shift in the range of ~100–200 cm^{-1}. Similar values were observed for other types of molecules [40]. This implies that in addition to the two aforementioned band shift mechanisms, there is the third mechanism whose contribution decreases with a decrease in the triplet energy. As the energy of an excited triplet state decreases below ~46000 cm^{-1}, the values of β and $\Delta\Gamma$ sharply drop. The β value is reduced by an order of magnitude as the energy of the triplet state decreases by ~5000 cm^{-1}, with the decrement in $\Delta\Gamma$ being greater than 1000 cm^{-1}.

Intermolecular interactions in these systems in the ground state involve the dispersion interaction of π electrons and weak interaction of the dipole moment of the toluene molecule, which is 0.4 D [41], with the negatively charged carbon atoms of aromatic rings, whose charge is due to the displacement of σ-electron density of the C–H bonds from the hydrogen to the carbon atom. Despite the small magnitude of this interaction, which is not manifested in electronic absorption spectra, it plays an important part because it ensures the existence of weakly bound donor–acceptor pairs, the role of which strongly increases in the excited state, as will be seen below. The increase in β correlates with both the increase in the width $\Delta\Gamma$ of vibronic triplet–triplet absorption bands of electronic-energy donor molecules and the value of the absorption band shift in the toluene matrix relative to solutions in ethanol (ΔE, Fig. 4, Table 2) [36, 38, 39]. These effects can be explained by significant enhancement of the intermolecular interaction by the excitation of an electronic-energy donor molecule to a high triplet state to form a triplet exciplex with a toluene molecule [42, 43].

To discuss this issue, it is necessary to have information on the triplet state energies of energy acceptor molecules. Unfortunately, there are few experimental data in the literature on the position of higher triplet states of the effective acceptors toluene and benzene. The position of the highly excited triplet state $^3E_{2g}$ is known only for benzene [44]. There are no such data for toluene molecule, which, in particular, is due to the difficulty of experimental observation of unlikely T–T optical transitions (e.g., of the π-σ* type). Note that the higher triplet states to which optical transition from the first T state is unlikely can take part in energy transfer processes in the case of appropriate orientation of energy donor and acceptor molecules. In connection with this, we have calculated the energies of the higher triplet states of toluene and benzene molecules using the quantum-chemical method of molecular orbitals with partial neglect of differential overlap
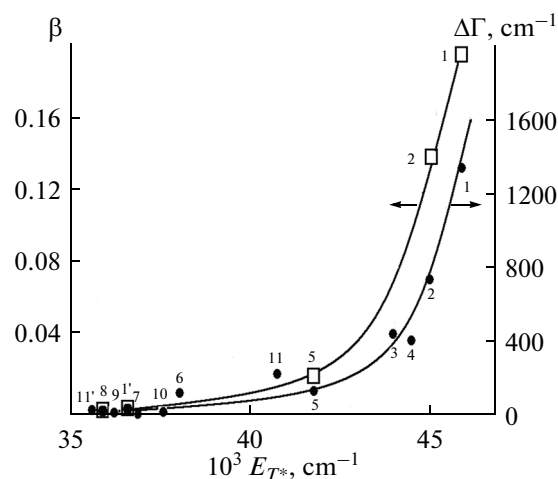

Fig. 4. Dependence of the width of the vibronic bands of T–T absorption spectra ($\Delta\Gamma$) and the probability of energy transfer from higher triplet levels (β) upon the energy of a highly excited triplet state (compound numbering is the same as that in Table 2).

and special spectroscopic parameterization [45]. The results are shown in Table 2. It can be seen that the theoretical and known experimental values agree well.

Let us turn to discussion of the mechanism of formation of this type of exciplex. Consider a system of electronic states including an excited triplet state of a triplet-energy donor molecule with a wave function φ_1 and an energy E_0 and a number of triplet electronic states of an energy acceptor molecule ψ_n, whose energies E_n are close to the energy E_0. The energy of states is measured from the energy of the lower triplet state of the donor. These states are coupled by exchange electronic interaction V_{1n}. The optical transition from the lower triplet state φ_0 of the donor molecule with the energy E_0 in this case is allowed only to the state φ_1 in the dipole approximation.

Representing the wave functions of the system as an expansion in functions ψ_n and φ_1, we have:

$$\psi_j = c_{j1}\varphi_i + \sum_n c_{jn}\psi_n, \qquad (4)$$

where c_{j1} and c_{jk} are coefficients. Assuming the functions in expansion (4) to be orthonormal, we get the following expression from the Eq. (4) normalization condition:

$$|c_{1j}|^2 + \sum_n |c_{nj}|^2 = 1. \qquad (5)$$

Along with the wave functions of the excited states of acceptor molecules, the functions corresponding to the states of electron transfer from an energy donor to a toluene molecule may also contribute to Eq. (4). The contribution of these states increases with an increase in excitation energy. However, their contribution can-

Table 3. Calculated energies of the triplet states of benzene and toluene molecules (cm⁻¹)*. Given in parentheses are known experimental values of the energy [19, 44]

State number	Toluene	Benzene
1	28850-ππ* (28705)	29620-ππ* B_{1u}^- (29500)
2	37050-ππ*	38430-ππ* E_{1u}^-
3	37620-πσ*	38430-ππ* E_{1u}^-
4	37680-ππ*	41540-πσ*
5	41980-πσ*	43980-πσ*
6	42480-πσ*	43980-πσ*
7	43750-πp*	44300-ππ* B_{2u}^-
8	45270-πσ*	46790-πσ*
9	45670-πσ*	46790-πσ*
10	50000-πσ*	52290-πσ*
11	52780-ππ*	54870-ππ* E_{2g}^+
12	54700-ππ*	54870-ππ* E_{2g}^+ (52950)

* In the case of the toluene molecule, the attribution of electronic states to the status ππ* or πσ* the type is an approximation because of the planar structure of the CH₃ group.

not be determining for molecules of the aromatic hydrocarbons under consideration, since the excitation energy of the T* states in question does not exceed 6 eV and the ionization potential is higher by 1.5–2 eV [46]. In addition, toluene (and benzene) has a negative electron affinity of about 1 eV [46]. Taking account of these states cannot lead to the splitting of the initial states of the donor and, hence, to broadening of the spectrum; it only leads to a shift.

Note that as far as highly excited states are concerned, Rydberg orbitals of the atoms making the molecule can contribute to their formation. The size of these orbitals increases with an increase in principal quantum number n as n^2 and their account may be significant in the calculation of intermolecular exchange interactions at large distances.

An analytical expression for the energy of a system with wave functions can be obtained only in special cases. Let us illustrate the general feature using the simplest example of two coupling states φ_1 and ψ_2. The expression for the energy of electronic states of the system can be written as:

$$E_{1,2} = \frac{E_0 + E_1}{2} \pm \frac{1}{2}\sqrt{4V^2 + (E_0 - E_1)^2}, \qquad (6)$$

where V is the coupling matrix element of states with energies E_0 and E_1. If $E_0 = E_1$, the energies of the electronic states are $E^{(1)} = E_0 + |V|$ and $E^{(2)} = E_0 - |V|$ and the splitting of the states that are degenerate without taking into account the coupling is $2|V|$. In this case, the lower (in energy) state is bonding and the higher state is repulsive. If $E_1 > E_0$ and $E_1 - E_0 \gg |V|$, then $E^{(1)} = E_0 + V^2/(E_1 - E_0)$ and $E^{(2)} = E_1 - V^2/(E_1 - E_0)$. From these expressions it follows that the energy shift in the states of the system of donor and acceptor molecules reaches a maximum at quasi-degeneracy of the energy of their electronic states. The excited state is delocalized over the entire system in this case. As the energy difference between the states increases, the shift decreases. If the coupling matrix element is constant, the decrement in the shift is inversely proportional to the energy difference of the coupling states.

The results of studies [36, 38, 39] on the dependence of the triplet–triplet absorption spectra of naphthalene, methylnaphthalenes, and triphenylene upon the solvent nature show that the maximum shift and broadening of the vibronic spectra on passing from ethanol to toluene as a solvent is observed at a T*-state energy of about 45500 cm⁻¹ (5.7 eV). The bathochromic shift is ~600 cm⁻¹ in this case (Table 2). The data in Table 2 show that two πσ* triplet states of toluene lie in the same region, with the energy gap between them being 400 cm⁻¹. The matrix element can be roughly estimated at $V \approx 600$ cm⁻¹. This value is intermediate between that of the matrix element of triplet–triplet energy transfer along C–C bonds in polymers (~3000 cm⁻¹ [47]) and the value of exchange interaction, which determines the width of the triplet exciton band in crystals of aromatic hydrocarbons (~10 cm⁻¹ [48]), a fact that is considered to be direct evidence for the existence of the exciplex. As the excitation energy of the triplet-energy donor decreases, the long-wavelength shift of the triplet–triplet absorption band decreases as it follows from Eq. (6).

The formation of the triplet exciplex with an excitation energy of about 5.7 eV gives rise to two or more closely located electronic states, to which optical transition is allowed from the T_1 state of the molecule, since their wave functions at $E_1^0 \approx E_2^0$ have similar contributions of wave function ψ_1, in which the transition from the lowest triplet state of the donor is allowed. The splitting of the states is less than the frequency of optically active molecular vibrations in the $T-T$ absorption spectrum (~1500 cm⁻¹). This leads to broadening of the vibronic spectra of triplet–triplet absorption of aromatic molecules when toluene is used as a solvent instead of ethanol. The closer in energy the triplet states of the donor and acceptor molecules, the greater the broadening, which is indeed the case observed experimentally [36, 38, 39]. As the

energy of the T^* state of the donor decreases, the broadening is reduced, since the splitting of the state disappears. According to published data [38], the oscillator strength of the $T-T$ transition for the molecules listed in Table 1 retains its value accurate to within 20% when the solvent alcohol, in which the exciplex cannot be detected, is replaced by toluene. The model proposed explains this effect [43].

Note that Bensasson and Land [49] observed a bathochromic shift and broadening of the $T-T$ absorption spectrum of naphthalene in benzene at ~23500 cm^{-1} compared with its solution in cyclohexane. The shift of the absorption band was found to be 570 cm^{-1}, and its broadening was 310 cm^{-1}. Processing the spectra reported in their paper shows that the oscillator strengths of the band in the cyclohexane and benzene solutions are identical (accurate to within ~5%). Since the positions of the triplet states of toluene and benzene molecules in this energy region of the T* state of naphthalene are close (Table 2), the effects observed in this case can be due to the formation of the triplet exciplex. One of the criteria for the formation of exciplexes of this type is approximate conservation of the $T-T$ transition oscillator strength during the formation of the exciplex.

It is worth to dwell on the results of study by Haertel et al. [50] who investigated the triplet−triplet absorption spectra of naphthalene in durene crystals. They found that unlike the case of solutions in toluene, there was no substantial broadening of the triplet−triplet absorption spectrum at ~25000 cm^{-1} in durene. This finding suggests the lack of excimer formation in the case of durene. The reason for this may be the absence of a dipole moment in the durene molecule and screening its π-system by CH$_3$ groups.

Thus, the set of experimental facts can be rationalized assuming that the primary step of triplet−triplet transfer of electronic excitation energy in the case of quasi-degeneracy of the electronic states of the donors and acceptors of electronic energy in the systems under consideration involves the formation of an exciplex by the energy donor and acceptor molecules. In the exciplex, the distance between the donor and acceptor molecules is shorter and the effective rate constant of energy transfer is higher. The mechanism of the process includes fast internal $T-T$ conversion in the exciplex to the lower T_1 state of the acceptor without changing the formal kinetics. Thus, the existence of the isotopic H/D effect in the energy transfer process cannot be ruled out. It should be emphasized that the exciplex is formed only in an excited triplet state, not in the T_1 state, and therefore does not prevent energy migration by the lower triplet states of the toluene matrix.

Note that the model proposed is close to the one describing excited singlet states of the dimers of dye molecules [51], when $E_1^0 = E_2^0$ in Eq. (4) and the coupling of the dye states is determined by dipole−dipole interaction. The difference is that the splitting of the states in the dimer is greater than that of the triplet states and the optical transition probability is usually very different for the two states of the dimer, since the optical transition from the ground state of the system to the excited state is allowed for both molecules forming the complex.

The formation of excimers and exciplexes of aromatic molecules in the singlet and triplet states was discussed in [51−55]. It is noteworthy that exciplexes take part in photochemical reactions, such as cycloaddition [55] and electron transfer [56]. However, this concerns lower singlet and triplet states, unlike the case of the present paper in which highly excited states are discussed.

Sensitization of photochemical processes by highly excited triplet states of aromatic compounds is the subject matter of two-quantum photochemistry. A detailed discussion of these processes can be found in [30, 31].

3. FORMATION OF TRIPLET STATES BY THE ACTION OF IONIZING RADIATION

The important role of the formation of triplet molecular states by the action of ionizing radiation was pointed out for the first time by Kaplan [57]. In radiation chemistry, there are two additional formation pathways for triplet molecular states as compared with photonics, (a) by the recombination of electrons and molecular cations generated during irradiation and (b) in the direct transition of the molecule from the ground state to triplet state, which is induced by fast electrons. The experimentally revealed features of electron−cation recombination processes in molecular systems are described in detail in [30, 58]. The theory of recombination of electrons with molecular ions yielding molecular entities in electronically excited states in the condensed phase was developed in [59]. The recombination rate constant of the solvated or trapped electron and the recombination cross section of the quasi-free electron in the conduction band are proportional to the square of the overlap integral of the vibrational wave functions of the initial i and final f states (Franck−Condon factor) and the electronic matrix element of the transition providing that certain additional conditions [59] are met. Since multiplicity of the states i and f is the same in this case, the relative probability for the formation of electronically excited singlet and triplet states will depend on the initial concentration of states i of a certain multiplicity. In the case of a high concentration of electrons and cations or fast spin relaxation [60, 61], the probability of occurrence of the triplet initial states is three times that of the singlet states in accordance with their statistical weight. Even this fact alone ensures a higher probability of the formation of triplet states by electron−cation recombination.

Together with the statistical reasons, there are energy factors that lead to an increased probability of the formation of triplet states in comparison with the singlet states. If the energy of the initial state E_i, which depends on the ionization potential of the molecule, polarity of the environment, the energy of its conduction band edge, the state of the electron, and the electron–cation separation distance [59], exceeds the energy of both the lower singlet and triplet states of the molecule, the recombination can produce the singlet and triplet states in the ratio of 1 : 3. If the energy E_i is greater than the triplet state energy but less than the energy of the lower singlet excited state, the recombination process can give the molecule in either the triplet state or the ground state. At last, when the energy of the initial state is less than the energy of the excited states, the molecule will be formed only in the ground electronic state. A detailed discussion of the feasibility of these cases for various systems can be found in [30, 58, 59].

A standard technique for studying the recombination processes is recombination luminescence. This technique is detailed in [30, 58]. For the present consideration, it is important to note that the ratio of the phosphorescence to the fluorescence yield is always much greater than that in the case of photoexcitation and often exceeds 3. This value clearly indicates a greater probability for the formation of triplet, rather than singlet states. Upon irradiation of molecular systems with ionizing radiation (γ-rays, fast electrons), there is another cause of the formation of molecular triplet states associated with their excitation by primary or secondary electrons via exchange interaction with the electrons of the molecule. However, the cross section of this process is appreciable only in a narrow region near the excitation threshold and rapidly decreases with the increasing energy of incident electrons, in contrast to excitation of singlet states [62, 63]; therefore, it is not to be expected that this process makes a large contribution in the balance of formation of triplet states.

A high probability for the formation of triplet states with bypassing the singlet states leads to a significant change in the direction of radiation-chemical processes of conversion of molecular systems as compared to photochemical processes. A particularly illustrative example of the difference in direction between photochemical and radiation-chemical decomposition of molecules to be noted here is given by saturated hydrocarbons, including polymeric compounds. In the case of photolysis of this class of compounds, the main degradation process is the detachment of molecular hydrogen H_2 from the same carbon atom to form the corresponding diradical in the first step. In the radiolysis of these compounds, the main product is radicals generated through C–H bond breaking. This difference is due to the fact that the H-atom detachment process is allowed only in triplet states and follows the predissociation mechanism [64], whereas the abstraction of the H_2 molecule is allowed in the singlet state as well [65]. This conclusion was directly proved in the study [66] undertaken to verify the results of the theoretical analysis [64]. It was found that the radicals generated during vacuum ultraviolet photolysis of polyethylene are not produced until electron–cation recombination. Various aspects of the dependence of radiation resistance of molecular compounds upon their electronic structure and triplet formation features were set out in [59].

4. PRACTICAL APPLICATIONS

Above we have considered the formation of triplet states in the molecular systems alone. Related systems—complexes of organic molecules with heavy metal ions—are also of great interest due to their wide use. The presence of a metal ion results in an increased intersystem crossing probability and effective population of triplet states. Here are a few examples of the use of excited triplet molecules.

4.1. Photodynamic Therapy

This treatment method is based on the sensitized generation of singlet oxygen and its reaction with tumor tissues. Molecules of a photosensitizer introduced into the body are selectively fixed on the membranes of tumor cells and in mitochondria. Laser irradiation of the photosensitized tumor tissue results in the transition of nontoxic oxygen from the triplet ground state $X^3\Sigma_g^-$ to the first singlet state a $a^1\Delta_g$, which lies 0.981 eV above the ground state [67]. In this state, the oxygen molecule is much more reactive and destroys the cell membranes of cancerous tumors. The basic requirements for a system that can be used as a sensitizer in photodynamic therapy are as follows [5, 6, 68, 69]. First, the sensitizer should have no phototoxicity at all or extremely low dark phototoxicity. Second, it is necessary that the pharmacokinetics of the medicament ensure the selectivity of its accumulation in the tumor compared to the normal tissue and rapid clearance after the therapy session to reduce overall phototoxicity. Third, the sensitizer should have a constant composition and be preferably composed of one substance. Fourth, it is desirable that the sensitizer have a high triplet quantum yield with a triplet energy of >94 kJ/mol (excitation energy required for the formation of singlet oxygen) and provide the transfer of energy sufficient for the formation of singlet oxygen. Finally, the drug should have a pronounced absorption in the red region of the visible spectrum in the range of 630 nm, since it this light that best penetrates into tissue. This class of photosensitizers includes porphyrins, chlorins, benzoporphyrins, phthalocyanines, and naphthalocyanines, which have found practical use in medicine.

4.2. Organic Light Emitting Diodes

Another area of application of compounds using triplet molecules is the design and fabrication of light-emitting diodes based on organic compounds (OLEDs) [70]. Complexes of organic molecules with heavy metal ions are used in these devices. The presence of a metal ion increases the probability of inter-system crossing and effective population of triplet states. Owing to a large value of spin−orbit coupling (~10^3 cm^{-1}), complexes with platinum and iridium ions [71, 72] have large quantum yields of triplet states and phosphorescence, a property that is used in light-emitting diodes.

4.3. Data Recording

Lashkov and Sukhanov [73] proposed to use pho-tosensitized processes involving triplet states in the creation of a phase recording medium on the mono-molecular level. The operation of this recording medium (called Reoksan) is based on the photo-oxi-dation reaction of anthracene compounds in solid polymer matrices, such as poly(methyl methacrylate). Excitation with light promotes anthracene into the triplet state, and the electronic energy is transferred to an oxygen molecule converting it into the singlet state. The singlet oxygen oxidizes anthracene in the 9,10-positions to give transannular peroxide with two unconjugated benzene rings. Spectral changes occur-ring in the sample form the basis for recording phase holograms. Reoksan is a material capable of cycling, thereby allowing sensitization of phase hologram recording over the entire visible range up to ~900 nm.

Tal'roze et al. [74] explored the possibility of using two-quantum photoionization through an intermedi-ate triplet level to record three-dimensional images. A sample in the form of a rectangular parallelepiped consisting of a glassy boric acid with a small admixture of an aromatic compound (4, 4-dihydroxybiohenyl) was irradiated with two light sources through masks on adjacent side faces. The first source (290 nm) excited the aromatic compound almost uniformly throughout the thickness (optical density of ~0.2). The wavelength of the second source corresponded to the quantum energy of ionization of the triplet excited molecule (365 nm). As a result of the absorption of two photons of light, the aromatic molecule is converted into the radical cation having an intense color in the visible spectral range of 580−670 nm. In the case of irradia-tion through a rectangular-shaped mask, a green-col-ored rectangular parallelepiped was formed in the sample after irradiation. Such two-photon process for recording a three-dimensional image using an inter-mediate triplet state can be carried out with two nar-row laser beams, and patterns of more complicated shapes can be thus obtained.

4.4. Some Diradicals

Molecular systems in which two unpaired electrons rest on the same atom (nitrenes, carbenes) or are con-jugated through the π-system typically have a triplet lower electronic state. The singlet−triplet energy gap is usually small, being about 10 kcal/mol. Nitrenes and carbenes are produced in the singlet state in photo-chemical reactions upon the direct excitation of the reactants (usually, azides), and triplet diradicals can be immediately formed in sensitized photolysis. In a short time, nitrenes and carbenes undergo transition from the singlet into the triplet state, which is the ground state for most of them. The S → T conversion in carbene occurs within ~10^{-9} s. The S−T splitting energy of carbenes is a few kcal/mol, and there is inversion of states in some cases. The S−T splitting energy in nitrenes is ~10−40 kcal/mol and is signifi-cantly higher than in carbenes, in which it is in the range of 700−3500 cm^{-1}. For example: HN: ~1260 cm^{-1} [75], PhN: ~6300 cm^{-1} [76], H$_2$C: ~3150 cm^{-1} [77], and PhCH: ~1000−1700 cm^{-1} [78−80].

In diradicals, triplet−triplet fluorescence is observed, whereas singlet−triplet phosphorescence is undetectable. Singlet and triplet diradicals enter into various chemical reactions, so that the S−T energy gap can play a significant role in thermally activated reac-tions. The possibility of using carbenes and nitrenes in molecular magnetics is explored in the literature [81−83].

4.5. Triplet Excitons

It is interesting to note the existence of triplet exci-tons in molecular crystals [48, 84]. The usual way of their formation is intersystem crossing, excitation with an intense light source, or initiation of an optical tran-sition from the ground state by paramagnetic dopants. Triplet excitons are detected using delayed fluores-cence, which is due to triplet−triplet annihilation of triplet excitons. Owing to a long lifetime, they play an important part in the migration of energy in molecular crystals. An example is an anisotropic anthracene crystal, in which excitons move mainly in the *ab* crys-tal plane. At temperatures above 120 K, the motion of triplet excitons becomes diffusion with the diffusion coefficient to be $D = 6.2 \times 10^{-6}$ cm^2/s at room temper-ature and the Davydov splitting of the exciton band of $\Delta = 17$ cm^{-1}. The excitation rests on one molecule for ~3×10^{-10} s, and the diffusion length is $l \approx 3.5 \times 10^4$ cm at a triplet exciton lifetime of $\tau \approx 10^{-2}$ s.

Molecular crystals can be compared with the glassy solid solution of toluene discussed above. In solid solu-tions, the efficiency of energy transfer from higher triplet levels (see Fig. 4) may be as high as $\beta \approx 0.1$. In this case, the migration rate constant of triplet excita-tion over the glassy toluene matrix can be close in value to the internal-conversion rate constant $k_{ic} \approx 10^{12}-$

10^{13} s^{-1} (see Eq. (3)), which is two to three orders of magnitude less than the triplet exciton lifetime on one molecule in the molecular crystal. At these values of the constants in solid solutions, the hopping mechanism of intermolecular migration of excitation or energy migration by small molecular associates should be expected.

4.6. Magnetoplasticity

It is known that the hardness, yield strength, ductility, and other mechanical properties of diamagnetic crystals (NaCl, PbS, LiF, etc.) decrease in a magnetic field. This phenomenon is termed magnetoplasticity [85]. It is due to the behavior of dislocations: the proportion of free dislocations and their range increase in a magnetic field. Buchachenko [86] explained this effect by the formation in a defect of a biradical pair, which is transformed into a long-lived triplet state by the action of magnetic field. As a result, the range of dislocations and ductility of the material increase in a (permanent or microwave) magnetic field. This model was also proposed for explaining earthquakes and the impact of magnetic storms on them [87].

CONCLUSIONS

This analysis shows the variety of pathways of the formation and evolution of triplet molecular states. The important role of triplet states in photochemistry and radiation chemistry is reflected in the references cited in the text. Recently published data on the practical application of triplet states of molecular systems have been summarized.

ACKNOWLEDGEMENTS

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