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SPECTROSCOPY OF TRIPLET EXCITONS IN ORGANIC COMPOUNDS: CRYSTALLINE AND GLASSY BENZOPHENONE

A brief overview of the main results obtained on the spectral-luminescence properties of triplet excitons in crystalline and glassy benzophenone is given. The studies were mainly performed at the Institute of Physics of the National Academy of Sciences of Ukraine. Brief information on the achievements in the physics of triplet excitons in organic semiconductors is also presented. The peculiarities of phosphorescence and the structure of the glassy benzophenone phase are discussed. The conditions for the existence of excitonic phosphorescence in molecular crystals are considered. The achievements of various authors in the molecular spectroscopy of triplet state have been analyzed. It is shown that among molecular crystals, benzophenone is one of the most convenient objects for studying phosphorescence and spectral properties of the triplet state of organic compounds.

K e y w o r d s: triplet excitons, phosphorescence, energy migration, molecular crystals, boson peak, disordered systems, benzophenone, organic semiconductors.

1. Electronic States and Transitions between the Levels of Different Multiplicities in Organic Molecules

The processes of absorption, fluorescence, and phosphorescence in aromatic compounds can be described by the well-known scheme of electronic energy levels (Fig. 1). The ground state of an aromatic molecule is usually a singlet. The system of excited singlet levels S_i, for which transitions from the ground level S_0 ($S_0 \to S_1$, $S_0 \to S_2$, *etc.*) are allowed, determines the electronic absorption bands. In most cases, after excitation, due to rapid non-radiative relaxation (10^{-12}–10^{-13} s), radiation is emitted from the lowest excited singlet state S_1, with a lifetime of $\sim 10^{-8}$–10^{-9} s; this radiation is called fluorescence. Along with singlet levels, organic molecules also have a system of excited triplet electronic levels T_i, where excited electrons change their initial spin orientation to the opposite one.

A radiationless transition from an excited singlet state to an excited triplet state occurs via intercombination conversion. The triplet level is always located below the corresponding excited singlet level. Triplet states are triply degenerate. In a magnetic field, these levels split into three levels, which correspond to three possible orientations of the total spin of two electrons: along the field, against it, and perpendicular to it. A transition between the singlet and triplet levels is prohibited by the spin selection rules. However, as a result of spin-orbit interaction, the triplet and singlet states become "mixed", and the transition becomes allowed.

Indeed, according to Ref. [1], the spin-orbit interaction operator for a system of n electrons and m nuclei has the form

$$H_{S0} = \frac{e^2}{2m^2c^2} \sum_i^k \sum_k^m \frac{Z_k(\mathbf{r}_{ik} \times \mathbf{P}_i) \cdot \mathbf{S}_i}{r_{ik}^3}, \qquad (1)$$

where Z_k is the atomic number of the k-th nucleus; r_{ik} is the distance of the i-th electron from the k-th nucleus, and P_i and S_i are the linear and spin momenta, respectively, of the i-th electron. The expression $\mathbf{r}_{ik} \times \mathbf{P}_i$ is the orbital moment $\boldsymbol{\ell}_{ik}$ of the i-th electron with respect to the k-th nucleus. Thus, $\boldsymbol{\ell}_{ik}$ and $\mathbf{S}_i$ are vector operators, and for each electron,

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the spin-orbit interaction operator can be written in the form

$$\frac{e^2}{2m^2c^2}\left[\left(\sum_k^m \frac{Z_k \boldsymbol{\ell}_{xk}}{r_k^3}\right)\mathbf{S}_x + \left(\sum_k^m \frac{Z_k \boldsymbol{\ell}_{yk}}{r_k^3}\right)\mathbf{S}_y + \right.$$
$$\left. + \left(\sum_k^m \frac{Z_k \boldsymbol{\ell}_{zk}}{r_k^3}\right)\mathbf{S}_z\right]. \quad (2)$$

In the first order of perturbation theory, the wave function of the lower triplet state, being perturbed by "mixing" with the singlet state, looks like

$$\Psi(T') = \psi(t') + \sum_k \frac{\left(S^0|H_{S0}|S^k\right)}{E(S^0) - E(S^k)}\,\psi(S^k), \quad (3)$$

and, accordingly, the wave function of the singlet ground state, being perturbed by the triplet state, looks like

$$\Psi(S^0) = \psi(S^0) + \sum_k \frac{\left(S^0|H_{S0}|t^k\right)}{E(S^0) - E(t^k)}\psi(t^k), \quad (4)$$

where $\psi(t')$ and $\psi(S^0)$ are the wave functions of the unperturbed lowest triplet and ground singlet states, respectively.

Using the wave functions (3) and (4), we can find the matrix element of the vibrationless triplet-singlet transition,

$$\mathbf{M}\left(S^0|e\mathbf{r}|T'\right) = \sum_k \left[S^0|e\mathbf{r}|\frac{t'|H_{S0}|S'}{E(t') - E(S^k)}\right] +$$
$$+ \sum_k \left[t'|e\mathbf{r}|\frac{S^0|H_{S0}|t^k}{E(S^0) - E(t^k)}\right]. \quad (5)$$

Thus, due to the spin-orbit interaction, a "mixing" of the triplet and singlet states takes place, so transitions between levels of different multiplicity become possible. The radiative transition from the triplet state to the ground state, $T_1 \to S_0$, which is called phosphorescence, has a lifetime of the order of $\sim(10^{-3} \div 1)$ s or longer.

Numerous studies of the triplet states of the molecules of organic compounds began in the late 1940s and early 1950s at various laboratories around the world. Various phosphorescent properties of many organic molecules have been studied: emission and triplet-triplet absorption spectra, lifetimes and their dependence on various factors (concentrations, exciting light intensities, *etc.*), and so forth. Paramagnetism of organic molecules in the triplet state

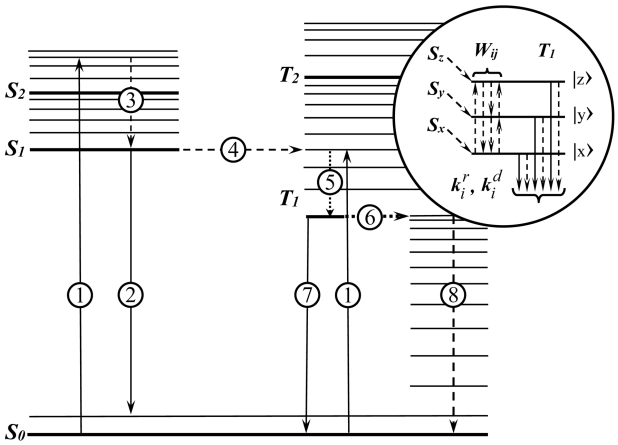

Fig. 1. Schematic diagram of electronic vibrational levels in molecules of organic compounds and transitions between them

was first observed. A large body of miscellaneous materials on those issues has been published in a number of reviews and monographs; see, e.g., Refs. [1–3].

Later, systematic studies of physical processes in condensed matter with the participation of triplet states began. The specificity of the triplet state manifestation is that phosphorescence, which is quite easily observed in solid solutions of organic molecules, is almost completely absent in pure crystals of the same compounds. Various authors [4] have formulated and substantiated the thesis that the low phosphorescence quantum yield of hydrocarbon molecular crystals or its complete absence is associated with effective migration processes and triplet-triplet annihilation.

Despite substantial progress in the study of various photophysical processes involving triplet states of molecules, the issue of the possibility of excitonic phosphorescence in pure molecular crystals remained open for a long time. Among the experimental studies aimed at detecting and studying the intrinsic phosphorescence of molecular crystals, Refs. [5–8] were among the first. Besides the trivial case of impurity-induced phosphorescence, the properties of triplet-singlet radiation of crystalline naphthalene and benzophenone, caused by the so-called X-traps of triplet excitons, were considered there.

2. Triplet and Singlet Excitons in Molecular Crystals

Triplet excitons in molecular crystals are collective currentless excitations with spins equal to unity. The foundations of the theory of triplet excitons were de-

veloped by Merrifield [9] and Jortner [10], by analogy with the theory of singlet excitons proposed by O.S. Davydov [11].

One of the significant differences between triplet and singlet excitons is that the width of the triplet exciton bands and their Davydov splitting are much smaller than those of singlet excitons. This is due to the fact that the matrix elements of resonance interaction for triplet-excited molecules are determined by exchange integrals between the electrons in different molecules [3].

Due to their long lifetime, triplet excitons play an important role in the migration processes of electron excitation energy in a crystal. The migration efficiency is determined by the ratio of the lifetime of a given excited state to the residence time of the corresponding excitation in that state. The lifetime of singlet excitons is $\sim(10^{-8} \div 10^{-9})$ s, and that of triplet excitons $\sim(10^{-3} \div 1)$ s and more. The residence time of an exciton at a certain crystal site can be estimated using the uncertainty principle $\Delta t\ \Delta E \approx \hbar$, where ΔE is the exciton band width. For singlet excitons, $\Delta E = (10^2 \div 10^3)$ cm^{-1}, and for triplet excitons, $\Delta E = (1 \div 10)$ cm^{-1}. Then, a singlet exciton is capable of making 10^4–10^5 jumps from one site to another, and a triplet exciton can make several orders of magnitude more (10^8–10^9 jumps).

Molecular crystals form a large class of compounds consisting of molecules with van der Waals interaction forces between them. The energy of such molecular interactions is very small compared to the binding energy of electrons in the molecules. In this regard, molecules in crystal lattices retain their individuality to a certain extent. Molecular crystals include a huge number of organic compounds (for example, anthracene, naphthalene, phenanthrene, benzophenone, and many others).

Molecular crystals are convenient model objects for studying both molecular and crystalline properties. On the other hand, they can be considered as relatively simple physical models of more complicated biological objects. Molecular crystals have a number of important practical applications. They are used as scintillators, in devices for converting and recording information, and for nonlinear conversion of radiation emitted by optical quantum generators. Since in most aromatic compounds, a substantial part of molecules that absorb light transit into the triplet state, and due to a more efficient energy migration via triplet states than via singlet ones, the luminescence properties of many organic molecular crystals are mainly governed by the spectral-kinetic features of the triplet states in those systems.

Triplet states play an important role in the conversion and transfer processes of electron excitation energy in organic molecular systems. Cooperative and nonlinear processes also occur with their participation. Triplet states are essential in bioenergetics, sensitization of photosensitive materials, photochemistry, and so forth. The properties of triplet states of organic molecules are widely used in biology, in particular, for studying the processes of photosynthesis, oxidation reactions, the energy and electron transfer in complicated biochemical systems (enzymes, micelles, *etc.*), and for analyzing the properties and performing the quality control of therapeutic biological products.

Works in the domain of triplet-state physics are characterized by an extremely wide variety in both their directions and the content of specific scientific developments and research: the nature and identification of triplet states, triplet-triplet annihilation processes, mechanisms of radiative and non-radiative processes, spin-lattice relaxation in the triplet state, the phenomenon of optical spin orientation, nonlinear effects, the influence of magnetic and electric fields, and others. One of the most striking achievements among the huge number of diverse results was the discovery in the mid-1960s of the optical spin orientation of the triplet state in organic molecular crystals [12, 13]. This led to the development and effective application of a new method in molecular spectroscopy, the phosphorescence microwave double resonance (PMDR) spectroscopy, which makes it possible to obtain unique information about the magnetic, radiative, and non-radiative properties of triplet excited molecules, their geometry, the pathways and mechanisms of intramolecular intercombination conversion, and so on. The objects of research are gases, liquid and solid solutions, pure and doped organic and inorganic crystals, polymers, glassy and amorphous disordered structures, thin films, biological objects, and others. Various experimental techniques are used: phosphorescence, EPR spectroscopy, luminescence, laser pulse photolysis, triplet-triplet adsorption spectroscopy, kinetics of phosphorescence growth and decay, *etc.*

Thus, nowadays it is completely impossible to give a complete, or even a partial, review of scientific research in triplet state physics. This domain has split into a number of essentially independent original directions with their own goals and experimental methods.

Historically, the physics of singlet excitons and the physics of triplet excitons were not developed in parallel, but one after another. By the beginning of the 1960s, the main regularities in the absorption and fluorescence processes of molecular crystals had been explained on the basis of the exciton theory developed by Academician O.S. Davydov. The experimental confirmation of this theory was mostly obtained in the works of spectroscopists belonging to the Kyiv school (Institute of Physics of the Academy of Sciences of the Ukrainian SSR, IP AS UkrSSR) under the supervision of Academician A.F. Prykhot'ko. The results of numerous experimental and theoretical studies of the spectroscopy of singlet excitons in pure and doped molecular crystals, which were carried out both at the IP AS UkrSSR and in other scientific centers of the former USSR, were afterwards presented and summarized in monographs [14–16].

The cycle of experimental and theoretical works "Excitons in Crystals" was awarded the Lenin Prize in 1966. The main provisions of the concept of molecular excitons are currently widely used in various branches of condensed matter physics, as well as in modern biology and biophysics.

It was in the early 1960s that systematic studies of physical processes involving triplet states in molecular crystals were initiated in many laboratories. At first glance, the situation seemed paradoxical: as the molecular crystals were purified, the intensity of their fluorescence increased, but that of phosphorescence decreased (later it was found that in most cases this phosphorescence was caused by impurities or defects). For some time, these results were considered controversial. Later, in Refs. [17, 18], it was shown that the absence of phosphorescence in pure molecular crystals is a result of the effective migration of triplet excitations; the latter gives rise to the pairwise triplet-triplet annihilation and, consequently, to the appearance of delayed fluorescence. In due course, this interpretation was repeatedly confirmed experimentally [1–3].

Further studies showed that not all molecular crystals are prone to phosphorescence. It turned out that among the factors contributing to the phosphorescence of these objects, the most essential are the low interaction energy in the triplet state and the short lifetime. These parameters, in turn, depend on the nature of electronic states ($\pi\pi^*$ or $n\pi^*$) and the crystal lattice structure. These conditions are combined very successfully in benzophenone: here, the diffuse displacement length and the triplet exciton lifetime are appreciably shorter than those in other crystals. Furthermore, the almost complete internal radiation-free conversion $S_1^* \rightarrow \rightarrow T_1$ leads to a high concentration of triplet excited molecules.

It should be noted that studies of low-temperature spectroscopy of triplet states began at the IP AS UkrSSR in the mid-1960s under the supervision of Academician M.T. Shpak. Initially, the task was to determine the conditions for the emergence of excitonic phosphorescence and to elucidate the mechanism of triplet-singlet emission in real molecular crystals [19]. The further development of those works led to the discovery of the intrinsic (excitonic) phosphorescence in molecular crystals (benzophenone, at $T = 4.2$ K) in 1969 [20].

Among further studies on this topic, it is worth noting a series of original Refs. [21, 22] performed at the IP AS UkrSSR in the 1980s. In particular, the effects of triplet exciton annihilation suppression in strong magnetic fields and at high levels of optical excitation were discovered and studied, and the influence of the magnetic field on the rate of spin-lattice relaxation of local triplet excitations in benzophenone crystals was measured for the first time.

In the early 2000s, at the Institute of Physics of the National Academy of Sciences of Ukraine (IP NANU), on the initiative of G.O. Puchkovska, the physical properties of organic-inorganic nanocomposite materials began to be studied with the help of spectral methods. In particular, using the previously discovered temperature peculiarities of benzophenone phosphorescence and taking into account the data of differential scanning calorimetry, atomic force microscopy, and IR spectroscopy, the dependence of the nanocomposite phase structure on the type of nanoparticles and the state of their surface was found [23, 24]. The limitations on the volume and format of this report did not allow the activity performed at the IP NANU in the field of triplet state physics to be considered in detail. A description

Table 1. **Main properties of various benzophenone phases**

Phase	Melting temperature (glass transition), K	Space group	Number of molecules in a unit cell	Density, g/cm^3	Unit cell parameters, Å
Stable α, α, rhombic	324	$P2_12_12_1$	4	1.233	$a = 10.27$ $b = 12.09$ $c = 7.90$ $\alpha = \beta = \gamma = 90°$
Metastable β, β, monoclinic	301	$C2_c$	8	1.212	$a = 16.23$ $b = 8.16$ $c = 16.36$ $\alpha = \gamma = 90°$ $\beta = 112.94°$
Metastable γ	296	–	–	–	–
Glassy X	217	–	–	–	–

Table 2. **Main parameters of triplet excitons in various molecular crystals**

Crystal	Diffusion coefficient D, cm^2/s	Diffusion displacement length, μm	Lifetime, s
Anthracene	2×10^{-4}	10–20	10^{-2}
Naphthalene	10^{-5}–10^{-6}	30–40	2.3
Tetracene	1.6×10^{-5}	2	10^{-4}
Benzophenone	5×10^{-7}	10^{-1}	10^{-3}

of some of the main achievements obtained in this field can be found in Refs. [25, 26].

3. Structure, Properties, and Spectroscopy of Benzophenone

Benzophenone $(C_6H_5)_2CO$ belongs to the class of aromatic ketones. It is currently known that benzophenone can exist in three crystalline modifications (one stable, α, and two metastable, β and γ) and in an amorphous glassy state (X-phase). X-ray structural studies of α-modification and metastable phases were performed in Refs. [27, 28]. In Table 1, some characteristics of various structural phases of benzophenone are presented. An analysis of the parameters of triplet excitons revealed some factors that favor the manifestation of phosphorescence in the spectra of pure molecular crystals. These are the low interaction energy in the triplet state and the short triplet lifetime.

One of the classes of organic crystals that satisfy these conditions is the class of crystals with a system of excited levels of the type $n\pi^*$, whose lifetime is much shorter than that of the $\pi\pi^*$-states. Benzophenone is a typical example of such crystals. The diffusion shift length of triplet excitons in benzophenone is one or two orders of magnitude shorter than that in other molecular crystals, which favors the detection of the intrinsic (exciton) phosphorescence of crystals (Table 2).

As for the studies of the spectral properties demonstrated by the triplet state of the benzophenone molecule, the paper by Terenin and Ermolaev [29] can be considered one of the first works in this direction. In this work, the nonradiative transfer of electronic excitation energy from triplet benzophenone molecules to unexcited naphthalene molecules in solid solvents at low temperatures was observed. High-resolution spectra of benzophenone phosphorescence under the conditions of the Shpolsky effect at the temperature $T = 4.2$ K were later obtained in Ref. [30].

Since the 1960s, the number of publications devoted to the study of various aspects of triplet states in the crystalline state, in general, and in crystalline benzophenone, in particular, has drastically increased. First of all, these are the works by O.M. Faidysh and collaborators devoted to the study of the processes of electron excitation energy transfer by triplet excitons and the influence of the phase state of benzophenone on its phosphorescence. Sharnoff and Hochstrasser performed theoretical and exper-

imental studies aimed at determining the population and deactivation probabilities for spin sublevels of triplet states in the benzophenone crystal. In the works of Laporte and Hochstrasser, the results of spectroscopic studies of benzophenone phosphorescence and absorption, as well as the results obtained for the influence of the benzophenone matrix disordering on the efficiency of triplet energy transfer to impurity molecules, were reported. The theoretical works of V.I. Sugakov and the experimental works of the Kharkiv school (Institute for Low Temperature Physics and Engineering of the NASU, ILTPE NASU) carried out by A.A. Avdeenko and collaborators had a significant impact on the development of the studies of triplet excitons in molecular crystals. Those results and the results obtained by other scientists in the triplet exciton physics were analyzed in more detail in the review [31].

The phosphorescence spectra of crystalline benzophenone were first reported by McClure in Ref. [32]. In due course, those studies became more and more extensive and diverse. Both phosphorescence and singlet-triplet absorption spectra, lifetimes, decay kinetics, and so forth were studied [33, 34]. As it turned out later, these spectra appear due to the presence of impurities and defects.

An analysis of the literature data in recent years has shown that research in triplet state spectroscopy and structural transformations of benzophenone has brought about new interesting fundamental results. In particular, in the works by M.O. Strzhemechny and collaborators (ILTPE NASU), comprehensive studies aimed at establishing a relation between the spectral-luminescence properties of benzophenone and its halogen derivatives, as well as between their crystal structures, were carried out [35]. It is essential that the temperature intervals of glass formation (217 K), crystallization (250–270 K), and melting (300–323 K) in all benzophenone phases are easily accessible for experiment, which makes benzophenone a convenient model object for studying phase transformations and their influence on the properties of triplet excitons. Later, the number of examined compounds with various properties of triplet excitons gradually increased. An analysis and summary of the results obtained by the beginning of the 2010s in the physics of triplet excitons in organic compounds can be found in a rather comprehensive review [36].

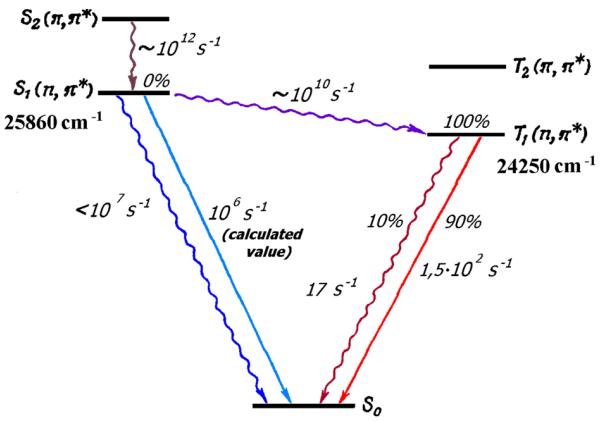

Fig. 2. Schematic diagram of energy levels in a benzophenone molecule

Despite the large number of publications on the triplet states of benzophenone, a fundamental issue remained open for a long time, namely, the existence of exciton phosphorescence in this crystal. For instance, some publications [37, 38] reported that the phosphorescence spectra were shifted to the long-wavelength region by 56 and 81 cm^{-1} as compared to the singlet-triplet absorption spectra.

Numerous studies showed that in order to obtain exciton phosphorescence, a fundamental condition must be satisfied: defect- and impurity-free benzophenone crystals of extremely high quality must be grown. In Ref. [20], these conditions were achieved, the exciton phosphorescence in crystalline benzophenone was observed, and its main characteristics were presented. The thickness of the crystalline specimens was 2–3 mm. Benzophenone was purified using the methods of zone melting and multiple crystallization from the solution. The schematic diagram of the benzophenone electronic levels is shown in Fig. 2.

In Fig. 3, the initial sections of the phosphorescence and singlet-triplet absorption spectra of benzophenone crystals are depicted. If we take the shortest-wavelength band in the phosphorescence spectrum at $\nu = 24195$ cm^{-1} as a purely electronic transition, then the frequency difference between this and the following bands corresponds, within the measurement errors, to the values of the vibrational frequencies of the benzophenone molecule obtained from the Raman and infrared absorption spectra. The phosphorescence spectrum consists of a large number of narrow quasilines, with a clearly pronounced periodicity in their arrangement. The periodicity interval is

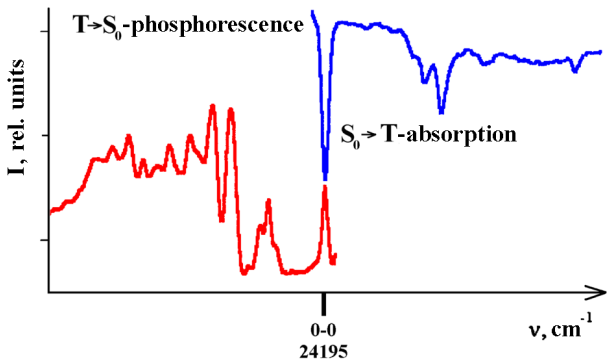

Fig. 3. Initial sections of the phosphorescence and singlet-triplet absorption spectra of benzophenone crystals at $T = 4.2$ K

1640 cm^{-1}, which corresponds to the stretching vibration of the carbonyl group C=O in the benzophenone molecule in the ground state. The most intensive vibrations form progressions with three-quantum repetitions in the spectrum.

As can be seen from Fig. 3, and this is essential, the 0–0 band in the phosphorescence spectrum resonantly coincides with the initial band in the singlet-triplet absorption spectrum (at $\nu = 24195$ cm^{-1}). The frequency of the most intensive oscillation (1218 cm^{-1}) is the repetition period of the main electronic-vibrational bands in the absorption spectrum.

The presence of an energy gap between the absorption and emission spectra, which was registered in Refs. [37, 38], testified to the defect origin of the obtained phosphorescence.

Thus, owing to the thorough purification of benzophenone, the growth of sufficiently high-quality crystals, and their protection from UV radiation, which leads to the emergence of undesirable impurities in the form of photochemical reaction products, it became possible for the first time to register the excitonic phosphorescence of a stable modification of crystalline benzophenone at $T = 4.2$ K [20].

4. Time-Resolved Phosphorescence Spectra

The application of time-resolved spectroscopy makes it possible, in a number of cases, to obtain new experimental results (unattainable under conventional conditions for spectrum registration), which are necessary for studying the mechanisms of such phenomena as spin-selective relaxation processes in excited triplet states, spectral migration, electronic excitation energy transfer in condensed media, determination of the nature of radiative centers, and so forth.

It should be noted that most information on the spectroscopy of triplet excitons in benzophenone crystals was obtained using the steady-state spectroscopy methods. Among the works known at that time, the non-stationary method for registering the phosphorescence spectra of benzophenone was applied only in Ref. [21] to analyze nonlinear effects at high pump levels. If time-resolved spectroscopy is used, it becomes possible to distinguish and analyze complicated bands that overlap and belong to different emission centers with correspondingly different lifetimes of excited states.

To obtain time-resolved phosphorescence spectra, the photomultiplier was short-circuited using a G5-15 generator, with various delay times with respect to the laser pulse. Phosphorescence was excited by radiation from a pulsed nitrogen laser LGI-21 with $\lambda = 337$ nm and a pulse duration of 10 ns. The output pulse power was approximately 1.5×10^4 W/cm^2. The locking pulse duration was 200 μs. The frequency of the exciting laser pulses was 25 pulses/s during the spectrum registration, and 10 pulse/s when measuring lifetime. This technique made it possible to register the phosphorescence intensity at various time intervals after the exciting pulse and resolve its "pure" spectral components with different lifetimes from the total spectrum.

An analysis of the obtained results allowed us to establish that along with exciton radiation, the phosphorescence spectrum of the benzophenone stable phase also contains two systems of bands with different lifetimes of the excited triplet state; those bands cannot be detected and registered against the background of much more intensive exciton radiation in conventional (integral) spectra. It was shown that as the delay time after the laser excitation pulse increases, the spectrum undergoes significant deformation and changes. In particular, at the later registration stages, only a wide, structureless emission band is available in the spectrum, whereas the exciton spectrum completely disappears.

In Fig. 4, the initial sections of the phosphorescence spectra of crystalline benzophenone, corresponding to various delay time intervals $\Delta t = 1$, 1.5, 2, 3, 5, and 10 ms between the laser pulse and the opening of the photomultiplier voltage pulse, are shown. The main feature of the obtained results is the strong depen-

dence of the spectral shape and structure on the delay time. It should be noted that this drastic time dependence is observed within the millisecond delay interval; for much shorter time delays, the structure of the phosphorescence spectrum is insensitive to their values. For example, the behavior of the phosphorescence spectra obtained for the stable modification of benzophenone at $\Delta t = 1$ ms and 0.1 μs is practically identical, but the spectrum intensity in the latter case is almost 60 times lower.

In our experiments at $\Delta t = 1$ ms, the spectrum coincides with the exciton phosphorescence spectrum obtained under stationary excitation. As the delay time increases, a new band (X-band) appears at about 23150 cm^{-1}, and its relative intensity with respect to the intensity of the 0–0 transition band in the exciton spectrum increases sharply.

At longer delay times, starting from $\Delta t = 3$ ms, the X-band remains dominant in intensity (the integral intensity of the spectrum decreases by approximately three orders of magnitude at that). At the same time, there appears a broad structureless band in the long-wavelength spectral interval, with a maximum at about 20000 cm^{-1}. At $\Delta t = 10$ ms, some "traces" of excitonic phosphorescence and the X-band still remain visible in the emission spectrum, but at $\Delta t = 30$ ms, the spectrum consists of only one broad band (Fig. 4, the inset). It follows from the above data that in the entire analyzed interval of time delays, the frequency of the excitonic phosphorescence maximum remains constant (24050 cm^{-1}), whereas the X-band shifts toward the long-wavelength region as the time delay increases. As Δt increases from 2 to 10 ms, the shift reaches a value of 127 cm^{-1}.

Thus, with the help of time-resolved spectroscopy, it was found that the integral phosphorescence spectrum of the stable benzophenone phase consists of three overlapping spectral band systems with different quenching times. The intensity ratios between the spectral components substantially depend on the delay time after the laser excitation pulse. One of those spectra corresponds to the emission by triplet excitons. The other spectrum is associated with the presence of the glassy benzophenone phase, which is formed at the sites of structural defects. The third spectrum is probably a result of the emission by excimers that were formed from the molecules of benzophenone or the products of its photochemical reactions [31].

5. Phosphorescence and Nanostructure of the Glassy Benzophenone Modification

The phosphorescence spectrum of the X-modification of benzophenone in a temperature interval of 4.2–200 K consists of a series of broad bands with a vibrational interval of 1640 cm^{-1}, characteristic of the C=O group. At a temperature of 220 K, the maximum of the short-wavelength band is located at about 23700 cm^{-1}. If the temperature is lowered to 97 K, the spectrum shifts toward the long-wavelength region by 370 cm^{-1}. As the temperature decreases further to 4.2 K, the maximum shifts in the opposite direction, toward the short-wavelength region, and also by 370 cm^{-1}. As a result, the positions of spectral maxima on the energy scale coincide at temperatures of 220 and 4.2 K (Fig. 5). This non-trivial result was studied in detail and appropriately interpreted in Ref. [39].

To interpret the "anomalous" temperature dependence of the phosphorescence spectrum of glassy benzophenone, model representations were used that de-

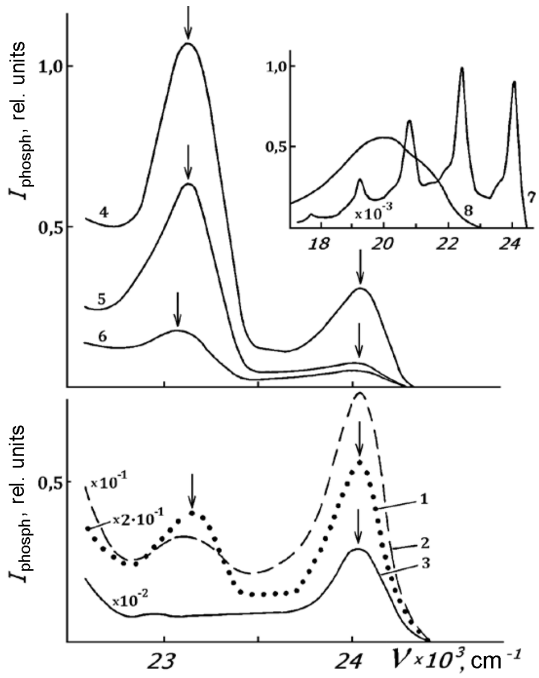

Fig. 4. Initial sections of time-resolved phosphorescence spectra of crystalline benzophenone; time-delay intervals are 1 (*1*), 1.5 (*2*), 2 (*3*), 3 (*4*), 5 (*5*), and 10 ms (*6*). Inset – Time-resolved phosphorescence spectra of crystalline benzophenone are shown in the inset; time-delay intervals are 0.1 (*7*) and 30 ms (*8*)

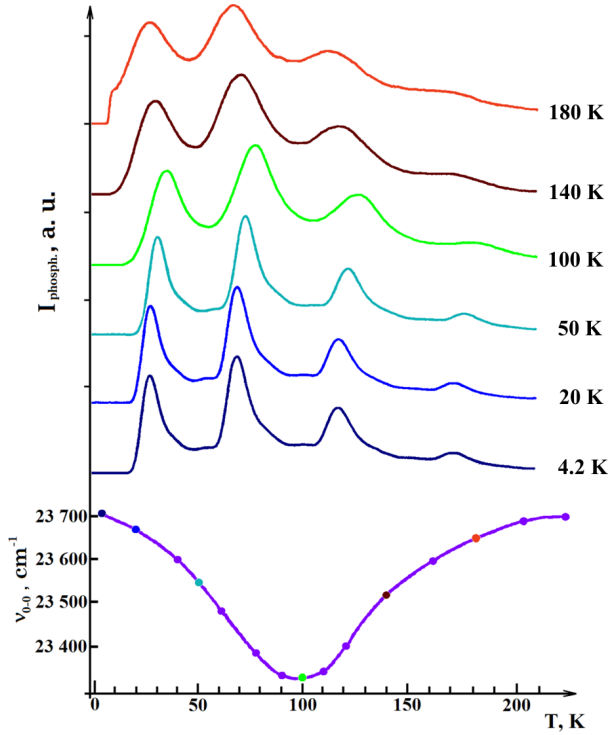

Fig. 5. Temperature dependence of the phosphorescence spectrum position of glassy benzophenone on the frequency scale

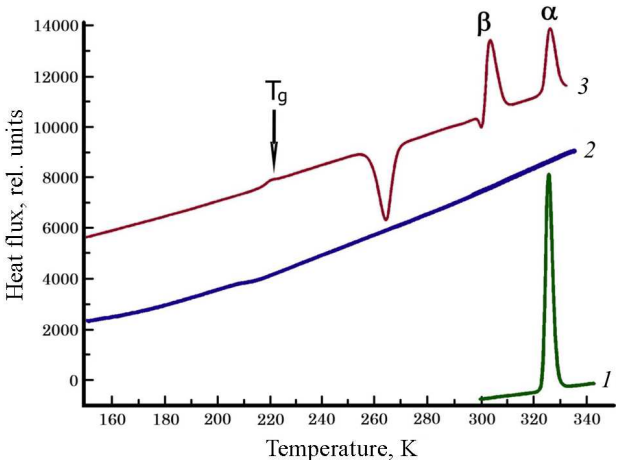

Fig. 6. DSC thermograms of benzophenone: heating of crystalline phase (*1*), cooling of the melt (*2*), heating of the glassy modification (*3*)

scribe the processes of charge carrier transport and electronic excitation energy transfer in disordered amorphous and glassy molecular structures [40, 41].

One of the challenging tasks of solid-state physics is the study of the nature and properties of disordered condensed systems with an amorphous or glassy structure. Their optical and electronic properties differ considerably from those of their crystalline counterparts. Despite the large number of publications on the glass structure, there is still no single theoretical concept of the substance structure in the glassy state, as well as no clear understanding of this issue. Therefore, additional experiments are needed to study various physical properties that may provide new information about the structure of glassy systems. In particular, in Ref. [42], the Raman spectra of benzophenone were studied in detail within a wide temperature interval. One of the main results of those studies consisted in the discovery of the so-called Boson peak in the low-frequency spectral interval, the presence of which is a fingerprint of the glassy structure of the substance.

To study the structure of glassy benzophenone, a comprehensive approach was used, in which the methods of differential scanning calorimetry (DSC), Raman spectroscopy, and luminescence and dielectric measurements were applied.

5.1. DSC thermograms

DSC measurements were carried out on a Perkin Elmer DSC7 calorimeter with a heating and cooling rate of 20 °C/min, in a temperature interval of 150–350 K. In Fig. 6, a typical DSC thermogram is presented, in which all phase transformations that occur in benzophenone within a temperature interval of 143–353 K are registered. Curve *1* demonstrates only one strong transition at 329.9 K, which corresponds to the melting point of α-benzophenone. When cooling the benzophenone melt (curve *2*), a low-energy transition is observed at about 211.7 K, which corresponds to the glass transition point, i.e., the X-phase formation.

The most informative is curve *3*, which illustrates the process of X-benzophenone heating. All temperature-induced structural transformations of glassy benzophenone are observed in this case. First of all, this is a temperature of 216.8 K, which corresponds to the transition of the glassy state into a supercooled liquid. Note that the phosphorescence spectra do not undergo noticeable structural changes at this point, except that the integral phosphorescence intensity of the supercooled liquid decreases by about 5 times. In a temperature interval of 240–261 K, the

β-phase is formed and subsequently transforms into the α-modification. The process is accompanied by the release of a large amount of heat. Two sharp narrow peaks at 301 and 323.9 K correspond to the melting points of the β- and α-phases of benzophenone, respectively.

It is also important to note that the thermal properties of benzophenone depend on the direction of temperature variation. In particular, in curve *2*, the crystallization process is not observed when liquid benzophenone is cooled. This is natural because there are no crystallization centers in the completely disordered liquid phase. At the same time, when the glass is heated, nanostructured fragments that arose during the glass formation process, owing to a reduction in viscosity and an increase in diffusion, become crystallization centers [39].

Nowadays, the concept of the relation between the physical properties of glass and its nanostructure is being successfully developed. Various experimental data testify to the existence of some universal structural formations in glasses with a size of several nanometers. Glassy and amorphous structures are characterized by the so-called medium-range order, whereas crystalline bodies with translational symmetry possess the long-range order.

In a number of both theoretical and experimental works, it was shown that the position of the Boson peak is related to the size of structural inhomogeneities, which is characterized by the medium-order radius [43]

$$R = K\frac{\upsilon_D}{\nu C},$$

where ν is the Boson peak frequency in cm^{-1} units, C is the speed of light, K is a dimensionless coefficient depending on the cluster shape, and

$$\upsilon_D = \left[\frac{1}{3}\left(\frac{2}{\upsilon_t^2} + \frac{1}{\upsilon_\ell^2}\right)\right]^{-1/3}$$

is the Debye velocity [43]. Hence, R is proportional to the ratio between the speed of sound and the Boson peak frequency.

In this way, using the experimentally measured values of the longitudinal, $\upsilon_\ell = 2.1$ km/s, and transverse, $\upsilon_t = 1.5$ km/s, sound velocities in glassy benzophenone and the Boson peak frequency in the Raman spectrum, $\nu = 17$ cm^{-1}, the value of R was calculated to be equal to (30 ± 5) Å.

6. Peculiarities in the Structure and Physical Properties of Glassy Benzophenone

In Fig. 7, the time-resolved phosphorescence spectra of glassy benzophenone registered at $T = 4.2$ K are shown. One can see that as the time delay Δt between the moment of laser excitation pulse arrival and the registration moment increases, the spectra shift toward the long-wavelength region. For example, at $\Delta t = 10$ ms, the shift is 100 cm^{-1}. To explain the experimental results, model representations were used. The latter were proposed by Bässler [40]. They explain the processes of charge carrier transport and energy transfer of electronic excitation in disordered amorphous and glassy molecular structures and are widely used to describe the electronic and optical properties of the compounds belonging to this class.

In Fig. 8, a schematic diagram of electronic excitation energy relaxation in glassy media is shown. Due to the energy and topological disorder in condensed molecular systems, their spectral bands undergo substantial inhomogeneous broadening and have a Gaussian distribution. Having arisen at an arbitrary site, an electronic excitation does not remain there, but it migrates within this distribution. At sufficiently low temperatures, when the inhomogeneous broadening of the distribution of centers is much larger than kT, the irreversible character of migration is strongly manifested. The transfer of excitation to centers with lower energy levels becomes much more probable than the reverse thermal activation process. As a result, the low-lying levels within the inhomogeneous con-

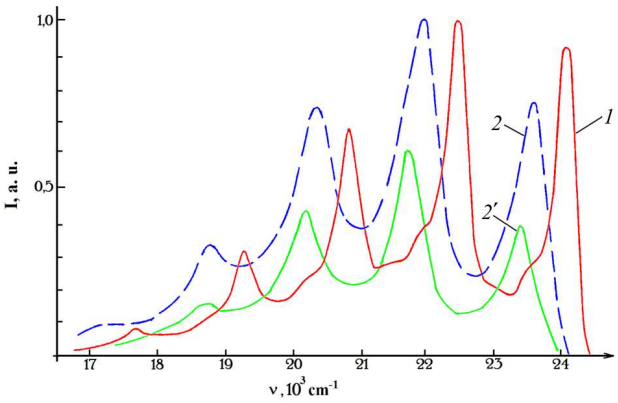

Fig. 7. Phosphorescence spectra of polycrystalline (*1*) and glassy (*2*, *2′*) benzophenone at delay times of 0.1 μs (*1*, *2*) and 10 ms (*2*)

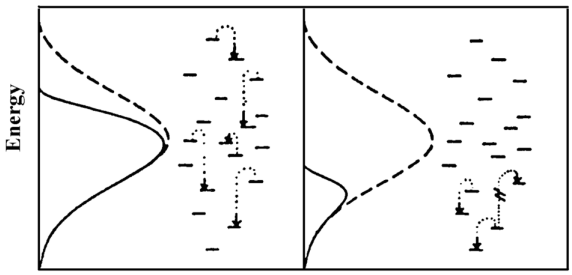

Fig. 8. Schematic diagrams of electronic excitation energy relaxation in disordered systems. Left panel: Gaussian distribution of energy states (dashed curve). Solid line: population distribution over energy states in a short time interval after the excitation pulse. Right panel: the same distribution after a long time interval [40]

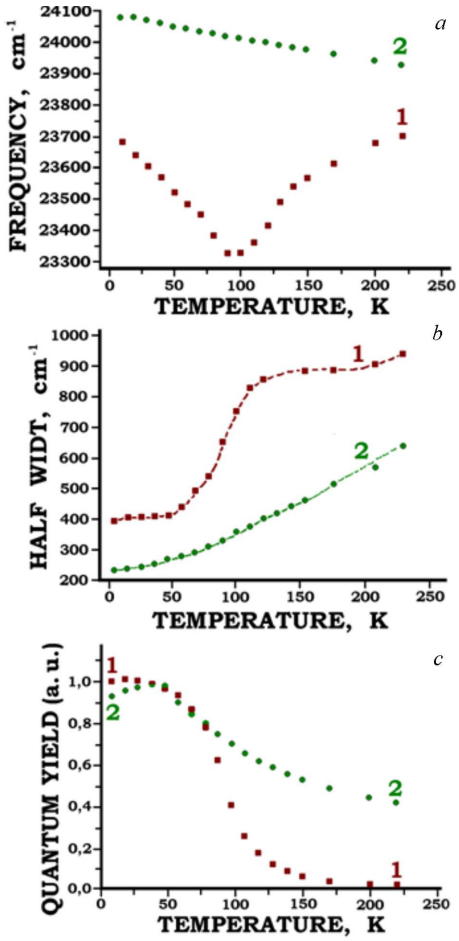

Fig. 9. Temperature dependences of the main spectral properties of glassy (*1*) and crystalline (*2*) benzophenone: (*a*) positions of the phosphorescence spectra on the frequency scale, (*b*) half-widths of the first short-wavelength bands in the spectra, (*c*) relative quantum yields

tour become predominantly populated. In addition, various centers of this ensemble have different decay rate constants; this fact induces spectral changes during the decay process over the excited state lifetime. The set of spectral and kinetic phenomena associated with the excitation transfer in disordered structures has been called spectral diffusion in the literature [44]. Thus, owing to the spectral diffusion of triplet excitations in glassy benzophenone, a long-wavelength shift of the spectra takes place.

The phosphorescence of glassy benzophenone is considerably different from that of crystalline benzophenone. In Fig. 9, the temperature dependences of the electronic transition frequencies, spectral band half-widths, and relative quantum yields of glassy and crystalline (α-phase) benzophenone are shown. First of all, attention is attracted by a peculiar temperature dependence of the electronic transition frequency in the glass phosphorescence spectrum.

One of the possible hypotheses explaining the observed phenomenon consists in the fact that the population density of excited electronic states is governed by two competing factors: triplet excitation energy migration, which causes a red shift, and thermal activation processes, which lead to the opposite shift. As was shown [45], a sharp (exponential) increase in the diffusion coefficient of triplet excitations is observed in glassy benzophenone at temperatures of 4.2–100 K, which causes a red shift of the spectrum. Starting from $T = 100$ K and above, the contribution of thermal activation processes becomes predominant, so the spectral shift toward the violet region is observed.

As for the comparative characteristics of the band half-widths and the relative quantum yields of phosphorescence in crystalline and glassy benzophenone, they are clearly presented in Fig. 9, *b* and 9, *c*. These results show that the temperature dependences of the main spectral characteristics of phosphorescence in glassy benzophenone have a number of distinctions compared with those in benzophenone crystals. Furthermore, the properties of glassy benzophenone drastically change in the temperature interval of 95–100 K. In particular, the temperature dependence of the spin-lattice relaxation time in glassy benzophenone, which was determined in Ref. [46] using the NMR method, undergoes a sharp increase also at about 100 K. It should be noted that the temperature dependence of the dielectric permittivity ε (the real component) of benzophenone, which was measured

by us, appreciably depends on the cooling rate. If the melt was cooled rapidly and a glassy structure was formed, the value of the relative jump-like change $\Delta\varepsilon/\varepsilon$ at about 95 K was found to equal 16%. In the case of slow melt cooling, the specimen was mainly a polycrystalline body, and the value of $\Delta\varepsilon/\varepsilon$ was only 7%.

From our experimental results presented above and from the results obtained by other authors, it follows that the physical properties of glassy benzophenone, which were obtained by independent experimental methods and exhibit different behaviors, surprisingly undergo jump-like changes exactly in a temperature interval of 95–100 K (Fig. 10). This fact may testify that certain structural changes occur at the microscopic level in glassy benzophenone within this temperature range. If we consider glass as a nonequilibrium state of a liquid with a long relaxation time at low temperatures, then its restructuring occurs in concordance with the diffusion mobility of atoms and molecules, as well as with other types of mobility.

In the cases of molecular glasses and polymers, these processes have been studied using the dielectric spectroscopy methods and described in the framework of the α- and β-relaxation concepts [47]. Currently, there is no single model and single interpretation of β-transitions at the microscopic level for different substances in the literature. At the same time, it is pointed out that β-transitions take place in almost all studied glassy and amorphous structures, being one of the universal and fundamental properties of disordered structures. Thus, all peculiarities and anomalies observed in glassy benzophenone in the temperature interval of about 90–100 K can be qualitatively related to a peculiar structural phase transition, which is a result of a jump-like change in the mobility of benzophenone molecules at this temperature.

At the IP NASU, under the supervision of A.K. Kadashchuk and in collaboration with foreign partners, a series of comprehensive studies on the physics of triplet excitons in organic semiconductor materials has been carried out. In particular, the phosphorescence of a number of classes of π-conjugated polymers, such as poly-fluorenes and poly-spirofluorenes [48], as well as ladder-type polymers, such as poly(para-phenylene-carbazole) [49], was discovered and studied for the first time. For the films of those materials, the contribution of triplet excitons to recombination and thermally stimulated luminescence was considered.

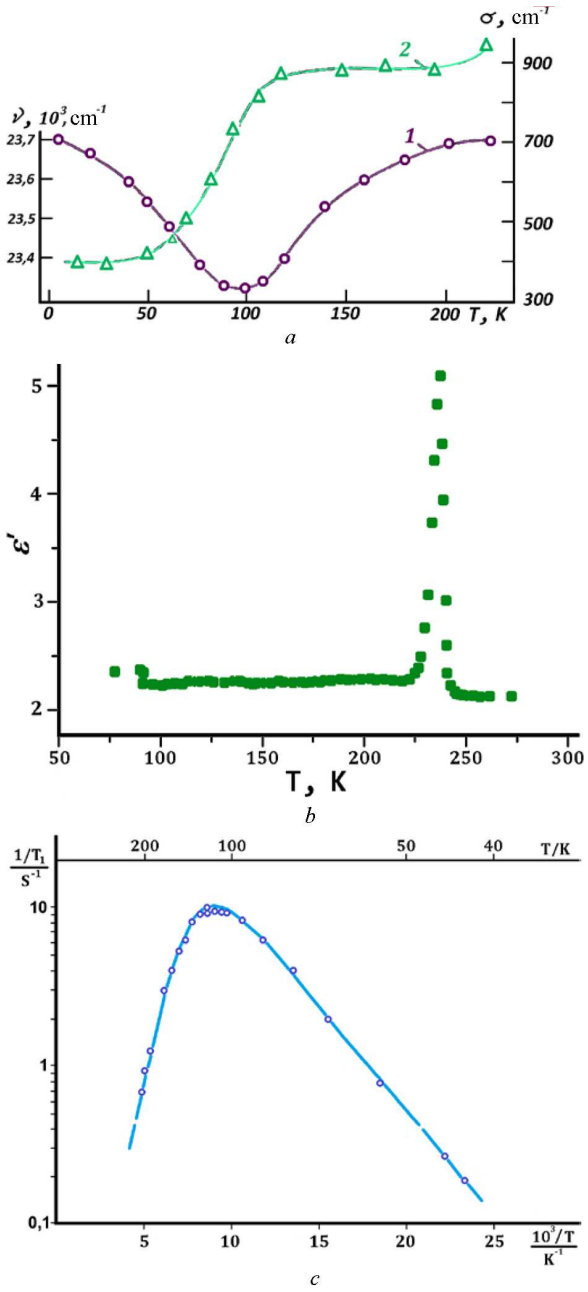

Fig. 10. Temperature dependences of some physical properties of glassy benzophenone: position of the phosphorescence spectrum on the frequency scale ν and the half-width σ of the first short-wavelength band in the spectrum (*a*), dielectric permittivity (*b*), spin-lattice relaxation rate (*c*)

The intrinsic phosphorescence of the organosilicon σ-conjugated polymer poly-(methylphenylsilane) (PMPSi) in the solution and the solid phase was also revealed [50]. Its spectrum looks like a broad, structureless band shifted by 0.85 eV below the excited singlet-state level of the polymer. The kinetics of the PMPSi phosphorescence decay and its temperature dependence were also studied [50]. Using some doping molecules as donors or acceptors of the triplet excitation energy, the triplet-triplet energy transfer in PMPSi films was quantitatively analyzed, and an appreciable spin-orbit splitting (about 6600 cm^{-1}) was found in PMPSi, which points to a strong correlation among σ-electrons and supports the Frenkel exciton concept for polymers of this type.

Original studies revealed extremely efficient intrinsic phosphorescence with a quantum yield of 15% in the conjugated polymer poly-(biphenyl-methylsilane) (PMBSi), which is at least 4–5 orders of magnitude higher than the quantum yield known for this class of materials, which do not contain heavy atoms. It was found that a high yield of intercombinational conversion in this polymer stems from the fact that the lowest excited singlet intramolecular charge-transfer state, and it has a very small singlet-triplet splitting in comparison with neutral exciton states [51].

In Ref. [52], the energy of singlet-triplet splitting of electron-hole pairs in conjugated polymers (these are an intermediate state preceding charge recombination and a precursor to the formation of excitons with a certain spin state) was experimentally determined for the first time. The obtained results made it possible to clarify the influence of polymer morphology on the ratio of singlet and triplet exciton yields at charge recombination in organic light-emitting diodes.

Using a model composite system based on a polymer matrix doped with molecules of metal-organic complexes (the so-called "triplet emitters"), the dynamics of triplet excitations was studied [53]. The spectral diffusion effect was revealed in the impurity phosphorescence, which proves the possibility of triplet exciton migration over a system of impurity molecules in energetically disordered states. These results support the recently proposed model of long-range dipole-dipole transfer of triplet excitations in such phosphorescent materials.

A comprehensive study [54] was also carried out of the dynamics of triplet excitons and the energy transfer mechanism in the films of the model 9,10-diphenylanthracene-based composite material doped with platinum porphyrin (PtOEP) complexes used as sensitizers of triplet excitations in the matrix. The phenomenon of incoherent upconversion of the exciting light energy at ultralow excitation levels due to the triplet-triplet annihilation process was revealed. It was found that the diffusion of triplet excitons in the aggregates of the PtOEP impurity determines the final rate of excitation energy transfer in solid-state systems of this type.

A phenomenon of the so-called "non-vertical" energy transfer of triplet excitations in solid matrices of organic semiconductors doped with molecules of cyclooctatetraene, the triplet excitation acceptor, was discovered for the first time in Ref. [55]. Earlier, such triplet acceptors were used only in liquid solutions in dye lasers. This effect opened the way to solving the challenging problem concerning the decrease of the electroluminescence quantum yield at high excitation levels, as well as the problem of parasitic losses due to triplet-triplet absorption in organic solid-state lasers with electrical pumping. Based on this research, US and EU patents were obtained for a method of effective quenching of triplet excitations in solid-state organic materials using "non-vertical" triplet acceptors [56].

An effective mechanism was proposed for the intrinsic photogeneration of charge carriers in organic single-component materials [57]. This phenomenon takes place owing to the bimolecular process of triplet excitation annihilation at relatively low levels of optical irradiation.

An analytical theory was developed for the diffusion of triplet excitations in disordered organic materials [58]. The model was applied to describe the temperature dependence of the diffusion of triplet excitons in a conjugated model polymer, which has a strong spin-orbit interaction due to the presence of heavy atoms (Pt) and is characterized by a very weak energy disorder. It was found that the transfer of triplet excitations in this system is a thermally activated process only above a certain critical temperature, while it is almost temperature-independent below this value. Additionally, the dependence of the critical temperature on the ratio between the energy disorder parameter and the polaron binding energy was determined.

In Refs. [59, 60], using some aromatic amine molecules introduced into polymer matrices as an exam-

ple, it was shown that the probability of intercombination conversion from the first excited singlet state into the triplet state depends on the chemical nature and configuration of the molecule. This probability increases if the polymer matrix density increases and if external uniaxial pressure is applied. It occurs due to the increased mixing of the wave functions of the amine and matrix molecules.

In Refs. [61–63], it was shown that the revealed and studied spectral diffusion effect relates to the triplet levels of metal-organic complex impurities in the neutral polymer matrix. This effect is evidence of a new mechanism that governs the transfer of triplet excitations in such materials and operates according to the Förster mechanism for the long-range dipole-dipole transfer. The latter was previously used only to explain the energy transfer of singlet excitations.

Finally, it is worth noting two recently published fundamental reviews on various issues of triplet exciton physics in various organic media [64, 65].

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СПЕКТРОСКОПІЯ ТРИПЛЕТНЫХ ЕКСИТОНІВ У ОРГАНІЧНИХ СПОЛУКАХ: КРИСТАЛІЧНИЙ І СКЛОПОДІБНИЙ БЕНЗОФЕНОН

Наведено стислий огляд основних результатів досліджень спектрально-люмінесцентних властивостей триплетних екситонів у кристалічному й склоподібному бензофеноні, переважно виконаних в Інституті фізики НАН України. Представлена також коротка інформація про досягнення в галузі досліджень триплетних екситонів у органічних напівпровідниках. Обговорюються особливості фосфоресценції й природа структури склоподібної фази бензофенону. Розглянуто умови існування екситонної фосфоресценції в молекулярних кристалах. Проведено аналіз досягнень різних авторів у галузі молекулярної спектроскопії триплетного стану. Показано, що серед молекулярних кристалів бензофенон є одним з найбільш зручних об'єктів для вивчення фосфоресценції й спектральних властивостей триплетного стану органічних сполук.

Ключові слова: триплетні екситони, фосфоресценція, міграція енергії, молекулярні кристали, бозонний пік, розупорядковані системи, бензофенон, органічні напівпровідники.