

in the range 10^{-7} – 10^{-9} sec.* Besides the excited fluorescent level, most aromatic molecules have a metastable or phosphorescent level $^3\Gamma$ situated somewhat lower. The concept of metastable levels in organic molecules was introduced by Jablonski^[9] in 1935 to explain the prolonged afterglow (phosphorescence) of aromatic molecules which appears when the molecules are fixed in a rigid solution or on an adsorbent at room temperature or below.

In 1943 Terenin^[6] gave reasons for the concept of the triplet (biradical) nature of the metastable (phosphorescent) state of aromatic molecules. The ground state and the fluorescent excited states of organic molecules are singlets. Thus, the low probability of radiative transition from the metastable state to the ground state is explained by the selection rule well-known in atomic spectroscopy† forbidding transitions between levels of different multiplicities (intercombination transitions). A year later, an analogous viewpoint was also set forth with detailed arguments in an article by Lewis and Kasha,^[10] and it is generally recognized at present.^[8,18,26-28] The molecule of the organic compound enters the triplet state upon excitation in the ordinary absorption bands, which correspond to transitions from the ground singlet level ($^1\Gamma$) to the first ($^1\Gamma^*$) or higher ($^1\Gamma^{**}$, $^1\Gamma^{***}$, etc.) excited singlet levels. Then, within a time 10^{-11} – 10^{-14} sec (k_9), the molecule, without emitting, goes over to the vibrational levels of the lowest singlet excited state,^[10] which come to thermal equilibrium with the surrounding medium. The molecule has three further possibilities: to go over to the ground state with emission of fluorescence (k_1 in Fig. 1), to be deactivated without emission (k_2)‡, and finally, to go over without emission to the triplet state (k_3).** The probability (rate constant) k_3 of this process, which we shall call intercombination conversion, is comparable in magnitude for most luminescent organic molecules with the probabilities k_1 and k_2 . Thus, ordinarily an appreciable fraction, and sometimes almost all of the molecules that have absorbed light go over to the triplet state.

As has been stated above, the direct radiative transition from the triplet state to the singlet ground state (k_4) is forbidden by the selection rule for transitions between levels having different multiplicities (the rate constant is 0.01 – 10^3 sec⁻¹). This transition is manifested as phosphorescence only when the molecule is fixed in a rigid solution, so as to reduce the proba-

bility of radiationless deactivation (k_5), which competes with the phosphorescence emission. We shall call the spectrum which is emitted in such a direct transition from the triplet state to the ground state phosphorescence.* Besides, at sufficiently high temperatures, the value of kT is comparable with the energy difference between the phosphorescent and fluorescent levels. Thus, a molecule can take up thermal energy to go from the triplet state to the lowest excited singlet state $^1\Gamma^*$ (process k_6). The transition of the molecule from the latter state to the ground state (k_1) will entail an emission identical in spectrum with the fluorescence, but relatively delayed by the time that the molecule has spent in the triplet state. We shall call this type of after-emission delayed fluorescence. Besides making observations of phosphorescence and delayed fluorescence, we can demonstrate the presence of metastable molecules in a solution by the triplet absorption from the lowest triplet level to the higher excited triplet states $^3\Gamma^*$, $^3\Gamma^{**}$, etc. (process k_7 in Fig. 1). This transition is allowed, since it takes place between states of the same multiplicity. The studies of McClure,^[10] Craig and Ross,^[8] and Porter and Windsor^[14] have shown that most aromatic molecules have highly characteristic $^3\Gamma^* \leftarrow ^3\Gamma$ spectra which differ sharply from the absorption spectra of the same molecules in the ground state. Owing to the use of flash lamps, the $^3\Gamma^* \leftarrow ^3\Gamma$ spectra have recently been used widely to detect and study the properties of triplet molecules in liquid solutions. Here the luminescence method is hardly suitable, since the triplet molecules are deactivated nonradiatively before they can emit. Nevertheless, the lifetimes of triplet molecules in degassed liquid solutions are 10^3 – 10^6 times greater^[14] than those of the singlet excited states of the same molecules. The triplet states of organic molecules have also been detected in the gaseous state, both by study of the after-luminescence (Dikun,^[14,38] Sveshnikov^[18]) and by use of flash lamps (triplet-triplet absorption).^[115]

The properties of molecules in the triplet state are currently being studied intensively in different countries by various methods: phosphorescence (spectra, yields, lifetime and decay mechanics), triplet-triplet

*See the monographs of Terenin,^[6] Levshin,^[5] Förster,^[10] Pringsheim,^[6] and the review by West.^[2]

†See, e. g., the monographs of Herzberg^[3] and Élyashevich.^[4]

‡We shall take k_2 to refer to both intramolecular processes of radiationless deactivation and various external quenching processes (chemical and physical).

**For proofs that the transition to the triplet state takes place from the lowest excited singlet (fluorescent) state, see the dissertation of Sveshnikov.^[18]

*To avoid confusion, we must make the qualification that different authors use here widely differing terminology. Terenin^[6] (p. 78) uses the term "phosphorescence" to denote the emission arising from direct transition from the triplet state to the ground state, while some American authors^[105] call it " β -phosphorescence." Pringsheim^[6] (p. 347) calls it "delayed fluorescence," while Sveshnikov^[18] calls it the "long-wavelength phosphorescence band." Terenin^[6] calls the after-emission due to transition from the fluorescent level to the ground level after the molecule has spent time in the triplet state "delayed fluorescence," while the American authors^[105] call it " α -phosphorescence," Pringsheim^[6] calls it "phosphorescence," and Sveshnikov^[18] calls it the "short-wavelength phosphorescence band." We shall use the terminology adopted in Terenin's monograph.^[6]

absorption, electron paramagnetic resonance, etc. The especial attention which has been paid to the study of the triplet state of organic molecules is due to the assumption that this state participates in many important photochemical reactions. Even in the initial article concerned with the interpretation of the metastable state of aromatic molecules as being the triplet state, Terenin^[55] indicated the unsaturated (biradical-like) nature of molecules in the triplet state, which must give rise to the high chemical reactivity of this state. In addition, the above-mentioned long lifetime of the phosphorescent (triplet) state, even in liquid solutions, has the consequence that a triplet molecule has a greater probability of meeting a chemical-reaction partner in diffusion-controlled reactions than a molecule in the fluorescent state does. Among the most important photochemical reactions assumed to take place with direct participation of the triplet state of organic molecules, we should cite: 1) photosynthesis in green plants (Terenin,^[66] Frank^[96]), 2) photooxidation and photoreduction of dyes (Terenin,^[8] Adelman and Oster^[111]), 3) photooxidation of derivatives of anthracene (Bowen and Tanner,^[80,81] Vember and Cherkasov^[33,74]) and benzaldehyde (Karyakin^[16,17]), 4) dye-sensitized oxidation of organic compounds (Terenin,^[8] Schenck and Koch^[117]).

1. CONCENTRATION QUENCHING, SHORTENING OF DECAY TIME, AND CONCENTRATION DEPOLARIZATION OF PHOSPHORESCENCE AND DELAYED FLUORESCENCE

The problem of whether electronic-excitation energy can be transferred nonradiatively from a molecule in the metastable (triplet) state to an unexcited molecule, raising the latter to the metastable level, was a topic for discussion for a long time. The experimental data obtained by studying the relation of the yield, lifetime, and polarization of phosphorescence to the dye concentration did not solve this problem unequivocally. The collection of information on processes of energy transfer from the metastable state of molecules by studying the concentration-dependence of their phosphorescence properties is greatly complicated by concentration effects involving the fluorescent state of the molecule.

a) Concentration quenching and shortening of the decay time of phosphorescence. In 1934 Shishlovskii and Vavilov^[75] found a decrease by a factor of 1-1/2 in the decay time τ of the delayed fluorescence of rhoduline orange in highly viscous sugar solutions as the concentration of the activator was increased from 7.5×10^{-4} M to 2.2×10^{-3} M (moles/liter). At concentrations below 7.5×10^{-4} M, the decay time does not depend on the dye concentration. Levshin and Vinokurov^[55] have also observed a shortening of the τ of the delayed fluorescence of fluorescein in boric acid as the dye concentration was increased from

3.7×10^{-4} to 1.1×10^{-2} M. Along with the shortening of the time τ , they observed a decrease in the delayed-fluorescence yield.* By analogy with the quenching and shortening of τ found in concentration quenching of fluorescence (Vavilov,^[1] Galanin^[33]), we might assume that here also these effects are due to a radiationless energy transfer between triplet and unexcited dye molecules accompanying the quenching. However, Lewis, Lipkin, and Magel^[104] studied the phosphorescence of fluorescein in a mixture of glycerol with 5% phosphoric acid at 90°K, and found only a very small shortening of the lifetime of the fluorescein molecules in the metastable state as the dye concentration was increased from 5×10^{-5} to 5×10^{-2} M† (τ decreased here from 1.96 to 1.72 sec).

In 1947 Sveshnikov^[59] confirmed again the occurrence of concentration quenching and shortening of the τ value for phosphorescence of fluorescein in boric acid with increase in the dye concentration at 173° and 290°K. Sveshnikov^[59] also showed that, in accord with what we would expect from kinetics, the decline in the delayed fluorescence of fluorescein in boric acid at 290°K due to quenching is considerably more rapid than that of phosphorescence and the total emission. Shortly thereafter, Sveshnikov, together with Dikun and Petrov,^[18,39] observed a shortening in the τ for phosphorescence of benzene, toluene, and other benzene derivatives on going from dilute alcoholic solutions to concentrated solutions and to the pure substances at 90°K. Concentration quenching and shortening of the τ for phosphorescence have also been observed by Kato^[102] for tryptaflavin adsorbed on filter paper at 290°K, and by Teplyakov^[64] for solutions of salicylic, cinnamic, and anthranilic acids at 90°K. In these studies, as in the earlier ones, however, no test was made of whether the change in the τ of the phosphorescence is due to the formation of aggregates of tryptaflavin or the aromatic acids at high concentrations, or to the effect of pH change in the solution on the luminescence, as is very likely in the concentration range studied. From this standpoint, the data of Dikun, Petrov, and Sveshnikov^[18,39] seem more reliable. They worked with benzene and toluene, which are less prone to association, although even this type of molecule is known to form aggregates consisting of an excited and a normal molecule (the so-called "excimers").^[37,95]

*The relative phosphorescence yield at various concentrations can be estimated most simply by measuring either the initial intensity of the after-emission upon prolonged excitation with $t \gg \tau_{\text{phos}}$, or from the total after-emission as obtained by integration of the intensity of the after-emission over time elapsed after a brief single excitation period with $\tau \ll \tau_{\text{phos}}$. A detailed account of the methods for determining the relative phosphorescence yield can be found in an article by Sveshnikov.^[61]

†All concentrations given in this section are for room temperature. No correction has been made for concentration increase due to contraction of the sample upon cooling.

Table I. The degree of polarization of the phosphorescence of tryptaflavin in alcohol at 90°K as a function of the time t elapsed after cessation of the excitation. Excitation at 4358 Å.* (From [18,62].)

t , sec	0	1	2	3	4	6
$C_T=1.9 \cdot 10^{-4}$ M	-12.8	-11.9	-12.2	-12.6	-12.7	-11.2
$C_T=3.5 \cdot 10^{-3}$ M	-7.7	-7.6	-7.3	-7.4	-7.8	-7.5

*The polarization of the phosphorescence of tryptaflavin with excitation at 4358 Å is negative.

Mokeyeva and Sveshnikov^[56] have made some very careful quantitative investigations of concentration quenching of phosphorescence. They measured the decay time, and also the delayed fluorescence and phosphorescence yields in boric acid-glycerol phosphors activated with fluorescein. They rejected a number of activators (tryptaflavin, acridine orange, etc.), since spectrophotometric measurements showed aggregation of dye molecules at high activator concentrations. No change in the spectra with concentration was observed for fluorescein. As in the study of Sveshnikov in 1947,^[59] they observed a shortening of the τ for phosphorescence at 90°K as the activator concentration was increased from 1.9×10^{-3} to 3.9×10^{-2} M. However, this decrease in τ is not accompanied by a decline in the phosphorescence yield, but even conversely, by an increase. This compelled these authors^[56] to conclude that at high activator concentrations groups of molecules with differing luminescent properties are formed. Here they did not observe any essential changes in the absorption spectra, as in the case of "classical" association of dye molecules (see Levshin^[5]), but the formation of the molecular groups is manifested in an increase in the initial phosphorescence intensity and a shortening of its lifetime. In this regard, we should point out that McRae and Kasha^[109] have theoretically demonstrated the possibility of an increase in the relative phosphorescence yield upon dimerization of a dye.

b) Concentration depolarization of phosphorescence. In addition to studying concentration quenching and shortening of the τ of phosphorescence, a number of attempts have also been made to detect a radiationless energy transfer from the metastable state by studying the concentration-dependence of the degree of polarization of the after-emission of dyes.* However, the application of this method, which is very fruitful in studying energy transfer from the fluorescent levels of molecules, has run up against considerable difficulties in the case of phosphorescence.

*In polarization measurements of phosphorescence, we must avoid light saturation, since the latter results in a marked decline in the degree of polarization of the emission of the phosphor (see Sveshnikov,^[18] Feofilov^[9]).

As was stated above, a molecule enters the metastable state via the fluorescent state. During the time that the molecule spends in the fluorescent state, energy transfer can ensue, leading to concentration depolarization of the fluorescence (Galanin^[13]). In studying whether energy transfer can take place from the metastable state by measuring the degree of polarization of the phosphorescence (process k_4 in Fig. 1), we must take into account the concentration depolarization of the fluorescence. Yet, if we investigate the delayed fluorescence, here the molecule has been in the fluorescent state twice, and must have been subjected twice thereby to depolarization. Sveshnikov^[59,60] was the first to consider this fact, and showed that the delayed fluorescence must be depolarized to a greater degree than the phosphorescence or the total emission. We must also take into account the possibility that the molecule can occupy the metastable level repeatedly. From this standpoint, the most direct proof of radiationless energy transfer from the metastable state would be the discovery of a depolarization that increases with decay of the phosphorescence at low temperatures.

Feofilov^[72] has performed experiments on the concentration depolarization of delayed fluorescence in the course of the decay process, which gave a negative result. That is, the degree of polarization of the phosphorescence was the same during all stages of the decay. Later, Sveshnikov and Ermolaev^[18,62] also found no decrease in the degree of polarization of the phosphorescence of tryptaflavin in alcohol at 90°K during the decay process (Table I). The measurements in the latter study were performed at tryptaflavin concentrations from 2.0×10^{-4} to 3.5×10^{-3} M. These values are below and above those for onset of concentration depolarization of the fluorescence of this dye ($\sim 8.0 \times 10^{-4}$ M).^[73] Finally, the most recent measurements by Kudryashov and Sveshnikov^[54] of the polarization of the phosphorescence of boric acid-glycerol phosphors activated with fluorescein have also shown no decline in the degree of polarization of the emission during the decay process.

We should state that according to current data (see the following section), processes of energy transfer between metastable and normal molecules with excitation of the triplet level are expected to set in at rela-

Table II. The degree of polarization of the total emission* (P_{total}) and the delayed fluorescence ($P_{\text{d.f.}}$) of boric acid-glycerol luminophors activated with fluorescein as a function of the activator concentration C at 290°K. (From^[54].)

		$3.9 \cdot 10^{-5}$	$1.9 \cdot 10^{-4}$	$3.9 \cdot 10^{-4}$	$1.9 \cdot 10^{-3}$	$3.9 \cdot 10^{-3}$	$7.8 \cdot 10^{-3}$	$1.9 \cdot 10^{-2}$
4800 Å	$P_{\text{total}}, \%$	38.9	37.3	38.9	26.3	23.0	15.8	6.6
	$P_{\text{d.f.}}, \%$	38.9	34.7	35.3	20.8	16.7	8.7	2.7

*The bulk of the total emission is fluorescence. The polarization measurements were made at $\lambda_{\text{lumin}} = 4800 \text{ \AA}$ with excitation by light at 4350 Å.

tively higher concentrations than energy transfer in which the fluorescent level is excited. Thus, the data given above cannot be considered to prove the absence of radiationless energy transfer between triplet and normal molecules. On the other hand, the design of experiments in which we could hope to obtain a concentration depolarization of phosphorescence during the decay process is exceedingly complex. We should expect appreciable effects (see the experiments on sensitized phosphorescence in Sec. 2 of this review) at dye concentrations of $5 \times 10^{-2} - 10^{-1} \text{ M}$ or greater. However, at such concentrations, repeated energy transfer will take place between the fluorescent levels before the molecule goes over to the triplet state. Consequently, the initial degree of polarization of the phosphorescence will decline to very low values, at which reliable measurements are impossible, and all the more so, in that a strong concentration quenching must take place at the same time. We can also expect complications due to dye association.

However, the study of the concentration depolarization of phosphorescence is of interest with regard to the theory of energy transfer between the fluorescent levels, and also as one of the methods to study processes of population of the metastable state. We shall take up some results of studies along this line below.

Feofilov^[9,72] has measured the degree of polarization of the total emission and that of the short-wavelength phosphorescence band at various concentrations of eosin in highly-viscous sugar solutions, and has found that their degrees of polarization coincide at all concentrations, in spite of the occurrence of an appreciable concentration depolarization. This fact, together with the absence of depolarization of the delayed phosphorescence during the decay process, led Feofilov to conclude that energy transfer could not occur between metastable and normal molecules. Feofilov assumed that the metastable state of the molecule is populated directly from the high vibrational levels of the excited dye molecule. Later Sveshnikov^[18,59,60] showed that the metastable state is populated via the fluorescent state. He considered the contradiction between the cited results of Feofilov and the idea that the probability of energy transfer depends on the time that the molecule spends in the fluorescent state (Galanin^[13]). The molecules which

take part in emission of delayed fluorescence enter the fluorescent state twice (or more times): once before they enter the metastable state, and a second time after they have spent time in that state. Consequently, the delayed fluorescence must be depolarized more than the total emission. The experiments of Sveshnikov^[18] have confirmed this conclusion for the example of boric acid phosphors activated with fluorescein, and highly-viscous sugar solutions activated with rhoduline orange. The concentration depolarization of the delayed fluorescence set in considerably more rapidly than that of the total emission. An analogous difference in the trends of the depolarization of the delayed fluorescence and the total emission has been observed by Laffite,^[103] and also by Bauer, Baczynski, and Czajkowski^[78] in boric acid phosphors activated by acridine yellow. The appreciable change in the ratio of quantum yields of the phosphorescence and the fluorescence which the latter authors observed at the same time greatly complicates the interpretation of their results.*

Very precise measurements of concentration depolarization of delayed fluorescence have been made recently by Kudryashov and Sveshnikov.^[54] They used a monochromator in their study to measure the degree of polarization in particular spectral regions (to separate the delayed fluorescence from the phosphorescence). They showed that at low activator concentrations the degree of polarization of the delayed fluorescence of boric acid-glycerol phosphors coincides with the degree of polarization of the total emission. However, as the activator concentration increases, the former is depolarized appreciably more rapidly than the total emission (Table II).

The data given in Table II indicate that the experimental facts here agree well with the current ideas

*Assuming that the transition to the phosphorescent state takes place from the upper vibrational levels of the fluorescent state, these authors infer from the fact that the phosphorescence shows concentration depolarization that energy transfer from metastable dye molecules takes place under the conditions of their experiments. However, as we have pointed out above, most of the experimental facts indicate that the molecule enters the triplet state via the fluorescent state. Hence we cannot consider the conclusion to be well-grounded that energy transfer between metastable levels takes place in this case.

concerning energy transfer between fluorescent levels and processes of population of the triplet state of organic molecules.

The problem of the concentration depolarization of phosphorescence is more complex. The degree of polarization of the phosphorescence, when excited in the first absorption band of the molecule, is considerably less than the polarization of the fluorescence or the delayed fluorescence (see the monographs of Feofilov^[9] and Levshin^[5]). Sveshnikov and Ermolaev^[62] have compared the sign and degree of polarization of the phosphorescence with the polarization of the fluorescence with excitation in various absorption bands of the dye molecules. Their experiments showed that this phenomenon is due to the markedly differing orientation within the dye molecules of the moments of the transitions from the fluorescent and phosphorescent states to the ground state. According to the calculations given at the beginning of this section, and the conclusion that there is no appreciable energy transfer between metastable and normal molecules under the experimental conditions, as follows from the experiments on concentration depolarization of the phosphorescence during the decay process (see above), the concentration depolarization of the phosphorescence must have a course identical to that of the fluorescence. Experimentally, the occurrence of concentration depolarization of the phosphorescence and the qualitative parallelism of the latter to the course of the concentration depolarization of the fluorescence have been established in^[62]. In the above-mentioned study, Kudryashov and Sveshnikov^[54] took up again the investigation of this problem; they showed that concentration depolarization of the phosphorescence takes place, but considerably more slowly than that of the fluorescence. The latter result is not in complete accord with the concepts presented at the beginning of this section, and requires further study.

In summing up the material in this section, we must note that, in contrast to the case of fluorescence, the study of concentration depolarization, concentration quenching, and the shortening of the τ of phosphorescence has not led to a solution of the problem of whether radiationless energy transfer can or cannot occur from a metastable molecule to a normal molecule, raising the latter directly to the metastable state. It has proved much more fruitful here to study the phenomenon of sensitized phosphorescence of organic compounds in solid solutions. We shall proceed to give an account of the results obtained by this method in the next section.

2. SENSITIZED PHOSPHORESCENCE OF ORGANIC COMPOUNDS AT LOW TEMPERATURES

In 1952 Terenin and Ermolaev^[40,67] discovered a new phenomenon, consisting in the fact that the structured phosphorescence spectrum in the visible of a

rigid solution of naphthalene at liquid-air temperature can be excited by the light of the mercury lines at 3650 Å, in a spectral region where naphthalene itself does not absorb, provided that one adds to the solution benzaldehyde or benzophenone, which absorb the exciting light (Fig. 2). The phenomenon was called sensitized phosphorescence. Terenin and Ermolaev^[40,67] interpreted this phenomenon as being radiationless transfer or electronic excitation energy from triplet-state molecules of benzaldehyde or benzophenone (energy donors) to unexcited naphthalene molecules (energy acceptors), raising the latter directly to the triplet state. That is, the process takes place according to the equation: ${}^3\Gamma_D + {}^1\Gamma_A \rightarrow {}^1\Gamma_D + {}^3\Gamma_A$.

When studying the phenomenon of sensitized fluorescence, we must, from energy considerations, select the energy donor and acceptor molecules such that the lowest excited singlet (or fluorescent ${}^1\Gamma^*$) level of the donor is higher than the fluorescent level of the acceptor. Owing to the diffuseness of the absorption spectra of organic compounds in solution, the result is that we cannot selectively excite the energy-donor molecules without affecting the acceptor. Furthermore, the probability of radiationless energy transfer between excited fluorescent and normal molecules increases with increasing overlap of the emission spectrum of the energy donor with the absorption spectrum of the acceptor. At the same time, this results in strong reabsorption and secondary fluorescence, which are very difficult to take into account under concrete experimental conditions. In the case

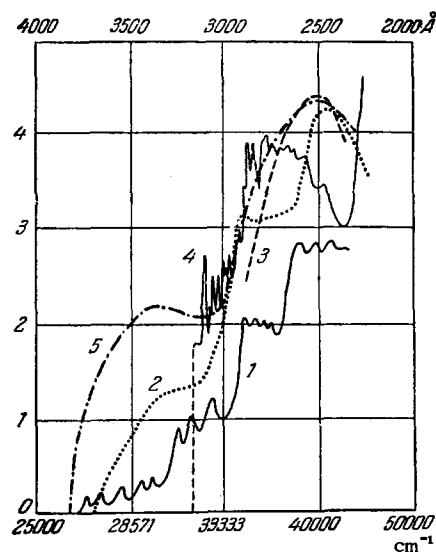


FIG. 2. Absorption spectra (with $\log \epsilon$ as ordinate). 1 - Benzaldehyde in pentane-propane mixture at 90°K.^[77] (owing to lack of data, the height of the bands is arbitrary, and has been obviously underestimated); 2 - benzaldehyde in ethanol at 293°K.^[12]; 3 - biphenyl in ethanol + methanol at 77°K^[64]; 4 - naphthalene in ethanol + methanol at 77°K^[64]; 5 - benzophenone in ethanol at 293°K.^[11] For the spectrum of benzophenone in alcohol-ether at 77°K, see reference^[43].

of sensitized phosphorescence, the circumstances are considerably more favorable, since one can excite the energy donor without affecting the acceptor. Furthermore, the acceptor shows no appreciable absorption in the emission region of the energy donor.* This is possible because the energy difference between the fluorescent and triplet levels in various classes of aromatic molecules varies over a broad range of values from 1000 to 10,000 cm^{-1} . This fact was used by Terenin and Ermolaev. They used as energy donors aromatic aldehydes and ketones (benzaldehyde, benzophenone, etc.), for which the triplet and singlet levels are separated by 1700–2000 cm^{-1} . The simple carbonyl derivatives of benzene in liquid solutions do not luminesce, while in solid solutions at low temperatures they show only an intense phosphorescence in the range 26,000–18,000 cm^{-1} , with a decay time of the order of 10^{-3} sec, arising from direct transition from the triplet state to the ground state. The long-wavelength absorption limit of these compounds is situated at 26,000–27,000 cm^{-1} .†

Naphthalene and its alkyl and halogen derivatives in solution show an ultraviolet fluorescence (32,000–28,000 cm^{-1}), while at low temperatures they also show a phosphorescence located in the visible (21,000–16,000 cm^{-1}) with a value $\tau \sim 2.0\text{--}10^{-3}$ sec.^[46] In the cited naphthalene derivatives, the spacing between the fluorescent and phosphorescent levels is much greater than in the carbonyl derivatives of benzene, being approximately 10,000 cm^{-1} . Thus, when one illuminates a mixed solution of benzaldehyde and naphthalene with the mercury lines at 3650 Å, only the benzaldehyde molecules will absorb light and be excited. The appearance in the emission spectrum of the phosphorescence bands of naphthalene can be explained only by radiationless energy transfer from benzaldehyde in the triplet state to naphthalene, raising the latter also to the triplet state. The fluorescence spectrum of naphthalene does not appear under these conditions. As control experiments showed, rigid solutions of naphthalene and the other energy acceptors used, in concentrations up to 0.1–0.5 M, do not emit their own fluorescence or phosphorescence spectra upon intense excitation by the light of the 3650 Å mercury lines.

The system of the lower excited electronic levels of the donor and acceptor molecules in the sensitized-phosphorescence phenomenon is shown in Fig. 3. On the left are drawn the ground, fluorescent, and phosphorescent levels of the energy donor, and at the

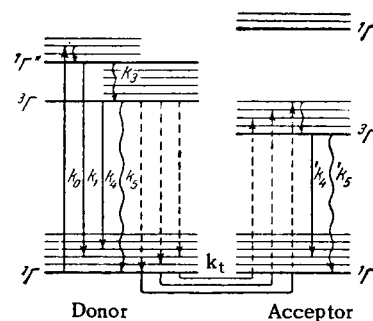


FIG. 3. The system of electronic-vibrational levels of the donor and acceptor molecules in the phenomenon of radiationless energy transfer via the triplet levels. The straight arrows denote radiative transitions, the wavy arrows are internal processes of radiationless degradation, and the dashed arrows are transitions involving radiationless transfer of electronic excitation energy from the donor to the acceptor. The symbols for the levels and rate constants are analogous to those in Fig. 1.

right, the same levels for the energy acceptor. The solid lines denote the electronic transitions involving absorption or emission of light, the wavy lines are the transitions in which the electronic energy is degraded into thermal motion, and finally, the dotted lines are the transitions involving radiationless transfer of electronic excitation energy from the donor to the acceptor. Figure 4 shows examples of the sensitized-phosphorescence spectra taken from reference^[15]. As we see from Fig. 4, the sensitized-emission spectra can be clearly distinguished on the background of the luminescence spectrum of the donor. Besides using the spectroscopic method, in some cases one can distinguish the phosphorescence of the acceptor (naphthalene, biphenyl, etc.) from that of the donor (benzaldehyde, benzophenone, etc.) by using a long-period phosphoroscope, making use of the difference in τ of the phosphorescence of the acceptor (τ for the phosphorescence of naphthalene and diphenyl amounts to several seconds) and that of the donor (τ for benzaldehyde and benzophenone amounts to several milliseconds).

Subsequent studies^[41,42,44,45,47,49,51] have extended considerably the number of combinations of substances for which the phenomenon of sensitized phosphorescence has been observed in rigid solutions at low temperatures.* These data are summarized in Table III. The upper part of the table gives the substances used as energy donors, and the lower part gives the energy acceptors. Table III also lists a number of the spectroscopic characteristics of the donors and acceptors: the height of the fluorescent level (${}^1\Gamma^*$) determined from the position of the long-wavelength ab-

*The ${}^3\Gamma \leftarrow {}^1\Gamma$ absorption spectrum of the acceptor situated in this region is so weak ($\epsilon_{\text{mol}} \leq 10^4$) that it cannot in practice give rise to any reabsorption.

†The long-wavelength absorption band and luminescence of the carbonyl derivatives of benzene is ascribed to an electronic transition of the $n\text{--}\pi^*$ type, i.e., the transition of a non-bonding 2p electron of the oxygen atom to an excited anti-bonding π^* orbital of the molecule.^[108,101,43,29]

*A commonly-used solvent freezing to a glass at liquid-air temperatures is a mixture of two volumes of 96% ethyl alcohol and one volume 98% diethyl ether (denoted below as alcohol-ether). Both solvents should be distilled repeatedly on a column beforehand. The phenomenon of sensitized phosphorescence has also been observed in other solvents.^[40]

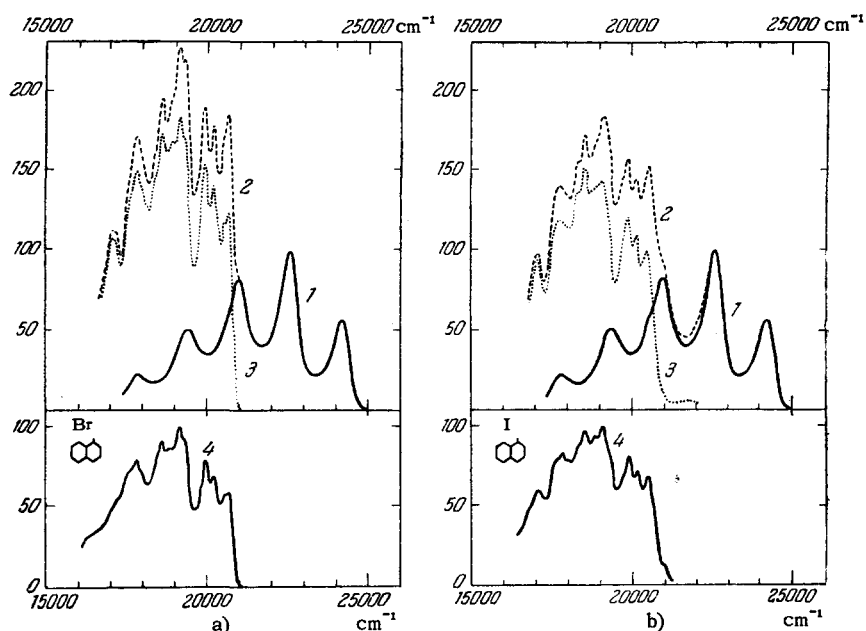


FIG. 4. A comparison of the phosphorescence spectra of 1-bromonaphthalene (a) and 1-iodonaphthalene (b) as obtained by direct excitation ($\lambda_{\text{excit}} \leq 3130 \text{ \AA}$) with their sensitized-phosphorescence spectra in the presence of benzophenone ($\lambda_{\text{excit}} = 3650 \text{ \AA}$). Here, the curves 4 = spectra under direct excitation; 3 = those calculated from the difference between the intensities of the total spectrum of benzophenone + 1-halonaphthalene (curve 2) and that of benzophenone (curve 1). Spectrum 2 has been matched in intensity with spectrum 1 at the two short-wavelength maxima of benzophenone. The spectra were recorded photoelectrically, and reduced to quantum intensities on a frequency scale. The solvent is alcohol-ether at 77°K ; concentrations: benzophenone = $2 \times 10^{-2} \text{ M}$; 1-bromonaphthalene = $4.8 \times 10^{-1} \text{ M}$; 1-iodonaphthalene = $3.2 \times 10^{-1} \text{ M}$ (from [15]).

Table III. Aromatic compounds for which a sensitized-phosphorescence phenomenon has been observed.* (From the data of references [70,47,51,49].)

Compound	$^3\Gamma, \text{ cm}^{-1}$	$^1\Gamma^*, \text{ cm}^{-1}$	$\tau_{\text{phos}}, \text{ sec}$	$\frac{q_{\text{phos}}}{q_{\text{fluor}}}$
Energy donors				
Benzaldehyde	24950	26750	$1.5 \cdot 10^{-3}$	>1000
Benzophenone	24250	26000	$4.7 \cdot 10^{-3}$	>1000
Acetophenone	25750	27500	$2.3 \cdot 10^{-3}$	>1000
Ethylphenylketone	26150	28000	$3.8 \cdot 10^{-3}$	>1000
p-Chlorobenzaldehyde	24750	—	—	>1000
o-Chlorobenzaldehyde	24350	—	—	>1000
m-Iodobenzaldehyde	24750	26250	$6.5 \cdot 10^{-4}$	>1000
Anthrone	25150	27000	$1.5 \cdot 10^{-3}$	>1000
Xanthone	24800	27000	$2 \cdot 10^{-2}$	>1000
Anthraquinone	21950	—	—	>1000
Triphenylamine	24500	29000	$7 \cdot 10^{-1}$	15
Carbazole	24600	29500	7.6	0.55
Phenanthrene	21700	28900	3.3	1.1
Energy acceptors				
Naphthalene	21250	31750	2.3	0.09
Octodeuteronaphthalene	21400	31850	9.5	0.21
1-Methylnaphthalene	21000	31450	2.1	0.05
1-Chloronaphthalene	20700	31360	$2.9 \cdot 10^{-1}$	5.2
1-Bromonaphthalene	20650	31280	$1.8 \cdot 10^{-2}$	164
1-Iodonaphthalene	20500	31000	$2.0 \cdot 10^{-3}$	>1000
Quinoline	21700	31900	1.4	1.9
Biphenyl	23000	33500	3.1	0.8
Decadeuterobiphenyl	23100	33650	11.3	1.9

*The data are for alcohol-ether at 77°K .

sorption band or the short-wavelength fluorescence band, the height of the lowest triplet level ($^3\Gamma$) determined from the position of the short-wavelength phosphorescence band, and finally, the phosphorescence decay time (τ_{phos}) and the ratio of the phosphorescence and fluorescence quantum yields ($q_{\text{phos}}/q_{\text{fluor}}$). In most cases, all these quantities have been determined for solutions in alcohol-ether at 77°K .

The following limitations are imposed on the choice of the substances used as the energy donors and acceptors in the sensitized-phosphorescence phenomenon:

1. The triplet level of the energy donor must be higher than that of the energy acceptor (from the law of conservation of energy). Adherence to this condition for complex organic compounds automatically entails an overlap of the $^3\Gamma_{\text{D}} \rightarrow ^1\Gamma_{\text{D}}$ emission spec-

trum of the donor with the ${}^3\Gamma_A \leftarrow {}^1\Gamma_A$ absorption spectrum of the acceptor.

2. In order that only the energy donor may be selectively excited, its fluorescent level must be lower than that of the acceptor.

3. Finally, the acceptor must be soluble enough in the chosen solid solvent to give high enough concentrations for radiationless energy transfer between triplet levels to become appreciable ($C_A \sim 10^{-2}$ – 5×10^{-1} M).

Of the three cited limitations, only the first one remains in force for the great majority of cases of energy transfer between triplet levels of organic molecules. In the other methods of observing this type of energy transfer (for the shortening of the τ_{phos} of the donor in rigid or liquid solutions, see below), it is not always necessary that the second and third conditions be satisfied. We can expect that the first limitation will be relaxed at high temperatures. For the substances cited in Table III, all three limitations are satisfied by the combination of any compound from the upper part of the table with any compound from the lower part, except for the pairs: phenanthrene-biphenyl, phenanthrene-quinoline, and anthraquinone-biphenyl, since in these cases the triplet level of the donor is below that of the acceptor.

In examining Table III, we see that there are various types of aromatic compounds among the energy donors. The most numerous among them are the representatives of the carbonyl derivatives of benzene. These substances are very convenient to study, since they absorb the light of the mercury lines at 3650 Å, and show an intense phosphorescence with a 0–0 band in the range 22,000–26,000 cm^{-1} .^[43] A second group consists of carbazole and triphenylamine. These compounds show rather large relative quantum yields.^[48] They are excited well by the mercury line at 3340 Å, which is not absorbed, or only very poorly absorbed, by the acceptors given in Table III. Finally, sensitized phosphorescence of naphthalene and its derivatives can be observed in the presence of phenanthrene, which is also excited by the light of the mercury line at 3340 Å. The selection of acceptors in Table III is more limited, since it is hard to find available compounds having a large gap between the fluorescent and phosphorescent levels, and having the latter level situated low enough.

To test the correctness of the explanation of the sensitized-phosphorescence phenomenon in terms of radiationless transfer of electronic excitation energy, the absorption spectra of benzophenone in petroleum ether at 293°K ($C_{\text{benzophenone}} = 2 \times 10^{-2}$ M) were studied in the presence of high concentrations of naphthalene (2 – 5×10^{-1} M). In the spectral range 3800–3300 Å, where the naphthalene molecule has no characteristic absorption, the absorption spectrum of the mixture showed no appreciable change as com-

pared with a benzophenone solution of the same concentration.^[15] The absence of strong mutual perturbations of the donor and acceptor molecules in the sensitized-phosphorescence phenomenon has also been demonstrated by the identity of the phosphorescence spectra of naphthalene and its derivatives under direct and sensitized excitation (see Fig. 4). Measurements^[15,68] have also shown that the short-wavelength bands of the phosphorescence spectrum of benzophenone (and other energy donors), which do not overlap with the superimposed sensitized-emission spectrum, do not change in shape in the presence of 1-bromonaphthalene at concentrations of 3.2×10^{-1} M and higher. However, when one combines benzophenone with naphthalene, a deep minimum appears at 24,000 cm^{-1} in the benzophenone luminescence spectrum. As has been explained,^[15,68] the reason for this is the triplet-triplet absorption of metastable naphthalene molecules (see the studies of McClure,^[107] and Craig and Ross^[85]); under the experimental conditions the concentration of the latter rises to appreciable values. One needs only to reduce the intensity of the exciting light to make these distortions in the spectrum disappear.

Measurements^[41] have also been made of the τ of phosphorescence of energy acceptors upon excitation in their own absorption band, and the τ of their phosphorescence when sensitized by benzaldehyde and benzophenone. The data from these measurements are given in Table IV. These measurements were made possible by the fact that the decay time of phosphorescence for the set of energy donors (benzaldehyde, benzophenone, etc.) is about 1000 times smaller than that for the acceptors (see Table III). At 0.1–0.2 sec after cessation of the excitation, the decay curve is already completely determined by the phosphorescence of the energy acceptor. As we see from Table IV, the lifetime of naphthalene and diphenyl in the triplet state is the same within the limits of experimental error, independently of whether the acceptor molecule gets into the metastable state through internal intercombination conversion from the fluorescent state (process k_3 in Fig. 1), or by radiationless energy transfer from a triplet molecule of the energy donor (process k_t in Fig. 3).

The set of facts presented above leads us to reject the possibility of explaining the phenomenon of sensitized phosphorescence by the formation of donor-acceptor complexes relaxing the rule forbidding transitions between the ground and phosphorescent levels of the acceptor molecule, or by other strong perturbations of the acceptor molecule.

Farmer, Gardner, and McDowell^[90] have confirmed the existence of an energy-transfer effect involving the triplet levels by means of electron para-magnetic resonance (EPR) spectra. A mixture of benzophenone and naphthalene ($C_{\text{naph}} = 5 \times 10^{-2}$) dissolved in E.P.A.

Table IV. A comparison of the decay times of the sensitized and the ordinary phosphorescence of naphthalene and biphenyl in ethanol at 90°K. (From the data of reference [41].)

Acceptors	τ for the ordinary phosphorescence (sec), $\lambda_{\text{excit}} = 3130 \text{ \AA}$	τ for sensitized phosphorescence (sec), $\lambda_{\text{excit}} = 3650 \text{ \AA}$	
		Donors	
		Benzaldehyde	Benzophenone
Naphthalene	2.3	2.3	2.3
Biphenyl	4.4	4.1	4.6

[Translator's note: a mixture of 5 parts ether, 5 parts isopentane, and 2 parts ethanol.] exhibited the EPR spectrum of naphthalene in the triplet state at 77°K, when excited by the 3650 Å mercury line. In the absence of benzophenone, this spectrum disappears. Benzophenone alone gives upon illumination the spectrum of the ketyl radical, which disappears in the presence of naphthalene.

In their initial studies, Terenin and Ermolaev [67] measured some quantitative characteristics of the sensitized-phosphorescence phenomenon. Figure 5 gives the relation of the intensity of sensitized phosphorescence of naphthalene in the presence of benzophenone to the concentration of the former*. The phosphorescence of the naphthalene was distinguished from the luminescence of the benzophenone by means of a long-period phosphoroscope. As we see from Fig. 5, the intensity of the sensitized phosphorescence initially increases linearly with the acceptor concentration, but then approaches a saturation point. Figure 6 gives the curve for the relation of the intensity

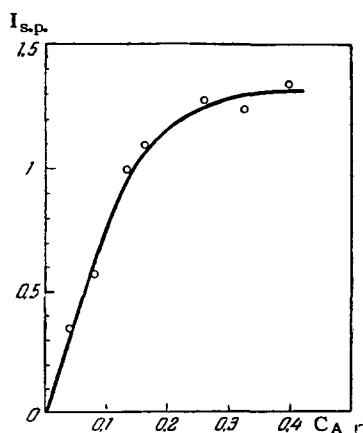


FIG. 5. The intensity of sensitized phosphorescence as a function of the acceptor concentration (naphthalene, $\tau_{\text{phos}} = 2.3$ sec). The measurements were made photoelectrically using a long-period phosphoroscope (1 rev/sec) to eliminate the quickly-decaying phosphorescence of the donor (benzophenone, $C = 2 \times 10^{-2}$ M, $\tau_{\text{phos}} = 4.7 \times 10^{-3}$ sec), in alcohol-ether solution at 90°K, $\lambda_{\text{excit}} = 3650 \text{ \AA}$ (from [66]).

*In Fig. 5 and hereinafter, the given concentrations in the rigid solutions take into account the contraction of the sample on cooling.

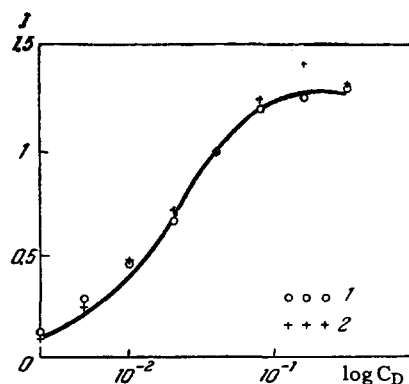


FIG. 6. The intensity of the sensitized phosphorescence of the acceptor naphthalene (1), the phosphorescence of the donor benzaldehyde (2), and the amount of light absorbed by the donor (solid curve) as functions of the logarithm of the donor concentration. Solution in ethanol, 90°K, $C_A = \text{const} = 10^{-2}$ M (from [67]).

of the phosphorescence of the acceptor naphthalene and that of the donor benzaldehyde to the concentration of the latter. The concentration of the energy acceptor was kept constant. The excitation in both cases was in the absorption band of the energy donor ($\lambda \approx 3650 \text{ \AA}$). The courses of the curves for the phosphorescence of benzaldehyde and the sensitized phosphorescence of naphthalene were identical, and are described by the formula

$$I = I_{\text{max}} (1 - e^{-aC}), \quad (1)$$

where C is the concentration of benzaldehyde, and a is a constant. Thus, the intensity of the sensitized phosphorescence is proportional to the number of quanta absorbed by the energy donor. None of these data contradict the interpretation of the sensitized-phosphorescence phenomenon as being a "physical" process of radiationless energy transfer involving excitation of the triplet level.

In 1952, a study was published by Ferguson and Tinson, [91] who tried to explain the changes in the luminescence spectrum of a frozen solution of benzophenone in petroleum ether at 90°K as the concentration of the substance was raised from 10^{-4} to 10^{-2} M in terms of energy transfer between triplet levels. They found that the phosphorescence spectrum of benzophenone is appreciably shifted to longer wavelengths

with increase in concentration, and at the same time, it changes in shape. These authors explain this fact by energy transfer to the triplet level of benzophenone. However, our measurements^[15] have shown that the spectrum of a concentrated solution of benzophenone in petroleum ether is very similar to that of crystalline benzophenone at 90°K (Fig. 7). Thus,

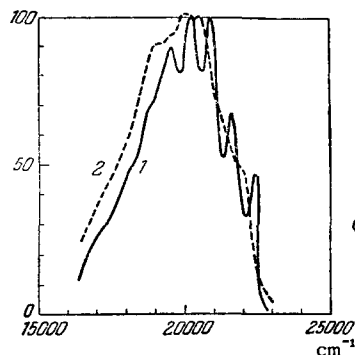
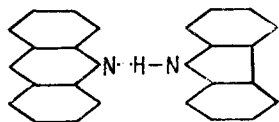


FIG. 7. The phosphorescence spectra at 77°K of: (1) benzophenone crystals; and (2) a concentrated solution of benzophenone in petroleum ether. $C_{\text{benzophenone}} = 10^{-2}$ M (from^[15]).



the phenomenon amounts to the precipitation of the benzophenone from the solution in petroleum ether upon freezing at concentrations 10^{-3} – 10^{-2} M in the form of a finely-crystalline suspension rather than being explained by energy transfer involving excitation of the triplet level, as Ferguson and Tinson suggested.^[91] The precipitation of the crystals can also be noted from the appearance of turbidity in a solution of the appropriate concentration upon freezing. In alcohol-ether mixture, in which benzophenone is considerably more soluble, such effects are not observed, and the luminescence spectrum of benzophenone remains unchanged up to $C = 2 \times 10^{-1}$ M.

El-Bayoumi and Kasha^[88] have tried to detect energy transfer between molecules of carbazole and acridine joined by a hydrogen bond. They showed that the fluorescence and phosphorescence of carbazole in a glassy hydrocarbon solvent at 77°K ($C_{\text{carbazole}} = 10^{-4}$) are strongly quenched in the presence of an equimolar amount of acridine. The quenching effect was ascribed to the formation of a carbazole-acridine complex. The effect of acridine on ethylcarbazole in a hydrocarbon solvent or the effect of acridine on carbazole in alcoholic solutions at a concentration of 10^{-4} M is negligibly small, confirming the requirement that a hydrogen-bonded complex must be formed. We must note that the quenching of fluorescence in hydrogen-bonded systems had been previously investigated in detail in the studies of Mataga and Tsuno.^[106]

a) Quenching and the shortening of the phosphorescence decay time of a donor in the presence of an ac-

ceptor. The radiationless transfer of electronic excitation energy in sensitized phosphorescence naturally entails quenching of the luminescence of the energy donor in the presence of the acceptor. At the same time, by analogy with resonance quenching by foreign absorbing substances (see Galanin^[33]), we might expect a shortening of the decay time of phosphorescence (τ) of the donor in the presence of the acceptor. The initial studies of Terenin and Ermolaev^[40,67] showed an appreciable decrease in the intensity of phosphorescence of benzaldehyde in the presence of naphthalene. In a series of later studies,^[15,41,42,44,45,47] these authors made quantitative measurements of the course of the quenching as a function of the acceptor concentration. They used monochromatic light absorbed only by the energy donor for excitation. They used diffraction-grating monochromators in order to isolate the required spectral regions in the exciting and emitted light.^[15] The quenching measurements were performed with high-aperture spectrometric apparatus using photoelectric recording.^[15] The decay times were determined with the oscillographic phosphoscope of Tolstoï and Feofilov^[71] ($\tau \sim 10^{-2}$ – 10^{-4} sec), and with an apparatus having an electromagnetic oscillograph ($\tau \sim 10$ – 10^{-2} sec).^[57]

It was shown^[15,44,45,47] that the curve for quenching of the phosphorescence of the energy donor as a function of the acceptor concentration is described well by the formula

$$\frac{q_0}{q} = e^{\alpha C}, \quad (2)$$

where q_0 is the quantum yield of phosphorescence of the donor in the absence of the acceptor, q is the same in the presence of the acceptor at a concentration C (molar), and α is a constant with the dimensions of reciprocal molarity. Figure 8 shows the relation of the quenching of the phosphorescence of carbazole and phenanthrene to the concentration of the acceptor naphthalene, as well as the quenching of the phosphorescence of benzophenone as a function of the concentration of the acceptor 1-bromonaphthalene. The plot is semilogarithmic. As we see from Fig. 8, the experimental points fit a straight line very well even up to the highest concentrations. Here the phosphorescence of carbazole has been quenched by a factor of 40, and that of benzophenone by a factor of ten. Unfortunately, the limited solubility of naphthalene and its derivatives in alcohol-ether mixtures at low temperatures prevented a test on whether Eq. (2) holds over an even broader range of concentrations.

The exponential concentration-dependence of the quenching q_0/q was first derived theoretically by F. Perrin^[112] for the concentration quenching of the fluorescence of dyes (see also Förster^[10]). Perrin suggested that, if an excited molecule has another quenching molecule within its "sphere of quenching action" v , the excited molecule is "instantaneously" deactivated without emitting. On the other hand, a

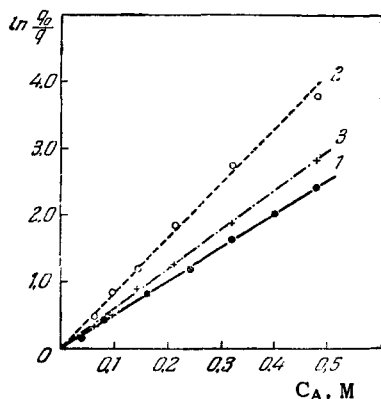


FIG. 8. The natural logarithm of the amount of quenching of the phosphorescence of the energy donor ($\ln q_0/q$) as a function of the acceptor concentration C_A for various donor-acceptor combinations. 1 - Benzophenone + 1-bromonaphthalene; 2 - carbazole + naphthalene; 3 - phenanthrene + naphthalene in alcohol-ether solution at 90°K. The excitation was carried out in a spectral region in which only the donor molecules absorb: $\lambda \approx 3650 \text{ \AA}$ for benzophenone (1), and $\lambda \approx 3340 \text{ \AA}$ for carbazole and phenanthrene (2 and 3) (from [47]).

molecule of the quenching agent located outside the given volume v about the excited molecule exerts no effect on the latter. Besides, one assumes that the molecules do not change their positions appreciably within the lifetime of the excited state. That is, one considers only very viscous or rigid solutions. In such a case, the only excited molecules which emit are those whose "spheres of action" v contain no molecules of a quenching agent. If the concentration of the quenching agent is C (molar), this corresponds to $N'C = 6.02 \times 10^{20} C$ molecules per cm^3 . According

to the laws of statistics, the probability that there is no molecule of the quenching agent in the volume v about the excited molecule is

$$p = \lim_{N'C \rightarrow \infty} (1 - v)^{N'C} = e^{-vN'C};$$

Since p is proportional to the fluorescence yield (q), we obtain Perrin's formula

$$\frac{q_0}{q} = \frac{I_0}{I} = e^{vN'C}. \quad (3)$$

Naturally, Perrin's formula (3) is valid only if the energy donor and acceptor molecules do not form aggregates (e. g., by a hydrogen bond) or molecular complexes of other types. For the donors and acceptors cited in Table III, the formation of such aggregates in the solvent used (alcohol-ether) is highly improbable.

The fact that Perrin's formula describes the decline in the phosphorescence yield of the donor with increasing acceptor concentration is evidence of a rather well delimited "sphere of action" of quenching in the phenomenon of sensitized phosphorescence. This formula also permits us to determine from the slope of the $\ln(q_0/q)$ line the "sphere of action" of quenching for various combinations of energy donors and acceptors:

$$v = \frac{\ln(q_0/q)}{CN'}. \quad (4)$$

Table V gives the "spheres of action of quenching" calculated by this formula in [47] for various combinations of energy donors and acceptors in rigid solutions at low temperatures.

Table V. The spheres of action of quenching and the quantum yields in the sensitized-phosphorescence phenomenon*. (From the data of reference [47].)

No.	Donor	Acceptor	$v \cdot 10^{21}$, cm^3	R , \AA	$\gamma = \frac{q_A}{q_{0D} - q_D}$
1	Benzaldehyde	Naphthalene	6.8**	12	0.13**
2	»	1-Chloronaphthalene	7.0	12	0.22
3	»	1-Bromonaphthalene	7.2	12	0.27
4	Benzophenone	Naphthalene	8.6	13	0.07
5	»	1-Methylnaphthalene	9.5	13	0.07
6	»	1-Chloronaphthalene	9.5	13	0.12
7	»	1-Bromonaphthalene	8.6	13	0.20
8	»	1-Iodonaphthalene	8.6	13	0.35
9	»	Quinoline	7.2	12	0.14
10	Acetophenone	Naphthalene	6.0	11	0.10
11	p-Chlorobenzaldehyde	»	6.7	12	0.14
12	»	1-Bromonaphthalene	6.2	11	0.49
13	o-Chlorobenzaldehyde	Naphthalene	5.4	11	0.11
14	m-Iodobenzaldehyde	»	5.8	11	0.11
15	»	1-Bromonaphthalene	5.7	11	0.30
16	Xanthone	Naphthalene	9.2	13	0.11
17	Antraquinone	»	5.9	11	0.10
18	»	1-Bromonaphthalene	7.6	12	0.27
19	Triphenylamine	Naphthalene	9.3	13	0.07
20	Carbazole	»	14	15	0.08
21	Phenanthrene	»	10	13	0.30
22	»	1-Chloronaphthalene	11	14	0.73
23	»	1-Bromonaphthalene	11	14	0.99

*All measurements were made in alcohol-ether mixture at 90° or 77°K. For Nos. 1-16, the 3650 \AA mercury line was used for excitation, and for Nos. 17-23, the 3340 \AA line.

**The accuracy of determination of the quantities v and $q_A/(q_{0D} - q_D)$ is 10-15%.

As we see from Table V, the dimensions of the spheres of action of quenching for energy transfer involving the triplet state are somewhat larger than the molecular volumes, as estimated from the dimensions of the interacting molecules. Table V also gives the values of the distance R between the centers of the interacting molecules taking part in the radiationless energy transfer. R was calculated under the assumption that both molecules are spherical in shape.

We must note that, whereas the presence of an acceptor in high concentration strongly quenches the phosphorescence of the donor, it does not affect the intensity of its fluorescence (Fig. 9) in the cases where the latter is observed (No. 19–23 in Table V).

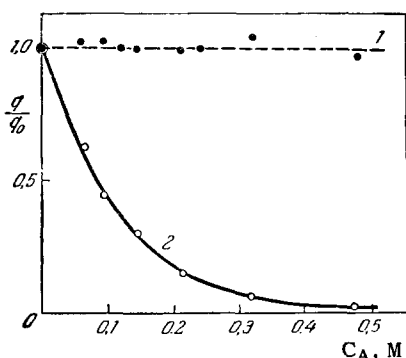


FIG. 9. The relation of the relative yields q/q_0 of the fluorescence (1) and the phosphorescence (2) of carbazole to the naphthalene concentration (C_A) in alcohol-ether solution at 90°K , $\lambda_{\text{excit}} = 3340 \text{ \AA}$, $C_{\text{carbazole}} = 8 \times 10^{-4} \text{ M}$.

As Vavilov^[1,32] has shown, the relation of the concentration quenching and the quenching by foreign absorbing substances of the fluorescence to the concentration of the quenching agent cannot be described by Perrin's formula (3). In this case the interaction force between the excited and unexcited molecules responsible for energy transfer by the dipole-dipole inductive-resonance mechanism decreases as the reciprocal sixth power of the distance between them. The exponential dependence of q_0/q on the acceptor concentration in sensitized phosphorescence indicates the relation of the interaction between a triplet donor molecule and an unexcited acceptor molecule to the distance between them agrees better with the hypothesis underlying Perrin's formula (3) than is the case with inductive-resonance interaction. Obviously, the relation of q_0/q to the concentration of quenching agent in viscous media will be better described by Eq. (3) when the interaction force between the donor and acceptor molecules declines more rapidly with distance. Hence we can conclude that the interaction force responsible for the radiationless energy transfer in sensitized phosphorescence decreases with increasing intermolecular distance more rapidly than R^{-6} .

A shortening of the decay time of phosphorescence of a donor in the presence of high concentrations of an acceptor was observed in^[41] (Fig. 10). We should immediately make the qualification that the existence of a shortening of τ is not in strict accord with the assumption of a well-delimited "sphere of action" of

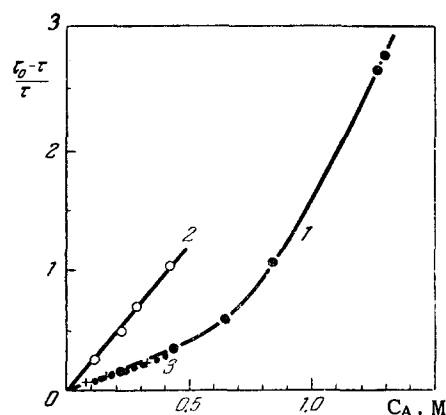


FIG. 10. The shortening of the decay time $(\tau_0 - \tau)/\tau$ of the phosphorescence of an energy donor in the presence of an acceptor as a function of the acceptor concentration in alcohol-ether solution at 90°K . 1 – Benzophenone ($C = 2 \times 10^{-2} \text{ M}$) + 1-methylnaphthalene; 2 – carbazole ($C = 10^{-2} \text{ M}$) + naphthalene; 3 – benzaldehyde ($C = 2 \times 10^{-2} \text{ M}$) + naphthalene (from [41]).

the quenching agent. On the other hand, the quantity τ_0/τ , which quantitatively characterizes the shortening of the decay time of the donor, increases much more slowly with the acceptor concentration than the quenching q_0/q does. The rate of decline in the decay time of the donor (τ_0/τ) is about ten times slower than that of the quenching of its phosphorescence (q_0/q).^[15] It was noted also^[15] that the decay law of the phosphorescence of the energy donor in the presence of the acceptor becomes highly non-exponential. The non-exponentiality reveals itself here in the fact that one cannot straighten the decay curve of the phosphorescence of the energy donor on the screen of the tube of the oscillographic phosphoroscope of Tolstoï and Feofilov.^[71]

The reasons for the discrepancy between the amount of quenching (q_0/q) and the shortening of the decay time (τ_0/τ) of the energy donor in the case of energy transfer in viscous or rigid solutions have been discussed (Galanin,^[37] Förster,^[93,94] Sveshnikov and Shirokov^[63]) as applied to concentration quenching and quenching by foreign absorbing substances of dye fluorescence. The studies explained the fact that the increase in the concentration of the quenching agent had a lesser influence on τ than on the intensity. Here they showed that it resulted from a decrease in the probability of energy transfer in the viscous solutions as a function of the time elapsed after the fluorescence began to decay. That is, they explained it by a so-called "depletion" effect. That is, as the decay proceeds, the excited molecules in the solution having unexcited quenching molecules in their close vicinity become exhausted. This latter fact arises from the rapid decline in the probability of energy transfer with increasing distance between the interacting molecules. This effect must lead to deviations from exponential decay of the luminescence, which will be

greatest with "instantaneous" excitation, i.e., brief in comparison with τ . It will also lead to the observed decline in the fluorescence yield q_0/q , which is about twice as rapid as the decrease in the fluorometric decay time τ_0/τ of the fluorescence of the donor.

As has been noted, in sensitized phosphorescence we observe a relative decline in τ of the after-emission of the donor which is about ten times as slow as the quenching in the presence of the same acceptor concentration. This latter fact, just like the exponential dependence of the quenching on the acceptor concentration, indicates a very rapid decline in the interaction force between the triplet and unexcited aromatic molecules responsible for the radiationless energy transfer between them. The swift decline in the interaction forces is manifested in the non-exponential decay of the phosphorescence of the donor in the presence of the energy acceptor, in spite of the unfavorable conditions for observing it when using the oscillographic phosphoroscope.*

b) Quantum yields of sensitized phosphorescence. The measurement of the coefficient of utilization of the electronic excitation energy which is radiationlessly transferred in the sensitized-phosphorescence phenomenon is also of great interest. This coefficient of utilization can be characterized by the ratio of the number of quanta radiated as sensitized phosphorescence of the acceptor to the number of quanta of phosphorescence of the donor which have been lost by quenching.

Studies^[15,42,44,45] have measured the ratio of the quantum intensity of the sensitized phosphorescence of the acceptor ($q_{s.p.A}$)† to the quantum intensity of the donor (q_D)† as a function of the concentrations of the donor and acceptor. The excitation was in the long-wavelength absorption band of the donor (the acceptor does not absorb the exciting light).

The value of $q_{s.p.A}/q_D$ was determined under these conditions from the ratio of the areas of the phosphorescence spectra of both substances, converted to quantum intensities. As we see from Fig. 4, the spectra are characteristic enough that the emission of the acceptor (1-bromonaphthalene in Fig. 4) can be reliably distinguished from the luminescence of the donor (benzophenone in Fig. 4). It was shown^[15] that an increase in the concentration of the donor (benzophenone) by two orders of magnitude from 2×10^{-3} to 2×10^{-1} M with a constant concentration of acceptor

*The most favorable case for observing deviations from exponential decay of emission when energy transfer occurs is the case of an "instantaneous" single excitation, i.e., brief in comparison with the decay time being studied. However, in the oscillographic phosphoroscope, the specimen is periodically excited by rather prolonged square pulses of the exciting light (see the description of the oscillographic phosphoroscope in^[11]).

†The quantities $q_{s.p.A}$ and q_D are proportional to the absolute quantum yields of the corresponding emission processes, though in this case we are interested only in their ratio.

does not affect the ratio of yields $q_{s.p.A}/q_D$ within the experimental limits of error. On the other hand, an increase in the concentration of the energy acceptor is accompanied by a rapid increase in the given ratio $q_{s.p.A}/q_D$ (Fig. 11).

If we know the values of $q_{s.p.A}/q_D$ and q_0D/q_D for a given acceptor concentration, we can determine the ratio $q_{s.p.A}/(q_0D - q_D)$ of the quantum intensity of the sensitized phosphorescence to the fraction of the emission of the donor lost by quenching. Here, q_0D and q_D are the quantum intensities of the phosphorescence of the donor in the absence and in the presence of the energy acceptor, respectively. We have termed the ratio $\gamma = q_{s.p.A}/(q_0D - q_D)$ the quantum yield of sensitized phosphorescence. It can be calculated from the directly-determined experimental data on $q_{s.p.A}/q_D$ and q_0D/q_D by the formula

$$\gamma = \frac{q_{s.p.A}}{q_0D - q_D} = \frac{q_{s.p.A}}{q_D} \left(\frac{q_0D}{q_D} - 1 \right)^{-1} \quad (5)$$

or can be determined graphically. An example is given in Fig. 12, where γ is equal to the ratio of the area under the sensitized-emission spectra (vertically cross-hatched) to the difference between the

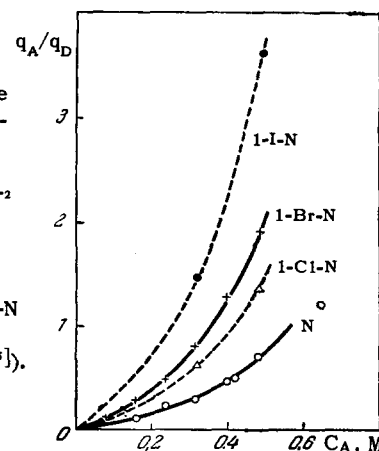


FIG. 11. The ratio of the yield of the sensitized phosphorescence to that of the donor phosphorescence (benzophenone at $C = 2 \times 10^{-2}$ M) as a function of the acceptor concentration C_A . N = naphthalene, 1-Cl-N = 1-chloronaphthalene, 1-Br-N = 1-bromonaphthalene, 1-I-N = 1-iodonaphthalene (from^[45]).

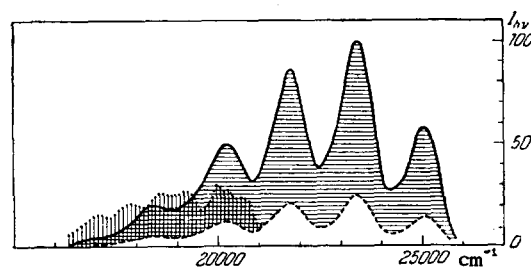


FIG. 12. Graphical determination of the quantum yield of sensitized phosphorescence γ . 1 - Phosphorescence spectrum of benzophenone at $C = 2 \times 10^{-2}$ M (solid line); 2 - spectrum of benzophenone at $C = 2 \times 10^{-2}$ M in the presence of 1-bromonaphthalene at $C = 3.2 \times 10^{-1}$ M (dashed line); 3 - sensitized-phosphorescence spectrum of 1-bromonaphthalene (dotted line). All the spectra have been reduced to quantum intensities on a ν scale. $\gamma = q_{s.p.A}/(q_0D - q_D)$ is equal to the ratio of the vertically-hatched to the horizontally-hatched area in the diagram.

Table VI. Quantum yields of sensitized phosphorescence $\gamma = q_{S.p.A}/(q_{0D} - q_D)$ for varying acceptor concentrations in alcohol-ether at 77°K. (Taken from reference [49].)

Donor + acceptor Acceptor concentration (M) at 77°K	$\gamma = q_{S.p.A}/(q_{0D} - q_D)$			
	Benzophenone* + 1-bromonaphthalene	Phenanthrene** + naphthalene	Phenanthrene** + 1-chloronaphthalene	Carbazole** + naphthalene
$6.3 \cdot 10^{-2}$	—	—	—	0.085***
$9.5 \cdot 10^{-2}$	0.21	0.32	—	0.083
$1.42 \cdot 10^{-1}$	0.16	0.31	—	0.080
$2.13 \cdot 10^{-1}$	0.21	0.32	0.73	0.070
$3.2 \cdot 10^{-1}$	0.20	0.30	0.67	0.074
$4.8 \cdot 10^{-1}$	0.19	0.26	0.67	0.075

* $\lambda_{excit} = 3650 \text{ \AA}$.
 ** $\lambda_{excit} = 3340 \text{ \AA}$.
 ***The error of measurement of the quantum yield of sensitized phosphorescence is 15-20%.

Table VII. The variation in the quantum yield of sensitized phosphorescence $\gamma = q_{S.p.A}/(q_{0D} - q_D)$ in the series of 1-halonaphthalenes as energy acceptors. All data are for alcohol-ether mixture at 77°K. (From the data of reference [47].)

Donor \ Acceptor	Benzo-phenone	Benz-aldehyde	m-Iodobenz-aldehyde	Phen-anthrene
Naphthalene	0.07	0.13	0.11	0.30
1-Chloronaphthalene	0.12	0.22	—	0.73
1-Bromonaphthalene	0.20	0.27	0.30	1.00
1-Iodonaphthalene	0.35	—	—	—

areas of the unquenched and quenched spectra of the donor (horizontally cross-hatched).

The values of the quenching (q_{0D}/q_D) and of $q_{S.p.A}/q_D$ have been stated above to be independent of the concentration of energy donor molecules in the solution. Naturally, the quantum yield of sensitized phosphorescence is independent of the concentration of the energy donor. The question of the relation of γ to the concentration C_A of the energy acceptor in the solution is more complex, since each of the quantities $q_{S.p.A}/q_D$ and q_{0D}/q_D entering into Eq. (5) by itself depends strongly on C_A .

Table VI gives the values of the quantum yield of sensitized phosphorescence at various acceptor concentrations in the range from 6×10^{-2} to 4.8×10^{-1} M for four combinations of energy donors and acceptors.

As we see from the data given in Table VI, the value of γ is independent of the concentration of the energy acceptor within the limits of experimental error for all the combinations studied.* Thus, the

*At the same time, the value of the absolute quantum yield of sensitized phosphorescence $q_{S.p.A}$ will depend on both the donor used and on the acceptor concentration.

value of the quantum yield of sensitized phosphorescence is a constant determined by the chosen combination of the energy donor and acceptor.* The average values of γ for a large set of different combinations of donor and acceptor molecules [47] are given in the last column of Table V. As is indicated there, the numerical values of the quantum yields of sensitized phosphorescence for the cases studied vary from 0.07 to 1.0, depending both on the donor molecule and the acceptor molecule. Interestingly, in combining any given donor with various acceptors, the value of γ always increases in the order of acceptors: naphthalene, 1-chloronaphthalene, 1-bromonaphthalene, and 1-iodonaphthalene (Table VII).

To find the factors determining the value of the quantum yield of sensitized phosphorescence γ , Ermolaev and Terenin [49, 51, 70] have made a comparison of the quantum yields of sensitized phosphorescence with the absolute quantum yields of the ordinary

*Perhaps the choice of solvent can affect the value of the quantum yield of sensitized phosphorescence, but this problem has not been studied. All of the quantitative measurements in [47, 49, 70] were made in alcohol-ether at 77° or 90°K.

Table VIII. Absolute quantum yields of fluorescence and phosphorescence of a set of aromatic compounds in alcohol-ether at 77°K; $\lambda_{\text{excit}} = 3030, 3340, \text{ or } 3650 \text{ \AA}$. (Taken from reference [49].)

Compound	q_{phos}^*	q_{fluor}^*
9,10-di-n-propylanthracene	0.00	1.00
Benzophenone	0.74	0.00
Benzaldehyde	0.49	0.00
Acetophenone	0.62	0.00
m-Iodobenzaldehyde	0.64	0.00
Phenanthrene	0.135	0.12
Naphthalene	0.03	0.29**
1-Chloronaphthalene	0.16	0.03
1-Bromonaphthalene	0.14	0.00
1-Iodonaphthalene	0.20	0.00
1-Methylnaphthalene	0.023	0.43
Quinoline	0.10	0.053

*The error of measurement of the yields is $\pm 20\%$.
 **The value of the yield is appreciably lower than that given in [9].

fluorescence and phosphorescence of the donor and acceptor molecules measured under the same conditions. The numerical values of the yields agree satisfactorily with one another if we assume that the process of radiationless transfer of electronic excitation energy between the triplet levels is not accompanied by quenching, [Translator's note: i.e., takes place without degradation of energy], and that all the quenching in the molecules used as energy donors and acceptors takes place only in the triplet state. Under these assumptions, the quantum yield of sensitized phosphorescence $\gamma_{\text{s.p.}}$ is related to the absolute quantum yields of fluorescence q_{fluor} and phosphorescence q_{phos} of the donor D and the acceptor A by the following equation:

$$\gamma_{\text{s.p.A}} = \frac{q_{\text{s.p.A}}}{q_{\text{0D}} - q_{\text{D}}} = \frac{q_{\text{phos A}}}{1 - q_{\text{fluor A}}} \frac{1 - q_{\text{fluor D}}}{q_{\text{phos D}}} \quad (6)$$

Equation (6) has been derived under the assumption that the process of radiationless deactivation of a molecule from the triplet state to the ground state (process k_5 in Fig. 1) is a rate process, and competes with the emission of phosphorescence (k_4).

At the same time, in a rigid solution in the presence of acceptor molecules, there is a statistical probability of finding an acceptor molecule in the "sphere of action" about a triplet donor molecule, as determined by Perrin's formula (3). In such a case, instead of undergoing process k_4 or k_5 , the donor molecule can be deactivated by giving its energy to the acceptor.

Table VIII gives the data of Ermolaev [49] on the absolute quantum yields of fluorescence and phosphorescence of a number of aromatic substances in alcohol-ether at 77°K. The yields were determined by comparison with the quantum yield of fluorescence of

9,10-di-n-propylanthracene, taken to be 1.00.*

Table IX compares the quantum yields of sensitized phosphorescence determined directly by experiment (last column of Table IX) with the values calculated by Eq. (6) from the data on the absolute quantum yields (next-to-last column). Comparison of the last two columns in the table shows fully satisfactory agreement. The discrepancies of 20–30% occurring in most cases can be ascribed to experimental error, especially in the measurement of the absolute quantum yields of fluorescence and phosphorescence at low temperatures. The greatest discrepancy (as much as 80%) is found when using 1-chloronaphthalene as the acceptor. The discrepancies are small for the other acceptors. These facts permit us to consider the assumptions made above to be confirmed, namely: 1) that the act of radiationless transfer of electronic excitation energy is not accompanied by quenching, and 2) that the processes of radiationless conversion of an electronically-excited molecule to the ground state studied in reference [49] in simple aromatic compounds involve the triplet state, and are independent of the manner in which the molecule got into the triplet state.

Thus, the study of quantum yields of sensitized phosphorescence [49] indicates that the deactivation of electronic excitation energy in simple aromatic molecules takes place via the triplet state.†

This conclusion is highly essential, since the most

*According to the data of Vember, [34] the quantum yield of fluorescence of 9,10-dipropylanthracene in deoxygenated alcohol at 293°K is 0.96.

†Robinson [116] has also come to an analogous conclusion that the radiationless deactivation of electronically-excited-naphthalene molecules occurs via the triplet state from comparing the decay times of phosphorescence of ordinary and completely-deuterated naphthalene.

Table IX. A comparison of the directly-measured quantum yields of sensitized phosphorescence with those calculated from the absolute quantum yields of the ordinary fluorescence and phosphorescence of the donor and acceptor molecules (all data for alcohol-ether at 77°K). (From the data of reference [49].)

Donor	$\frac{q_{\text{phos.D}}}{1-q_{\text{fluor.D}}}$	Acceptor	$\frac{q_{\text{phos.A}}}{1-q_{\text{fluor.A}}}$	$\frac{q_{\text{phos.A}}(1-q_{\text{fluor.D}})}{(1-q_{\text{fluor.A}})q_{\text{phos.D}}}$	$\gamma = \frac{q_{\text{s.p.A}}}{q_{0D}-q_D}$
Benzophenone	0.74	Naphthalene	0.042	0.057	0.07
»	0.74	1-Methylnaphthalene	0.04	0.054	0.07
»	0.74	1-Chloronaphthalene	0.165	0.22	0.12
»	0.74	1-Bromonaphthalene	0.14	0.19	0.20
»	0.74	1-Iodonaphthalene	0.20	0.27	0.35
»	0.74	Quinoline	0.105	0.14	0.14
Benzaldehyde	0.49	Naphthalene	0.042	0.036	0.13
»	0.49	1-Chloronaphthalene	0.165	0.34	0.22
»	0.49	1-Bromonaphthalene	0.14	0.29	0.27
Acetophenone	0.62	Naphthalene	0.042	0.068	0.10
m-Iodobenzaldehyde	0.64	Naphthalene	0.042	0.065	0.11
»	0.64	1-Bromonaphthalene	0.14	0.22	0.30
Phenanthrene	0.15	Naphthalene	0.042	0.28	0.30
»	0.15	1-Chloronaphthalene	0.165	1.1	0.73
»	0.15	1-Bromonaphthalene	0.14	0.94	0.99

contradictory opinions have been expressed in the literature up to the present on the question of the pathways of deactivation of excited aromatic molecules. Sveshnikov^[18,60] has suggested that direct radiationless deactivation to the ground state occurs either from the fluorescent ($^1I^*$) or the phosphorescent (3I) state. Kasha^[28] thinks that radiationless transitions in aromatic compounds in rigid solutions generally do not occur. Gilmore, Gibson, and McClure^[97] suggest that quenching occurs mainly in the triplet state. Zelinskiĭ, Kolobkov, et al.^[53] concluded from measurements of luminescence yields and τ of phosphorescence performed mainly with phthalimide derivatives that quenching does not occur in the metastable triplet level of aromatic compounds. These authors propose that quenching takes place in a hypothetical intermediate state into which the molecule enters before undergoing transition to the triplet state.

Subsequently^[51] the conclusion that all quenching occurs via the triplet state was tested by comparing

the quantum yields of ordinary and sensitized phosphorescence of naphthalene and biphenyl with those of their deuterated analogs. As was shown in^[98,116], deuteration of naphthalene leads to a several-fold increase in the τ of its phosphorescence (from 2.3 to 18 sec in E.P.A. at 77°K). It was suggested^[116] that the increase in τ is due to a decrease in the rate constant for degradation of the excitation energy of the triplet state into heat in the deuterated compounds. If this is true, then in the deuterated compounds the ratio $q_{\text{phos}}/q_{\text{fluor}}$ and the quantum yield of sensitized phosphorescence γ should increase at the same time that τ increases. The test experiments performed in^[51] showed an approximately parallel increase in $q_{\text{phos}}/q_{\text{fluor}}$ and in γ in going from naphthalene and biphenyl to octadeuteronaphthalene and decadeutero-biphenyl (Table X). This confirms the explanation given above for the values of the quantum yields of sensitized phosphorescence, and also provides another proof for the assumed existence of a rate process of radiationless degradation of the energy of the triplet

Table X. A comparison of the luminescent properties of ordinary and deuterated hydrocarbons in alcohol-ether at 77°K. (From the data of reference [51].)

	Naphthalenes		Biphenyls	
	C ₁₀ H ₈	C ₁₀ D ₈	C ₁₂ H ₁₀	C ₁₂ D ₁₀
τ_{phos} , sec	2.15 (2.1)	9.5 (17) *	3.1±0.1	11.3±0.4
q_{fluor} (relative)	1.00	0.97±0.07	1.00	0.84±0.18
q_{fluor} (absolute)	0.29	0.28±0.02	0.21	0.18±0.04
$q_{\text{phos}}/q_{\text{fluor}}$	0.083±0.005	0.21±0.03	0.79±0.06	1.9±0.2
$\gamma_{\text{s.p.}}$ **	0.07	0.21±0.05	0.16±0.05	0.34±0.08

*The value in parentheses is from the data of [98,116].
**Energy donor: benzophenone.

Table XI. Rate constants for radiative and radiationless intercombination transitions in aromatic molecules in alcohol-ether at 77° K*.

Compound	k_4 (sec ⁻¹) $^3\Gamma \rightarrow ^1\Gamma$	k_5 (sec ⁻¹) $^3\Gamma \rightarrow ^1\Gamma$	$\tau_{\text{emission}} = 1/k_4$ (sec)
m-Iodobenzaldehyde	$1.0 \cdot 10^3$	$5.5 \cdot 10^2$	$1.0 \cdot 10^{-3}$
Benzaldehyde	$3.4 \cdot 10^2$	$3.5 \cdot 10^2$	$2.9 \cdot 10^{-3}$
Acetophenone	$2.8 \cdot 10^2$	$1.7 \cdot 10^2$	$3.6 \cdot 10^{-3}$
Benzophenone	$1.6 \cdot 10^2$	$5.0 \cdot 10$	$6.2 \cdot 10^{-3}$
Ethylphenylketone	$\sim 1.5 \cdot 10^2$	$\sim 1.2 \cdot 10^2$	$\sim 6.7 \cdot 10^{-3}$
1-Iodonaphthalene	$1.0 \cdot 10^2$	$4.0 \cdot 10^2$	$1.0 \cdot 10^{-2}$
1-Bromonaphthalene	7.0	$4.3 \cdot 10$	$1.4 \cdot 10^{-1}$
4-Phenyl-4-methoxybenzophenone	2.3	1.3	$4.3 \cdot 10^{-1}$
4-Phenylbenzophenone	1.6	1.7	$6.2 \cdot 10^{-1}$
4-(p-Methoxyphenyl)-benzophenone	1.0	1.0	1.0
Triphenylamine	$8.6 \cdot 10^{-1}$	$5.7 \cdot 10^{-1}$	1.2
1-Nitronaphthalene	$8.6 \cdot 10^{-1}$	2.0 · 10	1.2
1-Chloronaphthalene	$5.7 \cdot 10^{-1}$	1.7	1.7
1-Naphthaldehyde	$3.8 \cdot 10^{-1}$	1.2 · 10	2.6
Quinoline	$7.7 \cdot 10^{-2}$	$6.6 \cdot 10^{-1}$	1.3 · 10
Carbazole	$6.9 \cdot 10^{-2}$	$6.3 \cdot 10^{-2}$	1.5 · 10
2-Naphthylmethylketone	$5.1 \cdot 10^{-2}$	$9.8 \cdot 10^{-1}$	2.0 · 10
Phenanthrene	$4.6 \cdot 10^{-2}$	$2.6 \cdot 10^{-1}$	2.2 · 10
Biphenyl	$3.7 \cdot 10^{-2}$	$2.9 \cdot 10^{-1}$	2.7 · 10
Decadeuterobiphenyl	$3.7 \cdot 10^{-2}$	$5.1 \cdot 10^{-2}$	2.7 · 10
1-Fluoronaphthalene	$3.6 \cdot 10^{-2}$	$6.3 \cdot 10^{-1}$	2.8 · 10
1-Methylnaphthalene	$2.0 \cdot 10^{-2}$	$4.5 \cdot 10^{-1}$	5.0 · 10
1-Naphthol	$1.6 \cdot 10^{-2}$	$5.1 \cdot 10^{-1}$	6.3 · 10
Naphthalene	$1.6 \cdot 10^{-2}$	$4.2 \cdot 10^{-1}$	6.3 · 10
Octadeuteronaphthalene	$1.6 \cdot 10^{-2}$	$9.0 \cdot 10^{-2}$	6.3 · 10

*The experimental data on τ_{phos} , ϕ_{fluor} , ϕ_{phos} , and $\gamma_{\text{s.p.A}}$ are taken from [15, 49, 45, 46, 51].

state into heat. The lack of a strict quantitative agreement between all the values given in Table X is apparently due to an insufficiently high percent deuteration of the substances (the naphthalene was 80% deuterated, and the biphenyl 85%) as well as to the low degree of accuracy of measurements of the yields, especially for biphenyl.

On the basis of the conclusion that the radiationless degradation of electronic excitation energy in aromatic molecules in rigid solutions at low temperatures occurs only via the triplet state, calculations were made in [51] of the constants for radiative and radiationless transitions from the triplet state to the ground state for 25 aromatic molecules. These data are given in Table XI. The last column gives the data on the natural lifetime of the triplet state of the studied molecules. We shall not discuss the data in the table, since that would be outside the limits of this review. We shall only note that, in contradiction to the opinion expressed in [116] that naphthalene does not show radiationless degradation from the triplet state, our data (see Table XI) indicate that the rate constant of the radiationless transition $^3\Gamma \rightarrow ^1\Gamma$ for $C_{10}D_8$ is six times as great as that of the corresponding radiative transition.

The described facts indicate that one can use measurements of quantum yields of sensitized phosphorescence to estimate the amount of quenching in the triplet state of one of the compounds taking part in the transfer of energy from donor to acceptor when this magnitude is unknown for the other component.

c) The mechanism of the intermolecular interaction responsible for radiationless energy transfer involving excitation of the triplet state. The material presented in the previous sections indicates that the sensitized phosphorescence of aromatic compounds is due to radiationless transfer of electronic excitation energy from a triplet donor molecule to an unexcited acceptor molecule, directly exciting the latter to the triplet level. The question arises of the nature of the interaction responsible for the energy transfer here.

A large number of studies by Vavilov, [1, 32] Galanin, [36] Förster, [10, 92-94] et al. [19, 20, 23] had shown previously that inductive-resonance interactions between the excited and unexcited molecules are responsible for the radiationless energy transfer manifested in concentration depolarization, concentration quenching of fluorescence, quenching of fluorescence by foreign absorbing substances, and sensitized fluorescence.

Interactions of this type have been discussed theoretically by F. Perrin, [113] Förster, [10, 92] Galanin and Frank, [36] Galanin, [13] and Dexter. [36] Dexter's formula [36] determining the rate constant (probability) of radiationless energy transfer is given below [Eq. (7)]. The interaction is of inductive-resonance dipole-dipole type with an excited donor molecule and an unexcited acceptor molecule situated at a distance RDA apart.

$$k_{D^* \rightarrow A^*} = \frac{B k_{D^* \rightarrow D^* A^* \leftarrow A}}{n^2 R_{DA}^6 v_{av}^2} \int_0^\infty F_D(\nu) \epsilon_A(\nu) d\nu, \quad (7)$$

where B is a constant, and $F_D(\nu)$ and $\epsilon_A(\nu)$ are the

emission spectrum of the donor and the absorption spectrum of the acceptor normalized to unit area. As we see from Eq. (7), the rate of transfer is directly proportional to the oscillator strengths of the energy donor and acceptor, to the overlap of the emission spectrum of the donor with the absorption spectrum of the acceptor normalized to unit area, and also to R_{DA}^{-6} .

If we now take the ratio of the transfer rate to the rate of radiative transition in the donor molecule, $k_{D^* \rightarrow A^*}/k_{D^* \rightarrow D}$, we obtain a formula giving the quenching of the luminescence of the donor in the presence of the acceptor $(q_{0D} - q_D)/q_D$. If the distance between the excited donor molecule and the unexcited acceptor molecule remains constant (or, going over to mean values, if the concentration of the acceptor in the solution remains the same*), the amount of quenching $(q_{0D} - q_D)/q_D$ of the luminescence of the donor will be directly proportional to the overlap of the normalized spectra and to the oscillator strength of the electronic transition in the energy acceptor being excited in the energy transfer. An analogous dependence on the oscillator strength of the transitions in the acceptor and donor is also found in the case of interaction of an electric quadrupole with a dipole, of a magnetic dipole with a dipole, and other cases of electromagnetic interactions. The difference consists in the variation of the strength of the interaction as a different power of the distance between the energy donor and acceptor.

These conclusions have been experimentally tested by Galanin and L. V. Levshin,^[35] who showed that the value of the shortening of the lifetime $(\tau_{0D} - \tau_D)/\tau_D$ in quenching of the fluorescence by foreign absorbing substances is approximately proportional to the mean absorption coefficient of the quenching agent, as averaged over the fluorescence spectrum. It is almost independent of the τ for fluorescence of the donor, in spite of the variation in τ by several orders of magnitude.

In addition to interactions of the inductive-resonance type, exchange-resonance interactions can also lead to radiationless energy transfer. This type of interaction has been investigated by Dexter.^[36] In the case of exchange-resonance interactions between a triplet and an unexcited molecule, the probability of radiationless energy transfer will no longer be directly proportional to the oscillator strength of the triplet-singlet transition in the donor molecule.

In order to find the mechanism of the interaction responsible for energy transfer between triplet and unexcited molecules, Ermolaev and Terenin^[35,44,45] have studied the relation of the amount of quenching of the luminescence of the energy donor to the oscillator strength of the triplet-singlet transition in the

acceptor. In addition to depending on the oscillator strength of the electronic transition excited in the acceptor, the amount of quenching, as defined by the expression $(q_{0D} - q_D)/q_D$, depends also on the overlap between the emission spectrum of the donor with the absorption spectrum of the acceptor; in the present case, the latter corresponds to the direct transition from the ground state of the molecule to the triplet state. It is very difficult to measure directly the absorption spectrum corresponding to the $^3\Gamma \leftarrow ^1\Gamma_A$ transition, owing to its very low intensity. However, we may assume that it shows approximate mirror symmetry with the emission spectrum of the phosphorescence.

Thus, in order to determine the effect of the oscillator strength of the triplet-singlet transition in the energy acceptor on the amount of quenching, we must use as acceptors substances having widely differing constants k_4 for radiative transition from the triplet state to the ground state, but having phosphorescence spectra which are identical in position and structure. These conditions are satisfied well by naphthalene and its halo-derivatives: 1-chloronaphthalene, 1-bromonaphthalene, and 1-iodonaphthalene. As we see from Fig. 13, the phosphorescence spectra of these acceptors are very similar to one another in position and

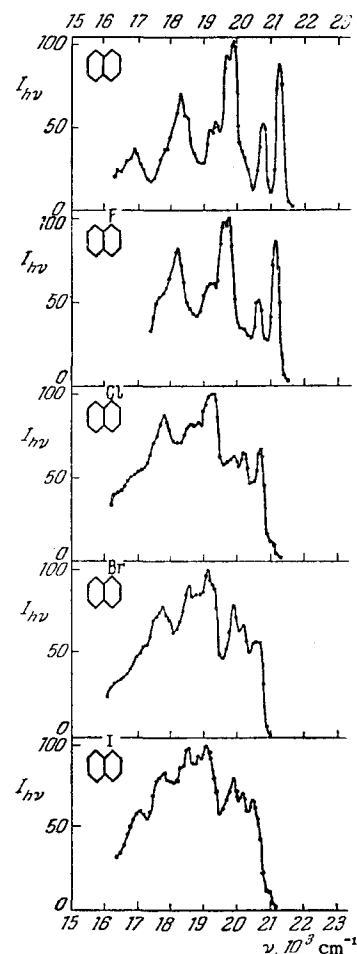


FIG. 13. The phosphorescence spectra of naphthalene and 1-fluoro-, 1-chloro-, 1-bromo, and 1-iodonaphthalene in alcohol-ether at 77°K; $\lambda_{\text{excit}} \approx 3030\text{--}3130 \text{ \AA}$, $C = 10^{-2}\text{--}10^{-1} \text{ M}$. The ordinate is the quantum intensity distribution. The abscissa is ν in units of 1000 cm^{-1} (from [15]).

*It is assumed here that there is no transfer between excited and unexcited molecules of the donor.

Table XII. The quenching of the phosphorescence of some donors ($C_D = 2 \times 10^{-2}$ M, $\lambda_{\text{excit}} = 3650 \text{ \AA}$) in the presence of various energy acceptors at a concentration 3.2×10^{-1} M. Solvent: Alcohol-ether at 77°K . (Taken from reference [45].)

Acceptor	Donor k_{4A} (sec^{-1}) $^3\Gamma_A \rightarrow ^1\Gamma_A$	$\frac{q_{0D} - q_D}{q_D}$	
		Benzophenone	Benzaldehyde
Naphthalene	$1.6 \cdot 10^{-2}$	$4.3 \pm 0.9^*$	2.7 ± 0.6
1-Methylnaphthalene	$2.0 \cdot 10^{-2}$	5.2 ± 1.2	—
1-Chloronaphthalene	$5.7 \cdot 10^{-1}$	5.2 ± 1.2	2.8 ± 0.7
1-Bromonaphthalene	7.0	4.3 ± 0.9	3.0 ± 0.8
1-Iodonaphthalene	$1.0 \cdot 10^2$	4.3 ± 0.9	—

*The considerable error was due to difficulties in quantitative measurement of the luminescence intensities at liquid-nitrogen temperature.

structure, but they differ greatly in their rate constants k_{4A} (Table XII). Hence, if we take an energy donor having its triplet level situated $3000\text{--}4000 \text{ cm}^{-1}$ higher than for the cited naphthalene derivatives, e.g., benzaldehyde or benzophenone,* we can assume that the overlap of the emission spectrum of the donor molecule with all of the cited naphthalene derivatives is approximately constant. This permits us to isolate the effect of the changes in the probability of the radiative $^3\Gamma_A \leftrightarrow ^1\Gamma_A$ transition of the acceptor on the energy transfer occurring in sensitized phosphorescence.

Measurements [15,44,45] of the quenching of the phosphorescence of benzophenone and benzaldehyde by naphthalene and its 1-halo-derivatives have shown that the amount of quenching of the emission of the donor in the presence of various acceptors at the same molar concentration is the same within the experimental limits of error for naphthalene, 1-chloronaphthalene, 1-bromonaphthalene, and 1-iodonaphthalene. This is so, in spite of the several thousand-fold increase in the oscillator strength of the $^3\Gamma \rightarrow ^1\Gamma$ transition in 1-iodonaphthalene, as compared with naphthalene. The quenching data are given in Table XII.

The amount of quenching of the luminescence of the donor by two acceptors (1-chloronaphthalene and 1-bromonaphthalene) having oscillator strengths of the $^3\Gamma \leftrightarrow ^1\Gamma$ transition differing by a factor of twelve is shown in Fig. 14 to be the same at all acceptor concentrations.

All this indicates that the probability of radiationless energy transfer in sensitized phosphorescence

*If we use an energy donor whose triplet level is only a little higher than that of naphthalene (e.g., phenanthrene or anthraquinone), then small changes in the height of the triplet levels of the 1-halo-derivatives of naphthalene will affect appreciably the value of the overlap integral, which can then be no longer taken to be even approximately constant.

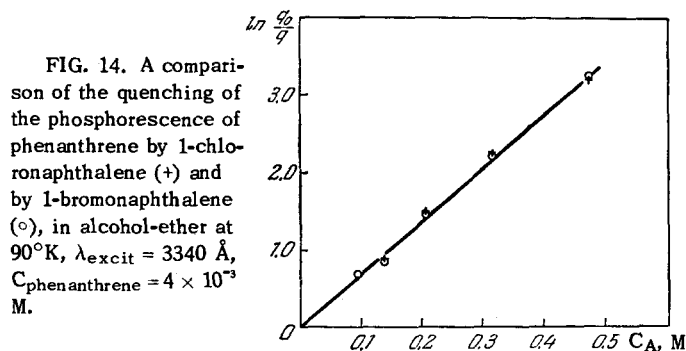


FIG. 14. A comparison of the quenching of the phosphorescence of phenanthrene by 1-chloronaphthalene (+) and by 1-bromonaphthalene (o), in alcohol-ether at 90°K , $\lambda_{\text{excit}} = 3340 \text{ \AA}$, $C_{\text{phenanthrene}} = 4 \times 10^{-3}$ M.

is independent of the oscillator strength of the $^3\Gamma \leftrightarrow ^1\Gamma$ electronic transition of the acceptor. Thus, sensitized phosphorescence cannot be explained by an inductive-resonance interaction of any type (electric dipole-dipole, electric quadrupole-dipole, magnetic dipole-dipole interaction, etc.).

The estimate of the "critical distance" for energy transfer made by Ermolaev [15,45] by Förster's formula for the interaction of two electric dipoles also gave a value $R = 1.1 \text{ \AA}$ for the pair benzophenone + naphthalene.* This is smaller by more than an order of magnitude than the experimental value $R = 13 \text{ \AA}$ for the same pair of substances.

On the basis of these facts, Ermolaev and Terenin [15,44,45] interpreted the phenomenon of energy transfer in sensitized phosphorescence in terms of exchange-resonance interactions between a triplet donor molecule and an unexcited acceptor molecule. Intermolecular interactions of the exchange-resonance type resulting in radiationless transfer of electronic excitation energy in condensed systems have been studied theoretically by Dexter. [86] The exchange-resonance effects are of quantum nature, and cannot be understood from the standpoint of classical physics, in

*We must note that Förster's formula is no longer applicable at such distances.

distinction from the inductive-resonance interactions.^[86] The exchange-resonance interactions are manifested when the peripheral parts of the electron shells of the donor and acceptor molecules overlap. The matrix element of the exchange interaction between an excited donor molecule D^* and an unexcited acceptor molecule A has the form^[86]

$$\langle H \rangle = \int \psi_D^*(\mathbf{r}_1) \psi_A^*(\mathbf{r}_2) H \psi_A'(\mathbf{r}_1) \psi_D(\mathbf{r}_2) \chi_D^*(\sigma_1) \chi_A^*(\sigma_2) \chi_A'(\sigma_1) \times \chi_D(\sigma_2) d\tau, \quad (8)$$

where the prime indicates the excited state, and the asterisk indicates the complex conjugate of a quantity. The spin portions $\chi(\sigma)$ have been factored out of the wave functions of the molecular states: $\psi(\mathbf{r}, \sigma) = \varphi(\mathbf{r}) \chi(\sigma)$. Since H does not operate on $\chi(\sigma)$, the stated integral does not vanish only when the spin portion does not vanish. Thus we derive the selection rule: the exchange integral does not vanish only when $\chi_D' = \chi_A'$, and $\chi_A = \chi_D$, while χ' is not necessarily equal to χ . That is, the spin functions of the two molecules can undergo the same type of change. The latter rule is analogous to Wigner's rule;^[120] Terenin and Ermolaev^[40,67] pointed out that this rule was satisfied in sensitized phosphorescence in the initial papers on this phenomenon.

According to Dexter,^[86] the probability of energy transfer by the exchange-resonance mechanism can be written in the form

$$k_{D^* \rightarrow A^*}(\text{exch.}) = \frac{2\pi}{\hbar} Z^2 \int_0^\infty F_D(\nu) \epsilon_A(\nu) d\nu, \quad (9)$$

where $F_D(\nu)$ is the quantum emission spectrum of the donor, and $\epsilon_A(\nu)$ is the absorption spectrum of the acceptor, with both spectra normalized to unit area. This integral is analogous to the overlap integral in the formula for the probability of energy transfer by the inductive-resonance mechanism [see Eq. (7)].

According to Galanin,^[33] the meaning of the overlap integral can be treated as being a manifestation of the Franck-Condon principle in the radiationless energy transfer between the molecules.* In distinction from the case of inductive-resonance interaction, where all the terms entering into the expression for the probability of radiationless transfer can be determined from optical experiments, we cannot determine Z^2 in Eq. (9) directly from optical data. According to Dexter's estimate,^[86] Z^2 varies approximately as $Y e^{-2R/L}$, where Y is a dimensionless quantity much

smaller than unity, R is the distance between the donor and acceptor molecules, and L is the mean effective Bohr radius of the excited donor molecule and the unexcited acceptor. The exponential factor arises from the fact that the electron density in a molecule falls exponentially with distance beyond a certain point. Thus, in exchange-resonance interactions the probability of energy transfer declines exponentially with increase in the intermolecular distance, i.e., much more rapidly than in the case of interaction of two electric dipoles [Eq. (7)]. Thus we can treat the situation as if the triplet donor molecule in exchange-resonance interactions had a quite well delimited sphere of action, and when an acceptor molecule enters it, "instantaneous" energy transfer from the former to the latter molecule would take place. These ideas agree well with the exponential increase observed in the sensitized-phosphorescence case in the amount of quenching of the donor emission as the acceptor concentration is increased. They are also in accord with the large deviations in the amount of quenching and the shortening of the decay time of the donor in the presence of identical acceptor concentrations (see above, Sec. 2a).

We must make the immediate qualification that an overlap of the electron shells of the energy donor and acceptor sufficient to permit the process of energy transfer by the exchange-resonance mechanism has no appreciable effect on the positions of the energy levels of the acceptor molecule or on the probabilities of transitions between them.* As was shown at the beginning of this section (see Fig. 4), the phosphorescence spectrum of the energy acceptor remains unchanged, regardless of whether it is excited in its own absorption band or by radiationless energy transfer from a donor which has absorbed the exciting radiation.* The decay time of the after-emission of the acceptor also remains constant in both cases discussed (see Table IV).

Exchange-resonance interactions must take place not only in the energy transfer from a triplet molecule to an unexcited molecule, but also in that from a singlet excited molecule surrounded by unexcited singlet molecules of an acceptor having a lower fluorescent level. Radiationless energy transfer by the exchange-resonance mechanism is also allowed in this case by the spin selection rules. However, in this case the transitions are allowed even before the excited donor molecule approaches the acceptor molecule, as is necessary for their electron shells to overlap. Thus, forces from the inductive-resonance interaction of the electromagnetic fields appear and give rise to radiationless transfer of the electronic excitation energy. The inductive-resonance interac-

The overlap of the $^3\Gamma \leftarrow ^1\Gamma$ absorption spectrum of the acceptor with the $^3\Gamma \rightarrow ^1\Gamma$ emission spectrum of the donor is an additional condition which must be satisfied in order to permit triplet-triplet energy transfer between the molecules (in addition to the conditions mentioned on p. 341). However, in practice it would seem to be always satisfied whenever condition (1) is satisfied, i.e., the triplet level of the donor must be higher than that of the acceptor. This is because the spectra of the transitions $^3\Gamma_A \leftarrow ^1\Gamma_A$, $^3\Gamma_A^ \leftarrow ^1\Gamma_A$, $^3\Gamma_A^{**} \leftarrow ^1\Gamma_A$, etc., in aromatic molecules are diffuse in structure, and overlap one another.

*We shall not consider the very insignificant spectral shifts brought about by the change in the refractive index and the dielectric constant of the medium upon addition to the solvent of molecules of the energy acceptor.

tion forces decline much more slowly with increasing intermolecular distance than the exchange-resonance forces. Hence, energy transfer takes place at distances of the order of 40–60 Å, or appreciably farther than the distances necessary for energy transfer by the exchange-resonance mechanism ($R \sim 10\text{--}15$ Å). The exchange-resonance interactions emerge when the corresponding electronic transition in the acceptor is forbidden (by the intercombination selection rule or other rules). Exchange-resonance interactions can be manifested also in the close interactions of molecules at high acceptor concentrations, such as occur, e.g., in liquid scintillators with aggregation of molecules, or in crystals.

At the same time, as Förster^[24] first noted, the rule forbidding radiative transition in the donor molecule will not interfere with the occurrence of radiationless energy transfer by the inductive-resonance mechanism if the metastable donor molecule is close enough to an acceptor molecule having an absorption spectrum overlapping the phosphorescence spectrum of the donor, and the transition responsible for this spectrum is allowed. This conclusion is implicit in Eq. (7), from which we see that the ratio of the probability of radiationless energy transfer by the inductive-resonance mechanism to that for the emission of luminescence by the energy donor is independent of the oscillator strength of the transition of the donor. Thus, if we add to a solution of a phosphorescent substance a dye absorbing in the region of emission of the phosphorescence, then at high enough dye concentrations (about the same concentrations as in the quenching of fluorescence by foreign absorbing substances) we should expect the appearance of quenching and shortening of the τ of the phosphorescence due to energy transfer from the triplet donor molecule to the quenching agent, exciting the latter to the fluorescent level. The phenomenon will be accompanied by the trivial reabsorption of the light of the donor phosphorescence by the acceptor. These consequences have been tested experimentally by Ermolaev and Sveshnikova.^[50,52]

Radiationless energy transfer from a triplet to a singlet level in rigid solutions at 90°K has been observed by the shortening of the decay time of phosphorescence of a donor (triphenylamine) in the presence of acceptor molecules (chrysoidine, etc.) which absorb the light of the phosphorescence of the donor. This indicates that an additional possibility for deactivation of a triplet donor molecule appears in the presence of an acceptor. The energy-transfer diagram for this case is given in Fig. 15. In a paper presented at the 11th Conference on Luminescence, Ermolaev and Sveshnikova^[52] studied triplet-singlet energy transfer in a large number of various combinations of substances. They described also the appearance of a sensitized after-emission in the dianion of fluorescein, coinciding with its fluorescence spectrum, in the presence of 2-naphthylmethyl-

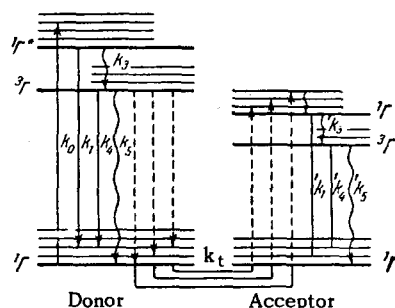


FIG. 15. The system of molecular levels for radiationless energy transfer from a triplet to a singlet level. The straight arrows denote radiative transitions, the wavy arrows denote intramolecular radiationless degradation, and the dashed arrows are transitions involving radiationless energy transfer from the donor molecule to the acceptor. The symbols for the levels and rate constants are analogous to those of Fig. 1.

ketone. The quantum yield of the sensitized after-emission $q_{s.a.}/(q_{0D} - q_D)$ (that is, the ratio of the number of quanta emitted by the acceptor to the number of quanta of phosphorescence of the donor lost by quenching) was equal to twenty here. Thus, the effect cannot be explained by reabsorption and secondary fluorescence. The relation of the quenching and the shortening of τ_{phos} to the acceptor concentration, as well as the transfer distances, unequivocally indicate the inductive-resonance nature of the interactions producing this type of energy transfer. It was also shown that this type of energy transfer occurs efficiently among biologically-important compounds (tryptophan, chlorophyll, pheophytin).

A number of papers^[58,82] have suggested using energy accumulated in organic molecules in the triplet state to obtain a stimulated-emission effect. Finally, very recently two short notes were published,^[110] describing the experimental observation of this effect. Since the problem of using organic compounds to obtain a laser effect has already been treated in a review by Shpol'skiĭ,^[22] in this review I shall take up this problem very briefly. The stimulated-emission effect was obtained by the authors of^[110] in glassy solutions of aromatic aldehydes and ketones at 77°K (benzaldehyde, acetophenone, benzophenone). The effect was also obtained in naphthalene in which the triplet state was filled up by triplet-level radiationless energy transfer from benzophenone. However, in these communications,^[110] one is puzzled by the fact that they were able to get a stimulated-emission effect in naphthalene, a molecule having a very low probability of radiationless transition from the triplet state to the ground state (τ for emission of phosphorescence = 63 sec; see Table XI).

3. ENERGY TRANSFER INVOLVING TRIPLET LEVELS IN CRYSTALLINE MEDIA

The first to point out the possibility of existence of a "triplet exciton" in organic crystals was Terenin^[68]

in a comment at a Discussion of the Faraday Society in 1958. By using these ideas, one can interpret a number of qualitative observations described in the literature.^[118,121] Sidman^[118] found in 1956 that the phosphorescence spectrum of naphthalene crystals at 20°K manifest very intensely the spectrum of an unknown impurity ($\nu_{0,0} = 18,000 \text{ cm}^{-1}$), and the phosphorescence spectrum of naphthalene itself ($\nu_{0,0} = 21,000 \text{ cm}^{-1}$) very weakly. If one adds a little 2-chloro- or 2-bromonaphthalene to the naphthalene, then the spectrum of the crystal shows their phosphorescence spectra. The phenomenon can be interpreted in terms of energy transfer with excitation of the triplet state. Kanda, Sponer, and Blackwell^[79,100] have found marked differences between the phosphorescence spectra of solid toluene and xylene at 4° and 77°K, probably due to energy transfer at 77°K to traces of benzaldehyde. However, we must note that the radiationless transfer of electronic excitation energy in these cases could also involve the singlet excited levels. Zmerli^[121] applied the phenomenon of sensitized phosphorescence to obtain the phosphorescence spectrum for transition from the lowest triplet level in naphthalene crystals at 20°K by adding small amounts of benzophenone to the crystal. The ordinary phosphorescence spectrum of naphthalene appeared at 20°K in the naphthalene crystal to which benzophenone had been added, providing evidence that the energy transfer in naphthalene crystals at 20°K involves the singlet levels, since otherwise the energy of the triplet molecules of naphthalene, in migrating, would undergo quenching by the impurities. However, the phosphorescence spectrum may possibly be emitted by naphthalene molecules occurring in crystal lattice defects near a benzophenone molecule incorporated in the crystal. In such a case, the appearance of the sensitized-phosphorescence spectrum of naphthalene would not indicate the absence of energy transfer involving triplet levels among the unexcited naphthalene molecules.

Some experimental facts from recent studies have proved anew the existence of energy migration involving triplet levels in crystals. A recent study^[88] dealt with energy transfer from a benzophenone crystal containing incorporated naphthalene molecules. The efficiency of this transfer increases as the mole fraction of naphthalene varies from 10^{-5} to 10^{-3} . A calculation of the sphere of action for energy transfer leads to the conclusion that one naphthalene molecule can be excited by 10^3 donor molecules. Interestingly, the sensitized-phosphorescence spectrum of naphthalene under these conditions has a quasilinear structure as defined by Shpol'skiĭ.^[21]

Some rather convincing proofs of efficient energy migration involving the triplet levels of molecules in crystals have been given in^[89]; here crystals of octa-deuteronaphthalene were studied in the pure state and containing 0.5% naphthalene. The $^1\Gamma^*$ and $^3\Gamma$ levels

of C_{10}H_8 lie about 100 cm^{-1} lower than the corresponding levels of C_{10}D_8 . In addition, analogous crystals ($\text{C}_{10}\text{D}_8-0.5\% \text{ C}_{10}\text{H}_8$) containing unidentified chemical impurities were studied.

The following facts were found: 1) At 4.2°K, one finds a linear-structured phosphorescence from C_{10}H_8 , but not from C_{10}D_8 ; here $\nu_{0,0} = 21208.7 \text{ cm}^{-1}$. 2) The phosphorescence disappears when the temperature rises to 77°K. 3) When the C_{10}H_8 concentration is decreased or the temperature is increased, points occur at which one observes simultaneously the fluorescence of C_{10}H_8 and C_{10}D_8 , but the phosphorescence of only C_{10}H_8 . In the crystal contaminated with a chemical impurity, the phosphorescence comes only from the impurity, either at 4.2°K or at 77°K.

The observed facts led these authors^[89] to the following conclusions:

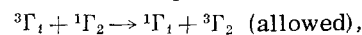
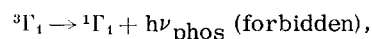
1. Since the crystal $\text{C}_{10}\text{D}_8-0.5\% \text{ C}_{10}\text{H}_8$ (+ chemical impurity) shows the fluorescence of C_{10}H_8 , but not that of the impurity, then the impurity concentration is not high enough for the energy transfer to the latter to compete with the intercombination conversion to the triplet state in C_{10}H_8 .

2. The most reasonable mechanism for filling the singlet and triplet states of the chemical impurity is energy transfer between the C_{10}H_8 molecules by "long-range tunneling". The energy transfer is markedly accelerated when kT approaches the depth of the isotopic trap level (100 cm^{-1}).

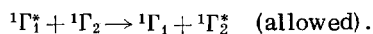
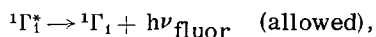
3. The tunneling at 4.2°K of the triplet excitation between the C_{10}H_8 centers and the chemical-impurity centers takes place within a time which is short in comparison with $\tau_{\text{phos}} = 2.6 \text{ sec}$. This results in the disappearance of the C_{10}H_8 phosphorescence in the "impure" crystal, even at 4.2°K, and in the appearance of the phosphorescence of the impurity. The fact that the fluorescence of C_{10}H_8 persists under these conditions indicates that we cannot explain this fact by migration involving the singlet levels. The theoretical problem of energy migration among impurity molecules has been studied by Agranovich^[31] within the framework of the virtual-exciton concept.

Migration involving triplet levels can explain the lack of phosphorescence in many "pure" organic crystals.

It seems to us that we can understand the great efficiency of radiationless energy transfer involving triplet levels if we take into account the following fact. Namely, in triplet-triplet migration the radiative transition in the donor molecule, which is forbidden by the multiplicity rule, competes with the allowed energy-transfer process:



while in energy transfer involving the singlet levels, both processes (emission and energy transfer) are allowed:



To be sure, the interaction declines more abruptly with increasing distance in the first type of interaction than in the second (see above). However, in a crystal this may not be essential.

This viewpoint is corroborated by the experiments of Hochstrasser,^[25] who showed that the τ_{phos} of triphenylene at 77°K in the crystal is non-exponential, and is about 15 times shorter than that in rigid solutions (15 sec). At the same time, the ratio $q_{\text{phos}}/q_{\text{fluor}}$ of the phosphorescence to the fluorescence yields of the crystal depends strongly on the degree of purification of the crystal, and possibly on the presence of defects ($0.05 \leq q_{\text{phos}}/q_{\text{fluor}} \leq 0.8$). This author also showed that energy transfer from the intensely phosphorescing crystals of benzophenone to naphthalene, triphenylene, chrysene, phenanthrene, anthracene, and pyrene occurs in the same way via the triplet levels. For the latter two molecules, the energy transfer could occur via the singlet levels, since their fluorescent ${}^1\Gamma^*$ levels are situated below the ${}^1\Gamma^*$ level of benzophenone (see Table III). However, even in this case one does not observe the fluorescence of the impurity; this indicates that energy transfer occurs only via the triplet levels. We must note that intercombination conversion competes with the singlet-singlet energy transfer from benzophenone, and the probability of the former in benzophenone is about a thousand times as great as that of the emission of fluorescence by the benzophenone molecule.^[43]

Sternlicht and McConnell^[119] have recently made a theoretical study of the problem of the triplet exciton as applied to electron paramagnetic resonance spectra.

¹ S. I. Vavilov, *Mikrostruktura sveta (Microstructure of Light)*, Collected Works, Vol. 2, AN SSSR (1952), p. 383; also see articles, *ibid*.

² W. West, Ed. *Chemical Applications of Spectroscopy*, Vol. IX, *Technique of Organic Chemistry*, Interscience, New York (1956), p. 707; Russ. Transl., IL (1959), p. 590.

³ G. Herzberg, *Atomic Spectra and Atomic Structure*, Prentice-Hall, New York (1937).

⁴ M. A. El'yashevich, *Atomnaya i molekulyarnaya spektroskopiya (Atomic and Molecular Spectroscopy)*, Fizmatgiz (1962).

⁵ V. L. Levshin, *Fotoluminescenciya zhidkikh i tverdykh veshchestv (Photoluminescence of Liquids and Solids)*, Gostekhzdat (1951).

⁶ P. Pringsheim, *Fluorescence and Phosphorescence*, Interscience, New York (1949).

⁷ C. Reid, *Excited States in Chemistry and Biology*, Academic Press, New York (1957); Russ. Transl., M., IL (1960).

⁸ A. N. Terenin, *Fotokhimiya krasitelei i rodstvennykh organicheskikh soedinenii (Photochemistry of Dyes and Related Organic Compounds)*, AN SSSR (1947).

⁹ P. P. Feofilov, *Polyarizovannaya lyuminescenciya atomov, molekul i kristallov (Polarized Luminescence of Atoms, Molecules, and Crystals)*, Fizmatgiz (1959); Engl. Transl., *The Physical Basis of Polarized Emission*, Consultants Bureau, New York (1961).

¹⁰ Th. Förster, *Fluorescenz organischer Verbindungen (Fluorescence of Organic Compounds)*, Vandenhoeck und Ruprecht, Göttingen (1951).

¹¹ R. A. Friedel and M. Orchin, *Ultraviolet Spectra of Aromatic Compounds*, Wiley, New York (1951), Fig. 140.

¹² Landolt-Bornstein, *Tabelle*, Vol. 1, Part 3, Springer-Verlag, Berlin (1951), Fig. 131, p. 270.

Reviews and dissertations

¹³ M. D. Galanin, *Rezonansnyy perenos energii voz-buzhdeniya v lyuminescencii rastvorakh (Resonance Energy Transfer in Luminescent Solutions)*, Dissertation, Institute of Physics, Academy of Sciences of the USSR, (1955); *Trudy FIAN SSSR* 12, 3 (1960).

¹⁴ P. P. Dikun, *Fosforestsentsiya parov organicheskikh soedinenii (Phosphorescence of Vapors of Organic Compounds)*, Dissertation, GOI (State Optical Institute) (1958).

¹⁵ V. L. Ermolaev, *Sensibilizovannaya fosforestsentsiya organicheskikh soedinenii pri nizkikh temperaturakh (Sensitized Phosphorescence of Organic Compounds at Low Temperatures)*, Dissertation, GOI (State Optical Institute), (1958).

¹⁶ A. V. Karyakin, *Spektralnoe izuchenie reaktsii fotookisleniya organicheskikh soedinenii i rol' metastabil'nykh sostoyaniy (A Spectral Study of the Reaction of Photooxidation of Organic Compounds and the Role of Metastable States)*, Dissertation, MGU (Moscow State University), (1958).

¹⁷ A. V. Karyakin, *Uspekhi khimii* 30, 1050 (1961).

¹⁸ B. Ya. Sveshnikov, *Fosforestsentsiya organicheskikh soedinenii (Phosphorescence of Organic Compounds)*, Dissertation, FIAN (1951).

¹⁹ A. N. Terenin, *UFN* 44, 347 (1951).

²⁰ A. N. Terenin and V. L. Ermolaev, *UFN* 58, 37 (1956).

²¹ É. V. Shpol'skiy, *UFN* 77, 321 (1962); *Soviet Phys. Uspekhi* 5, 522 (1962).

²² E. V. Shpol'skiy, *UFN* 77, 553 (1962); *Soviet Phys. Uspekhi* 5, 612 (1963).

²³ L. G. Augenstine, Ed. *Bioenergetics, Radiation Research*, Suppl. 2 (1960).

²⁴ Th. Förster, *Disc. Faraday Soc.*, 27, 7 (1959); *Z. Elektrochem.* 64, 157 (1960).

²⁵ R. M. Hochstrasser, *Revs. Mod. Phys.* 34, 531 (1962).

- ²⁶ M. Kasha, *Chem. Revs.* **41**, 401 (1947).
- ²⁷ M. Kasha and S. P. McGlynn, *Ann. Rev. Phys. Chem.* **7**, 403 (1956).
- ²⁸ M. Kasha, *Radiation Research*, Suppl. **2**, 243 (1960).
- ²⁹ J. W. Sidman, *Chem. Revs.* **58**, 689 (1958).
- ³⁰ H. Spöner and E. Teller, *Revs. Mod. Phys.* **13**, 75 (1941).
- Original papers**
- ³¹ V. M. Agranovich, *Optika i Spektroskopiya* **9**, 113, 798 (1960); Engl. Transl. (Optical Society of America), pp. 59, 421.
- ³² S. I. Vavilov, *JETP* **13**, 13 (1943); see also other articles in his *Collected Works*, Vol. 2, AN SSSR (1952).
- ³³ T. M. Vember and A. S. Cherkasov, *Izv. AN SSSR, ser. Fiz.* **24**, 577 (1960), *Columbia Tech. Transl.* p. 583.
- ³⁴ T. M. Vember, *DAN SSSR* **147**, 123 (1962).
- ³⁵ M. D. Galanin and L. V. Levshin, *JETP* **21**, 121 (1951).
- ³⁶ M. D. Galanin and I. M. Frank, *JETP* **21**, 114 (1951).
- ³⁷ M. D. Galanin, *JETP* **28**, 485 (1955), *Soviet Phys. JETP* **1**, 317 (1955).
- ³⁸ P. P. Dikun, *JETP* **20**, 193 (1950).
- ³⁹ Dikun, Petrov, and Sveshnikov, *JETP* **21**, 150 (1951).
- ⁴⁰ V. L. Ermolaev and A. N. Terenin, in *Collected Volume in Memory of S. I. Vavilov*, AN SSSR (1952), p. 137.
- ⁴¹ V. L. Ermolaev, *DAN SSSR* **102**, 925 (1955).
- ⁴² V. L. Ermolaev, *Izv. AN SSSR, ser. Fiz.* **20**, 514 (1956), *Columbia Tech. Transl.* p. 471.
- ⁴³ V. L. Ermolaev, *Optika i Spektroskopiya* **1**, 523 (1956).
- ⁴⁴ V. L. Ermolaev and A. N. Terenin, *J. chim. phys. et phys.-chim. biol.* **55**, 698 (1958).
- ⁴⁵ V. L. Ermolaev, *Optika i Spektroskopiya* **6**, 642 (1959); Engl. Transl. (Optical Society of America), p. 417.
- ⁴⁶ V. L. Ermolaev and K. K. Svitashv, *ibid.* **7**, 664 (1959); Engl. Transl. *ibid.*, p. 399.
- ⁴⁷ V. L. Ermolaev, *DAN SSSR* **139**, 348 (1961); *Soviet Phys. Doklady* **6**, 600 (1962).
- ⁴⁸ V. L. Ermolaev, *Optika i Spektroskopiya* **11**, 492 (1961); Engl. Transl. (Optical Society of America), p. 266.
- ⁴⁹ V. L. Ermolaev, *ibid.* **13**, 90 (1962); Engl. Transl., *ibid.*, p. 49.
- ⁵⁰ V. L. Ermolaev and E. B. Sveshnikova, *Izv. AN SSSR, ser. Fiz.* **26**, 29 (1962) [sic!]
- ⁵¹ V. L. Ermolaev, Paper presented at the 11th Conference on Luminescence (Minsk, September 1962), *Abstracts of papers*, AN SSSR, p. 25.
- ⁵² V. L. Ermolaev and E. B. Sveshnikova, *ibid.*, p. 26.
- ⁵³ Zelinskiĭ, Kolobkov, Borgman, and Zhmyreva, *Izv. AN SSSR, ser. Fiz.* **24**, 601 (1960), *Columbia Tech. Transl.* p. 607. Viktorova, Zhmyreva, Kolobkov, and Saganenko, *Optika i Spektroskopiya* **9**, 349 (1960); Engl. Transl. (Optical Society of America), p. 181.
- ⁵⁴ P. I. Kuryashov and B. Ya. Sveshnikov, *Optika i Spektroskopiya* **8**, 651 (1960); Engl. Transl. (Optical Society of America), p. 344.
- ⁵⁵ V. L. Levshin and L. A. Vinokurov, *Phys. Z. Sowjetunion* **10**, 10 (1936).
- ⁵⁶ G. A. Mokeeva and B. Ya. Sveshnikov, *Optika i Spektroskopiya* **9**, 601 (1960); Engl. Transl. (Optical Society of America), p. 317.
- ⁵⁷ V. A. Pilipovich and B. Ya. Sveshnikov, *ibid.* **4**, 116 (1958).
- ⁵⁸ S. G. Rautian and I. I. Sobel'man, *ibid.* **10**, 134 (1961); Engl. Transl., *ibid.*, p. 65.
- ⁵⁹ B. Ya. Sveshnikov, *DAN SSSR* **58**, 49 (1947).
- ⁶⁰ B. Ya. Sveshnikov, *JETP* **18**, 878 (1948).
- ⁶¹ B. Ya. Sveshnikov, *DAN SSSR* **105**, 1208 (1955).
- ⁶² B. Ya. Sveshnikov and V. L. Ermolaev, *DAN SSSR* **71**, 647 (1950).
- ⁶³ B. Ya. Sveshnikov and V. I. Shirokov, *Optika i Spektroskopiya* **12**, 576 (1962); Engl. Transl. (Optical Society of America), p. 320.
- ⁶⁴ P. A. Teplyakov, *ibid.* **2**, 269 (1957).
- ⁶⁵ A. N. Terenin, *Acta physicochim. URSS* **18**, 210 (1943); *Zhur. Fiz. Khim.* **18**, 1 (1944).
- ⁶⁶ A. N. Terenin, *Fotokhimiya khlorofilla i fotosintez* (Photochemistry of Chlorophyll and Photosynthesis), 6th Bakh Lectures, AN SSSR (1951).
- ⁶⁷ A. N. Terenin and V. L. Ermolaev, *DAN SSSR* **85**, 547 (1952).
- ⁶⁸ A. N. Terenin and V. L. Ermolaev, *Trans. Faraday Soc.* **52**, 1042 (1956).
- ⁶⁹ A. N. Terenin, *Disc. Faraday Soc.* **27**, 97 (1959).
- ⁷⁰ A. N. Terenin and V. L. Ermolaev, *Izv. AN SSSR, ser. Fiz.* **26**, 21 (1962), *Columbia Technical Translations*, p. 21.
- ⁷¹ N. A. Tolstoĭ and P. P. Feofilov, *UFN* **41**, 44 (1950).
- ⁷² P. P. Feofilov, *DAN SSSR* **44**, 159 (1944).
- ⁷³ P. P. Feofilov and B. Ya. Sveshnikov, *JETP* **10**, 1372 (1940).
- ⁷⁴ A. S. Cherkasov and T. M. Vember, *Optika i Spektroskopiya* **6**, 503 (1959); Engl. Transl. (Optical Society of America), p. 319.
- ⁷⁵ A. A. Shishlovskii and S. I. Vavilov, *Phys. Z. Sowjetunion* **5**, 379 (1934).
- ⁷⁶ A. H. Adelman and G. Oster, *J. Am. Chem. Soc.* **78**, 3977 (1956).
- ⁷⁷ L. Arnold and G. Kistiakowsky, *J. Am. Chem. Soc.* **54**, 1713 (1932).
- ⁷⁸ Bauer, Baczynski, and Czajkowski, *Bull. Acad. Polon. Sci., Ser. sci. math. astr. et phys.* **6**, 653 (1958).

- ⁷⁹ Blackwell, Kanda, and Sponer, *J. Chem. Phys.* **32**, 1465 (1960).
- ⁸⁰ E. J. Bowen, *Disc. Faraday Soc.* **14**, 143 (1953).
- ⁸¹ E. J. Bowen and D. W. Tanner, *Trans. Faraday Soc.* **51**, 475 (1955).
- ⁸² Brock, Czavinsky, Hormats, Nedderman, Stirpe, and Unterleitner, *J. Chem. Phys.* **35**, 759 (1961).
- ⁸³ Cadas, Courpron, Lochet, and Rousset, *Compt. rend.* **254**, 2490 (1962).
- ⁸⁴ E. Clar, *Spectrochim. Acta* **4**, 116 (1950).
- ⁸⁵ D. P. Craig and I. G. Ross, *J. Chem. Soc. (London)* 1589 (1954).
- ⁸⁶ D. L. Dexter, *J. Chem. Phys.* **21**, 836 (1953).
- ⁸⁷ E. Döller and Th. Förster, *Z. phys. Chem. (New Series)* **31**, 274 (1962).
- ⁸⁸ M. A. El-Bayoumi and M. Kasha, *J. Chem. Phys.* **34**, 2181 (1961).
- ⁸⁹ El-Sayed, Wauk, and Robinson, *Molec. Phys.* **5**, 205 (1962).
- ⁹⁰ Farmer, Gardner, and McDowell, *J. Chem. Phys.* **34**, 1058 (1961).
- ⁹¹ J. Ferguson and H. J. Tinson, *J. Chem. Soc. (London)* 3083 (1952).
- ⁹² Th. Förster, *Ann. Physik* **2**, 55 (1948).
- ⁹³ Th. Förster, *Z. Elektrochem.* **53**, 93 (1949).
- ⁹⁴ Th. Förster, *Z. Naturforsch.* **4a**, 321 (1949).
- ⁹⁵ Th. Förster and K. Kasper, *Z. Elektrochem.* **59**, 976 (1955).
- ⁹⁶ J. Frank, *Proc. Natl. Acad. Sci. USA* **44**, 941 (1958).
- ⁹⁷ Gilmore, Gibson, and McClure, *J. Chem. Phys.* **20**, 829 (1952); **23**, 399 (1955).
- ⁹⁸ C. A. Hutchinson, Jr., and B. W. Mangum, *J. Chem. Phys.* **32**, 1261 (1960); M. S. DeGroot and J. H. Van der Waals, *Molec. Phys.* **4**, 189 (1961).
- ⁹⁹ A. Jablonski, *Z. Physik* **94**, 38 (1935).
- ¹⁰⁰ Y. Kanda and H. Sponer, *J. Chem. Phys.* **28**, 798 (1958).
- ¹⁰¹ M. Kasha, *Disc. Faraday Soc.* **9**, 14 (1950).
- ¹⁰² S. Kato, *J. Inst. Polytech. Osaka City Univ.* **4c**, 155 (1953).
- ¹⁰³ E. Laffite, *Ann. physique* **10**, 71 (1955).
- ¹⁰⁴ Lewis, Lipkin, and Magel, *J. Am. Chem. Soc.* **63**, 3005 (1941).
- ¹⁰⁵ G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.* **66**, 2100 (1944).
- ¹⁰⁶ N. Mataga and Sh. Tsuno, *Bull. Chem. Soc. Japan* **30**, 368 (1957); N. Mataga, *ibid.* **31**, 459, 487 (1958).
- ¹⁰⁷ D. S. McClure, *J. Chem. Phys.* **19**, 670 (1951).
- ¹⁰⁸ H. L. McMurry, *J. Chem. Phys.* **9**, 241 (1941).
- ¹⁰⁹ E. G. McRae and M. Kasha, *J. Chem. Phys.* **28**, 721 (1958).
- ¹¹⁰ Morantz, White, and Wright, *Phys. Rev. Letters* **8**, 23 (1962); *Proc. Chem. Soc. (London)* 26 (1962); *J. Chem. Phys.* **37**, 2041 (1962).
- ¹¹¹ G. Oster and A. H. Adelman, *J. Am. Chem. Soc.* **78**, 913 (1956).
- ¹¹² F. Perrin, *Compt. rend.* **178**, 1978 (1924).
- ¹¹³ F. Perrin, *Ann. physique, Ser. 10*, **17**, 283 (1932).
- ¹¹⁴ G. Porter and M. W. Windsor, *J. Chem. Phys.* **21**, 2088 (1953); *Disc. Faraday Soc.* **17**, 178 (1954).
- ¹¹⁵ G. Porter and F. J. Wright, *Trans. Faraday Soc.* **51**, 1205 (1955).
- ¹¹⁶ G. W. Robinson, *J. Mol. Spectr.* **6**, 58 (1961).
- ¹¹⁷ G. O. Schenck and E. Koch, *Z. Elektrochem.* **64**, 170 (1960).
- ¹¹⁸ J. W. Sidman, *J. Chem. Phys.* **25**, 229 (1956).
- ¹¹⁹ H. Sternlicht and H. M. McConnell, *J. Chem. Phys.* **35**, 1793 (1961).
- ¹²⁰ E. Wigner, *Nachrichten von Gesellschaft der Wissenschaft zu Göttingen, Jahre 1927, Math.-Phys. Klasse, 1928, Heft. 4*, p. 375.
- ¹²¹ A. Zmerli, *J. chim. phys. et phys.-chim. biol.* **56**, 405 (1959).

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