FLUORESCENCE OF BINARY MIXTURES OF POLYATOMIC MOLECULES

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The increase in the temperature of complicated organic molecules upon electrical excitation [1, 2] creates the problem of increasing their stability in the excited state and of diminishing the quantity of vibrational energy in excess of the amount stored at equilibrium. It was previously shown in [2] that utilization of the phenomenon of stabilization—labilization [3] in an electric discharge results in a decrease in the amount of vibrational energy stored in excited molecules and makes it possible to optimize the excitation conditions by forming a suitable distribution function of the electrons with respect to their energies. The use of vapors of complicated organic compounds as stabilizers in electric discharges has been found to be especially effective [4]. However, in the case of electrical excitation, it is difficult to isolate the effect of the foreign vapors on the stabilization of fluorescing molecules due to the occurrence of various attendant processes. In order to examine the special features of the luminescence of binary mixtures of polyatomic molecules used for electrical excitation in a pure form, we used monochromatic optical excitation in the present work.

The luminescence of the vapor was excited by the emission of a DRSh-500 mercury lamp. The time characteristics of the fluorescence were studied on a PRA-3000 pulse fluorometer with excitation by flashes from a hydrogen lamp and a lamp with a small pressure of oxygen having half-width pulse lifetimes from 1.6 to 4 nsec. Quartz cuvettes with a branch for the substance were prepared for the investigations in the gaseous phase. Each cuvette with a substance was evacuated to a pressure of $\sim 10^{-4}$ Pa and sealed. Specially designed furnaces, in which the cuvettes were placed, were inserted into the cuvette section of the instrument. The vapor pressure in the cuvettes was assigned by the temperature of the lower furnace. The results of the measurements were treated on a MINC-11 minicomputer with consideration of the form of the exciting pulse. The error in the determination of the fluorescence lifetime was no greater than 5%.

The fluorescence of mixtures of perylene and pyrene vapors and of perylene and p-terphenyl vapors, which differ significantly with respect to the values of their partial pressure p at the same temperatures, was investigated.

The fluorescence spectra of perylene, pyrene, and p-terphenyl vapors vary only slightly at low partial pressures (Fig. 1).

Significant changes occur in them in binary mixtures of the molecules.

Figure 2 presents the fluorescence spectra of a mixture of perylene and pyrene. When the temperature of the lower furnace has the low value $T_\ell = 427$ K, at which the vapor pressure of pyrene p is equal to 53 Pa, that of perylene is equal to $8 \cdot 10^{-2}$ Pa, and the ratio between the pressures of perylene and pyrene is on the order of $1.5 \cdot 10^{-3}$, the fluorescence is produced mainly by pyrene, whose long-wavelength wing is broadened by the contribution of the fluorescence of perylene (spectrum 1). A further increase in the pressure of the mixture results in more distinct display of the fluorescence spectrum of perylene (spectra 2 and 3), since the fluorescence of pyrene is strongly absorbed by perylene as a consequence of the overlap of the absorption band of perylene (spectrum 5) and the luminescence band of pyrene. At significant pressures the fluorescence of pyrene is completely absorbed by perylene, and the band of perylene is strongly reabsorbed (spectrum 4), but the vibrational structure is clearly expressed.

Fluorescence spectra 3 and 4 of perylene in mixtures with pyrene in Fig. 2 are displaced toward longer wavelengths in comparison to spectra 1 and 2 in Fig. 1, which were obtained under similar conditions in the absence of foreign gases, and they display a significant vibrational structure, as in the case of a decrease in the value of ν_{exc} [5]. A structure

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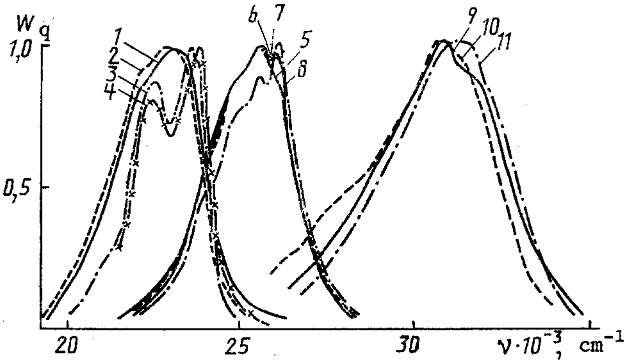

Fig. 1. Fluorescence spectra of vapors at various pressures. Perylene excited at λ_{exc} = 248 (1, 2, 4) and 365 nm (3) and T = 485 (1) and 493 K (2, 3): 1) p = 1.2 Pa; 2) 5.3 Pa; 3) 1.3 Pa; 4) in a mixture with pyrene at p = 1200 Pa. Pyrene excited at λ_{exc} = 248 (5-7) and 365 nm (8) and T = 448 (5), 473 (6), and 493 K (7, 8): 5) p = 5.3 Pa; 6) 387 Pa; 7, 8) 1200 Pa. p-Terphenyl excited at λ_{exc} = 248 (9, 10) and 302 nm (11) and T = 473 (9), 493 (10), and 453 K (11): 9, 11) p = 6.7 Pa; 10) 240 Pa.

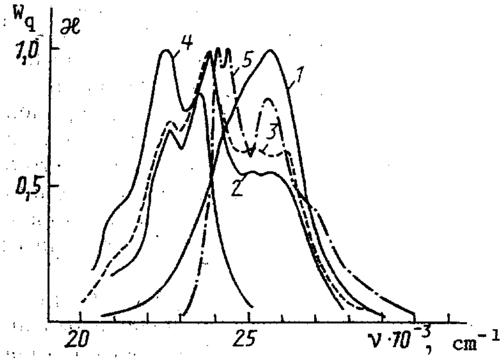

Fig. 2. Fluorescence spectra of a perylene—pyrene mixture (λ_{exc} = 248 nm): 1) p = $8 \cdot 10^{-2}$ and 53.3 Pa; 2) 0.4 and 387 Pa; 3) 5.3 and 1200 Pa; 4) 113 and $6.8 \cdot 10^3$ Pa; T = 448 (1), 473 (2), 493 (3), and 530 K (4); 5) absorption spectrum of perylene, T = 495 K.

is also displayed in the spectra of pyrene, but it is difficult to trace the changes in it due to the absorption of its fluorescence by perylene. The factor by which the concentration of the pyrene vapor exceeded the concentration of the perylene vapor in the present case was fairly high ($2.2 \cdot 10^2$).

Figure 1 presents the fluorescence spectrum of perylene vapor obtained by subtracting the fluorescence spectrum of pyrene from the overall spectrum of the mixture with consideration of the absorption of the fluorescence of pyrene by perylene (spectrum 4). A comparison of spectrum 4 with spectrum 3, which was obtained upon the excitation of pure perylene vapor by radiation with ν_{exc} = 27,400 cm^{-1}, i.e., with a frequency close to the inversion frequency of this compound ν_{inv} = 24,390 cm^{-1} [5], reveals that they are similar within the range of error of the method used to obtain spectrum 4. The value of the excess of vibrational energy which can be lost by the excited perylene molecules in a mixture with pyrene molecules determined from these data ΔE^* = 13,900 cm^{-1} is fairly large.

The fluorescence spectra of the perylene and p-terphenyl molecules do not overlap, and the fluorescence band of p-terphenyl falls in a region of weak absorption by perylene; therefore, in the case of a mixture of these molecules, manifestations of the vibrational structure can be traced in the spectra of both compounds (Fig. 3). The change in the fluorescence spectrum of perylene in this case is smaller than the change in its mixture with pyrene (compare spectrum 1 in Fig. 3 and spectrum 4 in Fig. 1). The is possibly due to the fact that in the present case, the ratio between the vapor pressures of p-terphenyl and perylene was approximately 5 times smaller than the ratio for pyrene and perylene. It should be noted that the

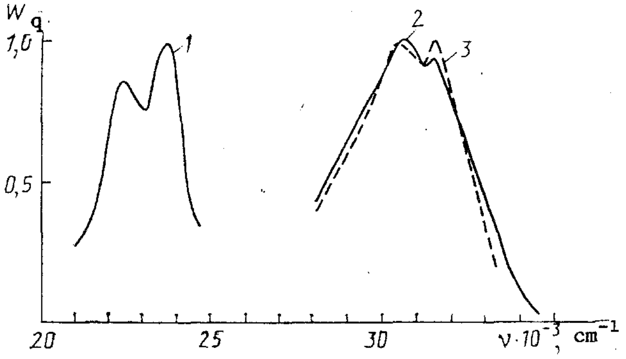

Fig. 3. Fluorescence spectra of a perylene–p-terphenyl mixtire (λ_{exc} = 248 nm): p = 6.7 and 267 (1, 3), $8 \cdot 10^{-2}$ and 6.7 Pa (2); T = 493 (1, 3) and 453 K (2).

TABLE 1. Lifetime of the Fluorescence of Perylene and p-Terphenyl Vapors at Various Pressures in Binary Mixtures

Substance	T, K	p of perylene, Pa	p of p-terphenyl, Pa	λ_{exc}, nm	τ_1, nsec	τ_2, nsec
Perylene	493	5,3	0	405	3,65	
	493	5,3	0	296	3,59	
	493	5,3	0	248	3,37	
	493	5,3	240	405	3,59	
	493	5,3	240	296	5,18	
	493	5,3	240	248	5,35	
	528	113	$3{,}3 \cdot 10^3$	280	5,89	
p-Terphenyl	493	0	240	302	1,2	5,11
	493	0	240	296	1,7	5,34
	493	0	240	248	1,54	5,56
	513	53,3	467	280	4,59	
	528	113	$3{,}3 \cdot 10^3$	280	3,17	
Solution of p-terphenyl in cyclohexane				302	0,9	

fluorescence spectrum of p-terphenyl in the presence of perylene (Fig. 3) has a more pronounced vibrational structure than the spectrum excited at ν_{exc} = 33,110 cm^{-1}, which is close to ν_{00}.

The observed changes in the fluorescence spectra of the vapors of the compounds considered indicate that the exchange of vibrational energy between the component of the mixture occurs in the binary mixtures.

In order to study the character of the emission of polyatomic molecules in binary mixtures in greater detail, we carried out measurements of the time characteristics of the fluorescence for a perylene–p-terphenyl vapor. The lifetimes τ of the excited states of the perylene and p-terphenyl molecules were recorded at the wavelengths of the fluorescence maximum, i.e., at λ_{rec} = 425 and 325 nm, respectively.

The values of τ for perylene and p-terphenyl molecules in the absence of foreign molecules, as well as in mixture, for various wavelengths of the exciting radiation and pressures of the components of the mixture are presented in Table 1.

When p-terphenyl is present in perylene vapor, a considerable increase in the lifetime of the excited state is observed for excitation at $\lambda_{exc} < \lambda_{inv}$. In the case of p-terphenyl vapor, an addition of perylene vapor results in a transition from the nonexponential character of the fluorescence decay process to an exponential character. These findings attest to the fact that the interaction of the perylene and p-terphenyl molecules in a mixture of these two substances takes place over the course of a certain time period and depends on the quantity of vibrational energy stored in the excited molecules and the pressures of the components of the mixture. In cases in which polyatomic molecules participate in the process of the transfer of vibrational energy, their interaction has a complicated character. For example, in [6] the high efficiency of naphthalene molecules in the removal of the excess of vibrational energy from perylene molecules was noted, and it was postulated that the molecules undergo a quasichemical interaction with one another, which results in the prolongation of their collisional interaction.

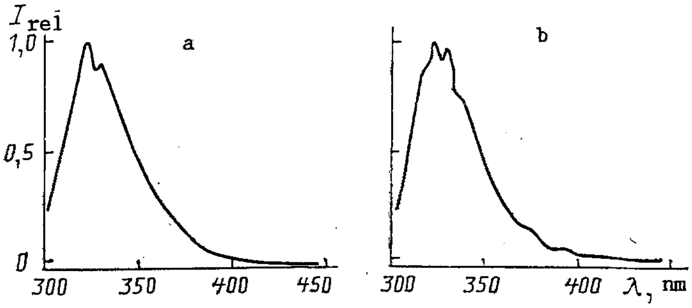

Fig. 4. Instantaneous fluorescence spectra of p-terphenyl vapor for λ_{exc} = 296.7 nm, T = 493 K, and p = 240 Pa in the presence of perylene vapor (p = 5.3 Pa) recorded 0.6 (a) and 11.2 nsec (b) after the maximum of the exciting pulse over a period of 2.5 (a) and 19.2 nsec (b).

Figure 4 presents instantaneous fluorescence spectra of p-terphenyl vapor mixed with perylene recorded in different time intervals of the decay curve. It is seen that spectrum b, which was obtained in the later period of the fluorescence decay process, displays clear manifestations of the vibrational structure, which attests to a decrease in the quantity of vibrational energy stored in the p-terphenyl molecules. It should be noted that the analogous spectrum for a pure vapor of p-terphenyl has a less pronounced vibrational structure.

Unfortunately, it was not possible to record the instantaneous spectra of perylene vapor in a mixture with p-terphenyl, since the luminescence of perylene in the mixture is much weaker than that of p-terphenyl (even if the pressure of the latter is an order of magnitude smaller). A slight increase in intensity is observed in instantaneous spectrum b on the long-wavelength wing in the region of the fluorescence spectrum of the perylene vapor (Fig. 4).

The calculation of the number of collisions of the excited molecules of one kind with the molecules of the other kind was carried out with the use of the well-known gas-kinetic formula

$$Z = 4{,}43\cdot 10^{23}\left(\frac{r_1+r_2}{\sqrt{T}}\right)^2 \sqrt{\frac{M_1+M_2}{M_1\cdot M_2}}\,p_g,$$

where r_1 and r_2 are the radii of the colliding particles (cm), M_1 and M_2 are the molecular weights of the particles, T is the absolute temperature, and p is the pressure of the foreign gas. The radii of the pyrene, perylene, and p-terphenyl molecules were evaluated on the basis of structural models and were assumed to be equal to 0.458, 0.467, and 0.682 nm, respectively. The number of collisions of excited perylene molecules at T = 493 K with pyrene molecules (p ~ 1200 Pa) was found to be Z ~ 10^8, and the number of collisions with p-terphenyl molecules (p ~ 240 Pa) was found to be Z ~ $4\cdot 10^7$, i.e., the changes in the fluorescence spectra of perylene vapor begin to be displayed at the values $\tau\cdot Z \sim 3.4\cdot 10^{-1}$ and $\tau\cdot Z \sim 1.4\cdot 10^{-1}$ for perylene—pyrene and perylene—p-terphenyl vapor mixtures, respectively. Appreciable changes in the time characteristics of these molecules are also significant when $\tau\cdot Z \sim 10^{-1}$. Thus, the data obtained attest to the great efficiency of the action of polyatomic molecules on one another in mixtures even at low concentrations. In all likelihood, significant mutual stabilization of polyatomic molecules occurs owing to the intermolecular interactions [7], as well as the collisions take place with the participation of molecules having a mean velocity greater than that assumed in the calculation of Z [8]. The effectiveness of the process of the stabilization of complicated molecules is high as a consequence of their high heat capacities. These data are of great importance in the selection of stabilizers for obtaining the optimal operating conditions for electric discharge in complicated molecules.

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QUENCHING OF THE LUMINESCENCE OF BENZOPHENONE VAPOR BY FOREIGN GASES

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Investigations of bimolecular interactions in the condensed phase have demonstrated the significant influence of the solvent on the mechanism and rate of the relaxation of photoexcitation energy in complicated organic compounds [1]. Therefore, the study of bimolecular interactions in the gaseous phase, where the influence of the medium may be neglected and the motion of the molecules is described well in the framework of the gas-kinetic model, would be of great interest.

In the case of polyatomic molecules in the gaseous phase, the bimolecular process of photoinduced electron transfer with the formation of an excited complex (an exciplex) has been studied very extensively [2-6]. As was shown in [4], the relaxation processes occurring in such systems are influenced to a considerable extent by the amount of stored vibrational energy acquired as a result of the absorption of a quantum of light. The yield of a photochemical reaction can, in principle, be regulated by varying the quantity of vibrational energy in the interacting molecules. A universal technique for altering the amount of stored vibrational energy is to add a chemically inactive foreign gas to the vapor of the compound under investigation (to utilize the phenomenon of stabilization—labilization [7]).

The influence of foreign gases on molecules in the triplet state was studied in [8-11]. It was established that the dependence of the $T_1 \rightarrow T_n$ absorption spectra on the concentration of the foreign gas is related to the process of intermolecular vibrational relaxation. In addition, a photochemical channel for the deactivation of the excitation energy of triplet states has not previously been detected.

It was shown in [12] that the photoexcitation of molecules of benzophenone (BP) in the gaseous phase in the presence of the hydrogen-containing foreign gas pentane (H—R) results in the transfer of a hydrogen atom from H—R to a molecule of benzophenone in the triplet state ($^3BP^*$) with the formation of a ketyl radical ($\cdot{}^2BP{-}H$) in a doublet state. The $D_1 \rightarrow D_0$ luminescence of the ketyl radical was observed with the aid of laser excitation. It was established that the main mechanism for the excitation of the liminescence of the ketyl radical is the radiationless intermolecular triplet-doublet transfer of energy from $^3BP^*$ to $\cdot{}^2BP{-}H$. These processes are described by the scheme

$$^3BP^* + H{-}R \rightarrow \cdot{}^2BP{-}H + \cdot R, \qquad (1)$$

$$^3BP^* + \cdot{}^2BP{-}H \rightarrow {}^1BP + \cdot{}^2BP{-}H^*, \qquad (2)$$

where $^2BP{-}H^*$ denotes an electronically excited ketyl radical.

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