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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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INTERACTION OF TRIPLET EXCITONS WITH EXCITED IMPURITY MOLECULES

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Physics

1. At high intensities of the exciting light in organic crystals, annihilation of triplet excitons may occur, or their interaction with excited molecules ([1–6]). In impurity crystals the latter process will be sufficiently effective only when the triplet state of the impurity molecules is appreciably populated. The intensity of the exciting light at which this condition is fulfilled can be considerably reduced by using transfer of the energy of the triplet state from the crystal lattice to the impurity molecules and the long lifetime of their triplet state. In the present work this method was applied to the investigation of the interaction of triplet excitons with excited impurity molecules in benzophenone crystals.

Purified benzophenone ([16]) was used for the investigation; in it the phosphorescence intensity of an unknown impurity Z does not exceed 10% of the intensity of the intrinsic phosphorescence of benzophenone crystals. It is interesting to note that in such crystals the quantum yield of phosphorescence upon heating from 90 to 293° K decreases by a factor of 3.5–4, whereas in crystals of unpurified benzophenone it decreases by a factor of 50–100. In "pure" crystals, on going from 90 to 293° K, a considerable broadening of the band, a shift of the spectrum to the long-wavelength side by 50–100 cm^{-1}, and the disappearance of impurity bands are observed (Fig. 1).

Luminescence of benzophenone crystals was excited by PRK-7 and DRSh-250 lamps. To investigate luminescence spectra and determine quantum yields, ISP-51 and ISP-28 spectrographs with photoelectric attachments were used ([7]).

Fig. 1. Phosphorescence spectra of purified benzophenone at 90° K *(1)* and at 293° K *(2)*. The arrows indicate the positions of impurity bands.

2. To study the processes of interaction of triplet excitons with excited impurity molecules, the dependence of the phosphorescence of benzophenone crystals with impurities Z, phenanthrene, naphthalene, and α-bromonaphthalene on the intensity of the exciting light L, 365 mμ, was investigated at 90° K. In benzophe-

Fig. 2 and Fig. 3 spectra

Figure 2: Fig. 2 and Fig. 3 spectra

none with impurity Z, whose phosphorescence decay time is approximately 0.1 sec, decreasing L by a factor of 11 noticeably increases the relative intensity of the impurity phosphorescence bands, while the intensity of the total phosphorescence of the crystal, within the accuracy of the measurements ($\approx 20\%$), does not change. The illumination of the sample under irradiation with the unattenuated light flux L_0 is equal to $\sim 5 \cdot 10^{16}$ photons $\cdot$ cm^{-2} $\cdot$ sec^{-1}.

In benzophenone crystals with a phenanthrene impurity ($C_\phi = 10^{-4}$ g/g), decreasing L by a factor of 11 does not noticeably change the quantum yield of phosphorescence of benzophenone B_b and the energy distribution in its spectrum, but slightly changes the phosphorescence spectrum of phenanthrene and increases its quantum yield B_ϕ by a factor of 4-4.5 (Fig. 2).

Changing the excitation from 365 to 313 mµ leads to a threefold increase in B_ϕ / B_b. This phenomenon is evidently due to a decrease in L under the indicated change in excitation. Attenuating the 313 mµ light by a factor of 14 also leads to an increase in B_ϕ by approximately 100-150%.

Increasing the concentration of phenanthrene in benzophenone noticeably decreases the above-discussed change in B_ϕ. In benzophenone crystals with admixtures of phenanthrene 0.1 g/g and anthracene ≈ 0.001 g/g, changing L by a factor of 11 does not noticeably change the fluorescence quantum yield of anthracene, which arises as a result of anthracene’ s own absorption of the exciting light, and increases B_ϕ by a factor of 2.

Fig. 2. Phosphorescence spectra of benzophenone crystals with an admixture of 10^{-4} g/g phenanthrene at $L = L_0$ (1) and $L = \frac{1}{11} L_0$ (2); b—benzophenone bands, ϕ—phenanthrene bands.

Fig. 3. Phosphorescence spectra of benzophenone crystals with an admixture of 10^{-4} g/g naphthalene at $L = L_0$ (1) and $L = \frac{1}{11} L_0$; b—benzophenone bands, n—naphthalene bands.

When benzophenone crystals with phenanthrene are heated from 90 to 293°K, the phosphorescence practically disappears. This quenching of phosphorescence is due to the small B_ϕ and to efficient energy transfer from benzophenone to phenanthrene at 293°K.

In benzophenone crystals with a naphthalene admixture 10^{-4} g/g at 90°K, decreasing L (365 mµ) by a factor of 11 increases B_ϕ approximately fourfold (Fig. 3). The strengthening observed at large L of the relative intensity of the second and third bands in the phosphorescence spectrum of naphthalene is probably due to superposition of benzophenone phosphorescence bands.

In benzophenone crystals with α-bromonaphthalene (a) $\approx 10^{-4}$ g/g, decreasing L by a factor of 11, within the accuracy of the measurements, does not change B_a, but leads to a noticeable change in the energy distribution in the impurity spectrum. In these crystals the phosphorescence of benzophenone and α-bromonaphthalene is also observed at 293°K.

3. Upon excitation of benzophenone crystals at 365 mμ, the phosphorescence of the impurities Z, phenanthrene, naphthalene, and α-bromonaphthalene is entirely due to capture of triplet excitons by the molecules of these impurities (7-10). Therefore the dependence of B on L found in the present work can be explained either by a change in the interaction of triplet excitons with impurity molecules, or by reabsorption of the impurity radiation.

In both cases, a strong dependence of B on L can occur only when a significant fraction of the impurity molecules has been transferred from the normal to the triplet state. In the experiments carried out, this condition is fulfilled for phenanthrene and naphthalene. Indeed, in these experiments

(at $C = 10^{-4}$ g/g) the number of impurity molecules in the absorbing layer with an area of 1 cm^2 is approximately $5 \cdot 10^{15}$, while the number of photons absorbed by them in 1 sec (at $L = L_0$) is $\approx 2 \cdot 10^{16}$. For phenanthrene and naphthalene the lifetime of the triplet state τ is several seconds, and therefore at $L = L_0$ the majority of triplet excitons will interact with impurity molecules that are in the triplet state. The population of the triplet state will be considerably smaller for impurity Z ($\tau \approx 0.1$ sec), and for α-bromonaphthalene ($\tau \approx 0.01$–0.02 sec. (^{11,12})) the overwhelming majority of molecules will be in the normal state.

Thus, the observed strong influence of the nature of the impurity molecules on the dependence of B on L is mainly determined by the difference in the lifetimes of their triplet states, which determines the degree of population of the triplet states.

For phenanthrene and naphthalene impurities, reabsorption due to triplet-triplet absorption ($T \rightarrow T_1$) cannot appreciably change their phosphorescence quantum yield. Indeed, for naphthalene such a process is energetically impossible, since the energy of the excited triplet state T_1 (45400 cm^{-1} (^{13,14})) is greater than twice the energy of the first triplet state. For phenanthrene such absorption is possible ($^{13-15}$), but its effect is small.

This gives grounds for asserting that the observed dependence of B on L is due to a change in the interaction of triplet excitons in benzophenone crystals with impurity molecules, which arises as a result of the increase in the population of triplet states with increasing intensity of the exciting light. The interaction of triplet excitons with impurity molecules in the normal state transfers them, as a result of energy transfer from benzophenone to the impurity, into the triplet state. Energy transfer from excitons to impurity molecules in the triplet state, apart from a possible change in the probability of exciton trapping, can transfer them from the first triplet state T to the excited singlet S_1 or triplet T_1 states.

Under the conditions of the experiments performed, fluorescence of phenanthrene and naphthalene was not observed. This can be explained either by a low probability of the transition $T \rightarrow S_1$, or by energy transfer from the excited impurity molecule S_1 to the surrounding benzophenone molecules. The absence of a significant change in the phosphorescence quantum yield of benzophenone when the intensity of the exciting light is changed evidently argues in favor of the first assumption. Therefore, it should be considered that the interaction of triplet excitons with impurity molecules already in the triplet state T mainly transfers them to the excited triplet state T_1. Since radiation corresponding to the transition $T_1 \rightarrow T$ is not observed, this transition is consequently nonradiative.

Thus, the decrease in the phosphorescence quantum yields of phenanthrene and naphthalene with increasing intensity of the exciting light is explained by the expenditure of exciton energy on carrying out the transition $T \rightarrow T_1$, with subsequent return of the impurity molecule to the initial state without emission of light. The decrease in the indicated quantum yields by more than a factor of two is probably due to the successive collision of several triplet excitons with one and the same impurity molecule during the time it remains in the triplet state.

A considerable decrease in B_ϕ and B with changing L is also observed at high impurity concentrations, when the relative population of the triplet states of the impurity molecules is small. In this case, the strong quenching of phosphorescence is possibly due to migration of the energy of the triplet state between impurity molecules located close to one another or forming impurity microcrystals.

inside a benzophenone crystal, which increases the probability of collision of a benzophenone triplet exciton with an impurity molecule in the triplet state.

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