Migration of Triplet-Level Energy in Benzophenone Crystals

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Migration of Triplet-Level Energy in Benzophenone Crystals

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1. The existence of transfer of triplet-level energy from donor molecules to acceptor molecules in frozen solutions was proved and studied in detail in a number of works ($^{1-5}$), which are of particular interest, since in them a new exchange-resonance mechanism of energy transfer between molecules was established. The results of these investigations give grounds to assume that triplet-level energy transfer can also occur between identical molecules. In the case of crystals such transfer may be multistep; i.e., the triplet-level energy may migrate along a considerable number of molecules. In the present work, to prove the existence of such a "triplet exciton" (^{5,10}), energy transfer in benzophenone crystals from the host substance to impurities of naphthalene and naphthacene is used.

Transfer of triplet-level energy from benzophenone to naphthalene in frozen solutions was established in the above-mentioned works. On passing to the crystal, the triplet level of benzophenone is lowered, but still remains higher than the triplet level of naphthalene molecules dissolved in it. Therefore, in crystals as well one may expect efficient energy transfer from benzophenone to naphthalene.

In the case of benzophenone with naphthacene, energetic considerations make possible the transfer of energy from the triplet level of benzophenone to the excited singlet level of naphthacene molecules. The possibility of energy transfer from a triplet level to a singlet level was noted in papers (^{6,8}) and experimentally proved in work (^{7}).

2. Chemically pure benzophenone was used for the investigations; it was additionally purified by recrystallization and by double distillation under vacuum. Benzophenone crystals with naphthalene were obtained by melting under vacuum the corresponding mixtures of the indicated compounds. The thickness of the crystals was usually 0.2–0.3 mm.

Absorption and luminescence spectra were recorded on a photoelectric setup in which an ISP-28 spectrograph was used as the monochromator. Since the phosphorescence spectrum of naphthalene consists of narrow bands, the slit widths and the rate of scanning of the spectrum were taken sufficiently small (the spectral slit width was about 5 cm^{-1}, and the scanning rate was 2 $\text{cm}^{-1} \cdot \text{sec}^{-1}$). The spectral sensitivity of the setup was determined from the spectrum

Fig. 1. Phosphorescence spectra of a benzophenone crystal with naphthalene impurity

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of an incandescent lamp with known brightness temperature. For excitation of luminescence, a PRK-7 lamp with a filter selecting the region around 365 mμ was used.

3. Preliminary investigations of the phosphorescence spectra, lifetimes, and quantum yields of solutions of benzophenone and naphthalene in a mixture of alcohol and ether at 90° K gave results close to those of ($^{1-5}$).

The absorption of a pure benzophenone crystal was studied at 20° C. In this case the absorption spectrum consists of four broad bands located in the region 26,400-30,000 cm^{-1}. In the region of 365 mμ the absorption coefficient is approximately 350 cm^{-1}.

At room temperature very weak phosphorescence is observed; lowering the temperature to 90° K leads to a considerable increase in its intensity. Investigations with an END-1 oscillograph showed that there are two kinds of emission. The principal emission has a duration

τ_b = 10–15 msec, while the weaker one (with an intensity approximately 10 times less than the first) has $\tau \approx$ 2–3 sec.

The phosphorescence spectra of benzophenone crystals with naphthalene impurity, for some of the investigated concentrations of the latter, are presented in Fig. 1. The phosphorescence spectra of benzophenone and naphthalene overlap strongly, and this makes it difficult to determine the quantum yields of phosphorescence of the individual components. However, significant differences in the band widths,

Fig. 1. Phosphorescence spectra of a benzophenone crystal with naphthalene impurity at $\lambda_{\text{ex}} = 365$ mμ; $T = 90°$ K.
a–$C_{\text{H}} = 0$; b–$C_{\text{H}} = 3 \cdot 10^{-4}$ g/g; v–$C_{\text{H}} = 10^{-3}$ g/g; g–$C_{\text{H}} = 10^{-2}$ g/g.

some displacement of the maxima of the benzophenone bands relative to the naphthalene bands, and the absence of overlap in the short-wavelength part of the benzophenone phosphorescence spectrum make it possible to determine these quantum yields with satisfactory accuracy (20–25%). It should be noted, however, that the values of the quantum yields of naphthalene may be considerably overestimated owing to possible distortion of the band contour during recording, caused by the small band width and the low dispersion of the instrument. The dependence of the quantum yields of benzophenone (B_b) and naphthalene (B_{H}) on the concentration of naphthalene (C_{H}) is presented in Table 1. For pure benzophenone the quantum yield is conventionally taken

Fig. 2. Phosphorescence spectra of benzophenone with naphthacene impurity

Figure 2: Fig. 2. Phosphorescence spectra of benzophenone with naphthacene impurity

to be equal to 1.00. At higher concentrations of naphthalene, a nonuniform distribution of its molecules in benzophenone is possible.

Table 1

$C_H, \frac{mol}{mol}$	0	$2 \cdot 10^{-4}$	$3 \cdot 10^{-4}$	$5 \cdot 10^{-4}$	$1 \cdot 10^{-3}$	$3 \cdot 10^{-3}$	$7 \cdot 10^{-3}$	$1 \cdot 10^{-2}$	$1.5 \cdot 10^{-2}$
B_b, measured	1.00	0.87	0.76	0.51	0.30	0.16	0.11	0.09	0.08
B_b, calculated	1	0.77	0.69	0.57	0.40	0.18	0.09	0.065	0.045
B_H, measured	0.00	0.08	0.14	0.24	0.34	0.43	0.47	0.48	0.49

In the case of a mixture of benzophenone with naphthalene, slow cooling of the melt leads to separation of naphthalene into a separate phase in the form of microcrystals. In this case there is no appreciable luminescence of naphthacene. To obtain a molecular solution of naphthacene in benzophenone, the molten mixture must be cooled very rapidly by immersing the test tube containing it in liquid oxygen. With such cooling the structure of benzophenone differs from the usual one. The presence of a change is indicated by the phosphorescence spectrum of benzophenone, which differs considerably from the spectrum of the stable modification of a benzophenone crystal and resembles the spectrum of a frozen solution of benzophenone.

Fig. 2. Phosphorescence spectra of benzophenone with naphthacene impurity at $\lambda_B 365$ mμ;
$T = 90°$ K. 1—$C_{naph} = 0$; 2—$C_{naph} = 4 \cdot 10^{-5}$ g/g; 3—extrapolated spectrum of benzophenone; 4—luminescence spectrum of naphthacene

The luminescence spectra of benzophenone and naphthacene also overlap strongly (Fig. 2). These spectra can be separated owing to the fact that there is no overlap in the short-wavelength region of the benzophenone spectrum. This circumstance, in combination with the assumption that the energy distribution in the benzophenone spectrum does not change upon addition of naphthacene, makes it possible to isolate the benzophenone spectrum. By subtracting this spectrum from the total spectrum of benzophenone with naphthacene, one can obtain the spectrum due to emission of naphthacene. The spectrum obtained in this way agrees rather well with the luminescence spectrum of naphthacene directly excited by λ 436 mμ (in this case benzophenone phosphorescence does not occur). The quantum yields, determined from the areas of the separated spectra, are given in Table 2. At high concentrations, part of the naphthacene may separate in the form of microcrystals, and this may lead to underestimated values of the quantum yield of naphthacene.

Table 2

$C_{\text{naph}}, \frac{\text{mol}}{\text{mol}}$	0	$4 \cdot 10^{-5}$	$2 \cdot 10^{-4}$	10^{-3}
$\bar{P}_{\text{b}}$	1.00	0.94	0.73	0.25
B_{naph}	0.00	0.02	0.07	0.22

At a naphthacene concentration of 10^{-3} mol/mol, the duration of the total emission is approximately 25% less than the emission duration of pure benzophenone. The duration of the total emission approximately coincides with the duration of emission in the region 19 000 cm^{-1}, which is due mainly to naphthacene. When naphthacene luminescence is excited by 436 mμ, no afterglow is observed.

4. Since naphthalene does not absorb λ 365 mμ, it is clear that in the indicated emis-

under our conditions its emission is due to energy transfer from benzophenone. Such energy transfer can only be radiationless, since in the region of benzophenone phosphorescence there is only very weak triplet absorption of naphthalene.

In work (5) it was shown that energy transfer from the triplet level of benzophenone to the triplet level of naphthalene occurs as a result of exchange-resonance interaction. In this case the transfer radius is equal to 13 Å, which is in approximate agreement with our data.

Quenching of donor phosphorescence in solution is well (5, 9) described by Perrin' s formula: $B_6 = B_{60} e^{-\alpha N' C}$, where B_{60} is the quantum yield of benzophenone (donor) in the absence of naphthalene (acceptor); α is the volume of the sphere of action of quenching, which for the benzophenone—naphthalene pair is $9.2 \cdot 10^{-21}$ cm^3; N' is the number of naphthalene molecules in 1 cm^3 of solvent at a naphthalene concentration $C_{\text{n}} = 1$ g/g. In our case the solvent is the donor itself—benzophenone. Assuming the indicated formula to be valid for this case as well, at naphthalene concentrations $5 \cdot 10^{-4}$, 10^{-3}, and 10^{-2} g/g we obtain for B_6/B_{60} the following values: 0.98, 0.95, and 0.61. In reality, as our experiments show, B_6/B_{06} for the indicated concentrations is equal to 0.51; 0.30; and 0.10.

To explain this discrepancy, it is evidently necessary to assume the existence of energy migration in benzophenone crystals. As a result of such migration, energy will be brought to the sites where naphthalene molecules are located.

Upon excitation of benzophenone, only phosphorescence is observed, which indicates very rapid internal conversion of the excited singlet level into a triplet level. It follows from this that energy migration must occur over triplet levels. The absence of energy migration of the excited singlet level is confirmed by the absence, established by us, of energy transfer from benzophenone to anthracene.

The dependence of the quantum yield of benzophenone on the concentration of naphthalene is satisfactorily (Table 1) described by the formula $B_6 = B_{60}/(1 + \beta C_\mathrm{n})$, where β determines the probability of capture of a "triplet exciton" by naphthalene molecules at a concentration of 1 mole/mole. For the pair under consideration, β is approximately equal to $1.5 \cdot 10^3$.

Energy transfer is also observed in benzophenone containing naphthacene as an impurity. In this case energy transfer occurs from the triplet level of benzophenone molecules to the first excited singlet level of naphthacene molecules. Direct proof of such transfer is the presence of naphthacene afterglow, which is absent upon direct excitation of naphthacene ($\lambda_\mathrm{v} = 436$ mμ). This afterglow is due to a delay in the supply of energy to naphthacene molecules. The presence of energy transfer from the triplet level is also confirmed by a decrease in the duration of benzophenone phosphorescence upon addition of naphthacene.

Note added in proof. After the article had been submitted for publication, we became aware of works (11, 12), in which evidence is also given for the existence of a triplet exciton. It should also be noted that a brief communication on the existence of a triplet exciton in benzophenone crystals was made by us as early as September 1962 at the XI Conference on Luminescence.

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