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CONCENTRATION DEPOLARIZATION OF PHOSPHORESCENCE AND ENERGY TRANSFER BETWEEN LIKE MOLECULES

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Two new findings are reported on the energy transfer between like molecules in rigid glass at 77 K: The depolarization of the phosphorescence is not mainly caused by the triplet-triplet energy transfer, but essentially by the singlet-singlet transfer. And the concentration where the depolarization starts to take place depends on the individual phosphor compounds.

We here report two new findings on the energy transfer between like molecules obtained from observation of the concentration depolarization in the phosphorescence and fluorescence of some aromatic compounds through populating the luminescent states via excited singlet states. One is the finding that essentially the triplet-triplet energy transfer is not responsible for the concentration depolarization of the phosphorescence,[1)] which is definitely contrary to the statement accepted in the literature;[2)] as Fig. 1 shows, the depolarization of the phosphorescence was found to behave in the same way as that of the fluo-

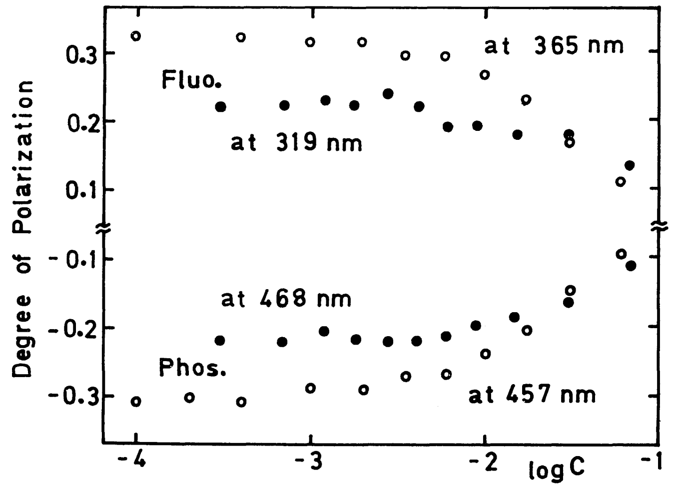

Fig. 1. Concentration depolarization of the phosphorescence and fluorescence of naphthalene-d_8 (●) and benzo(f)quinoline (o) observed in ethanol glass at 77 K. C denotes molar concentration at room temperature.

rescence, which implies that mainly the singlet-singlet transfer causes the depolarization, as will be detailed later on. The other is the finding that the depolarization of the phosphorescence starts to take place at different concentrations ranging from 10^{-3} to 10^{-2} M, depending on the phosphor compounds,$^{1)}$ in a keen contrast to the fixed starting concentration of 10^{-2} M claimed in a previous study;$^{2)}$ this fixed concentration was regarded as consistent with the exchange mechanism for the triplet-triplet energy transfer. It should be noted that this second finding is apparently compatible with the first one.

These two findings are based on the results of this study on the various phosphor compounds appropriately chosen, benzo(f)quinoline, benzo(h)quinoline, phenanthrene-h_{10}, phenanthrene-d_{10}, naphthalene-d_8, 1-chloronaphthalene, 1-bromonaphthalene, quinoxaline, benzophenone, and pyrazine. The last five compounds have been chosen because they are practically non-fluorescent.

As for the solvent, ethanol was used as obtained from Wako Pure Chemical Industries, Ltd. (the super special grade, 99.5 vol%). The phosphor compounds studied were obtained from Tokyo Kasei Kogyo Co., Ltd. unless otherwise specified. Benzo(f)quinoline as well as benzo(h)quinoline was treated with sulfuric acid and sodium hydroxide as described previously,$^{3)}$ and then sublimed under reduced pressure. Phenanthrene-h_{10} obtained from Yoneyama Yakuhin Kogyo Co., Ltd. was recrystallized from ethanol three times, subjected to oxidation with chromic acid, distilled under reduced pressure over metallic sodium, and finally zone refined. Perdeuterated naphthalene and phenanthrene were obtained from E. Merck Ag., Darmstadt, Germany, and were used without further purification. Quinoxaline, 1-chloronaphthalene, and 1-bromonaphthalene were distilled under vacuum. Benzophenone was recrystallized from ethanol and zone refined with 250 passes. Pyrazine was sublimed twice in a vacuum.

All the measurements were made at 77 K in ethanol glass. Emission spectra were recorded with a Bausch & Lomb 500-mm grating monochromator equipped with an RCA 1P28 photomultiplier, and a Hitachi recorder model QPD-54. A rotating-disk phosphoroscope was used to observe phosphorescence.

Excitation radiation was obtained from a 1-kW super-high-pressure mercury arc lamp, model Orc-CH-612. Excitation wavelengths were selected by means of a Farrand 160-mm grating monochromator and appropriate filter combinations; for exciting phosphorescence, we used a combination of a Corning glass filter 7-54 and a saturated aqueous solution of nickel sulfate, while for exciting fluorescence we further used an aqueous solution of D_3P (0.3g/l) which is known as a band-pass filter for the 2537-Å mercury line.$^{4)}$ This low concentration was chosen so as to enable us to observe fluorescence from the samples sealed in the Pyrex cells (1-2 mm thickness) after degassing by the freeze-pump-thaw cycles.

A Glan-Thompson prism polarized the excitation radiation, while a Polaroid UV sheet polarizer, HNP-B, analyzed the emitted radiation. Corrections were taken into account to the polarization introduced by the analyzing monochromator. A neutral filter of 10% transmittance made of four pieces of brass-wire gauze was used to study the effect of the excitation intensity on the depolarization. The fluorescence depolarization was observed at the vibronic bands

Table 1. Summary of the typical results

Phosphor compound	Depol. concn. (10^{-3}M)$^{a)}$ Phos.	Fluo.	Phosphorescence lifetime (sec)	Quantum yield$^{b)}$ Phos.	Fluo.
naphthalene-d_8	5	5	21.0	0.41	0.23
phenanthrene-h_{10}	3	(c)	3.8	0.09	0.12
phenanthrene-d_{10}	3	(c)	15.5	0.24	0.10
benzo(f)quinoline	2	2	3.1	(f)	0.41
benzophenone	15	(d)	0.0058	0.75	$\sim$0
pyrazine	(e)	(d)	0.020	0.30	0.0006
1-bromonaphthalene	10	(d)	0.016	0.27	0.0016

a) Room-temperature molar concentration where the depolarization starts to take place.
b) Refs. 5 and 6.
c) Parallel and perpendicular components are equal in intensity. See text.
d) Too weak to be observed.
e) No depolarization was found up to 10^{-1} M, the highest concentration studied.
f) Numerical value is not available. The phosphorescence is very strong.

next to the 0,0-band.

Now, we turn to the description of the important results obtained, inclusive of the above-mentioned two findings. A summary of the typical results is presented in Table 1, where the quantum yields are cited from Refs. 5 and 6.

(1) As Fig. 1 shows, and as mentioned at the beginning of this report, the concentration depolarization of the phosphorescence was found to coincide with that of the fluorescence. The fluorescence was excited via the second excited singlet state, while the phosphorescence was excited via the first excited singlet state. Therefore, it is clear that the energy transfer from the molecules in the fluorescent state to those in the ground state is responsible for the observed depolarization. This coincidence was found for the two benzoquinolines and naphthalene-d_8. In the case of phenanthrene-h_{10} and phenanthrene-d_{10}, the parallel and perpendicular components of the fluorescence were practically equal in intensity even at the lowest concentrations studied, and hence no concentration dependence could be investigated.

(2) The concentration where the depolarization starts to take place depends on the phosphor compounds, as mentioned above and as can be seen from Table 1.

(3) In the concentration depolarization of the phosphorescence, no appreciable variation was found from vibronic band to band, that is, no appreciable wavelength dependence was found. This would mean, together with the results described in (1), that the scattering of light is not important in the depolarization observed. Visual inspection also could not find any sign of occurrence of the microcrystals or precipitations. Thus, the microcrystal or precipitation formation would not be involved.

(4) No concentration dependence was found in the phosphorescence lifetime up

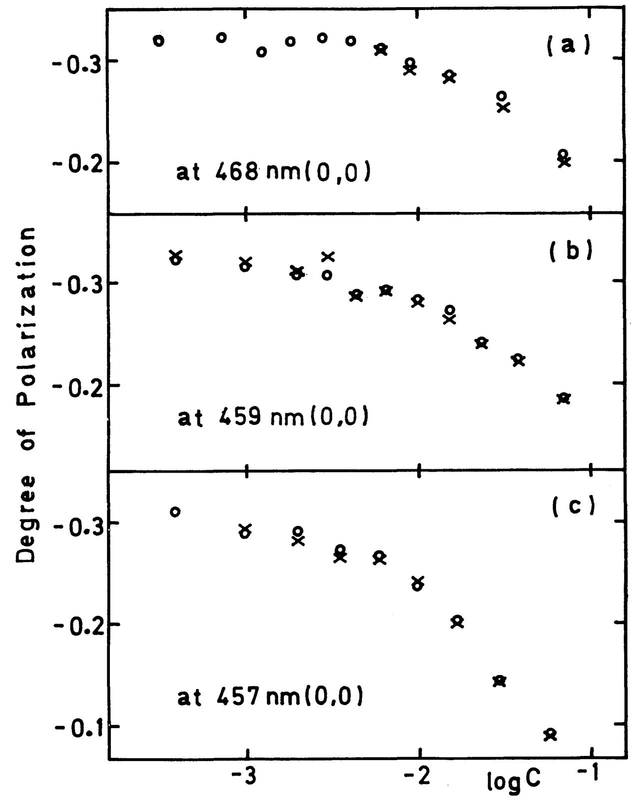

Fig. 2. Effect of the excitation intensity, I_{exc}, on the depolarization of the phosphorescence observed in ethanol glass at 77 K. C denotes molar concentration at room temperature. $I_{exc}(o)/I_{exc}(x) = 10$.
(a) Naphthalene-d_8,
(b) phenanthrene-d_{10},
(c) benzo(f)quinoline.

to the concentrations as high as 10^{-1} M for any one of the phosphor compounds studied, which implies that no process leading to the phosphorescence quenching is involved in the observed depolarization.

(5) As Fig. 2 shows, the depolarization observed is independent of the excitation intensity, at least under the excitation conditions of this study. Therefore, as implicitly assumed in (1), it may be concluded that the interaction between the excited molecules, say the triplet-triplet annihilation, is not involved essentially.

(6) The slope of the curve representing the concentration depolarization is independent of the phosphorescence lifetime, contrary to the description found in Ref. 2(a). Therefore, the depolarization is not of the phenomenon on the time scale of the phosphorescence decay. Observations with the perdeuterated compounds particularly contributed to this finding.

(7) Perdeuterated phenanthrene has the same concentration depolarization of the phosphorescence as that found for the corresponding perprotonated compound in spite of its much longer lifetime.

(8) In addition to (7), the degree of polarization of the phosphorescence is independent of the time interval subsequent to the cessation of excitation. As in the case of (6), this as well as (7) also means that the depolarization observed is not of the time scale of the phosphorescence duration.

(9) No excimer fluorescence was found in this study. This implies, in accordance with the contents of (3), that the phosphor molecules were so well distributed in rigid glass that the formation of dimer or aggregates was

improbable, or at least, insignificant.

(10) In the case of pyrazine, a practically non-fluorescent compound, the concentration depolarization of the phosphorescence was not found up to the concentrations as high as 10^{-1} M, contrary to the results published in Ref.2(a). This is another manifestation of the importance of the singlet-singlet energy transfer in the concentration depolarization in question. Here, it should be noted that the phosphorescence of pyrazine has a considerably high quantum yield.

(11) The phosphorescence quantum yield seems to be indifferent to the depolarization in question, as can be seen from Table 1.

All the results listed above are consistent with the singlet-singlet energy transfer. However, as for 1-chloronaphthalene, 1-bromonaphthalene, and quinoxaline, the concentration depolarization of the phosphorescence starts around 10^{-2}, 10^{-2}, and 5×10^{-3} M, respectively. As shown in Table 1, the starting concentration was found to be 1.5×10^{-2} M for benzophenone. Therefore, the results obtained for these four practically non-fluorescent compounds should be interpreted with some reservation. This is the reason why we do not affirmatively claim that the concentration depolarization of the phosphorescence is caused exclusively by the singlet-singlet energy transfer. In this connection, it would be significant to point out the importance of measuring the quantum yield of very weak fluorescence as precisely as possible. For lack of these data, we can not go into the details of the mechanism involved in the phosphorescence depolarization found for these non-fluorescent compounds. Incidentally, it would also be significant to perform a direct excitation into the phosphorescent state so that we may directly investigate the effect of the triplet-triplet energy transfer, if any, without being bothered by the participation of the excited singlet states.

Finally, it can be suggested that the famous experiment of Terenin and Ermolaev7) on the benzophenone-naphthalene system may be re-examined in the light of the results of this study. In other words, formation of the molecular complexes might be responsible for the energy transfer observed, since now the triplet-triplet energy transfer has been found to be inefficient and it should be of the short range phenomenon, and since the appreciable energy transfer occurred at the very high concentrations of the order of 10^{-1} M in their study.

Detailed description of the results and discussion will be presented elsewhere.

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