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Phosphorescence Characteristics of Benzophenone under High-Power Excitation

(Received May 20, 1966)

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Abstract

Emission characteristics of phosphorescence of benzophenone in alcohol solid solution are studied at the temperature of about -150°C . Under low excitation a decay curve of phosphorescence intensity is exponential, but under high excitation it deviates from the exponential and the enhancement of decay is observed. The result may be explained in terms of the induced emission and the triplet-triplet reabsorption.

I. Introduction

Feasibility of an organic laser making use of an organic material as an active element has been discussed in many places^{1), 2), 3)}. Except for a Ramman laser and a rare earth chelate laser, however, no success of a laser oscillation has been obtained.

In principle, fluorescence or phosphorescence phenomenon of an organic material may be considered to be useful for a laser action. Brock et al.⁴⁾ first suggested an utility of organic molecules with conjugated bonds as potential laser materials. Because of the spin selection rules, in the case of phosphorescence, the decay time is longer than that in the case of fluorescence. Therefore, making use of organic phosphors, the population inversion may be more easily obtained.

Morantz et al.^{5), 6), 7)} reported observations of the stimulated emission from several organic phosphors. They showed the oscillographic traces of "spikes" or oscillations of phosphorescence emission, but they did not examine the wave length

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1) E. J. Schimitschek and E. G. K. Schwarz, *Nature*, 196, 832, (1962).

2) D. L. Stockman, W. R. Mallory and K. F. Tittel, *Proc. IEEE.*, 52, 318, (1964).

3) H. Winston, O. J. Marsh, C. K. Suzuki and C. L. Telk, *J. Chem. Phys.*, 39, 267, (1963).

4) E. G. Brock, P. Csavinszki, E. Hormats, H. C. Nedderman, O. Stirpe and F. Unteroeitner, *J. Chem. Phys.*, 35, 759, (1961).

5) D. J. Morantz, B. G. White and A. J. C. Wright, *Phys. Rev. Lett.*, 8, 23, (1962).

6) D. J. Morantz, B. G. White and A. J. C. Wright, *J. Chem. Phys.*, 37, 2041, (1963).

7) D. J. Morantz, "Optical Maser", Polytechnic Press, Brooklyn, N. Y., pp 491, (1963).

and coherency of this oscillation.

Lempicki⁸⁾ and Wilkinson⁹⁾ have attempted to detect again these results, but they have failed in. They showed theoretically that the amplified stimulated emission was very difficult.

In this work we have also attempted to realize this amplified stimulated emission and studied in more detail the emission characteristics of benzophenone in rigid glass solution under high power excitation by Xenon flash lamp.

II. Experimental results

(A) Sample material and apparatus

The active element used in this investigation was guaranteed reagent grade benzophenone which was commercially obtained from the Tokyo Kasei Co.. It was used without any further purification. This active element was dissolved in the mixture of ethylalcohol and methylalcohol (1:1 in volume) and then this solution was refrigerated gradually in a quartz cell to form a glassy transparent sample.

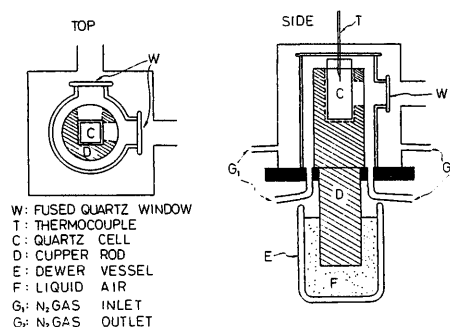


Fig. 1. Sample holder for low temperature measurements.

The sample holder used for low temperature measurements is schematically depicted in Fig. 1. A copper rod (30 mm ϕ) is drilled parallel to the rod axis to make a hollow cavity, in which the quartz cell containing the sample solution is held.

Two windows are opened perpendicularly to the rod axis. The sample is irradiated by an incident light for excitation through one of the windows and a phosphorescence emission is detected through the other. The lower part of the copper rod is put in a Dewar vessel containing liquid air, then the sample in the hollow cavity is refrigerated by thermal contact with the rod. Thus the temperature of the sample drops down to about -150°C from room temperature in about half an hour. The spectral analysis on the emission and absorption was carried out with Hitachi 139 spectrophotometer and its fluorescence measuring attachments.

8) A. Lempicki and H. Samelson, *Appl. Phys. Lett.*, 2, 159, (1963).

9) F. Wilkinson and E. B. Smith, *Nature*, 199, 691, (1963).

Before the measurements the spectral sensitivity of the photomultiplier, which is a part of the spectrophotometer, was examined by means of the incandescent standard light source.

(B) Absorption and emission spectrum

The molar extinction coefficient of benzophenone, which is calculated from the transparency measurement, is shown in Fig. 2 over the range of $300\text{ m}\mu$ to $400\text{ m}\mu$ at room temperature.

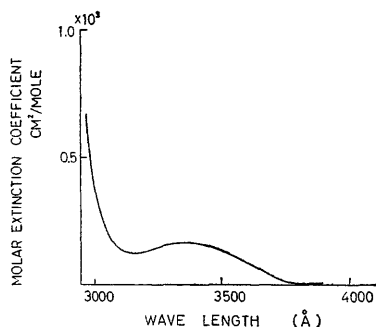


Fig. 2. Absorption Spectrum.

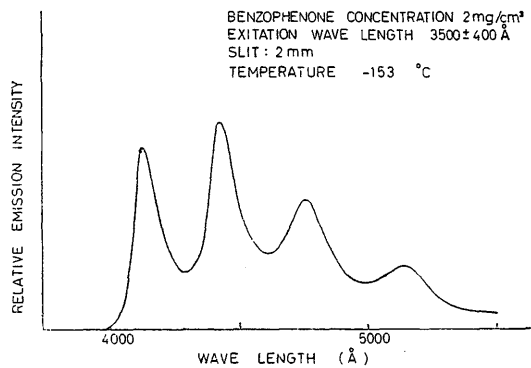


Fig. 3. Emission spectrum (benzophenone)

The excitation wave length for emission measurements was selected so that the emission intensity became maximum and it was $350 \pm 40\text{ m}\mu$. The slit of the monochromator was fixed to 2 mm in width. The emission spectrum is shown in Fig. 3 for the benzophenone concentration of 2 mg/cm^3 (1.1×10^{-2} mole/l.) at -153°C . The spectrum has peaks at 414, 443, 476 and $515\text{ m}\mu$. According to the results of Ferguson and Tinson¹⁰, the phosphorescence of benzophenone dissolved in light petroleum has blue and green emission bands. For the low concentrations, the blue emission band is dominant and the green is faint. For the high concentration, however, the green band emission increases and the emission spectrum loses its vibrational structure near the concentration of 10^{-2} mole/l.. Comparing with these results, emission peaks obtained in our measurements at low temperature rather correspond, even though with a blue shift, to those of the blue band and not to those of the green band reported by Ferguson and Tinson. The fifth peak of the blue band, which was pointed out by Ferguson and Tinson, was not observed in our measurements and also was not reported by Lewis and Kasha¹¹.

Ferguson and Tinson suggested also the excitation mechanism due to intermolecular energy migration for the green band of the phosphorescence of benzophenone in light petroleum. To make an intermolecular energy exchange possible,

10) J. Ferguson and J. Tinson, J. Chem. Soc., 3083, (1952).

11) G. N. Lewis and M. Kasha, J. Amer. Chem. Soc., 67, 944, (1945).

two molecules must approach within the critical distance below which the exchange can occur¹²⁾. In our rigid solution, however, the frozen benzophenone molecules are hindered to approach within this distance in spite of the high concentration of 1.1×10^{-2} mole/l.. Therefore, we could not observe the emission corresponding to the green band that was reported by Ferguson and Tinson.

(C) Phosphorescence emission intensity

The phosphorescence emission intensity at the wave length of $443 \text{ m}\mu$ was examined for various concentrations of benzophenone at low temperatures.

The conditions in measurement, that is, the wave length for excitation, the slit width of the monochrometer and so on, were the same as those of emission spectral measurements. The concentration dependence of the emission intensity at -153°C is shown in Fig. 4. In the lower concentration region, the emission intensity increases in proportion to the solute concentration, but in the higher region the increment of the emission intensity becomes small and finally the intensity begins

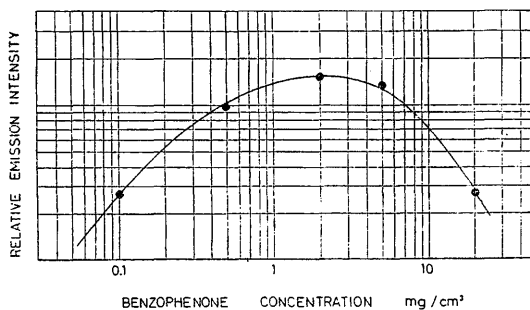


Fig. 4. Concentration dependence of emission intensity.

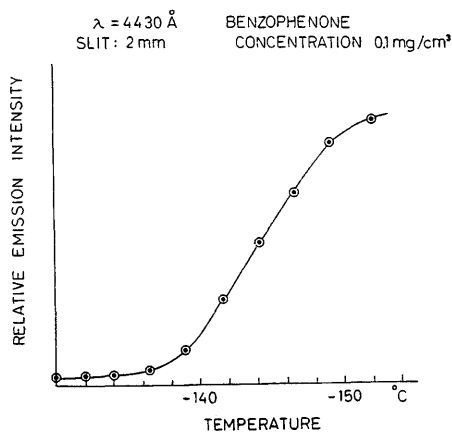


Fig. 5. Temperature dependence of emission intensity.

12) T. Förster, Ann. Physk., 2, 55, (1948).

to decrease because of the so called concentration quenching. The maximum of the emission intensity appears at the concentration of 2.0 mg/cm^3 ($1.1 \times 10^{-2} \text{ mole/l.}$).

In general, phosphorescence emission intensity depends strongly upon the temperature of phosphor. In our measurements, we could observed no appreciable emission in the benzophenone-alcohol solution at room temperature. However, the emission intensity increased abruptly below about -140°C . The temperature dependence of the emission intensity is shown in Fig. 5 at the concentration of 0.1 mg/cm^3 .

(D) Phosphorescence decay time

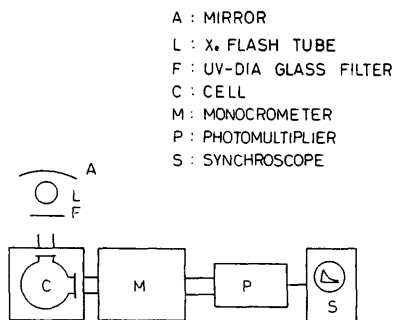


Fig. 6. Decay time measurement apparatus.

The schematic diagram of the apparatus for phosphorescence decay time measurement is shown in Fig. 6. A Xenon flash tube was fired by discharging oil condensers through an 100mH choke coil. The total capacity of the condensers was $400 \mu\text{F}$ and the condensers were charged up to 1000 volts. In this case the fire duration of the tube was about 0.6msec. It may be considered that this duration of decay time is not a serious objection for the rough estimation of decay time, the magnitude of which is a few milliseconds. A mirror was set behind the flash tube so that the flash light for excitation might impinge upon the sample effectively. A UV-

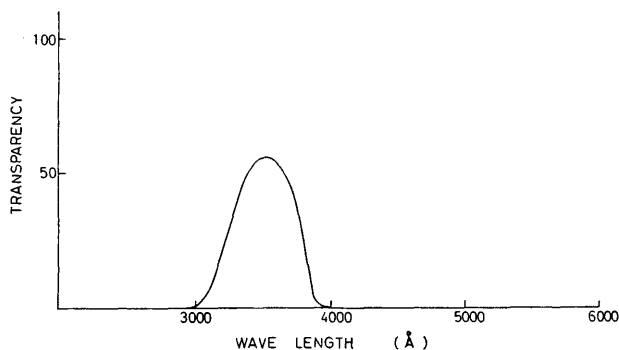
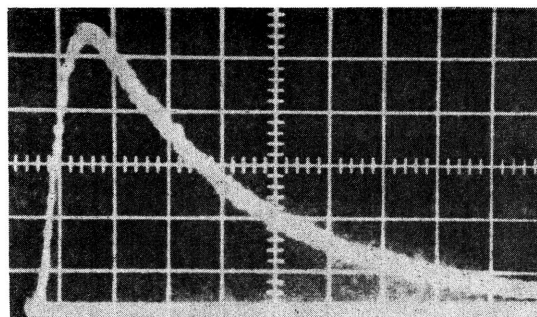


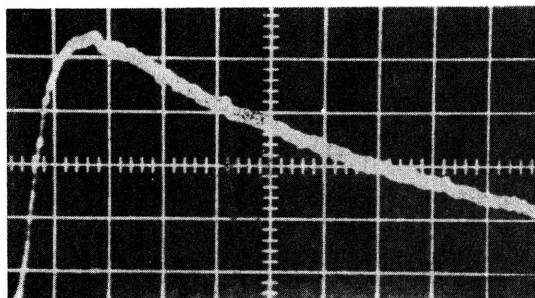
Fig. 7. Transparency of UV-D1A glass filter.

D1A glass filter was used to cut off the spectral region of the flash unnecessary for excitation of the sample material. The transparency of the UV-D1A filter is shown in Fig. 7. The emission of $443\text{ m}\mu$ wave length was detected by the photomultiplier after the phosphorescence emission from the sample passes through the monochromator. The time variation of emission intensity was traced by a synchroscope.

We examined the scattered light from the source with use of a cell containing only alcohol instead of the sample cell under the same conditions, and we observed no appreciable scattered light. As a result of this observation, it may be considered that no scattered light from the source was superposed on the observed



Sweep 0.5 msec/div.
Vertical gain 0.1 v/div.
(a) Supply voltage 1000 v (200 joules)
Temp. -144°C .
Decay time 1.6 msec.



Sweep 0.5 msec/div.
Vertical gain 0.1 v/div.
(b) Supply voltage 1000 v.
Temp. -151°C .
Decay time 4.2 msec.

Fig. 8. Time variation of the phosphorescence intensity of benzophenone under low excitation.

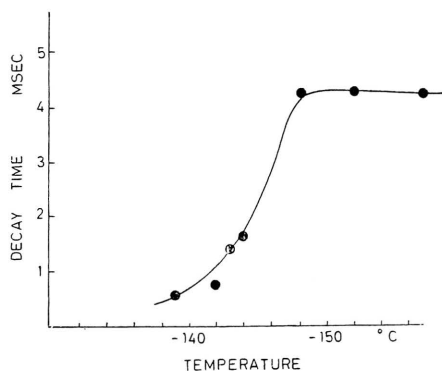


Fig. 9. Temperature dependence of emission decay time (benzophenone).

phosphorescence emission from the sample.

The typical traces of the time variation on the synchroscope are shown in Fig. 8. The decay time of the phosphorescence emission of benzophenone in the rigid glass solution can be computed from these traces. The computed values, together with the measurement conditions, are given in the caption of Fig. 9.

(E) Phosphorescence decay rate under high-power excitation

The time variation of the phosphorescence intensity at the wave length of $443\text{ m}\mu$ was oscillographically traced under high-power excitation. The experimental ap-

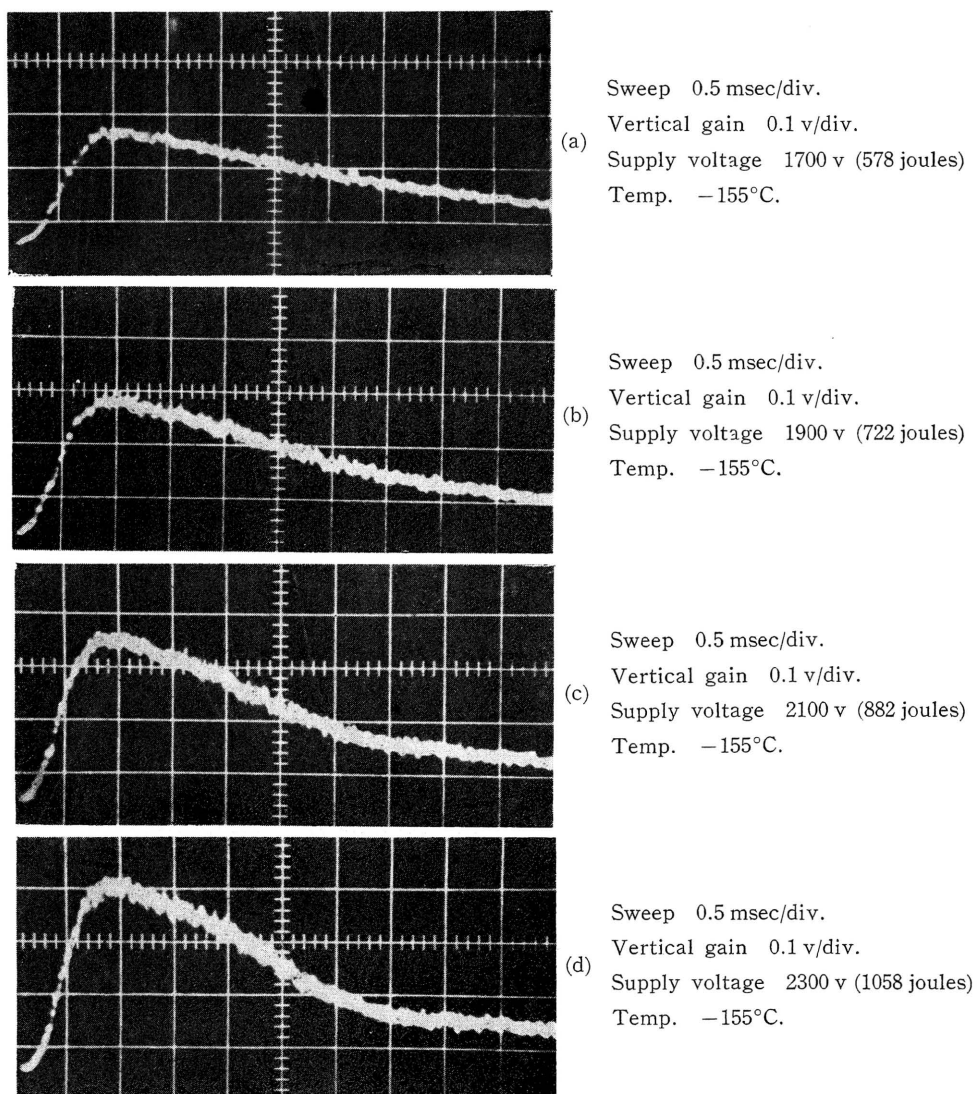


Fig. 10. Time variation of the phosphorescence intensity of benzophenone under high excitation.

paratus was arranged in the same way as the decay time measurements with a slight improvement for much strong excitation. The quartz cell used in this experiment was $1 \times 1 \times 4.5$ cm in size. A pair of parallel side plates of the quartz cell were coated with thin silver film in order to increase the radiation density in the cell by reflection. One of these parallel side plates has the transparency of 2% (nearly 98% reflection) and the other has no transparency (nearly 100% reflection) at the wave length under consideration. The degree of parallelism of the cell was about 5 minutes. The phosphorescence emission was observed through the 2% transmitting side plate. The sample was irradiated through one of the unsilvered side plates of the cell. The power supplied to the Xenon flash tube was up to about 1K joule which was obtained from condensers of $400 \mu\text{F}$ charged up to 2300 volts.

The traces of the time variation of the phosphorescence intensity at $443 \text{ m}\mu$ are shown in (a), (b), (c) and (d) of Fig. 10) for excitation powers of 578, 722, 882 and 1058 joules respectively. It is seen that the phosphorescence intensities increase according to the input power into the Xenon flash tube, but in 3.5 msec after the start of excitation the residual phosphorescence has the same intensity in all cases of (a), (b), (c) and (d). In the case of (d), there appears a remarkable feature in the time variation curve of the phosphorescence intensity in comparison with the curves in the cases of (a) and (b). It is seen that the emission intensity decreases abruptly in 2 msec after the start of excitation.

In our benzophenone-alcohol solid solution system, we could not observe such a "spikes" that was reported in the cases of pyrazine and α -bromonaphthalene by Morantz et al..

The fire duration of the flash does not change seriously in a range of the excitation energy used in this investigation. It was below 1.0 msec. Therefore the change in form of the decay curves mentioned above may not be attributed to the flash light duration for excitation but to their emission characteristics themselves. Finally it may be said that in the cases of (a) and (b) of Fig. 10 the decay form of the phosphorescence emission is normal and similar to those obtained in the decay time measurements, and in the cases of (c) and (d) the decay curve deviates from the normal exponential one.

III. Discussion and conclusion

For energy levels of benzophenone molecule we refer to a Jablonski-type energy level diagram of organic phosphors shown in Fig. 11. Just after the excitation ceases, the population n_T at the lowest triplet level varies as the following equation

$$\frac{dn_T}{dt} = -An_T + B \cdot \rho(\nu) \cdot \left(n_S - \frac{g_S}{g_T} n_T \right), \quad (1)$$

phosphorescence shown in Fig. 10 can be also explained by this induced emission.

We have hitherto supposed implicitly no occurrence of the reabsorption from the lowest triplet state to an upper triplet state. According to Naboikin et al.¹⁴⁾, benzophenone doped in polymethylmethacrylate has the reabsorption of the induced triplet-triplet transition. Although this induced absorption has its peak at 553 m μ , the absorption of about 20% of the peak still remains at 443 m μ . We must now take into account of this triplet-triplet transition. Though the emission spectrum of benzophenone in polymethylmethacrylate is broader than that observed in our benzophenone-alcohol solid system, the wave length of the emission peaks in both cases shows a fairly good agreement. Therefore it may be considered that the emission characteristics of benzophenone in both solid solvents do not differ seriously. On this assumption, if the triplet-triplet reabsorption at 443 m μ occurs in the case of polymethylmethacrylate, it may also take place at the same wave length in the case of the alcohol solid solution. It is considered that the enhancement of decay under high excitation may be partly attributed to the triplet-triplet absorption.

In conclusion, we could not detect the "spikes" within the excitation power of 1K joule, but we could observe the enhancement of decay of the phosphorescence emission from benzophenone in rigid glass solution under high-power excitation. This results may be explained in terms of the induced emission and the triplet-triplet absorption.

14) Yu. V. Naboikin, L. A. Ogurtosva and K. T. Pechii, *Optics and Spectroscopy*, 16, 298, (1964).