591. *The Phosphorescence Emission of Benzophenone.*

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The phosphorescence emission of benzophenone has been examined and recorded. The emission was found to be of two different types, the proportion of each depending on the concentration of benzophenone. An attempt has been made to explain this dependency by consideration of intermolecular migration of excitation energy.

That the phosphorescence emission observed from many organic molecules is a transition from a triplet to the ground singlet state of the molecule was suggested by Lewis and Kasha (*J. Amer. Chem. Soc.*, 1945, **67**, 994; 1944, **66**, 2100). Before this work very little was known about such states and no systematic investigation of them had been attempted. The field has been reviewed by Kasha (*Chem. Reviews*, 1947, **41**, 401). Since then, however, further work has been published by a group of American workers and a number of Russian authors.

The phosphorescence emission of benzene has been analysed by Shull (*J. Chem. Phys.*, 1949, **17**, 295) and the perturbing singlet claimed to be of symmetry $^1B_{1u}$. Much stronger spectroscopic evidence, however, points to this level as having the symmetry $^1B_{2u}$. McClure (*ibid.*, p. 905) has measured the lifetimes of the emissions of a number of molecules. He has attempted to calculate theoretically these lifetimes, but finds them to be in bad agreement with experiment. McClure has also derived selection rules for the mixing of singlet and triplet states (*ibid.*, p. 665), but their validity has yet to be proved.

These workers have assumed that the mechanism of population of the triplet state is that given by Kasha (*loc. cit.*), *i.e.*, a spin-orbit interaction operator controls an internal conversion between singlet and triplet states. Our observations with benzophenone, however, show evidence for a mechanism by means of which the triplet state is populated by intermolecular migration of excitation energy.

The phosphorescence emission of benzophenone was photographed, solutions in light petroleum which ranged from 10^{-2} to 10^{-4}M being used. The resulting tracings are shown in Figs. 1, 2, and 3. As can be seen, the spectrum is changing between these two values. At low concentrations the emission appears blue when viewed through the phosphoroscope but becomes progressively green as the concentration is increased. As the blue emission has the shorter life, a photograph of the green emission was obtained by revolving the phosphoroscope by hand and using a solution which had a predominantly green emission, *i.e.*, of concentration about 10^{-2}M. The tracing of the green emission is shown in Fig. 4. Although the green emission is present at low concentrations it is so weak that the tracing in Fig. 1 was taken to represent the blue emission. The positions of the peaks in the blue and the green emissions are shown in the table.

Positions of peaks, in Å

Blue emission		Green emission		
4190	5310	4480	5060	5360
4500	5700	4600	5120	5500
4860		4780	5280	5660
		4900		

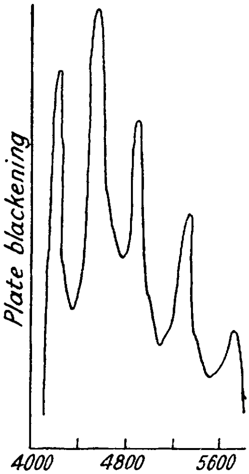
Only a preliminary attempt was made to compare frequency differences with known Raman frequencies. A favourable comparison was obtained with both emissions, but the accuracy of measurement is low and so little is known about the vibrational modes of a molecule the size of benzophenone that the subject was not pursued further.

There seems to be no doubt that the blue emission corresponds to that obtained by Lewis and Kasha (*loc. cit.*) with the exception that we have obtained a fifth band at longer wave-lengths which they did not report.

Visual scanning of the spectrum by means of a monochromator gives an "excitation spectrum " different from that observed with other compounds not allied to benzophenone, *e.g.*, aromatic hydrocarbons, amines, etc. In these cases the excitation spectra are similar to those usually found, owing to the phenomenon of internal conversion, in fluorescence (Pringsheim, " Fluorescence and Phosphorescence," Interscience Publ., New York, 1949, p. 306). The excitation spectrum of benzophenone, however, has two maxima corresponding to the two regions of absorption lying above 2300 Å. This suggests that internal conversion between the first two singlets is a process of low probability and the two singlets differ in character. The first region of absorption has been shown by McMurray (*J. Chem. Phys.*, 1941, **9**, 231) to be of the type N–E_1, involving a non-bonding electron from the oxygen atom, and the second of the type N–V_1 peculiar to the aromatic ring system.

The effect of change in concentration on the relative intensities of the phosphorescence excited in the two regions is most noticeable; that excited in the first region of absorption increasing greatly in intensity with increase in concentration.

FIG. 1.

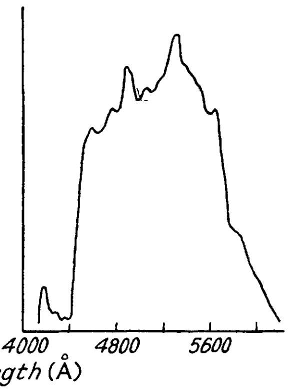


Benzophenone at the concentration of 1·2 × 10⁻⁴M.

FIG. 2.

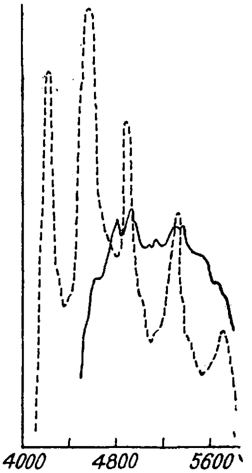
Benzophenone at the concentration of 9·3 × 10⁻⁴M.

FIG. 3.



Benzophenone at the concentration of 9·5 × 10⁻³M.

FIG. 4.



The two phosphorescences of benzophenone.

Behaviour similar to that of benzophenone was also observed with allied substances such as acetophenone, benzoin, and benzil.

Benzophenone, then, as a representative of a class of compounds is unique in that phosphorescence from two different triplet levels is observed. This is because internal conversion is a process of low probability. Although there is no proof of the nature of these levels, we have assumed them to be triplet in accordance with the ideas of Lewis and Kasha (*loc. cit.*). It remains then to discuss the mechanism of population of these levels. At all the concentrations we have employed both emissions are present in varying degrees, although at concentrations of the order 10^{-4}M the glow has only a very faint trace of green.

The change in nature of the emission is most noticeable between 10^{-3} and 10^{-4}M-concentration. This comparatively abrupt change suggests energy transfer. Franck and Livingston (*Rev. Mod. Physics*, 1949, **21**, 505) state that a molecule, excited by light of wave-length shorter than that absorbed by a second compound which is also present in the system, should be able to transfer its energy to a molecule of the latter type. The efficiency of this transfer should be high if the fluorescence spectrum of the primarily excited molecule overlaps the absorption spectrum of the second molecule.

Förster (*Ann. Physik*, 1948, **2**, 55) has approached the problem of energy exchange and fluorescence by means of quantum mechanics and has obtained expressions for the critical distance between similar molecules below which exchange can occur. He has considered only exchange between similar molecules in the same region of the spectrum.

If, in a system containing the one species of molecule, the fluorescence spectrum of the first singlet overlaps the absorption spectrum of the first (or higher) triplet, then energy transfer should be possible between molecules excited in the lowest singlet level (through internal conversion or direct transition from the ground state) and unexcited molecules lying within the critical region. The latter, on being transferred to the lowest triplet level, would be capable of returning to the ground state and emitting their characteristic phosphorescence.

We consider that the above explanation can be applied to the emission observed with benzophenone. It is the general rule that the difference in energy between the lowest singlet and triplet is low enough for the fluorescence spectrum of the former to overlap the absorption spectrum of the latter.

The possibility of energy migration in phosphorescence has been considered by Weissman (*J. Chem. Phys.*, 1950, **18**, 1258) in a study of various metal complexes. He dismissed this, however, when he found no appreciable change in the degree of polarisation when the concentration was changed from 10^{-4} to 10^{-6}M. The range of concentrations he used, however, was very limited and we feel that a more thorough investigation was needed to reach the conclusion of no energy transfer.

We do not as yet know the extent to which migration of energy populates the triplet states of other molecules, but a preliminary observation with the benzene phosphorescence shows that energy can definitely be transferred. This is shown by the quenching of the phosphorescence of benzene by the presence of iodobenzene, which does not have a phosphorescence emission (unpublished work).

We suggest that the difficulties so far experienced in attempted theoretical work may lie in the neglect of energy transfer. Work is proceeding along these lines.

EXPERIMENTAL

Benzophenone.—A B.D.H. sample, recrystallised from alcohol, then light petroleum, and three times sublimed, had m. p. 49°.

Light Petroleum.—This solvent was used for the work as it sets to a transparent glass at the temperature of boiling nitrogen. It was purified by treatment with 20% oleum until the acid layer was no longer coloured, washed with sodium hydroxide solution and then water, dried, and distilled; it boiled at 58—63°/760 mm. and then had no phosphorescence emission, this being the criterion of purity.

Apparatus.—The method and apparatus for recording the phosphorescence emissions were essentially as used by Lewis and Kasha (*loc. cit.*). A Pyrex Dewar vessel with Corex windows, of short-wave transmission limit about 2300 Å, and, instead of a rotating can, two discs, with four holes in each staggered in relation to one another rotating at about 1800 r.p.m. were employed.

The spectrograph was a Hilger F4 high-aperture instrument with non-linear dispersion. All photographs were taken on thin glass panchromatic super XX Kodak plates. The slit width used in all cases was 0·2 mm. with exposures of 10 and 30 minutes. The spectrogram densities were determined with a Baird Associates non-recording densitometer. A Hanovia mercury ultra-violet lamp was used as a source of exciting radiation.

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