

naphthalene have been measured from -30 to 180° .

2. When $\log \eta$ is plotted against $1/T$ straight lines are not obtained and there is evidence that the *cis*-form undergoes some change at 110° .

3. An attempt is made to explain the high values of η and E_{vis} , and also the effect of *cis-trans* isomerism on these.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Electromagnetic Mechanism of the Beta Phosphorescence of Fluorescein in Acid Solution

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Introduction

The peculiar nature of the beta phosphorescence of fluorescein in acid solution, investigated recently by Lewis, Lipkin and Magel,² suggested to us the desirability of studying the mechanism of this emission process. The peculiarities made themselves evident in several ways. Firstly, the luminescence is of unusually long duration. Secondly, no absorption band corresponding to a transition from the normal to the phosphorescent state has been found.³ Thirdly, although the fluorescein molecules in the phosphorescent state have been found to be oriented when excited to that state by polarized light, the beta phosphorescence from such molecules is but little polarized.²

It is possible to describe the radiation processes from a source which is small compared with the wave length of the emitted waves in terms of the electric and magnetic multipole moments of the source. In the case of most of the familiar sources the only significant contribution to the radiation arises from an oscillating electric dipole. Indeed, most of the selection rules used in interpreting atomic and molecular spectra are not applicable in the case of transitions other than those involving electric dipoles. Thus, many spectral lines have been observed which appear to arise from processes which are forbidden by these selection rules. Two explanations may be advanced for the occurrence of these processes. In the first place, as we have just indicated, these seeming violations may occur because a given transition involves a multipole other than an electric dipole. Secondly, they may occur because of the invalidation of the rules by external perturbations of the emitting system. The $^2S_{1/2}$ - $^2D_{3/2, 5/2}$ doublet of potassium studied by Segrè and Bakker,⁴ the 1S_0 - 3P_2

and 1D_2 - 3P_0 transitions of lead studied by Jenkins and Mrozowski,⁵ and the 1S_0 - 1D_2 transition of oxygen studied by Frerichs and Campbell⁶ may be cited as examples of breakdowns of the first type. On the other hand, the 6^3P_2 - 7^3P_2 transition of mercury,⁷ which is induced by external electric fields, may be cited as an example of a breakdown of the second type.

In the case of the transitions just mentioned, the investigators were able to determine the nature of the emission mechanism (magnetic dipole, electric dipole and electric quadrupole) by a study of the Zeeman effect. Obviously, this method cannot be used to study broad spectral bands such as those of large organic molecules. In this case it becomes necessary to use the wide-angle interference method of Selényi.⁸ This method, the interpretation of which depends on characteristic differences in directional distribution of radiation about the various elementary multipoles,⁹ involves the study of the coherence properties of rays issuing in widely diverging directions from small sources.

Experimental

In order to obtain interference between two beams of light issuing at a wide angle from a source, it must be of such dimensions that the interference patterns from different parts of the source do not obliterate each other. The most critical requirement as to the size of the source is that one dimension be not more than about one-twentieth of the wave length of the light. The other dimensions may be much larger and are determined by various optical characteristics of the interference apparatus. Selényi⁸ has devised a simple experimental set-up which admirably fulfills the above requirements. We have used essentially

(5) Jenkins and Mrozowski, *Phys. Rev.*, **59**, 808 (1941).

(6) Frerichs and Campbell, *ibid.*, **36**, 151 (1930); **36**, 1460 (1930).

(7) Segrè and Bakker, *Nature*, **128**, 1076 (1931).

(8) Selényi, *Ann. Physik*, **85**, 444 (1911); *Z. Physik*, **108**, 401 (1938); *Phys. Rev.*, **56**, 477 (1939).

(9) Halpern and Doermann, *ibid.*, **52**, 937 (1937); Doermann, *ibid.*, **53**, 420 (1938); Doermann and Halpern, *ibid.*, **55**, 486 (1939).

(1) National Research Council Fellow, 1941-1942.

(2) Lewis, Lipkin and Magel, *THIS JOURNAL*, **63**, 3005 (1941).

(3) These last two observations are, of course, interrelated.

(4) Segrè and Bakker, *Naturwiss.*, **19**, 738 (1931); *Z. Physik*, **72**, 724 (1931).

his set-up, but have adapted it so that the emitting source could be examined at liquid air temperatures.

A saturated solution of fluorescein in a phosphoric acid approximating metaphosphoric acid in composition was found satisfactory for preparing the small source necessary for the wide-angle interference study.¹⁰ This source was obtained by placing a droplet (*ca.* 10^{-4} ml.) of the solution on the hypotenuse of a right angle prism and covering with a freshly split sheet of mica 0.005–0.010 mm. thick. The prism was maintained at a temperature of 110° until the film spread to the required thickness. The other dimensions of the source were determined by a pinhole in a sheet of black paper placed in contact with the mica (see Fig. 1B).

The experimental arrangement for the excitation and examination of the phosphorescence of the fluorescein film is depicted schematically in Fig. 1A. Light from a high-pressure mercury arc (1) was focused on the pinhole by means of a large aperture lens (2). The right angle prism (5)¹¹ was suspended in an unsilvered dewar (4) fitted with a balsa wood cover (7). The interfering beams of phosphorescent light from the film passed through a glass window in the cover (6). The fringe system was focused on the slit of the spectrograph (13) by means of a lens (9) and totally reflecting prism (11). The polarization of the fringe system was studied with the aid of a Polaroid disk (12) placed before the slit of the spectrograph.¹²

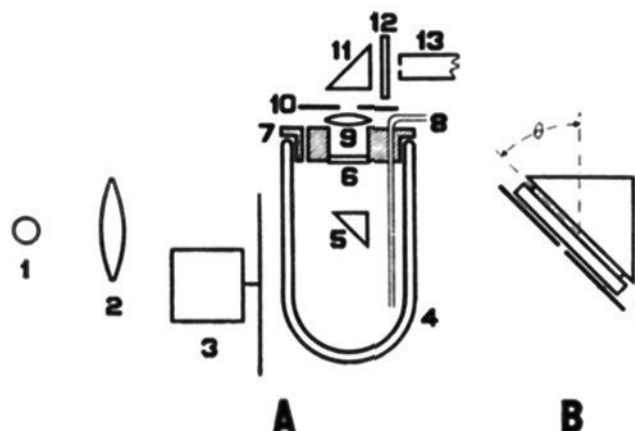


Fig. 1.—Schematic representation of the apparatus used for wide-angle interference studies at low temperatures.

The fluorescein film which served as the source of phosphorescent light was maintained at the desired temperature (95°K.) by a stream of cold air produced by boiling the liquid air contained in the dewar. This method of cooling was found necessary in preference to the usual method of immersion in liquid air in order to prevent disturbance of the exciting and emitted light beams.

In order that only phosphorescent light might enter the spectrograph a phosphoscope was used which consisted of two synchronized shutters. A disk (3) with a 50° sector

(10) It was necessary to use such a concentrated solution of fluorescein in order to obtain phosphorescence of sufficient intensity. The low intensity of the phosphorescence as compared with the fluorescence is accounted for by the fact that the fluorescein molecules spend such a long time in the phosphorescent state.

(11) For observations at an angle of $2\theta = 90^\circ$ (Fig. 1B) the 45° prism was used. At $2\theta = 45^\circ$ a glass half cylinder was used such as the one described by Freed and Weissman [*Phys. Rev.*, **60**, 440 (1941)].

(12) Since the only polarizations studied were perpendicular and parallel to the plane of incidence of the totally reflecting prism (11), it was permissible to place the Polaroid disk in this position.

of an annulus cut out of it, rotating at the rate of one revolution per second, served as the shutter for the exciting beam. A Packard Ideal shutter (10) placed in the phosphorescent beam was operated in synchronism with the first shutter by means of electrical contacts placed at properly spaced intervals on the disk.

The fringes arising from the broad band of wave lengths contained in the phosphorescent light were separated and photographed in the spectrograph (13), which was a small Bausch and Lomb constant deviation spectrometer fitted with a camera.

The Nature of the Emission Process

Observations of the interference patterns formed by pairs of rays diverging at angles of 90° and 45° sufficed for an unambiguous assignment of the multipole nature of the source. At an angle of divergence $2\theta = 90^\circ$ (see Fig. 1B) and with the Polaroid set to transmit light polarized with its electric vector perpendicular to the plane of the two interfering beams, we obtained a picture of the emission spectrum crossed by interference fringes of high visibility. The photograph showing these fringes is reproduced in Fig. 2(a). At the same angle of divergence, but with the Polaroid turned through 90° from its first position, interference fringes no longer appeared in the photograph of the emission spectrum (Fig. 2(b)). These results, when interpreted in the light of the theoretical

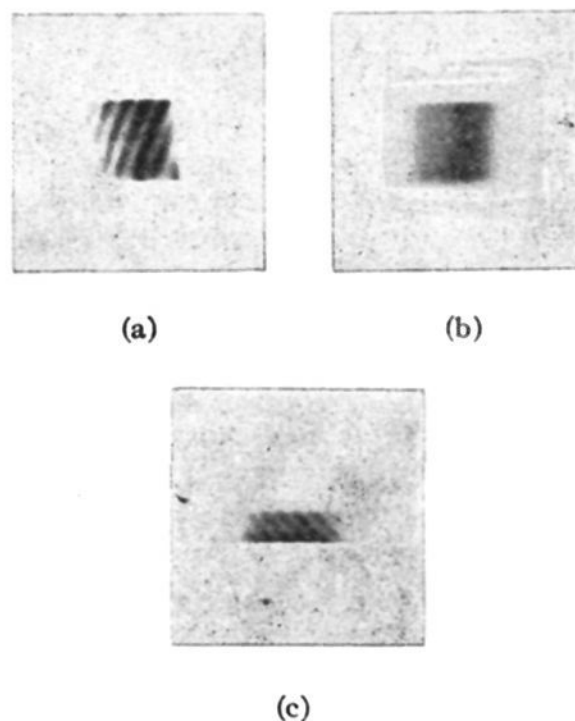


Fig. 2.—Phosphorescence ($5400\text{--}6200 \text{ \AA.}$) of fluorescein in phosphoric acid at 95°K. (a) $2\theta = 90^\circ$, electric vector perpendicular to plane of interfering beams. (b) $2\theta = 90^\circ$, electric vector parallel to plane of interfering beams. (c) $2\theta = 45^\circ$, electric vector perpendicular to plane of interfering beams. The photograph obtained with $2\theta = 45^\circ$ and the electric vector parallel to plane of interfering beams is indistinguishable from this one.

investigations of Doermann and Halpern,⁹ show that the emission process involved in the beta phosphorescence may be either an electric dipole or magnetic quadrupole transition. Furthermore, the theory definitely excluded transitions involving magnetic dipoles, electric quadrupoles, electric octopoles and magnetic octopoles. Detailed predictions of the interference properties of still higher multipoles have not as yet been made and, therefore, we cannot definitely exclude these on the basis of our photographs. However, these can be excluded on the basis of reasoning involving the lifetime of the phosphorescent state and the intensity of the emission.

In order to decide between the two alternatives allowed us by the results described above, *i. e.*, electric dipole and magnetic quadrupole, it was but necessary to observe the interference patterns at an angle of divergence $2\theta = 45^\circ$. At this angle of divergence we again made observations with the Polaroid set to transmit light polarized with its electric vector perpendicular to, and parallel with, the plane of the two interfering beams. In each case we obtained photographs of the spectrum crossed with fringes of high visibility (Fig. 2(c)). These photographs definitely show the emission process to be electric dipole in nature.¹³

Had our wide-angle interference experiments shown that the transition giving rise to the beta phosphorescence involved a multipole of higher order than a dipole, there would have been no great difficulty in explaining the long lifetime and small polarization of this process.¹⁴ However, the unambiguous results of these experiments confront us with this question: how can the long-lived beta dipole process occur with only slightly preferred

(13) The results of Doermann and Halpern are applicable to isotropic sources. Our source fulfilled this requirement of isotropy for two reasons. In the first place, a highly convergent beam of exciting light was used. Second, almost complete saturation of the source was achieved and, therefore, even molecules whose axes approach parallelism with the axis of the exciting light beam are activated.

(14) It has been shown by means of electromagnetic theory that the lifetime of an oscillator increases markedly with increase in the order of the multipole. Thus, the ratio of the lifetimes of two successive multipoles, *i. e.*, dipole and quadrupole, is approximately equal to $(\lambda/a)^2$, where λ is equal to the wave length of the emitted radiation and a is equal to the amplitude of the oscillation.

directional properties in the same oriented molecule which gives rise to highly selective directional properties for the short-lived dipole fluorescence? Let us suppose that the two states involved in the beta transition resemble non-degenerate states of zero total electronic angular momentum encountered in atomic spectra. Transitions of any multipole order between such highly symmetrical states are forbidden. However, a perturbation possessing sufficiently low symmetry may induce an electric dipole transition between such states. In the case here being considered such a perturbation may arise from zero point fluctuations in the medium or the molecule, as suggested by Lewis, Lipkin and Magel.² The direction of the oscillating moment associated with such an induced transition would be determined principally by the direction of the perturbation and little by the molecular axes, giving rise to phosphorescence with little polarization. On the other hand, in the fluorescence the upper state may be thought of as arising from a degenerate electronic state. Presumably there would be no prohibition against an electric dipole transition between this state and the ground state, and the observed lifetime of the fluorescence¹⁵ is actually found to be in good agreement with this presumption. Furthermore, such a state would partake of the symmetry of the molecule and the oscillating dipole moment associated with the transitions in which it is involved would be expected to be oriented with respect to the molecular axes. This would readily account for the high degree of polarization observed in the fluorescence and alpha phosphorescence.

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Summary

A wide-angle interference study of the beta phosphorescence of fluorescein in phosphoric acid at 95°K . has shown that the process involves an electric dipole transition.

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(15) Gaviola, *Z. Physik*, **42**, 853 (1927).