# ON THE POSSIBILITY OF THE EXISTENCE OF SEVERAL PHOSPHORESCENT LEVELS IN ORGANO-LUMINOPHORES

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## Abstract

## Full Text

## PHYSICS

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# ON THE POSSIBILITY OF THE EXISTENCE OF SEVERAL PHOSPHORESCENT LEVELS IN ORGANOLUMINOPHORES

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One of the fundamental propositions of the theory of fluorescence is the assertion that only one excited level is manifested in the radiation. The most graphic proof of this proposition was given by S. I. Vavilov as early as 1925 (^1). He showed that all portions of the fluorescence spectrum of solutions of complex organic substances have the same degree of polarization, i.e., the entire emission band belongs to a single electronic transition. A second, very important proof of the stated assertion is the exponential law of decay of luminescence. This proof is less graphic, since the fluorescence decay curve of solutions has not yet been obtained because of experimental difficulties; however, the assumption of an exponential law of fluorescence decay agrees well with a number of experimental facts from fluorometric and polarization measurements and from the quenching of fluorescence by foreign substances.

It is quite natural that the proposition set forth above was also extended to the case of phosphorescence of organic compounds. In the thirties and at the beginning of the forties this extrapolation seemed fully justified by the experiments of S. I. Vavilov and A. A. Shishlovskii (^2), V. L. Levshin and L. A. Vinokurov (^3), and Lewis, Lipkin, and Magel (^4), in which it was shown that the law of decay of long-duration afterglow is exponential and that the decay constant does not depend on the choice of the spectral region of phosphorescence*.

However, a repeated study of the law of decay of the afterglow of the same organoluminophores, carried out in the forties by one of us (^6) by means of a more refined method and therefore over a considerably broader interval of variation of the initial intensity of the afterglow, showed that the law of decay of the phosphorescence of organoluminophores differs noticeably from the exponential law**. Later these results were confirmed by many authors, and still more substantial violations of the exponential law of phosphorescence decay were found by them. Moreover, some authors (^8) proved the untenability of the assertion that the phosphorescence decay constant is independent of the choice of the spectral region of emission.

In recent years a number of hypotheses have been proposed to explain these phenomena. If one does not go into details and restricts oneself to the case of

Fig. 1. 1—copper rod; 2—windows; 3—sample; 4—flat walls of a Dewar made of uviolet glass; 5—liquid air or nitrogen

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long-wave phosphorescence, these hypotheses may be divided into three groups. To the first group (^9) belong hypotheses which suppose that the luminescence involves two processes: spontaneous emission, corresponding to a transition from the triplet (metastable) level to the normal one, and recombination emission, in whose spectrum, in the general case, there could evidently be both fluorescence-type emission and long-wavelength phosphorescence-type emission. To the second group (10) belong hypotheses that assume the existence of two metastable levels in the activator molecule. To the third group (8) belong hypotheses which suppose that the metastable (electronic) level of the molecule can be very strongly and variously deformed by the solvent, as a result of which in the solution there exists a set of emitting centers having different spectral composition and different emission duration.

Having carried out an extensive study of the decay kinetics of phosphorescence* of a series of organoluminophores, we came to the conclusion that the phosphorescent (metastable) level is at least double. In search of independent and clear evidence for this proposition, we naturally turned to polarization experiments, i.e., to the study of the degree of polarization of long-wavelength phosphorescence in different regions of the emission spectrum.

**Fig. 1.** 1—copper rod; 2—windows; 3—sample; 4—flat walls of a Dewar made of uviolet glass; 5—liquid air or nitrogen

The objects of our investigation were sugar candies activated with esculin and carbazole, and boric candies activated with fluorescein. The first two, at all temperatures, give only long-wavelength phosphorescence, and they were studied at 20° and $-180°$; the third only at $-180°$.

The apparatus with which the experiments were performed consisted of a super-high-pressure mercury lamp stabilized with respect to luminous flux (12); a water filter for absorbing thermal radiation; a light filter for isolating the exciting light**; two Glan prisms 20 × 20 mm; a rapidly rotating two-disk phosphoro-

* This latter circumstance was also indicated in the work of Carelli and Pringsheim (^5).

** It should be noted that the nonexponential character of the phosphorescence decay law of solid solutions and crystalline powders of certain organic substances had been shown even earlier in the works of Kennard and Tomashek (^7). At that time their results seemed to be exceptions for which an explanation had to be sought in contamination of the matrix or of the crystals.

scope; a glass monochromator UM-2; and a recording device consisting of a photomultiplier and a self-recording instrument.

The degree of polarization was determined from successive measurements at two positions of the polarizer. This method, which makes it possible to avoid errors introduced into the measurements by the monochromator, we borrowed from the work of S. I. Vavilov (1).

For experiments at low temperatures, a Dewar with flat windows of special design was used (Fig. 1), in which the passage of light through opalescent liquid air was eliminated. The temperature of the sample in this Dewar was 10 −15° higher than the temperature of liquid air.

**Table 1**

Dependence of the degree of polarization of the long-duration luminescence of esculin in a sugar candy at room temperature on the wavelength of phosphorescence

| $\lambda$, mμ | 600 | 594 | 582 | 571 | 560 | 550 | 541 | 532 | 523 | 511 | 501 | 491 | 480 | 472 | 462 | 450 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $P_1$, % | 0 | 1.0 | 6 | 5.4 | 4.1 | 5.6 | 6.1 | 6.6 | 6.8 | 6 | 6.5 | 8.6 | 5.9 | 3.5 | 2.5 | 0 |
| $P_2$, % | 0 | 1.3 | 8.2 | 7.6 | 6.7 | 6.8 | 7.5 | 8.7 | 8.7 | 7.5 | 9 | 10 | 7 | 4 | 3.5 | 0 |

The reproducibility of measurements for one sample is very good. The situation is worse with the agreement of the values of the degree of polarization for samples of different batches***; however, the character of the change of polarization over the spectrum phosphorescence remains one and the same for all samples of the given luminophore. Table 1 gives the results of our measurements for two sugar candies, prepared at different times and activated with esculin.

The data given in Table 2 for the degree of polarization of phosphorescence in different parts of the emission spectrum refer to those samples of luminophores for which higher polarization values were obtained. The investigations at room temperature and at liquid-air temperature were carried out on the same samples.

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* A small part of this investigation is set forth in (11).

** Phosphors activated with fluorescein were excited by the 436 mμ line; phosphors activated with esculin, by the 366 mμ line; and those activated with carbazole, by the 313 mμ line.

*** Naturally, for polarization experiments candies with the best optical qualities were selected.

**Table 2**

Dependence of the degree of polarization $P$ (in %) of the long-wave phosphorescence of organic luminophores on the wavelength of the emission spectrum

| $\lambda$, mμ | Esculin at 20° | Esculin at −180° | Carbazole at 20° | Carbazole at −180° | Fluorescein at −180° |
|---|---|---|---|---|---|
| 600 | 0 | 0 | 2.5 | −1.3 | 3.8 |
| 594 | 1.3 | | 2.5 | | 2.6 |
| 582 | 8.2 | 0 | 3.3 | −6.4 | 2.2 |
| 571 | 7.6 | | 3.2 | | 0 |
| 560 | 6.7 | −2.5 | 2.6 | −3.3 | 0 |
| 550 | 6.8 | | 2.5 | | −1.4 |
| 541 | 7.5 | −2.5 | 0 | −5.5 | −3.5 |
| 532 | 8.7 | | 0 | | −5.6 |
| 523 | 8.7 | −2.2 | 0 | −6.4 | −6.8 |
| 511 | 7.5 | | −3.2 | −8.1 | −5.6 |
| 501 | 9.0 | −4.1 | −3.2 | | |
| 491 | 10.0 | | −2.2 | | |
| 480 | 7.0 | −3.7 | −3.9 | −8.4 | |
| 472 | 4.0 | | −5.6 | | |
| 462 | 3.5 | −8 | −5.4 | −10.4 | |
| 450 | 0 | | | −8 | |
| 411 | | | | −20.8 | |
| 407 | | | | −19.4 | |
| 405 | | | | −19.2 | |
| 400 | | | | | |

It is evident from Table 2 that the degree of polarization of the long-wave phosphorescence changes very sharply on passing from one part of the phosphorescence spectrum to another. This makes it possible to assert that at least two phosphorescent levels are manifested in the long-duration emission. This assertion considerably facilitates the explanation of deviations of the phosphorescence decay curve from an exponential and of the difference in the decay constants of individual spectral regions of the phosphorescence*. It goes without saying that the discovery of two phosphorescent levels immediately raises the question of their nature, of their interaction with one another, and of their interaction with the fluorescent level. All these questions remain open.

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## CITED LITERATURE

1. S. I. Vavilov, *Zs. Phys.*, **32**, 721 (1925); S. I. Vavilov, *Collected Works*, **1**, 1954.

2. S. I. Vavilov, A. A. Shishlovskii, *Phys. Zs. Sowjetun.*, **5**, 379 (1934).
3. V. L. Levshin, L. A. Vinokurov, *Phys. Zs. Sowjetun.*, **10**, 10 (1936).
4. G. Lewis, D. Lipkin, T. Magel, *J. Am. Chem. Soc.*, **63**, 3005 (1941).
5. A. Carelli, P. Pringsheim, *Zs. Phys.*, **17**, 287 (1923).
6. B. Ya. Sveshnikov, *DAN*, **51**, 429, 675 (1946).
7. E. Kennard, *Phys. Rev.*, **4**, 278 (1914); R. Tomaschek, *Ann. Phys.*, **67**, 612 (1922).
8. V. V. Bredel, *DAN*, **103**, 788 (1955).
9. V. A. Yastrebov, *DAN*, **90**, 1015 (1953); D. Yamamoto, *J. Chem. Soc. Japan*, **74**, 173 (1953); P. Debay, J. Edwards, *J. Chem. Phys.*, **20**, 236 (1952).
10. S. Kato, M. Koizumi, *Bull. Chem. Soc. Japan*, **27**, 189 (1954); **30**, 27 (1957).
11. V. A. Pilipovich, B. Ya. Sveshnikov, *Optics and Spectroscopy*, **4**, No. 4 (1958).
12. V. I. Shirokov, *Izv. AN SSSR, ser. fiz.*, **20**, 605 (1956).
13. J. Kowalski, *Phys. Zs.*, **12**, 956 (1911).

* A change in the phosphorescence spectrum during the decay process was noted earlier in the work of Kowalski ($^{13}$).

*Note: Figure translations are in progress. See original paper for figures.*

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