

## Photomagnetism. Determination of the Paramagnetic Susceptibility of a Dye in Its Phosphorescent State\*

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The molar paramagnetic susceptibility of acid fluorescein dye in its 2-sec. phosphorescent state in boric acid glass at 25°C has been measured directly by means of a modified Theorell microbalance. The steady state concentration of phosphorescent state molecules was  $1.96 \times 10^{-8}$  mole per cm length of sample, calculated from optical intensity integrals and phosphorescence saturation curve data. The measured boom displacement was  $4.04 \times 10^{-3}$  cm, corresponding to a force of  $1.07 \times 10^{-2}$  dyne. The calculated value of the molar paramagnetic susceptibility is  $3090 \times 10^{-6}$  c.g.s. units, which agrees with the measured value for the susceptibility of the  $^3\Sigma$  ground state of oxygen within the estimated maximum experimental error of 13 percent.

### I. INTRODUCTION

THE phenomenon of phosphorescence of complex molecules was interpreted to be a lowest-triplet  $\rightarrow$  singlet emission as the result of a spectroscopic study of this luminescence.<sup>1,2</sup> Simultaneously, the inviting possibility of measuring the paramagnetic susceptibility of the molecule in the phosphorescent state presented itself. Preliminary experiments demonstrated the existence of a genuine photomagnetism and indicated that this was within a measurable range, although requiring experiments of great delicacy.<sup>3</sup> The present report marks the completion of the quantitative determination of the molar paramagnetic susceptibility of acid fluorescein dye in its phosphorescent state.<sup>4,5</sup>

Although the present experiments were done on a dye molecule, it is to be emphasized that the phenomena studied are characteristic of unsaturated complex molecules in general, rather than being peculiar to dyes. The absorption bands usually observed in the near ultraviolet spectra of unsaturated complex molecules are attributed to singlet-singlet transitions between the  $\pi$ -electron energy levels of the molecule. When these bands are intense and occur in the visible region, the molecule is called a dye. In addition to the set of singlet levels, there is commonly a corresponding set of triplet levels. The lowest triplet level and the ground level are involved in the phosphorescence emission. The paramagnetism of the molecule in this lowest triplet level is the subject of this study.

A direct measurement of the paramagnetic suscepti-

bility of the phosphorescent state is possible in the case of complex molecules as a consequence of the phosphorescence saturation phenomenon.<sup>6,7</sup> Because of the relatively long phosphorescence lifetime (seconds) and the large quantum yield of phosphorescence (approaching unity) of many complex molecules, a large concentration of molecules may be maintained in the phosphorescent state by illumination with an intense light source. All such experiments require the use of rigid glass solutions of the molecule, in order that viscosity dependent quenching processes be limited or eliminated. The name "phosphor" has been given to these rigid glass materials because of their luminescence properties (by analogy to inorganic phosphorescent materials), but it must be remembered that the properties of the dissolved molecule, and not of the rigid glass system, are so studied.<sup>5</sup>

A quantitative determination of a molar property of a molecule in its phosphorescent state requires a knowledge of the absolute concentration of the molecules in this state. The straightforward approach to this measurement would be to determine the absolute quantum efficiency of the phosphorescence as a primary datum; this, however, involves geometry-dependent factors which greatly complicate the evaluation. The need for a determination of absolute quantum efficiency has been disposed of in the present work by making use of the mathematical properties of the equations for the phosphorescence saturation curve. This permitted a direct evaluation of the absolute concentration of molecules in the phosphorescent state by a simple measurement of source intensity used in the paramagnetic apparatus relative to the maximum source intensity used in ob-

\* Most of the experimental work of this paper was done after the death of Professor Lewis; however, the theoretical treatment and design of the experiments are largely his.

† Work done during first four months as a University Post-doctoral Fellow. The large part of this author's work was done subsequently under a contract between the Office of Naval Research and the University of California.

<sup>1</sup> G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.* **66**, 2100 (1944).

<sup>2</sup> G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.* **67**, 994 (1945).

<sup>3</sup> G. N. Lewis and M. Calvin, *J. Am. Chem. Soc.* **67**, 1232 (1945).

<sup>4</sup> A preliminary report of this work was made by M. Calvin, Symposium on the Color and Electronic Structure of Complex Molecules, Northwestern University, Chicago, December 31, 1946. See reference 5, Section V.

<sup>5</sup> M. Kasha, *Chem. Rev.* **41**, 401 (1947).

<sup>6</sup> V. L. Levshin and L. A. Vinokurov, *Physik. Zeits. Sowjetunion* **10**, 10 (1936) (English); L. A. Vinokurov and V. L. Levshin, *J. Phys. Chem. (U.S.S.R.)* **8**, 181 (1936) (Russian). [The two articles are identical in content; nevertheless, although the abstract of the first (*Chem. Abs.* **31**, 2100 (1937)) is exemplary for its accuracy and completeness, the abstract of the Russian version (*Chem. Abs.* **31**, 1298 (1937)) is ambiguous and in error, owing partly to the mistranslation of the word for decay as quenching.]

<sup>7</sup> G. N. Lewis, D. Lipkin, and T. T. Magel, *J. Am. Chem. Soc.* **63**, 3005 (1941).

aining the phosphorescence saturation curve. We now consider these points in detail.

## II. THEORY AND EXPERIMENTAL DETERMINATION OF PARAMAGNETISM

### A. The Phosphorescence Saturation Curve

#### Theory

Consider the energy level scheme of Fig. 1 which represents the three lowest electronic states of a typical complex molecule (zero-point vibrational levels). The phosphorescent or triplet state  $T$  is reached by primary absorption  $S' \leftarrow S$  followed by the radiationless transition  $S' \rightarrow T$ . The excitation of the triplet state by direct absorption  $T \leftarrow S$  is improbable in most molecules containing atoms of low atomic number.

The ratio of the concentration of molecules in the triplet state relative to those in the ground state is given by

$$C_T/C_S = k_1 I_s,$$

where  $I_s$  is the source intensity used in the optical excitation, and  $k_1$  is a collection of constants. Now define the magnitude

$$i = C_T/C_S = I_s/I_{s,m}, \quad (1)$$

where  $I_{s,m}$  is a median source intensity corresponding to the half-value of the maximum phosphorescence intensity (see Fig. 2). Let  $C = C_S + C_T$ , then from (1)

$$C_T = C(i/i+1). \quad (2)$$

The intensity of phosphorescence is given by<sup>8</sup>

$$I_p = k_2 C_T$$

which by (2) is equivalent to

$$I_p = k_2 C(i/i+1). \quad (3)$$

Now define the half- or median-phosphorescence intensity  $I_{p,m} = I_p$  when  $C_T = C_S$ ; i.e., when  $i=1$ . Then<sup>8</sup>

$$I_{p,m} = k_2(C/2). \quad (4)$$

Defining the magnitude

$$j = I_p/I_{p,m}, \quad (5)$$

we obtain from (3) and (4)

$$j = 2i/(i+1). \quad (6)$$

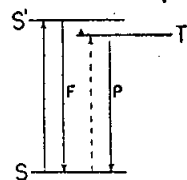
This is the equation of the phosphorescence saturation curve. Using (1) and (5), the equation may be written in terms of  $I_p$  and  $I_s$ :

$$\frac{I_p}{I_{p,m}} = \frac{2I_s}{I_s + I_{s,m}}, \quad (7)$$

expressing the relation of the phosphorescence intensity

<sup>8</sup> The term for induced emission is omitted since the new elements introduced by it cancel in taking the ratio, Eq. (5).

FIG. 1. Schematic energy level diagram for the three lowest electronic states of a complex molecule (zero-point levels).



to the exciting source intensity. This is next compared with experiment.

#### Experimental

A sample of fluorescein dye dissolved in boric acid glass of dimensions 3 cm  $\times$  1 cm  $\times$  0.2 mm was prepared by means of the extrusion process described elsewhere.<sup>9</sup> The concentration of dye was extremely low, so that  $\log_{10} I_0/I < 0.005$ , as measured by means of the Beckman spectrophotometer at 4390Å (absorption maximum, see below). In a phosphorescence saturation experiment it is essential that a concentration approaching infinite dilution of the complex molecule be used, in order that >90 percent of the molecules may become excited to the phosphorescent state with the light sources available in the laboratory. As a light source, the AH6 high pressure mercury arc was used, together with a chromium reflector and a 5 cm path of concentrated aqueous solution of  $\text{Cu}(\text{NO}_3)_2$  as a heat absorbing filter (see below). Between the light source and the filter a 10 cm dia. f1. quartz condensing lens was placed, concentrating the light of the mercury arc on a  $0.5 \times 0.5$  cm square of the fluorescein-boric acid sample. The sample was carefully masked with aluminum foil to fix the geometry of the sample. A stream of air was directed at the sample as a further precaution against warming. The phosphorescence light, observed from the back face of the sample by means of a Weston photronic cell (Model 594, barrier layer photocell) and measured by a Rubicon galvanometer (Ser. 805B, resistance 1067 $\omega$ , sensitivity 0.004 $\mu\text{A}/\text{mm}$ ), was separated from the exciting light by means of a rotating drum phosphoroscope, previously described.<sup>1</sup> The source intensity was diminished successively for the various readings by means of a calibrated set of oxidized copper screens. The galvanometer and photronic cell combination were tested for linearity of response in the range of measurement. Despite the high dilution of the dye in the glass, the phosphorescence at the maximum source intensity was visible as a strong yellow green emission through the phosphoroscope. The phosphorescence saturation curve obtained is given in Fig. 2. The observed maximum  $I_p = 4.10$  is 0.92(4) times the limiting value of  $I_p$  (4.44, see below). Thus, in this experiment 88.5 percent of the molecules were in the triplet state at the maximum value of the source intensity used.

#### Calculations

The saturation curve Eq. (7) in  $I_p$  and  $I_s$  may be written in the reciprocal form<sup>10</sup>

$$\frac{1}{I_p} = \frac{1}{2I_{p,m}} + \frac{I_{s,m}}{2I_{p,m} I_s}. \quad (8)$$

Then, if  $1/I_p$  is plotted against  $1/I_s$ , a straight line intersecting the  $1/I_p$  axis should be obtained, with  $(1/2I_{p,m})$  as the intercept and  $(I_{s,m}/2I_{p,m})$  as the slope. Accordingly the phosphorescence saturation curve data of Fig. 2 were replotted in the reciprocal form in Fig. 3.

<sup>9</sup> M. Kasha, "Fabrication of boric acid glass for luminescence studies," J. Opt. Soc. Am. 38, 1068 (1948).

<sup>10</sup> We are indebted to Dr. Harrison Shull for suggestions regarding the form of this equation.

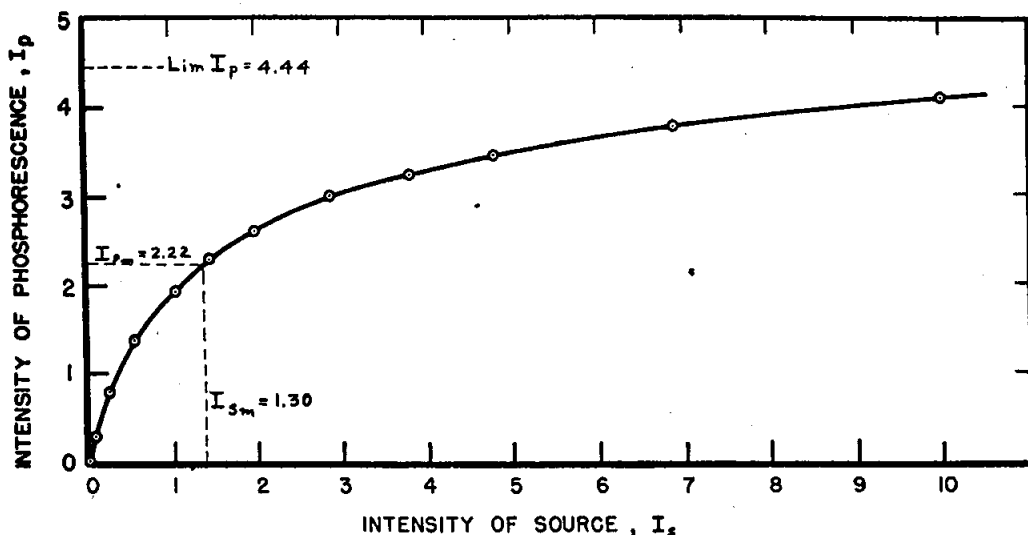


FIG. 2. Phosphorescence saturation curve for an extremely dilute solution of acid fluorescein dye (I) (see Part B, *Experimental*) in boric acid glass at room temperature.

The fit of the points to a straight line verifies the form of the saturation curve equation. The intercept on the  $1/I_p$  axis is 0.225, so that  $I_{p,m}$  is 2.22. From the slope (0.292) the value of  $I_{s,m}$  is calculated to be 1.30. The value of  $I_s$  measured in the paramagnetic apparatus (see below) is 0.205 of the maximum value of  $I_s$  used in the saturation curve determination. Since the latter value of  $I_s = 10$  arbitrary units, the value of  $I_s = 2.05$  for the paramagnetic experiment. Thus, according to equation (1)  $i = 2.05/1.30$ , or 1.58.

## B. Concentration of Triplet State Molecules

### Theory

We begin the development of the expression giving the concentration of molecules excited to the triplet state by first considering that the absorbing layer is (a) *very thin*, so that the fraction of the incident light absorbed will be negligibly small, and (b) *very dilute*, so that interaction between excited molecules and neighboring non-excited molecules, which leads to the concentration dependent quenching of the phosphorescent state (see *Calculations*, end of section B, and Fig. 7), will be negligibly small.

For a very thin, very dilute layer of absorbing centers (as used in the determination of the phosphorescence saturation curve) *per unit area* ( $\text{cm}^2$ ) the ratio *moles of triplets/moles of absorption acts* is

$$\frac{C_T}{C_S \int_{\nu_1}^{\nu_2} I_{(\nu)} \epsilon_{(\nu)}' d\nu} = \frac{i}{\int_{\nu_1}^{\nu_2} I_{(\nu)} \epsilon_{(\nu)}' d\nu} \quad (9)$$

in which the value of  $i = C_T/C_S$  is used to obtain the right member of the equation.

For a very thick, very dilute sample, *per unit area*,

the ratio (*total moles of triplets/moles of absorption acts*) is

$$\frac{N_{T'}}{\int_{\nu_1}^{\nu_2} I_{(\nu)} d\nu} \quad (10)$$

if the light is totally absorbed. In expressions (9) and (10),  $I_{(\nu)}$  is the function representing the dependence of intensity of the exciting light on frequency, and  $\epsilon_{(\nu)}'$  is the corresponding function for the absorption curve of the complex molecule.

The first ratio (9) is valid for each very thin layer of a thick sample. Although  $I_{(\nu)}$  diminishes in each successive layer, ratio (9) remains constant for each very thin layer, since  $C_T/C_S = k_1 I$ . Therefore, ratio (9) is valid for the whole sample, and we may equate it to ratio (10). Then after converting the units of  $\epsilon_{(\nu)}'$  to give the ordinary molar absorption coefficient, by

$$\epsilon_{(\nu)}' = 1000 \cdot 2.303 \epsilon_{(\nu)},$$

we obtain

$$N_{T'} = \frac{i \int_{\nu_1}^{\nu_2} I_{(\nu)} d\nu}{1000 \cdot 2.303 \int_{\nu_1}^{\nu_2} I_{(\nu)} \epsilon_{(\nu)} d\nu} \quad (11)$$

If the exciting light were monochromatic the corresponding expression would be

$$N_{T'} = \frac{i}{1000 \cdot 2.303 \epsilon_0} \quad (12)$$

where  $\epsilon_0$  is the molar absorption coefficient at the frequency of the exciting light. The values of the integrals

of Eq. (11) are determined experimentally as described below.

### Experimental

A sample of fluorescein dye mixed with crystalline boric acid was fused at 240°C and fabricated into glass strips by the extrusion process described elsewhere.<sup>9</sup> The concentration of the dye in the glass was determined by two independent methods. In the *dry* method the concentration is given by

$$C = \frac{1000wd}{WfM},$$

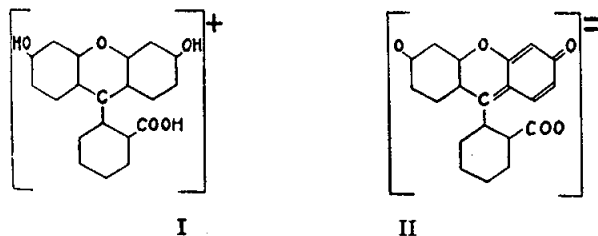
where  $C$  = moles of dye/liter of glass,  $w$  is the weight of the dye in grams,  $d$  is the density<sup>9</sup> of boric acid glass, 1.830 g/cm<sup>3</sup>,  $W$  is the weight of boric acid crystals used,  $f$  is the weight fraction of boric acid remaining after fusion,<sup>9</sup> 0.660, and  $M$  is the molecular weight of the dye or substance used.

In the *wet* method, a weighed sample of the glass containing the dye was dissolved in alkali of known concentration and the optical density of the solution measured at an appropriate wave-length by means of a spectrophotometer. The concentration of the dye is given by the usual equation

$$C = \frac{\log_{10} I_0/I}{\epsilon_0 d},$$

where  $C$  is concentration of dye in moles per liter of solution,  $\log_{10} I_0/I$  is determined by the spectrophotometer,  $d$  is the cell length in cm, and  $\epsilon_0$  is the molar absorption coefficient for the solution at the wave-length used for calibration.

For purposes of analysis and comparison, the absorption spectrum of fluorescein dye was measured in various media and after varied preliminary treatment. The results are summarized in Table I. Comparing experiments (2) and (3) it is evident that fusion of the dye with the boric acid does not destroy the dye, as may be expected from the mode of synthesis of such dyes as fluorescein. Comparison of experiments (4) and (5) shows the close similarity of the absorption spectra of the dye in these two different *acid* media. It is to be emphasized<sup>7</sup> that the species in this latter case is the positive ion (I), whereas in *alkaline* solution the doubly-negative ion (II) is present. Dye I and dye II have quite distinct optical properties as may be seen by comparing experiments (2) and (4) of Table I and by the fact that (I) has a quantum efficiency of *phosphorescence* approaching unity, while (II) has a quantum efficiency of *fluorescence* approaching unity.



The absorption spectrum of acid fluorescein dye (I) in boric acid glass at room temperature is given in Fig. 4, curve 1. The maximum molar absorption coefficient was calculated to be  $\epsilon = 23640$  (experiment 5, Table I) by the methods outlined above.

The light source used for excitation of the phosphorescence was an AH6 high pressure mercury arc. Figure 4, curve 2, gives the frequency dependence of emission intensity, determined spectrographically. The light was filtered by 5 cm of a concentrated aqueous solution of  $\text{Cu}(\text{NO}_3)_2$ . The transmission curve of this filter solution is given by Fig. 5; by comparison with curve 1, Fig. 4, it may be seen that the transmission region of this filter coincides with the first absorption region of acid fluorescein dye. Figure 4, Curve 3 gives the relative transmission of this filter in the region important in the evaluation of the intensity integrals.

### Calculations

In evaluating the integral for the source intensity of Eq. (11) we must multiply each ordinate of curve 2, Fig. 4, by the ordinates for the relative transmission of the  $\text{Cu}(\text{NO}_3)_2$  filter, curve 3. The resulting ordinates are plotted in Fig. 6, curve 1. The value of the intensity integral, determined graphically from this curve is, in arbitrary units

$$\int_{21500}^{25300} I_{(\nu)} d\nu = 2.26 \times 10^7. \quad (13)$$

The value of the integral for the  $\epsilon I_{\nu}$ -product curve, obtained by multiplying the ordinates of curves 1, 2, and 3 of Fig. 4 together, plotted as curve 2 of Fig. 6, is, in arbitrary units

$$\int_{21500}^{25300} I_{(\nu)} \epsilon_{(\nu)} d\nu = 3.86 \times 10^{11}. \quad (14)$$

The value of the integral ratio  $2.26 \times 10^7 / 3.86 \times 10^{11} = 5.86 \times 10^{-5}$ , which is to be used in Eq. (11), may be compared with  $1/\epsilon_{\text{max}} = 4.23 \times 10^{-5}$  (experiment (5), Table I) which would be used in Eq. (12) if monochromatic light of wave-length 4390Å had been used in the excitation of the phosphorescence.

The absolute concentration of triplet molecules may now be calculated using a modification of Eq. (11):

$$N_T = \frac{isq \int_{\nu_1}^{\nu_2} I_{(\nu)} d\nu}{1000 \cdot 2.303 \int_{\nu_1}^{\nu_2} I_{(\nu)} \epsilon_{(\nu)} d\nu}, \quad (15)$$

in which  $N_T$  is the concentration of triplet molecules in moles/cm length for a strip of width  $s$  cm, and  $q$  is a "concentration quenching" factor. The factor  $q$  must be taken into consideration in order to convert Eq. (11), which is valid for a very thick, very dilute, sample, to an equation valid for a sample of finite thickness and finite concentration. The need for such a correction is occasioned by the concentration-dependent quenching of luminescence which occurs in the solid state, as found by Dixon<sup>11</sup> and by Levshin and Vinokurov.<sup>6</sup> A plot of data from the paper by the latter authors for the phosphorescence of fluorescein dye in boric acid glass is given in Fig. 7. The ordinate is light sum (plotted as relative values with  $L_{p, \text{max}} = 1$ ),

$$L_p = \int_0^{\infty} I_{p,0} e^{-t/\tau_p} dt = I_{p,0} \tau_p,$$

which is a measure of relative quantum efficiency if the exciting pulse is of constant magnitude in comparable

<sup>11</sup> A. A. Dixon, J. Opt. Soc. Am. 21, 250 (1931).

experiments. In the previous considerations in this paper it has been assumed that the mean lifetime of phosphorescence is independent of experimental conditions.<sup>12</sup> Here, however,  $\tau_p$  changes with concentration of the dissolved dye, so light sum must be used in making comparisons, instead of merely the intensity. The abscissa of Fig. 7 is concentration of dye in grams per grams of boric acid glass. The concentration of dye used in the sample for the paramagnetic experiment was  $7.90 \times 10^{-4}$  g/g glass. Considering the value of  $L$  determined by means of a blue filter is low owing to self-absorption of the phosphorescence light, the value of  $q$  is determined from the curve for  $L_{red}$  of Fig. 7 to be 0.65 at the pertinent concentration.

Therefore, by Eq. (15), with  $i=1.58$ ,  $s=0.75$  cm (measured by vernier caliper),  $q=0.65$  and the integral

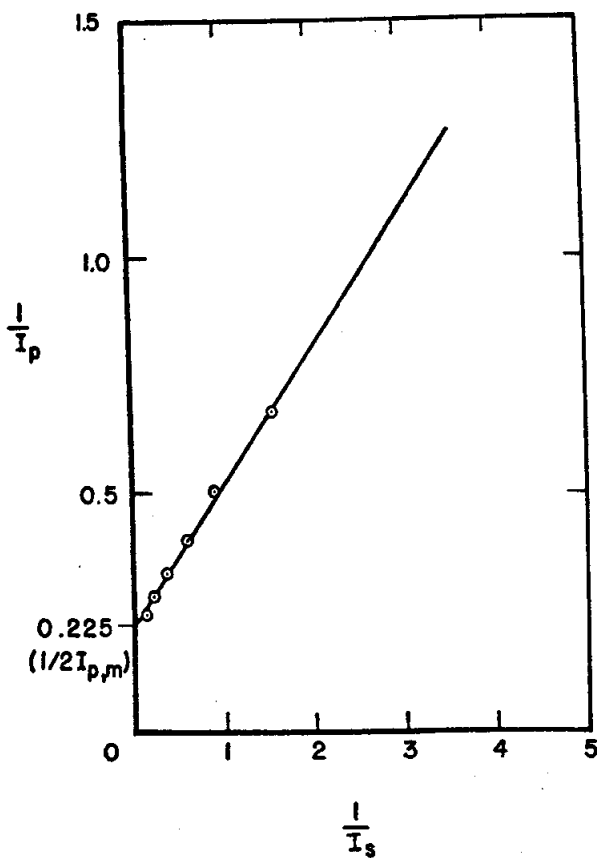


FIG. 3. Straight line form of the phosphorescence saturation curve (see Fig. 2).

ratio  $= 5.86 \times 10^{-5}$ , we calculate

$$N_T = 1.96 \times 10^{-8} \text{ mole/cm}$$

as the absolute concentration of molecules excited to the triplet state in the paramagnetic apparatus.

<sup>12</sup> B. Ya. Sveshnikov [Comptes Rendus Acad. Sci. URSS 51, 429 (1946)] reports a slight dependence of lifetime on initial phosphorescence intensity, for example (see reference 5, Section IV). This is a negligible effect in comparison with the concentration quenching effect.

## C. Measurement of Paramagnetism

### Theory

The horizontal boom microbalance used in the paramagnetic measurement (see experimental part, below) was in the form of a double pendulum. From the equations of the pendulum, in which the period is given by

$$T = 2\pi(l/g)^{1/2},$$

where  $l$  is the length and  $g$  the gravitational constant, and the force is given by

$$F = (mg/l)\delta,$$

where  $m$  is the mass of the pendulum and  $\delta$  is the displacement, the force in dynes may be calculated by

$$F = (4\pi^2 m/T^2)\delta. \quad (16)$$

The molar paramagnetic susceptibility of a substance whose magnetic pull is measured in the pendulum balance is then given by

$$\chi_M = \frac{2F}{N_T p (H_m^2 - H_0^2)}, \quad (17)$$

where  $N_T$  is the concentration per cm length (here, triplet state molecules) as before,  $(H_m^2 - H_0^2)$  is the field-square-difference for the magnet, and  $p$  is an empirical correction factor for percent of maximum pull as a function of the length of the sample.

### Experimental

Figure 8 shows a curve depicting the dependence of percent of maximum pull on the length of the sample as measured from the center of the pole piece of the magnet. This was determined experimentally by measuring the pull on a uniform tube filled to different heights with a standard paramagnetic salt solution. The sample of fluorescein in boric acid glass used in the paramagnetic determination protruded 3.1 cm out from each side, measured from the center of the pole pieces. Reading from the curve of Fig. 8, this corresponds to a value of  $p=0.84$ .

The apparatus used in measuring the magnetic pull was hori-

TABLE I. Optical absorption data for fluorescein dye in various media (using sodium salt of fluorescein as starting material).

Solution or Treatment	Concentration of Dye	Wave-length of max. Absorption $\lambda_{max}$	Character of Band	Molar Absorption Coefficient $\epsilon_{max}$
1. Dye dissolved in water	$1.628 \times 10^{-5}$ M	4550A 4850	shoulder peak	12500 16220
2. Dye dissolved in 0.500 M NaOH	$1.960 \times 10^{-5}$ M	4920	peak	39800
3. Dye fused with boric acid 20 min. at 240°C. Final solution 0.440N NaOH and 0.0858 M $\text{B}_2\text{O}_3$	$2.960 \times 10^{-5}$ M	4920	peak	40900
4. Dye dissolved in 0.264 M $\text{HClO}_4$	$3.89 \times 10^{-5}$ M	4375	peak	22030
5. Dye in boric acid glass, 0.055 cm thick	$(3.94 \times 10^{-5})$ M	4390	peak	23640

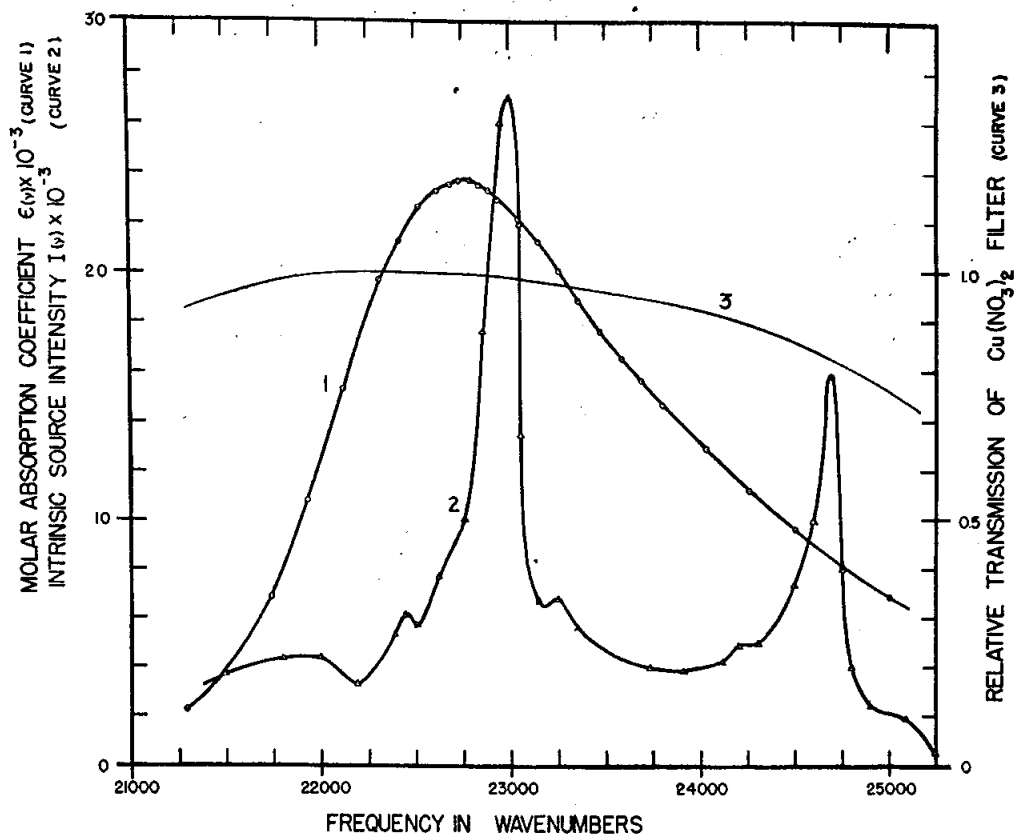


FIG. 4. Miscellaneous spectral curves. Curve 1, absorption curve of acid fluorescein dye (I) in boric acid glass at 25°C. Curve 2, intensity distribution of AH6 high pressure mercury arc. Curve 3, relative transmission of  $\text{Cu}(\text{NO}_3)_2$  filter (see Fig. 5).

zontal boom microbalance patterned after the balance of Theorell,<sup>13</sup> and except for some minor modifications, is identical with that used in the preliminary experiments.<sup>3</sup> This apparatus is diagrammed in Fig. 9. The components are as follows: (1) vernier eyepiece micrometer for measuring displacement of boom, (2) jacket of 20 mm glass tubing for protection against draughts. Inside may be seen the double pendulum suspension, consisting of a horizontal capillary boom—just stout enough to support its own weight plus the weight of the thin strip of phosphor—supported by two extremely fine glass threads (1.40 m long) by means of two hooks of very fine platinum wire. The upper ends of the suspension were the section of 8 mm Pyrex tubing from which the glass thread had been drawn; these sections of tubing were cemented by means of de Khotinsky cement to the glass jacket, so that warming of the cement allowed adjustment of the boom height. The magnet (3), consisting of copper tube conductors cooled by internally circulating kerosene oil, generated a field of about 20,000 gauss ( $H_m^2 - H_0^2 = 4.20 \times 10^8$ ; calibrated by a standard paramagnetic salt solution) with a current of 35.0 amperes. The tapered pole pieces (4), depicted in end view in Fig. 8, were fitted close to each side of the glass jacket of the apparatus. As a light source, the AH6 high pressure mercury arc was mounted in the bed of the magnet (5). The light was directed toward the phosphor sample by means of an  $f/1.0$  quartz condensing lens (10 cm dia.) (6), then passed through a 5 cm quartz cell (7) of a concentrated aqueous solution of  $\text{Cu}(\text{NO}_3)_2$ , for purposes of cooling the light beam (see Fig. 5).

The glass phosphor sample for the paramagnetic determination was a strip of dimensions 6.3 cm  $\times$  0.75 cm  $\times$  0.035 cm, prepared by an extrusion process.<sup>9</sup> The weight of the sample and its capil-

lary boom was 0.370 g. The concentration of dye was  $7.90 \times 10^{-4}$  g/g boric acid glass, or  $6.79 \times 10^{-3}$  mole of dye/l glass. For a thickness of 0.035 cm, using  $\epsilon = 23640$  (Table I), we calculate that  $\log_{10} I_0/I > 5$ , so that the light may be considered to have been totally absorbed.

The period of the pendulum, consisting of the glass phosphor strip mounted on the capillary boom and suspended by the two glass thread suspensions, was determined to be 2.35 sec.

After the optics were adjusted to give a uniform and intense illumination of the glass phosphor sample, the paramagnetic apparatus was lifted out of its mount and a piece of glass tubing (of the same size as used in the apparatus and cut to give a half-round end view) was mounted between the pole pieces of the magnet. A small flat rectangular barrier-layer photocell, covered with a dense, uniform screen, and masked to leave a  $0.5 \times 1$  cm aperture, was adjusted to occupy the same position as the phosphor sample, and the measurements of source intensity were thus

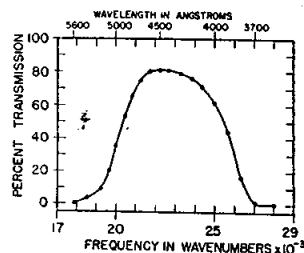


FIG. 5. Transmission curve of a 5-cm path of a concentrated aqueous solution of  $\text{Cu}(\text{NO}_3)_2$  used as a heat absorbing and "monochromatizing" filter.

<sup>13</sup> H. Theorell, Arkiv. f. Kemi. Min. Geol. 16A, 1 (1943).

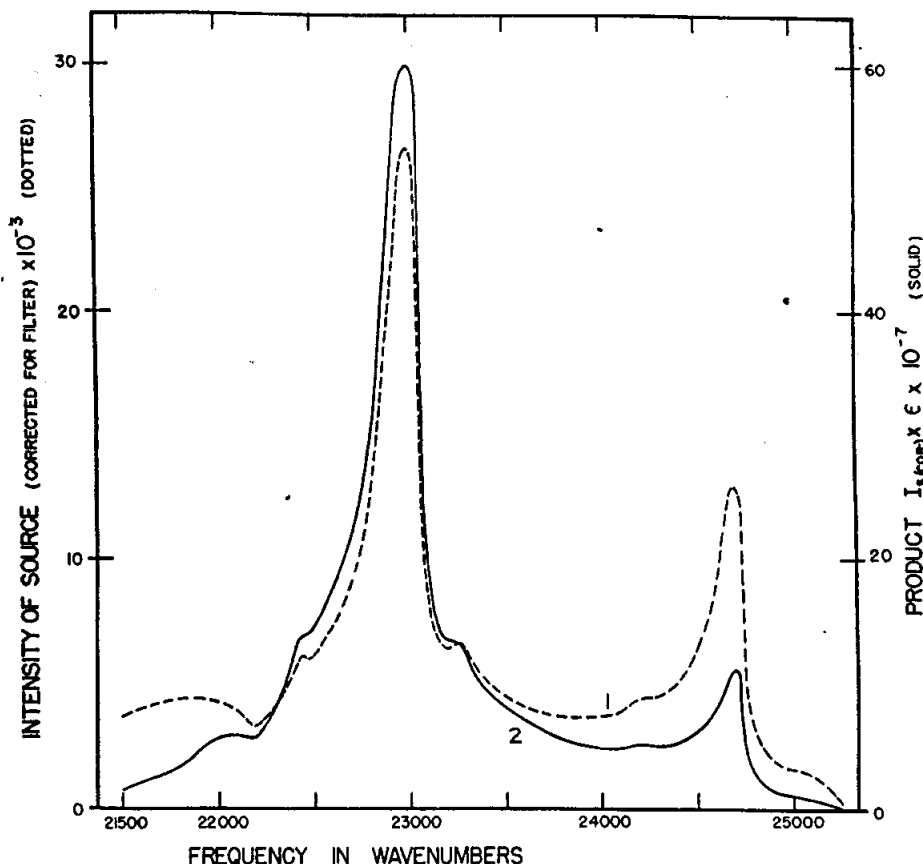


FIG. 6. Intensity curves used in the graphical integration of the theoretical intensity integrals (see Eq. (11)).

obtained. The same masked and screened photocell and galvanometer were used to measure the intense source used in the previous phosphorescence saturation curve determination. By such measurements it was found that the source intensity in the paramagnetic apparatus was 0.205 of the source intensity used in the saturation curve experiment, as previously indicated.

After mounting the phosphor sample in the magnetic balance and adjusting the position of the glass housing for freedom of swing of the suspension, the apparatus was pumped out to a high vacuum. In order to prevent recurrence of the oxygen effect<sup>3</sup> (see below) the apparatus was swept out with hydrogen gas several times and then filled with hydrogen gas to a pressure of 1 atmosphere. In addition to its being diamagnetic, hydrogen presents the additional virtue of relatively high heat conductivity.

The apparatus was covered with opaque black paper in such a way that one half of the phosphor sample would receive the full beam of the filtered high intensity mercury arc and that the other half would be kept dark. A simple shutter permitted complete shutting-off of the light. If the molecules excited to the phosphorescent state were paramagnetic, the illuminated half should be pulled into the field and the deflection could be observed by means of the eyepiece micrometer.

#### Observations and Calculations

The various experiments performed and the deflections observed with the magnetic balance are summarized in Table II. Experiment 1 was performed to test the effect of the light on the null point of the balance; the effect of the beam was found to be negligible in the absence of the magnetic field. In Experiment 2 observations were made alternately with both halves of the sample dark, and with one half dark and the other illu-

minated by the full exciting beam. Although a mean deflection of only 0.47 of the smallest scale division of the eye-piece micrometer was observed (read by vernier), the readings were exceptionally steady and reproducible. Experiment 3 repeated Experiment 2, except that the observations were made independently by a second observer. Experiments 4 and 5 were done at a later time at a significantly higher room temperature and were designed to test the effect of a 50 percent screen in the light beam; approximately a half deflection was obtained with the screen, as expected from the kinetics of excitation.

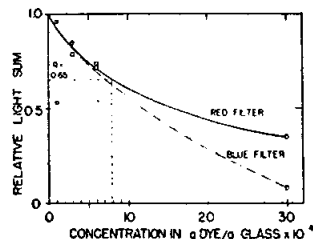


FIG. 7. Concentration quenching curves for the solid state; phosphorescence of acid fluorescein dye in boric acid glass at room temperature (data of Levshin and Vinokurov, reference 6).

From Experiments 2 and 3 of Table II, the average measured displacement is 0.48(5) scale divisions. One division on the eyepiece micrometer corresponds to  $\frac{1}{2}$  mm or 0.00833 cm. Therefore,  $\delta$  (Eq. 16) = 0.0040(4)

cm is the absolute displacement. Since the mass of the pendulum  $m=0.370$  g, and the period  $T=2.35$  sec., by Eq. (16) the magnetic pull  $F$  is  $1.07 \times 10^{-2}$  dyne.

To calculate the molar paramagnetic susceptibility of acid fluorescein dye in its phosphorescent state, we use Eq. (17), for which  $F$  has just been found to be  $1.07 \times 10^{-2}$  dyne,  $N_T=1.96 \times 10^{-8}$  mole/cm length,  $\beta=0.84$ , and  $(H_m^2 - H_0^2)=4.20 \times 10^8$ . From these data we calculate

$$\chi_{M,P^+} = 3090 \times 10^{-6} \text{ c.g.s. unit}$$

for the molar paramagnetic susceptibility of acid fluorescein dye in its phosphorescent state at 25°C. For comparison we give the molar paramagnetic susceptibility of molecular oxygen at 25°C, which has a triplet ground state,

$$\chi_{M,O_2} = 3340 \times 10^{-6} \text{ c.g.s. unit.}^{14}$$

### III. DISCUSSION AND CONCLUSION

The measurement of the paramagnetic susceptibility of a complex molecule in its phosphorescent state gives direct physical evidence for the triplet character of the associated electronic level. However, the phenomenon of photomagnetism is a delicate one whose quantitative investigation is susceptible to numerous possibilities for error; a discussion of these is therefore appropriate.

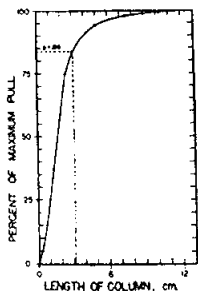


FIG. 8. Magnetic correction curve for length of sample.

#### Errors

Aside from offering a possibility of measuring extremely small paramagnetic effects, the Theorell balance presents several other desirable features. Not the least of these is the fact that in the present application the angle of incidence of the light beam relative to the direction of displacement of the boom is 90°. This dispenses of troublesome corrections for simple thermal effects (see below), radiation pressure, etc.

The largest errors in the present determination are anticipated to occur in  $F$ , the force in the magnetic balance; in the integral ratio of Eq. (15); and in  $q$ , the concentration quenching factor. Estimating respective errors of 10 percent, 5 percent, and 5 percent in these quantities (all other errors are estimated to be less than

<sup>14</sup> Calculated from data for the gas at 20°C by Curie's law [*Handbook of Chemistry and Physics* (Chemical Rubber Publishing Company, Cleveland, Ohio, 1944), 28th ed., p. 1912].

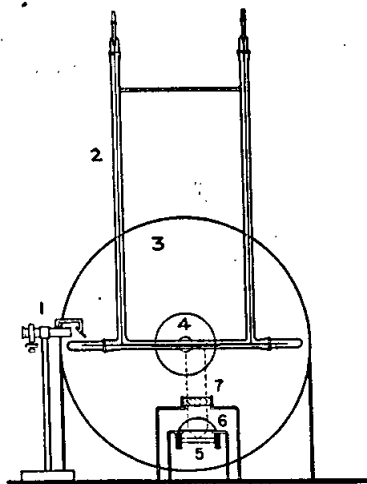


FIG. 9. Modified Theorell horizontal magnetic microbalance for photomagnetism determinations. In actual practice the illuminated half is entirely within the light beam.

1 percent), a propagated error calculation indicates that the error in  $\chi_M$ , the molar paramagnetic susceptibility, may be a maximum of 13 percent. Thus the precision of measurement is indicated to be

$$\chi_{M,P^+} = 3090 \times 10^{-6} \pm 400,$$

which covers the theoretical value of  $3340 \times 10^{-6}$ .

#### Temperature Effect

In the case of phosphorescence of dyes, for which the lowest excited singlet and the lowest triplet levels are often less than 10 kcal. apart in energy, there are characteristic phenomena<sup>5,7</sup> associated with changes of temperature of the phosphor. Of importance here is the thermal depopulation which takes place in such a phosphor at temperatures in the range of 290°K. From this, one may anticipate that the chief effect of a temperature increase in the sample, such as may occur in an intense light beam, would be to cause a *diminution* in the concentration of triplet state molecules.<sup>15</sup>

In order to determine whether there was any significant warming of the phosphor, despite the use of the  $\text{Cu}(\text{NO}_3)_2$  filter, a thermocouple element was imbedded in the front surface of a strip of fluorescein-boric acid glass. With the full beam turned on the strip in the paramagnetic apparatus, a temperature rise of less than 2° in five minutes occurred.

As a second approach, a thin strip of mica was covered with carbon black and suspended on the boom of the balance. Duplicating the technique of the paramagnetism determination (hydrogen atmosphere) readings were taken with the strip in total darkness and with half the strip illuminated by the full beam of the AH6 arc (filtered by the  $\text{Cu}(\text{NO}_3)_2$  filter). No measurable deflection occurred.

<sup>15</sup> At the time the preliminary report of the present determination was made (see references 4 and 5) it was thought that this was the reason for the low value of  $\chi_M$  obtained. However, the "concentration quenching" correction was not made at that time. If we divide the previously reported result  $\chi_M = 2100 \times 10^{-6}$  by 0.65, we obtain  $3230 \times 10^{-6}$ . This corresponds to a value of  $N_T = 2.10 \times 10^{-8}$  mole/cm, which also is not corrected for the  $\text{Cu}(\text{NO}_3)_2$  transmission (the corrected value is  $1.96 \times 10^{-8}$  mole/cm). Aside from these two corrections and some minor arithmetical corrections, the present results are the same as those previously reported (see reference 5).



TABLE II. Deflections in the Theorell balance.\*

Experiment 1, no field		Experiment 2, † field on ‡		Experiment 3, † field on		Experiment 4, field on		Experiment 5, field on	
dark	2.12	dark	1.87	dark	2.91	dark	3.77	50% beam	3.59
full beam	2.08	full beam	2.39 > 0.52	full beam	3.46 > 0.55	full beam	3.35 > 0.42	dark	3.43 > 0.16
dark	2.10	dark	1.98 > 0.41	dark	2.97 > 0.49	dark	3.71 > 0.36	50% beam	3.60 > 0.17
		full beam	2.52 > 0.54	-----	-----	full beam	3.30 > 0.41	dark	3.44 > 0.16
		dark	2.11 > 0.41	dark	3.03 > 0.48	dark	3.66 > 0.36		-----
		mean	0.47	full beam	3.51 > 0.46	mean	0.39	mean	0.16
				dark	3.05 > 0.46				
				mean	0.50				

\* Each reading is a mean of six settings of the eyepiece micrometer, in units 0.00833 cm.

† Room temperature, 25°C.

‡ The field is turned on before readings are taken, since the null point changes with field owing to diamagnetic asymmetry of the sample.

From these results it was concluded that both thermal depopulation of the excited state, and simple thermal effects, could be disregarded in these experiments.

### Oxygen Effect

In the first experiments<sup>3</sup> on the photomagnetism of acid fluorescein in its phosphorescent state, a large negative deflection (the illuminated half of the boom was pushed out of the field) was observed if the gas surrounding the boom of the microbalance was oxygen (or air). A strip of mica, covered with carbon black, and similarly illuminated in an oxygen atmosphere, was driven violently out of the field. With non-paramagnetic atmospheres (argon, carbon dioxide, or hydrogen) the phenomenon was absent.

The explanation of this queer phenomenon may be traced to the warming of a small layer of oxygen close to the surface of the illuminated part of the sample. The resulting diminution of the volume paramagnetic susceptibility of the oxygen should have a square dependence on the temperature according to Curie's and Charles' law. The more highly paramagnetic cool gas surrounding the dark half of the sample then would be pulled into the field, the flow of gas along the sample dragging it in the indicated direction. This "magnetic wind" phenomenon was avoided in the serious experiments by filling the apparatus with hydrogen gas as described above.

The satisfactory result obtained in this paramagnetism determination for a molecule in its phosphorescent state substantiates the validity of the theoretical treatment. This method may thus be extended to other cases in which the electronic character of a metastable level is in doubt. An independent determination of the present result would also be desirable, especially since the various determinations were not all carried to the highest refinement.

The specific molecular properties which are requisite for the application of this method are (a) a phosphorescence lifetime on the order of seconds, (b) a high relative quantum yield of phosphorescence, (c) a strong lowest normal absorption band, or a high solubility in the rigid glass medium, and (d) light absorption in an accessible range.

On the other hand, the extended sequence of determinations required for the quantitative evaluation of the paramagnetic susceptibility will put practical limits on its extensive application. In many cases purely qualitative results would be sufficient to deduce the multiplet character of a metastable level. Moreover, purely spectroscopic criteria which are now being developed offer methods of great experimental simplicity for deductions concerning the electronic characteristics of the energy levels of complex molecules.

<sup>16</sup> We are indebted to Professor W. F. Giaque for this explanation.