THE FORM OF THE ABSORPTION BANDS IN SOLUTIONS OF THE ORGANIC DYES, AND A RELATION BETWEEN ABSORPTION AND FLUORESCENCE

By Ernest Merritt

Abstract

To account for the breadth of the absorption and fluorescence bands in solutions and for the fact that the absorption and emission bands are not coincident it is assumed that for a given position relative to the solvent molecules the potential energy of an excited molecule is different from that of a normal molecule, and that the change in the potential energy that occurs during excitation or emission is to be counted as a part of the energy that determines $h\nu$. This leads to a general relation between the intensity of fluorescence F for the frequency ν and the coefficient of absorption for the same frequency, viz.

$$F=K'\nu e^{-h\nu/kT} \quad (1)$$

in which K' is a function of T and probably of ν.

The assumed conditions are met if the active molecule acts as an electric doublet whose moment changes from μ_1 in the normal state to μ_2 when excited. In this case it is shown that on the red side of the absorption band we have approximately

$$\alpha=\alpha_0 e^{ph\nu/kT}, \quad \text{where} \quad p=\mu_1/\mu_1-\mu_2 \quad (2)$$

Measurements made with Rhodamine-β and with Uranine show that Eq. (2) holds through a wide range with p nearly equal to unity, i. e. with μ_2 small compared with μ_1.

Eq. (1) has been tested by plotting log F—log α against $1/\lambda$. The result is in each case a straight line. The slant of the line is found to be 1.49×10^{-13} for rhodamine-B and 1.59×10^{-13} for uranine as compared with 1.64×10^{-13} the computed value of h/kT.

To account for the observed breadth of the fluorescence band of uranine it is sufficient to assume that the electric moment of the active molecule is of the order 3×10^{-19} e.s.u. This is about one-sixth of the value found by Jona for the electric moment of water.

IN THE case of solutions of the fluorescent organic dyes the fluorescence band is accompanied on the short wave side by a band of intense absorption. If the coefficient of absorption and the fluorescence intensity are plotted against wave-numbers the absorption band is always steeper on the long wave side, while the fluorescence band is steeper on the short wave side. There results from this fact a certain approach to symmetry in the appearance of the plot which is characteristic of all of the solutions of the organic dyes that have been studied.[1] It is usual also for the two bands to overlap; and in cases where this occurs it is found that Stokes' Law is violated: i.e., fluorescence may be excited by light whose wavelength is greater than that of a part of the fluorescence light emitted.

[1] E. L. Nichols, and E. Merritt, Studies in Luminescence, Carnegie Publication No. 298. 1912.

Since these relations are common to all cases of fluorescence in organic solutions it seems probable that they depend in some fundamental way upon the nature of the processes of absorption and fluorescence emission.

In attempting to account for these relations it is natural to assume,—and this assumption will be made in this discussion—that absorption occurs in quanta and that the absorption of a quantum results in an electron jump from one energy level to another, while the return of the electron to its normal state is accompanied by fluorescence emission. But in the case of liquids and solids this view leads to difficulties not met with in the case of gases, for the spectrum, instead of consisting of lines, is made up of bands, whose width is often as great as several hundred Ångström units. It is possible that the broad absorption band in a case like that of fluorescein is in reality a group of relatively narrow bands. But even if this is true we must account for the fact that each band has been sufficiently broadened to produce overlapping. If the quantum theory is to be applied to the absorption and fluorescence of liquids and solids there seems to be no escape from the necessity of introducing some hypothesis which will account for a continuous variation in the energy changes that occur.

A general explanation that is sometimes offered for the broadening of the absorption and emission lines in solutions is that the behavior of a given solute molecule is modified by the fact that it is surrounded by the solvent, and to a different extent depending on its configuration with reference to the solvent molecules. In other words the energy levels of the active molecules are altered by the presence of the solvent. In order to make this explanation quantitative I shall assume that for a given position relative to the solvent molecules, i.e., for a given electric field, the potential energy of an excited molecule is different from that of the normal molecule, and that the change in this potential energy which occurs during excitation or re-emission is to be counted as a part of the energy change that determines the frequency. If the potential energy of the normal molecule is u_1 and that of the excited molecule u_2 we have therefore

$$\begin{aligned} h\nu &= w_2+u_2-(w_1+u_1) \\ &= h\nu_0+u_2-u_1 \end{aligned} \tag{1}$$

where ν_0 is the frequency for a molecule that is free from the disturbing influence of neighboring molecules.

The number of molecules, N_1, that are so located as to absorb light whose frequency lies between ν and $\nu+d\nu$ is proportional (1) to the "a priori probability,"—disregarding the effects of thermal agitation,—that the configuration will be such as to give the necessary value to

u_2-u_1. This may be written $P(\nu)d\nu$; and (2) to the exponential factor $e^{-u1/kt}$ which determines the manner in which the distribution is modified by thermal agitation. Hence

$$N_1=K_1P(\nu)d\nu e^{-u_1/kT} \tag{2}$$

The number of excited molecules, N_2, which are so located as to emit the frequency ν is given by a similar expression in which u_2 takes the place of u_1

$$N_2=K_2P(\nu)d\nu e^{-u_2/kT} \tag{3}$$

It is here assumed that the time elapsing between absorption and re-emission is long enough to permit the excited molecules to reach the distribution corresponding to u_2 before emission occurs. And it is because this distribution is different from that of the normal molecules that the emission spectrum differs from the absorption spectrum.

Since the number of quanta absorbed is presumably proportional both to the number of quanta present in the incident beam and to the number of molecules capable of absorbing the particular frequency in question

$$\begin{aligned}\frac{\alpha I}{h\nu}&=A_1N_1\frac{I}{h\nu}\\ \alpha&=A_1N_1=\alpha_0P(\nu)e^{-u_1/kT}\end{aligned} \tag{4}$$

α being the coefficient of absorption. And since each electron returning to the w_1 level causes the emission $h\nu$ the intensity of the fluorescence light lying between ν and $\nu+d\nu$ is

$$Fd\nu=A_2N_2h\nu=F_0P(\nu)\nu d\nu e^{-u2/kT} \tag{5}$$

It should be pointed out that doubt may arise in the case of Eq. (4) as to whether the proportionality factor A_1 is independent of ν. The probability of the absorption of a quantum may depend not only upon N_1 and $I/h\nu$ but also upon the frequency. Again, in deriving Eq. (5) it is tacitly assumed that the probability of re-emission is independent of ν. This also is hardly likely to be true. In all probability α_0 and F_0 are both functions of ν.

If Eq. (5) is divided by Eq. (4) the fuction $P(\nu)$ is eliminated and we have

$$\frac{F}{\alpha}=K\nu e^{-(u_2-u_1)/kT} \tag{6}$$

Using the value of u_2-u_1 given by (1)

$$\frac{F}{\alpha}=K\nu e^{-h(\nu-\nu_0)/kT}=K'\nu e^{-h\nu/kT} \tag{7}$$

where K' is now a function of T and ν_0 and both K and K' may be functions of ν.

It is interesting to note that a relation somewhat similar to that of Eq. (7) has been derived by Kennard[2] by thermodynamic reasoning. Kennard finds that "the intensity at any point in a homogeneous fluorescence band is proportional to the intensity in the black body spectrum at that point multiplied by the power of light of that wave-length to excite fluorescence." Since the black body intensity, in the visible spectrum, is quite accurately represented by Wien's equation, we may therefore write

$$F = K\phi\nu^3 e^{-h\nu/kT} \tag{8}$$

where ϕ is the fluorescence exciting power.

If we put $\phi = \alpha f$, where f is the "specific exciting power," or the fluorescence produced per unit of absorbed energy, Eq. (8) may be written

$$\frac{F}{\alpha} = Kf\nu^3 e^{-h\nu/kT} \tag{9}$$

It will be noticed that if f is proportional to $1/\nu^2$ Eqs. (7) and (9) become identical. Unfortunately the few measurements that have been made of f have given conflicting results. Nichols and Merritt[3] find f approximately proportional to ν^{-3} for eosin, and to ν^{-6} for resorufin. Vavilov[4] finds f constant throughout the absorption band. The difficulty in determining f as a function of ν arises not only from the difficulties that are inherent in all fluorescence measurements but also from the fact that measurements can be made over only a small range of wavelengths. These same difficulties are met with in the experiments described later in the present paper, so that it is not possible to determine from these experiments what value should be assigned to the exponent of ν in Eqs. (7) and (9). The experimental results indicate, however, that these equations are correct so far as the exponential factor is concerned.

While Eqs. (7) and (9) indicate an interesting relation between absorption and fluorescence, neither equation is sufficient to determine the form of either the absorption or emission band unless one of the two is known. In order to predict the form of these bands we must go back to Eqs. (4) and (5) and make more definite assumptions regarding the dependence of u_1 and u_2 upon the configuration. In the discussion that follows I shall assume that both the active molecules and solvent molecules may be

[2] E. H. Kennard, Phys. Rev. **11**, 29–38 (1918).
[3] E. L. Nichols, and E. Merritt, Phys. Rev. Series I, **31**, 381 (1910).
[4] S. I. Vavilov, Phil. Mag. **43**, 307 (1922). (Also written Wawilow).

treated as electric doublets. In the case of the solvent molecules the correctness of such an assumption is made highly probable by the success of the Debye theory of dielectric polarization. And the complex structure of fluorescent organic compounds makes the assumption at least plausible for them. I shall assume also that the electric moment of the excited molecule is different from that of the normal molecule. We have therefore

$$u_1 = -\mu_1 E_0 \cos\theta, \qquad u_2 = -\mu_2 E_0 \cos\theta$$
$$h(\nu-\nu_0) = u_2 - u_1 = (\mu_1-\mu_2) E_0 \cos\theta \tag{10}$$

where μ_1 and μ_2 are the values of the electric moments of the active molecule in the normal and excited states respectively, E_0 is the electric field at the center of the active molecule, and θ the angle between μ_1 or μ_2 and E_0. We may therefore write

$$u_1 = -\frac{\mu_1}{\mu_1-\mu_2} h(\nu-\nu_0), \quad u_2 = -\frac{\mu_2}{\mu_1-\mu_2} h(\nu-\nu_0) \tag{11}$$

and Eqs. (4) and (5) become

$$\alpha = \alpha_0 P(\nu) e^{\mu_1/(\mu_1-\mu_2)\cdot h(\nu-\nu_0)/kT} \tag{12}$$

$$F = F_0 P(\nu) \nu e^{\mu_2/(\mu_1-\mu_2)\cdot h(\nu-\nu_0)kT} \tag{13}$$

The assumptions involved are subject to so many uncertainties that I have not attempted to determine the form of the function P throughout the band. Certain conclusions may be reached very simply, however, regarding the long wave side of the absorption band.

If an absorbing molecule is to be so located as to make the frequency ν possible we must have from (10)

$$\frac{h(\nu-\nu_0)}{\mu_1-\mu_2} = E_0 \cos\theta = E \tag{14}$$

where E is the component of E_0 in the direction of the doublet. By giving a suitable value to θ the molecule may always be brought into a position corresponding to a given ν, provided only that the required value of E is less than E_0. The probability, P, that ν will lie between ν and $\nu+d\nu$ is the same as the probability that E lies between E and $E+dE$, or that θ lies between θ and $\theta-d\theta$, where

$$dE = \frac{h d\nu}{\mu_1-\mu_2} = -E_0 \sin\theta \, d\theta$$

Since the probability that θ lies between θ and $\theta-d\theta$ is $\frac{1}{2}\sin\theta d\theta$.

$$P(\nu)d\nu=\frac{1}{2}\sin\theta\, d\,\theta=\frac{h d\nu}{2(\mu_2-\mu_1)E_0} \tag{15}$$

If therefore the active molecules were all located in a region where the field is E_0 we should have P proportional to V_0 where V_0 is the volume of this region of constant E_0, and for values of ν less than that corresponding to $E=E_0$ the function $P(\nu)$ would be independent of ν. It is hardly likely that this condition will be met. But there will be a tendency for the active molecules to move into positions where the field is strong, so that if V_0 is taken for the region in which E_0 is at least as great as some small value E_1 it is probable that nearly all the molecules will lie within this region. In this case $P(\nu)$ will be nearly equal to P_0V_0, where P_0 is the average value of P. As we approach one edge of the absorption band the function P therefore approaches a constant value and the expression for α (Eq. (4)) approaches the form

$$\alpha=K_3e^{+\mu_1/(\mu_1-\mu_2)\cdot h\nu/kT} \tag{15}$$

In this expression the constant exponential factor in ν_0 has been included in K_3.

The measurements made with solutions of uranine and rhodamine, which are described below, show that it is the long wave side of the absorption band for which this simplified expression holds. The coefficient $\mu_1/(\mu_1-\mu_2)$ must therefore be positive in order that the absorption shall increase with increasing ν. In other words the electric moment of the excited molecule must be less than that of the normal molecule. This seems not improbable, since when the electron moves away from the center of the molecule it is less firmly bound and therefore less likely to contribute to the electric moment.

In the region for which $P(\nu)$ is constant, i.e., the red side of the band, Eq. (13) takes the form

$$F=F_3\nu e^{\mu_2/(\mu_1-\mu_2)\cdot h\nu/kT} \tag{16}$$

where F_3 is probably a function of ν.

Experimental

In order to test the conclusions reached in the foregoing discussion measurements have been made, through as wide a range of wave-lengths as was practicable, of the fluorescence and absorption of aqueous solutions of rhodamine-B (National Analine Co.) and uranine (Heller and Merz)[5].

[5] Uranine is the sodium salt of fluorescen. The dye is made from fluorescein that is about 95% pure, sodium carbonate, and salt.

The results are shown in Figs. 1 and 2. Smooth curves have been drawn to indicate the form that the curves would probably take if accidental errors could be eliminated. The smoothed curves were not used, however, in making computations, which were in all cases based solely on the data directly observed. In computations involving graphical methods large scale plots were used. The width of the spectrophotometer slit was approximately 40 A.U. The frequency ν may be obtained from $1/\lambda$ (plotted horizontally) by multiplying by 3×10^{11}.

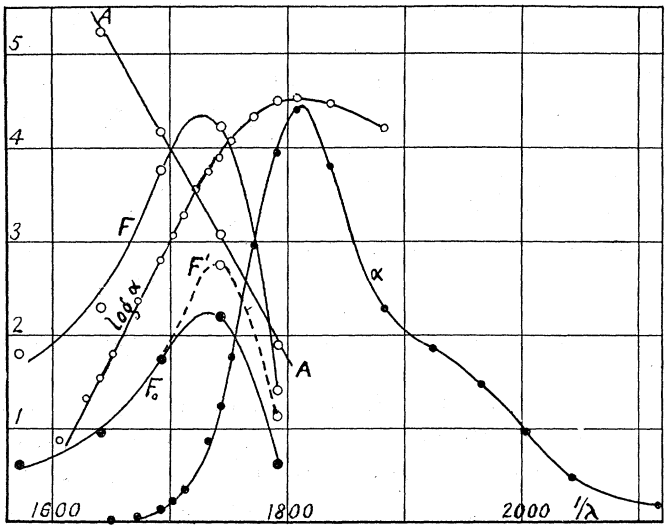

Fig. 1.

Rhodamine-B. Observed fluorescence, F_0. Fluorescence after correction for absorption, F'. Fluorescence intensity interms of an arbitrary energy unit, F. Coefficient of absorption α. In curve AA, $y=\log F/\alpha-\log \nu$.

Absorption. The intensity of the light of different wave-lengths transmitted by glass cells containing the solution was measured with a Lummer-Brodhun spectrophotometer, comparison being made with light from the same source which had passed through a similar cell containing distilled water. Several different cells were used ranging in thickness from 2 mm to 30 cm. To avoid errors arising from the possible failure of Beer's law the same solution was used throughout. The concentration for rhodamine-B was 111 mg per liter; for uranine, 47 mg per liter. The values of the coefficient of absorption α computed from these observations are shown in Figs. 1 and 2. The variation in α was so great—the largest value being more than two thousand times the smallest value—that it is quite impossible to show the lower part of the curve on so small a plot,

The general trend of the curve in the long wave region can be estimated, however, from the plotted values of log α.

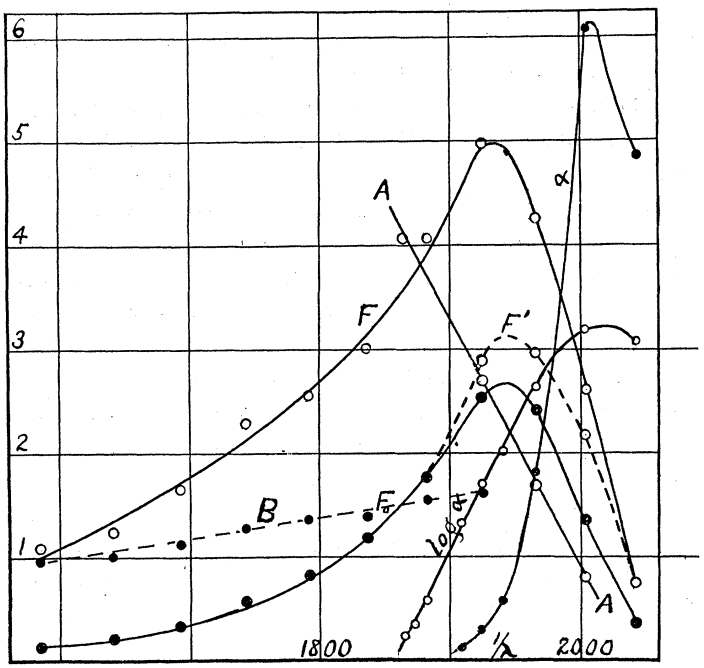

Fig. 2.

Uranine. Observed fluorescence, F_0. Fluorescence corrected for absorption, F'. Fluorescence intensity in terms of an arbitrary energy unit, F. Coefficient of absorption, α. In curve AA, $y=\log F/\alpha-\log \nu$. In curve B, $y=\log F-\log \nu$.

Test of Eq. (15). It will be seen from Figs. 1 and 2 that on the long wave side of the absorption band the relation between log α and $1/\lambda$ is very nearly linear. For extremely small values of α—in a region where the solution would ordinarily be called transparent—there is a deviation from the linear relation, which may be real but which, because of the uncertainty of the experimental results in this region, I am inclined to regard as accidental. We may conclude, therefore, that α is an exponential function of ν, as predicted in Eq. (15), through a considerable range; in fact, the exponential law holds until α has reached about one third of its maximum value. The multiplier of ν in the exponential factor of Eq. (15), as determined from the slant of the curve for log α, was found to be for rhodamine-B

$$s=\frac{\mu_1}{\mu_1-\mu_2}\frac{h}{kT}=1.60\times10^{-13}$$

and for uranine

$$s=\frac{\mu_1}{\mu_1-\mu_2}\frac{h}{kT}=1.62\times10^{-13}$$

For $T=18°C$ (the temperature of the solution), $h=6.56\times10^{-27}$ and $k=1.37\times10^{-16}$, $h/kT=1.644\times10^{-13}$.

For rhodamine s differs from h/kT by less than 3 percent, while for uranine the difference is still smaller. Since experimental errors as great as this are to be expected in measurements of this kind we can only conclude that the factor $\mu_1/(\mu_1-\mu_2)$ is nearly unity, and that μ_2 is therefore small compared to μ_1.

Fluorescence. In order to reduce the correction for absorption and to be able to extend the measurements as far as possible into the absorption band the fluorescence measurements were made with dilute solutions (rhodamine-B 0.67 mg per liter; uranine 0.5 mg per liter). The use of different concentrations for the absorption and fluorescence measurements is justified by the fact that in solutions of this type the form of the band, whether of absorption or of fluorescence, has been found to be independent of concentration.[6] Fluorescence was excited by a 400 watt gas filled lamp at a distance of about 30 cm. Since a small amount of scattered and diffusely reflected light was unavoidable, the correction to be applied on this account was determined by making measurements throughout the spectrum when the cell was filled with distilled water, everything else remaining the same. The stray light measured in this way was practically constant throughout the spectrum and was of the same intensity as the stray observed with the fluorescent solution at points outside the fluorescence band.

Correction for absorption. If the fluorescence excited per unit length of path is F', the intensity of the light emerging from the solution is

$$F_0=\int_0^a F'e^{-\alpha x}dx=\frac{F'}{\alpha}(1-e^{-\alpha a})$$

where a is the thickness of the cell.

α was determined by measurements of transmission made with the same cell and the same solution that were used in measuring F_0. The observed fluorescence F_0 and the corrected value F' are plotted in Figs. 1 and 2.

Energy distribution. In the fluorescence measurements the comparison source was a 40 watt tungsten lamp which had been calibrated for color

[6] E. L. Nichols, and E. Merritt, Studies in Luminescence, Carnegie Publication, No. 298, 1912. So far as I am aware, however, the assumed constancy of band form has not been tested through as wide a range of concentration as is here used.

temperature by the Bureau of Standards and which gave practically the same radiation as a black body at 2360°K when the potential difference between the terminals was maintained at 97.3 volts. The relative energy intensity for different values of $1/\lambda$ was computed by Wien's equation In the curves shown in Figs. 1 and 2 for the energy distribution in the fluorescence spectrum the ordinate is proportional to the value of the function F where $Fd\nu$ is the energy in that part of the spectrum lying between ν and $\nu+d\nu$.

Test of Eq. (7). The ratio F/α was computed from the experimentally determined values of F and α and $\log(F/\alpha)-\log\nu$ was plotted against $1/\lambda$ (see AA, Figs. 1 and 2). According to the theory here developed, assuming that K' in Eq. (7) is independent of ν, the slant of the line should be $h/kT=1.644\times10^{-13}$. The value computed from the plot is 1.49×10^{-13} for rhodamine and 1.59×10^{-13} for uranine. Since the fluorescence of uranine is in the yellow and green where spectrophotometric measurements are most accurate it is probable that the results obtained with uranine are the more reliable.

If we assume that K' in Eq. (7) is proportional to ν^2 so that Eq. (7) becomes identical with Eq. (9) (with K and f constant) a straight line should be obtained by plotting $\log F/\alpha-3\log\nu$ against $1/\lambda$. The variation in $\log\nu$ through the small range of frequencies used is so small that there is not much difference between these two plots. The slant of the line (not shown) for $F/\alpha-3\log\nu$ is, however, slightly larger than for the lines shown in Figs. 1 and 2. The form of Eq. (7) is such as to make it difficult to determine the multiplier of the exponential factor. But so far as it goes the experimental evidence is in favor of an exponent for ν considerably larger than unity.

Form of the fluorescence band. It is clear from the appearance of the curves for F that Eq. (16) is qualitatively correct. But it is also clear that the experimental errors are large so that a quantitative test cannot be expected to be very significant. However, when $\log F-\log\nu$ is plotted against $1/\lambda$ the result is roughly indicative of a linear relation (see curve B, Fig. 2). In the case of uranine the slant of the line gives

$$\frac{\mu_2}{\mu_1-\mu_2}\frac{h}{kt}=0.11\times10^{-13}$$

$$\mu_1=16\mu_2$$

Because of the small number of observed points such a calculation for rhodamine would have no significance.

Order of magnitude of the electric moments. In the expression $h(\nu-\nu_0)=(\mu_1-\mu_2)E_0\cos\theta$ (Eq. (14)) we may assume that the maximum value

of $\nu-\nu_0$ is determined by the extreme width of the fluorescence band, which we may estimate, in the case of uranine, as 600 units. If the minimum distance between the centers of the solvent and solute molecules is of the order 10^{-8} cm the maximum value of $E_0 \cos\theta$ will be of the order $2\mu_0\times 10^{+24}$ where μ_0 is the electric moment of the solvent molecule. Putting $\mu_0=1.9\times 10^{-18}$, this being the value found for water by Jona[7] we have

$$(15\mu_2)(3.8\times 10^{-18})\times 10^{24}=(6.56\times 10^{-27})(600\times 3\times 10^{11})$$
$$\mu_2=2\times 10^{-20}$$
$$\mu_1=3.2\times 10^{-19}$$

An electric moment about one sixth as great as that of water is thus sufficient to account for the observed broadening of the fluorescence band.

Discussion

The picture of the fluorescence process that is here suggested seems likely to prove helpful in overcoming the difficulties that have been met with in developing a theory of absorption and emission in liquids and solids. If, as has been assumed, one quantum is emitted for each quantum absorbed—but in general at a different wave-length—the energy emitted cannot in general be equal to the energy absorbed. If the exciting light is of short wave-length a considerable fraction of the absorbed energy is not reemitted but goes into the form of thermal agitation. On the other hand if Stokes' law is violated and the exciting wave-length is greater than the average wave-length of fluorescence, thermal agitation furnishes the energy that is necessary to make emission possible. When Stokes' law is violated fluorescence is a cooling process. The assumption that excitation changes the electric moment of the active molecule thus enables us to form a rough picture of a way in which radiant energy may be changed into the energy of thermal agitation, or thermal agitation into radiant energy.

It is clear that the proposed theory will have to be extended and modified in several particulars. For example it is not unlikely that more than two energy levels are involved in the fluorescence process. And it is possible that the excited state does not last long enough to permit a condition of thermal equilibrium to be reached. But in view of the difficulty of making precise measurements of fluorescence spectra the agreement between the simple form of theory here developed and the experimental results is not unsatisfactory.

Cornell University,
Ithaca, N. Y.
June 22, 1926.

[7] M. Jona, Phys. Zeits. **20**, 19 (1919). See also Marx, Handbuch der Radiologie, Vol. VI, p. 627.