

FLUORESCENCE AND PHOSPHORESCENCE

by PETER PRINGSHEIM

Argonne National Laboratory, Chicago, Illinois

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INTRODUCTION

A. General Theory

1. Postulates of Bohr's Quantum Theory. By absorption of light the energy of the absorbing system is increased. According to the laws of thermodynamics the inverse process, emission of energy in the form of radiation, must be possible. This inverse process *must* occur, if no other way of returning the system to its initial state of lower energy is available. Light emission excited by light absorption is called *photoluminescence*. For a long time photoluminescence was supposed to be an exceptional phenomenon characteristic of relatively few substances. The real problem is, however, to understand why so many substances are *not* photoluminescent.

Bohr's theory, first developed for interpretation of the spectra of the H atom and later adapted to more and more complicated systems, postulates that energy can be taken up by such a system only in certain definite steps; the system is stable only in discrete, more or less sharply defined energy levels. The lowest of these levels is the ground level or the ground state of the system. For all atoms and for many diatomic molecules the energy levels are perfectly known. For polyatomic molecules and for still more complicated systems like crystals, knowledge of the energy levels is still far from complete. Even for these systems however, the assumption of the existence of such energy levels has proved itself very fertile in developing an understanding of all processes connected with light absorption and light emission.

Only if the energy absorbed by a molecule is so large that one part of the system is completely separated from the remainder, as in a process of ionization or dissociation, can the separating particles take up undetermined amounts of kinetic energy, so that no discrete energy levels exist for the system as a whole.

In quantum mechanics a system in a given state is characterized by a "wave function" ψ which is the product of the wave functions ψ_i of all individual particles composing the system. These functions ψ_i determine the probability with which a particle is found at a point in space.

Apart from the introduction of discrete energy levels, Bohr's

theory postulated the following relation for a transition between two levels N and F with the energies E_N and E_F :

$$\nu_{FN} = 1/h \cdot (E_F - E_N) \quad (1)$$

h being Planck's constant = $6.63 \cdot 10^{-27}$ erg sec and ν_{FN} the frequency of the radiation which is emitted or absorbed by the transition.

In general, the wave number $\tilde{\nu} = 1/\lambda$ is used instead of the frequency ν , which has the dimension of sec^{-1} . $\tilde{\nu}$ is measured in cm^{-1} and is related to the frequency by the equation $\tilde{\nu} = \nu/c$. Hence a "term" T , which is characterized by its wave number $\tilde{\nu}$, has the energy $\tilde{\nu}hc$, but for the sake of brevity energies are frequently expressed in cm^{-1} . On the other hand, it is customary to measure energies in electron volts (eV), one electron volt being the energy which an electron acquires under the acceleration produced by a potential difference of one volt.

$$1 \text{ eV} \approx 8.11 \cdot 10^3 \text{ cm}^{-1} \approx 1.59 \cdot 10^{-12} \text{ ergs} \approx 23 \text{ kcal/mole}$$

2. Energy Levels. In the diagram of Figure 1 several energy levels of an atom or a more complicated system are represented by horizontal lines. The vertical distance between two of these lines is proportional

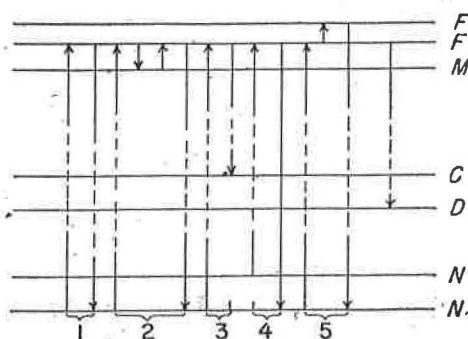


FIG. 1. Energy level diagram for the representation of fluorescence and phosphorescence.

- 1: resonance radiation.
- 2: phosphorescence.
- 3: fluorescence.
- 4 and 5: anti-Stokes fluorescence.

to the corresponding difference in energy; the level N represents the ground state. By absorption of light of frequency ν_{FN} the atom is raised to the level F and if no other energy levels exist between N and F , the atom can return to N only by re-emission of light of the same frequency ν_{NF} : theoretically this is the simplest case of photoluminescence; it is called "resonance radiation." In the diagram of Figure 1, however, several levels C, D, \dots are located between N and F . Under these conditions other transitions from F to C, D, \dots can

occur, resulting in the emission of spectral lines of frequency $\nu_{FC}, \nu_{FD}, \dots$. These frequencies are smaller than ν_{NF} . The law according to which the wavelength of fluorescence is always greater than, or in the limiting case equal to, the wavelength of the exciting light was first found empirically by Stokes (1852); the quantum theoretical expla-

nation was given by Einstein more than fifty years later (344). Small deviations from Stokes' law are possible if other energy levels N' or F' are located immediately above N or F respectively, so that the system can be raised by transfer of thermal energy either into N' before the exciting light is absorbed, or into F' during the lifetime of the system in the excited state F . Under these conditions the frequency of the exciting light $\nu_{FN'}$ is smaller than the frequency of the fluorescence ν_{FN} , or the frequency of the absorbed light ν_{FN} is smaller than the frequency of the fluorescence $\nu_{F'N}$: anti-Stokes fluorescence.

Such deviations from Stokes' law, by which additional energy is supplied by a body of low temperature to the radiation from a source of much higher temperature, of course in no way invalidates the second law of thermodynamics, as was suggested erroneously by Lenard (1284, 1293b, 1726, 1762b, 1762e).

3. Duration of the Luminescence Process. In the classical Lorentz-Drude theory the emission of monochromatic light by an atom or molecule originates from the oscillation of an electron which is bound to its position of equilibrium by a quasi-elastic force. The decrease in energy of the oscillating electric dipole which is caused by the emission of radiation, and the corresponding decrease in intensity of the radiation itself, follow an exponential law. The average duration of the emission, or the time after which the intensity has dropped from its initial value I_0 to $(1/e)I_0$, is:

$$\tau = \frac{3}{8\pi^2} \frac{mc}{e^2\nu^2} \text{ with } I_t = I_0 e^{-\frac{t}{\tau}} \quad (2)$$

For visible light, with $\nu \approx 5 \cdot 10^{14} \text{ sec}^{-1}$, τ is of the order of 10^{-8} sec .

In the absence of all external perturbations the lifetime of an excited state is determined, according to quantum theory, by the total probability of all possible transitions to lower energy levels. These transition probabilities A_{FK} can be calculated if the wave functions ψ' and ψ'' of the combining levels E_F and E_K are known:

$$A_{FK} = \left\{ \int_0^\infty \Psi' \Psi''^* \nu d\nu \right\}^2$$

The lifetime of a molecule in the excited state F is then:

$$\tau = \frac{1}{\sum_K A_{FK}} \quad (2a)$$

As in radioactive decay, the number of transitions per unit of time is at every instant proportional to the number of excited molecules and

thus the decay of the luminescence intensity again follows an exponential law, exactly as in the older theory.

The transition probabilities between various levels of one and the same molecule are of widely different magnitudes. While the Lorentz-Drude theory dealt only with electric dipole radiation, with a mean lifetime depending exclusively on the frequency of the oscillator, much weaker radiation of much longer duration can also be explained on the ground of classical electrodynamics by assuming electric quadrupoles or multipoles or magnetic dipoles or multipoles as sources of radiation. The emission by an electric quadrupole or a magnetic dipole lasts about 10^6 times longer than that of an electric dipole. In the quantum-mechanical models, however, an electric dipole can have a much smaller moment than the oscillating electron of the Lorentz theory and thus the decay of its radiation also can be much slower. Several experimental methods have been found which allow a discrimination between the radiation of electric and magnetic dipoles and multipoles (280a, 435, 1491, 1492, 1761a).

Transitions which have a very small probability because they correspond to the radiation of an electric dipole of small moment or of an electric multipole or a magnetic pole are called "forbidden" and the corresponding spectral lines are "forbidden lines." If no "allowed transition" from an excited state M to any lower energy level exists, the system, once brought into this state, must remain in it for a relatively long period. Such states are termed "metastable." If the system is absolutely unperturbed (as, for instance, in the highly rarefied atmospheres of stellar nebulas) light emission nevertheless occurs, but with very small intensity and slow decay. On the other hand, the transition from the ground state to the state M is also forbidden and the corresponding absorption line, if at all observable, is very weak. However, M can be reached indirectly; in the level scheme of Figure 1, this can occur by absorption of the line corresponding to the transition $F \leftarrow N$,* and by the subsequent transition $F \rightarrow M$. If M is separated by only a small amount of energy from F and if the excited system is in thermal equilibrium with the surrounding molecules a sufficient amount of energy can be provided to the system so that it can return to F . From there the emission of the lines corresponding to the transitions $F \rightarrow N$, $F \rightarrow C$, etc., may again take place. A photoluminescence

* The symbol for the higher level always precedes the symbol for the lower level; the direction of the transition is indicated by the arrow. This principle, which is generally used for the description of the spectra of diatomic molecules, is applied here similarly to the representation of atomic spectra.

process of this type, involving the passage through a metastable level, is called *phosphorescence*.

In the older literature, fluorescence and phosphorescence were distinguished only by the criterion of an observable afterglow: if the luminescence did not last longer than the irradiation, it was called fluorescence; if it was visible for an appreciable length of time after the end of the excitation, it was called phosphorescence. Modern experimental technique however, permits the measurement of the finite duration of any emission process, even if it is as short as 10^{-9} sec, and, on the other hand, the spontaneous transition probabilities, even in atomic processes, correspond to lifetimes which vary continuously from 10^{-8} sec to several seconds. Therefore, it is no longer possible to define some arbitrary duration of the emission process as the boundary between fluorescence and phosphorescence. (For a more complete definition of fluorescence and phosphorescence, see chapter IV.)

While, according to the definition given above, fluorescence and phosphorescence are first-order processes and follow exponential laws of decay, another kind of luminescence is a typical bimolecular reaction. If an electron is completely separated from its molecule by photoelectric ionization and if its recombination with any other ion produces the emission of light, the process is of the second order and decays, therefore, according to a hyperbolic law. Luminescence caused by recombination is observed in electrical discharge through gases or metal vapors under especially favorable conditions. These cannot be achieved in the case of excitation by light absorption. However, a phenomenon of the same kind occurs in certain phosphorescent crystals; it will be called "recombination afterglow" in the following treatment.

4. Effects of Perturbations. An excited system can be transferred to neighboring energy levels by outside perturbations, for instance by collisions or other interactions with surrounding molecules, and from these new levels transitions occur which produce emission lines not contained in the primary fluorescence spectrum. Furthermore, such perturbations may cause a momentary displacement of an energy level and if these displacements fluctuate with time and in space, broad and diffuse bands appear instead of sharp lines in the absorption and fluorescence spectra. This is true in particular for all condensed systems which are capable of luminescence (with the exception of certain crystals, especially at low temperatures). Under such conditions the peak of the emission band must be shifted with respect to the peak of the corresponding absorption band in the direction of greater

wavelengths. This consequence of Stokes' law will be dealt with in more detail in a later chapter.

If the whole energy of excited molecules can be lost as the result of collisions or other perturbations, the mean life of all excited molecules is shortened and the fluorescence yield is decreased.

The quantum yield of fluorescence is:

$$Q = I/A \quad (3)$$

where the fluorescence intensity I and the radiant energy A absorbed per unit time are measured by the number of light quanta contained in the emitted and absorbed radiation. In the case of resonance radiation, the quantum yield Q can be replaced by the "energy yield" Φ (I and A being given in ergs or calories), since in this case $Q \equiv \Phi$ (compare Section 105). [In general (namely in the case of Stokes fluorescence), the energy yield is smaller than the quantum yield, while in the case of anti-Stokes fluorescence Φ is slightly larger than Q .]

If no perturbations occur, the fluorescence intensity I_0 is equal to A when equilibrium is reached during the irradiation, and $Q = 1$. Under these conditions, the spontaneous transition probability α_0 alone determines the lifetime τ_0 , and the number n_0 of excited molecules in equilibrium is given by the equation:

$$A = I_0 = \alpha_0 n_0 = n_0/\tau_0 \text{ with } \tau_0 = 1/\alpha_0 \text{ and } n_0 = A/\alpha_0 \quad (4)$$

If the excitation energy can be lost by a second competing process with a probability α_1 , Equation (4) is replaced by:

$$A_1 = n_1(\alpha_0 + \alpha_1) = n_1/\tau_1 \text{ where } \tau_1 = 1/(\alpha_0 + \alpha_1) \text{ and } n_1 = A_1/(\alpha_0 + \alpha_1) \quad (5)$$

n_1 is smaller than n_0 . Supposing that the absorbing power of the molecules is not altered by the perturbations ($A_1 = A_0 = I_0$), the fluorescence intensity becomes:

$$I_1 = \alpha_0 n_1 = n_1/\tau_0 = I_0/(1 + \alpha_1 \tau_0) \quad (6)$$

and the yield:

$$Q_1 = I_1/A = \alpha_0 n_1/\alpha_0 n_0 = \tau_1/\tau_0 \quad (7)$$

$$\text{The "quenching constant" } \alpha_1 \text{ is: } \alpha_1 = \frac{\alpha_0(1-Q_1)}{Q_1} \quad (7a)$$

In the same way the yield is reduced by another perturbation with the probability α_2 to:

$$Q_2 = \tau_2/\tau_0 \text{ where } \tau_2 = 1/(\alpha_0 + \alpha_2) \quad (7b)$$

Hence the general relation:

$$Q_1:Q_2 = \tau_1:\tau_2 \quad (8)$$

The fluorescence yield of a given system is directly proportional to the actual lifetime of the excited state (I22I, I57I).

If several processes compete simultaneously with the radiating transition and if their probabilities are $\alpha_1, \alpha_2 \dots \alpha_n$, the lifetime of the excited state becomes:

$$\tau_n = \frac{1}{\alpha_0 + \alpha_1 + \alpha_2 + \dots + \alpha_n} \quad (9)$$

and the intensity of the luminescence:

$$\begin{aligned} I_n &= \frac{I_0}{1 + \tau_0(\alpha_1 + \alpha_2 + \dots + \alpha_n)} = \frac{I_1}{1 + \tau_1(\alpha_2 + \alpha_3 + \dots + \alpha_n)} \\ &= \frac{I_{n-1}}{1 + \tau_{n-1}\alpha_n} \end{aligned} \quad (10)$$

According to the classical theory, the width of a spectral line is proportional to the damping coefficient or inversely proportional to the mean life of the excited state. Qualitatively the same law holds in quantum theory. All perturbations by which the fluorescence is quenched increase the width of the corresponding emission line. The latter is determined, however, not only by the action of the perturbation on the excited state from which the emission process originates, but also by the action on the final state to which the system is transferred.

5. Coherence of the Secondary Radiation. The only photoluminescence process for which the classical wave theory of light could account without the introduction of rather artificial hypotheses was the excitation of resonance radiation. Existence of this phenomenon had been predicted on theoretical grounds by Lord Rayleigh long before its discovery by R. W. Wood. Resonance radiation was understood as special case of light scattering in which the scattering resonators were exactly in tune with the frequency of the primary radiation.

According to the original quantum theory only the average lifetime τ of an excited state could be determined, while for the individual molecule the time elapsing between the absorption and the re-emission of light obeyed the laws of statistics. Hence it seemed impossible that a definite phase relation could exist between the wave trains of the primary and the secondary light. Resonance radiation was considered to be incoherent. On the other hand Rayleigh scattering, which was known to be coherent, was ascribed to forced vibrations of "virtual oscillators" within the molecules. There was no

connection between the two phenomena. It was even assumed, for a time, that for radiation in resonance with the characteristic frequency of the scattering oscillators both processes might occur simultaneously and that it might be possible to separate them experimentally (e.g., by observing a different decay period for either of them) (129).

In the quantum-mechanical treatment, however, the electromagnetic field produced by the interaction of the primary radiation and the virtual oscillators of a molecule is exactly the same as that of the classical wave theory, and thus the steady transition from Rayleigh scattering to resonance radiation is restored. If various energy levels $C, D \dots$ exist in the molecule between the ground state N and the level F to which the molecule is raised by the absorption of the primary light, the resulting electromagnetic field surrounding the excited molecule is the same as if it contained a number of vibrating oscillators of frequency $\nu_{FC}, \nu_{FD} \dots$ in addition to the absorbing oscillator of frequency ν_{FN} . The "strength" of each oscillator is proportional to one of the transition probabilities $F \rightarrow C, F \rightarrow D \dots F \rightarrow N$. All phenomena related to the wave nature of the secondary radiation (coherence, interference, polarization) are to be derived from this model. However, the energy of the radiation is no longer spread continuously over the whole wave field and proportional everywhere to the square of the wave amplitude. The square of the amplitude determines only the probability for a photon of the corresponding frequency to be found at a given instant at a particular point. The absorption and emission of radiant energy occurs exactly as in Bohr's original theory, in quanta within practically infinitely short periods of time (1813).

Insofar as the problem of coherence is determined by the phase relation between primary and secondary radiation, only Rayleigh scattering and resonance radiation can be considered (1529). The existence of such coherence is not revealed by any experimental facts. Resonance radiation is observed exclusively in gases and vapors at low pressures. Under these conditions the coherence of the "classical" Rayleigh scattering with the primary radiation cannot be proved either, because of the random distribution of the molecules in a perfect gas.

If the fluorescence spectrum of a monatomic gas contains lines of wavelengths different from that of the exciting light, a constant phase relation between the waves of the primary and the secondary radiation is out of the question. However, a constant phase relation might still exist between the secondary wave trains originating at

different atoms; this kind of coherence could again only be observed by the angular distribution of the fluorescence intensity if the fluorescing atoms were fixed in space in a regular lattice.

Every kind of coherence between the radiation coming from different molecules must disappear in the fluorescence of molecules in which nuclear vibrations and rotations occur simultaneously with the electronic transition and independently in each individual molecule. The same is true if the molecules undergo external perturbations during their lifetime in the excited state. This is the case for the fluorescence of all liquids and solids. On the other hand, it has been proved by wide-angle interference experiments that the radiation emanating in different directions from an individual molecule of a liquid solution is coherent, exactly as the radiation emitted by a dipole as a spherical wave is coherent in itself according to the classical wave theory (435, 1489-1492, 1817).

• **6. Comparison with Other Excitation Processes.** The radiation emitted by an atom or a molecule depends only on its state of excitation and on the probabilities of transitions from this state to those of lower energy. It does not depend on the mode of excitation by which the system has been brought into the excited state. In this sense there is no difference between fluorescence and any other kind of light emission by the same atoms or molecules caused by collisions with electrons, by chemical processes, or by thermal agitation. The characteristic properties of a spectral line or a band (for instance, the dependence on temperature and pressure or the sensitivity to magnetic and electric fields) must be the same in every case.

A system emitting luminescence is not, however, in a state of thermal equilibrium; some of its molecules contain a much higher electronic energy than that corresponding to the actual temperature of the system and this is the essential feature of every luminescence process. It follows that the "excited" molecules can lose their excessive energy by collisions with other molecules: luminescence, for instance the photoluminescence of iodine vapor, can be suppressed or "quenched" by the addition of relatively small quantities of oxygen. If the same quantity of oxygen is added to iodine vapor heated in a quartz tube to a temperature of 1000° C at which it emits its characteristic bands as temperature radiation according to Kirchhoff's law, no appreciable change in the emission occurs, because now, in thermal equilibrium, the quenching collisions must be compensated by an equal number of exciting collisions (1284).

Photoluminescence is distinguished furthermore by an almost

complete control of the excitation process, since, among all atoms or molecules which are present, only those in a well-defined initial state are transferred into an equally defined excited state by the absorption of light of a given frequency. The complete spectrum of all atoms and molecules, modified within certain limits by the temperature, is emitted by a flame or an arc. By means of electron collisions in a gas at low pressure it is possible to exclude from the spectrum all lines which require an excitation energy surpassing the energy of the electrons under the applied voltage, but all levels lying below this energy are excited simultaneously. Besides, the accuracy of the method is not great enough to differentiate between the excitation of closely adjacent lines. On the other hand, the possibility of separately exciting neighboring energy states of a molecule by the absorption of monochromatic light is limited only by the degree to which the primary light can be made monochromatic. Even the state of polarization which is characteristic for a certain transition can be determined by this method of excitation; thus it becomes possible to ascertain the existence of the various Zeeman levels in very weak magnetic fields which are separated by such small intervals that they cannot be distinguished by other spectroscopic methods.

The same is still true, although to a smaller degree, for condensed systems; there, also, a much finer differentiation is obtained in the excitation of individual emission processes by light absorption than by any other mode of excitation.

B. Experimental Technique

7. Phosphoroscopes and Fluorometers. The experimental methods applied to the investigation of photoluminescence are, in general, very simple. The most important types of apparatus which have been especially designed for this purpose are the phosphoroscopes and fluorometers. These serve for measuring the duration of short or almost instantaneously decaying emission processes. All of these instruments are based on the principle of permitting the observation of the luminescence a short, and if desired, a variable time after the end of the excitation period.

The first phosphoroscope was invented by E. Becquerel (4,78); in a "Becquerel phosphoroscope" the luminescent substance is placed between two discs *M* and *N* (Figure 2), which are mounted on a common axis and have sector-shaped apertures *A* and *D* shifted with

CHAPTER IV

GENERAL SURVEY

A. Nature of Luminescent Substances

95. Conditions for Occurrence of Photoluminescence. Unperturbed fluorescence of gases and vapors is noted only at lowest pressures. At pressures at which collisions of excited molecules become sufficiently probable, either the secondary radiation is changed in frequency, or its intensity is weakened or even completely quenched. Polyatomic molecules seem to be less sensitive to quenching by collisions, in general, than monatomic vapors. In condensed states (pure liquid or solid, liquid or solid solution) the ability to fluoresce is lost, however, even in the majority of polyatomic compounds. The reasons for the absence of fluorescence due to the interaction of excited molecules with other molecules are, in principle, the same in condensed systems as in vapors: induced predissociation, chemical reactions, and "internal conversion." It is easily understood that the first of these processes has a greater chance of realization in condensed systems, where the excited molecules are in a constant state of collision.* In most instances no chemical reactions are produced by the absorption of light, and, especially if the nature of the surrounding molecules (of the solvent, for instance) has no marked influence on the optical properties of the absorbing substance, the re-emission of radiation must be suppressed by the third type of process (424).

The probability of internal conversion is greatly enhanced in condensed systems for two reasons. If, in a polyatomic vapor, the electronic excitation energy of an isolated molecule is converted to high vibrational energy of the electronic ground state, the inverse process must occur after some time. This fluctuation of energy from one form to the other may be repeated more than once, but as long as no collision takes place, the absorbed energy must eventually be re-emitted as radiation. Whenever a molecule has acquired a high

* It has already been pointed out that, on the other hand, the probability of spontaneous predissociation can be reduced by the stabilizing effect of collisions (see Section 83).

vibrational energy in a condensed system, this energy is almost immediately dissipated into thermal agitation of the surrounding medium and is never restored to the initially excited molecule. Also a molecule in a condensed system, especially in a solution, can never be treated as an isolated entity: in nearly every case it forms some sort of complex with surrounding molecules, e.g., of the solvent. Many metal ions exhibit, in aqueous solutions, absorption bands of much lower frequencies than those of the resonance lines in the vapor state and these may be due at least partially to electronic transitions between the dissolved molecules and the solvation envelope by which they are surrounded. In other instances the influence of the solvents on the absorption spectra of the dissolved molecules is relatively small, but none the less an interaction between the latter and the solvation envelope takes place and can greatly influence the fluorescence yield.

Since the existence of narrow absorption bands proves the corresponding electronic transitions to be well protected against perturbations from outside, one might assume that molecules exhibiting such bands should have a greater chance to be fluorescent than others. This is correct up to a point; among compounds with narrow absorption bands the number of fluorescing substances is relatively great, although fluorescence is by no means a general property of such compounds. For instance, the chromium alums and the uranous salts are not fluorescent. On the other hand, the absorption bands of many strongly fluorescent dye solutions are no less diffuse and broad than those of nonfluorescent dyes. Very small changes in the constitution of a molecule can have a great influence on the probability of internal conversion and, thus, on the occurrence or nonoccurrence of fluorescence without appreciably affecting the power of absorption.

96. Most Important Types of Luminescent Substances. If photoluminescence is a characteristic property of a compound as such, the molecules of this compound must be fluorescent under various conditions — for instance, when the compound is in the crystalline state, in a liquid solution, and in the vapor state. Practically all molecules which are photoluminescent in condensed states are more or less complex. The only exceptions are the positive ions of some rare-earth metals, the optical properties of which are so little perturbed by the surrounding medium that, even in crystals or in aqueous solutions, they behave almost like the atoms of a vapor. Among the complex inorganic molecules the positive ions UO^{++} are, with few exceptions, fluorescent in crystalline uranyl salts and in liquid solutions of such salts. A few other metallic ions (Tl^+ , Pb^{++} , and Sn^{++}) are able, in

aqueous solutions, to form complexes which can be excited to fluorescence (521,522,617,1304). In addition the cyanoplatinites are to be mentioned and, finally, some derivatives of siloxene which, owing to their ring structure, have much in common with aromatic compounds. It is doubtful whether the tungstates, molybdates, and some similar salts should be included in this class for, although many crystals containing these ions are strongly photoluminescent without being appreciably contaminated by an impurity, nothing is known about their fluorescence in other than the crystalline state. Thus, they may be classified as belonging to the mineral crystal phosphors.

Although only a relatively small number of inorganic compounds must be considered here, organic chemistry provides an almost unbounded wealth of examples, especially in the class of aromatic and polycyclic compounds, beginning with benzene and reaching to the most highly complex dyestuffs.

No less numerous are the substances belonging to the last main class of materials which are luminescent in the solid state. They are called "crystal phosphors."* As indicated by this designation, it is no longer an individual molecule which is luminescent by itself. The ability to re-emit absorbed radiation as light is intimately related to the condition that the molecules form a part of a crystal lattice; in most cases the luminescence is due to the incorporation of minute impurities into the "base material" of the crystal.

In general, only *fluorescence* is observed in liquids and most frequently it is a fluorescence of very short duration. Very weak phosphorescence has been obtained, however, with some liquid dye solutions (136,745,927b). Although a strong afterglow of considerable duration is observed with many solids (glasses as well as crystals), phosphorescence lasting many hours, and even days, after the end of the excitation seems to be a specific property of crystal phosphors "activated" by impurities.

97. Energy Transfer from the Absorbing to the Emitting Mechanism. In the isolated complex molecules of a vapor, radiant energy can be absorbed in one part of a molecule and pass into another part the characteristic fluorescence of which is subsequently emitted. If collisions occur, the electronic energy of an excited molecule can be transferred to the colliding molecule with subsequent emission of "sensitized fluorescence." Similar processes may take place in con-

* Many organic compounds are luminescent in the crystalline state, and so are uranyl salts and the platinous cyanides, but in these cases the crystalline form is not an essential condition for the occurrence of luminescence.

densed systems. The first type is observed at its best with certain complex rare-earth salts in liquid solutions.

The excitation and fluorescence spectra of crystalline or dissolved inorganic europium salts (nitrates, sulfates, etc.) are confined to several groups of narrow lines, and the fluorescence intensity which can be attained is weak. Organic salts of europium, such as the salicylaldehyde or the benzoyl acetate, have strong continuous absorption bands between 3200 and 4400A, and the characteristic europium line-fluorescence is excited with great intensity if the salt is irradiated with light of any wavelength between these limits. It is certain that the broad absorption bands which appear also in the absorption spectra of the organic compounds containing no rare earth are not connected with an electronic transition within the europium ion. The excitation of the internal electronic system of Eu^{+++} is caused by light absorption in another part of the complex molecule. The efficiency of the energy transfer seems to depend a great deal upon the nature of the bond between the rare-earth ion and the absorbing radical. It is best in the purely covalent, benzene-soluble benzoyl acetate, less good in the picrate, and completely missing in europium cyanoplatinite crystals with their purely ionic bonds (1816).

Probability of the energy transfer must also depend, however, on still other conditions, for the same compounds which provide the strongest europium fluorescence are quite inefficient with terbium. On the other hand, the green terbium line-fluorescence is excited with great brilliancy by light absorption in the u.v. bands of terbium acetoacetanilide, while the corresponding europium compound is very slightly fluorescent.

The converse effect has been obtained by Tomashek. The excitation of the blue-violet fluorescence characteristic of organic acids by the Hg-lines at 3130A is greatly enhanced in the gadolinium salts of these acids (for instance, gadolinium salicylate) which in addition to the normal absorption bands of the acids show the typical absorption lines of the trivalent gadolinium ion in the vicinity of 3130A (Section 140). The violet fluorescence of the europium salts of the same organic acids is only very slightly excited by the Hg-lines at 3130A, while the fluorescence of the gadolinium and of the europium salts is excited with equal rather low intensity by the Hg-lines at 3650A which are not selectively absorbed by either of the rare-earth ions (1698c).

While the phenomena described in the last paragraphs may be designated as internally sensitized fluorescence, the experimental

proofs for the occurrence of externally sensitized fluorescence in liquid solutions are rather unconvincing.

In crystals still other means of energy transfer from an absorbing to an emitting center must be taken under consideration: "internal photoelectric effect" and "exciton migration." These might be regarded as belonging to the category of energy transfer within a complex molecule, insofar as a crystal can be treated as a huge polyatomic molecule. In the first instance, an electron is completely detached by light absorption from its normal location and, transporting a certain amount of energy, it travels across the crystal lattice until it excites light emission at another point within the crystal. Exciton migration is a purely quantum-mechanical resonance phenomenon; in a certain way it is similar to the diffusion of a resonance light quantum in the "imprisoned radiation" of mercury vapor. However, the total time during which the photon remains within the vapor as imprisoned radiation is the sum of the individual lifetimes of the single excited atoms, while, in a crystal, the total lifetime corresponding to exciton migration becomes shorter in the same ratio as the number of identical crystal elements which take part in the resonance process becomes larger. The excitation energy does not belong to an individual element at any moment, but simultaneously to all of them; the probability of emission increases correspondingly, and if the crystal is homogeneous it is not possible to determine whether the absorbing and the emitting centers are the same or not. If the crystal contains an impurity with a characteristic emission band of its own, light absorption may be due to the base lattice, through which the energy travels as an exciton until it reaches the impurity center where, finally, the radiation is emitted.

Both phenomena are of special importance for crystal phosphors. As these differ in many respects from other classes of luminescent liquids and solids, it seems advisable to treat their properties separately. But photoconductivity and exciton migration can also occur in luminescent crystals which do not belong to the class of "crystal phosphors" and, thus, they should be mentioned here (143b, 428, 1803). Leaving the crystal phosphors aside, the properties more or less common to all other photoluminescent solids and liquids are collected in the following sections, while in later chapters the principal classes of fluorescent substances are treated. This division of the material, although leading to some repetition or overlapping, seems to be the best way by which a more general understanding of the phenomena can be attained. The crystal phosphors are dealt with in the last chapter.

B. Course of the Emission Process

98. Fluorescence and Phosphorescence. It has already been mentioned in the introductory chapter that, in the present state of knowledge and experimental technique, the duration of the emission process does not supply an unequivocal method of distinction between fluorescence and phosphorescence. J. Becquerel held the opinion that no essential difference really existed between the two kinds of photoluminescence, and that there was a continuous transition from the first to the second. As we know now, the situation is complicated by the fact that typical fluorescence is not inconsistent with a relatively long afterglow. For phenomena of this kind, F. Perrin introduced the term "fluorescence of long duration," which, for the sake of brevity, will be replaced here by "slow fluorescence" (*A, 272, 1221*).

An instance in which all possible luminescence processes can be observed and which corresponds to the energy-level diagram of Figure 1 is provided by mercury vapor which is excited, at room temperature and in the presence of nitrogen, by the absorption of the resonance line 2537Å. Some of the excited atoms re-emit the line as fluorescence within the normal lifetime (10^{-7} sec) of the state 6^3P_1 ; other atoms are transferred by collisions with nitrogen molecules into the metastable state 6^3P_0 . Some of these emit the forbidden line 2655Å and thus return to the ground state by a relatively improbable transition which has a much longer decay period and must be designated as slow fluorescence. Other 6^3P_0 -atoms are brought back to the 3P_1 -state by collisions with nitrogen molecules of sufficient energy, and the final process is, once more, emission of the resonance line. The duration of this afterglow depends primarily on the frequency of collisions with sufficient energy (in other words, on the temperature) and is a typical phosphorescence.

For the complex molecules which have to be considered in these paragraphs, the energy levels and the corresponding transition probabilities are almost never as well known as they are in the example of the mercury atom. Nevertheless, it is possible also to give here general criteria for the discrimination between fluorescence and phosphorescence. Becquerel's hypothesis seemed, at first, to be corroborated by an experimental result. Wiedemann and Schmidt found that while liquid dye solutions showed only fluorescence with no measurable afterglow, a phosphorescence could be observed and its duration could be increased if the viscosity of the solution was increased by the

addition of gelatin (1454,1835). A similar afterglow could be observed when the dye was dissolved in various solids such as sugar, benzoic acid, albumen, etc. Later, however, Vavilov and Levshin proved that there was no gradual increase of the duration of luminescence but that in the solid solutions the fluorescence retained the same short lifetime, of the order of magnitude of $5 \cdot 10^{-9}$ sec, and that a second process of much longer lifetime was superimposed on this fluorescence (1766). Boudin was the first to observe a phosphorescence lasting about 10^{-3} sec in a diluted eosin solution in glycerol free of oxygen which was placed in a Becquerel phosphoroscope. Kautsky obtained similar results with aqueous and alcoholic solutions of eosin, erythrosin, rose bengale, phloxin, and porphyrin; the relatively strong afterglow of chlorophyll could be observed only when the dye was dissolved in pure isoamylamine (136,469,750,1453,1454).

In every one of these cases the fluorescence and the phosphorescence are excited by light of the same wavelength and their emission spectra are identical: the light absorption leads to, and the emission starts from, the same excited level. It is obvious that the relatively stable state to which some of the excited molecules are transferred and which causes the appearance of phosphorescence is characteristic of the molecule itself; the phosphorescence is weak or completely missing in liquid solutions only because the probability of some sort of quenching process is much greater in this case. When phosphorescence occurs, the intensity of the luminescence drops to a much lower level at the moment when the primary radiation is cut off; from there on, it decays continuously to zero.

If an afterglow can be observed in a phosphoroscope or even without such an instrument, and if the intensity curve shows no discontinuous break immediately after the end of the excitation, the afterglow is not phosphorescence but a slow fluorescence [corresponding to the emission of the forbidden line by the Hg (6^3P_0)-atoms]. If this afterglow lasts only a few thousandths of a second or less, the bands corresponding to the same electronic transition are observable also in the absorption spectrum; and the slow fluorescence can be excited "directly" by light absorption in these bands (272 1218,1227,1767).

Many organic substances can be excited to emit a slow fluorescence different in color from their normal fluorescence and lasting several seconds. In general no band corresponding to the forbidden electronic transition which produces this slow fluorescence is found in the absorption spectrum; emission is excited by light absorption in

the normal absorption bands of the substance, exactly as emission of the forbidden Hg-line is excited by absorption of the mercury resonance line and a subsequent transfer of the atoms to the metastable state: it is an "indirectly excited" slow fluorescence. It has already been stated that the visible slow fluorescence of Eu^{+++} and Tb^{+++} which can be excited directly is excited indirectly, with much greater intensity, in certain complex organic compounds (1816).

The long lifetimes of the states M from which phosphorescence and indirectly excited slow fluorescence originate need not be due [as in the case of $\text{Hg}(6^3P_0)$], or at least may not be due exclusively, to electronic selection rules according to which certain transitions are forbidden or, rather, extremely improbable. Existence of longlived high-energy modifications of polyatomic molecules can also be explained by applying the Franck-Condon principle and by assuming that the atomic nuclei have an equilibrium configuration in state M which does not correspond to any configuration occurring in the electronic ground state. Under these conditions, a radiating spontaneous transition from M to N has an exceedingly small probability. Franck and Livingston, therefore, call the state M a tautomeric modification of the molecule. With a less specific designation, which may be applied also to the analogous phenomenon in crystal phosphors all states which owe their long life to the Franck-Condon principle will be classified as "quasi-stable," in contradistinction to those which are "metastable" because of an electronic selection rule (424).

The duration of a fluorescence process is essentially independent of external conditions insofar as this duration is determined by internal transition probabilities. If the mean life τ_0 of an excited state is shortened by a quenching process which might depend on the temperature this is, according to Equation (8), (compare Section 4, page 6) always accompanied by a proportional decrease in the total luminescence yield. Apart from such secondary effects, the temperature has no influence on the duration of fluorescence. As a matter of fact the afterglow of the uranyl salts or of the slow fluorescence bands of dyestuffs is very nearly the same at room temperature as at liquid-air temperature (927a, 1227, 1302). On the other hand, it follows from the energy-level diagram of Figure 1 that the duration of a real phosphorescence is fundamentally a function of temperature, since the energy deficiency $F - M = \epsilon$ must be provided by thermal fluctuations. The lower the temperature, the longer is the average time interval elapsing before the necessary energy is supplied to M . Below a certain temperature the return from M to F will practically not occur at all, while the

passage from N to F by light absorption and the transition from F to M is not impeded.

Thus, the phosphorescence is excited and "frozen in." If the temperature is subsequently raised, the absorbed energy is set free and re-emitted without new excitation as a brilliant flash. This phenomenon was discovered by Dewar when he immersed barium cyanoplatinite* in liquid air (283). Even if the platinite is kept after excitation in the dark at low temperature for an hour or more, a bright light emission takes place when the liquid air is removed. Similar phenomena occur in the phosphorescence of solid dye solutions, though with smaller efficiency. The most brilliant examples of "frozen-in" phosphorescence are found in certain crystal phosphors. All so-called thermoluminescence is nothing but phosphorescence which already is frozen in at room temperature.

99. Decay Curves. All emission processes treated in this chapter, normal and slow fluorescence as well as phosphorescence, are monomolecular (first-order) processes. Hence, according to theoretical expectation, their decay curves should all be simple exponentials:

$$I = I_0 e^{-at}, \text{ with } a = 1/\tau \quad (60)$$

From fluorometric measurements and other more indirect methods, the fluorescence of liquid dye solutions is known to have a lifetime usually not exceeding $5 \cdot 10^{-9}$ sec. The shape of the decay curve during so short a period has not yet been determined by direct experiments. However, the assumption of an exponential decay of the fluorescence of dye solutions is supported by the fact that calculations based on this hypothesis yield identical values for the lifetimes of excited dye molecules when widely differing shutter frequencies are used for obtaining the fluorometer curves, from which the τ -values are derived (compare Figure 4) (1623). Another result of fluorometric measurements, which was obtained by Cram and later confirmed by Thumerman, must be mentioned in this connection. Fluorometer curves corresponding to the fluorescence of various dye solutions at low temperatures could be interpreted only by supposing that a dark interval of the order of magnitude of 10^{-7} sec occurred between the end of the excitation and the beginning of the emission, while the latter proceeded from there on with the normal decay period of $5 \cdot 10^{-9}$ sec (243, 1709). The interpretation of several earlier experiments which seemed to prove the existence of a dark interval between the end

* At room temperature, this compound shows only a short-lived fluorescence.

of the excitation and the beginning of the emission in fluorescing solutions were based on erroneous assumptions concerning the methods used in these experiments (464,525,638,1884). Cram's and Thumerman's papers do not seem to contain any fallacies of this kind, but no theoretical interpretation of their unexpected results has been found so far (Compare Section 78).

For slower fluorescence processes a direct observation of the decay is possible and, in all cases in which measurements were made, the results were in satisfactory agreement with an exponential decay.

Nichols and Merritt, to whom we are indebted for much important research on the fluorescence of uranyl salts, were of the opinion that this luminescence originated from a bimolecular reaction and that its intensity after the end of the excitation should, therefore, be represented as a function of time by an equation of the type:

$$I = Ct^{-2} \quad (61)$$

From their experiments they derived for every uranyl salt several (in most instances, three) different values of the constant C for different intervals of time t , and so the curve representing $I^{-1/2}$ as a function of t was a broken line consisting of three straight branches (Figure 95).

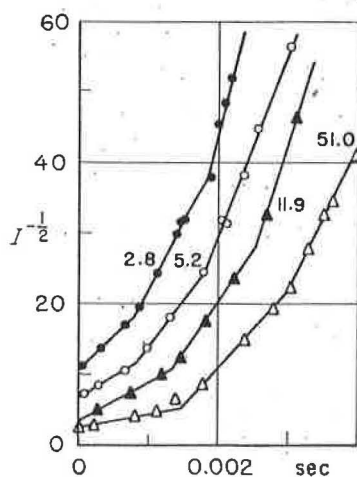


Fig. 95. Decay of fluorescence of uranyl salts at intensities of the exciting radiation varying from 2.8 to 51.0 (in arbitrary units) (Nichols and Merritt).

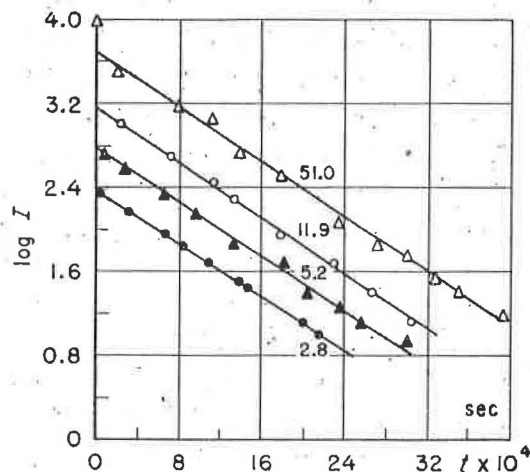


Fig. 96. The values of Figure 95 in a plot of $\log I$ versus t [Vavilov and Levshin (1767)].

Vavilov and Levshin showed, however, that all results published by Nichols and Merritt, as well as a great number of new observations of

their own, were represented without exception as straight lines on $\log I$ versus t diagrams, in accordance with Equation (60) (Figure 96) (*H*, III 3, III 6, I 767).

The same has been proved by various authors for the phosphorescence and for the slow fluorescence of solid dyestuff solutions, platinum cyanides, canary glass, and other luminescent compounds with values of τ larger than 10^{-4} sec (Figure 97). Minor deviations from strictly logarithmic decay curves which were occasionally observed probably can be ascribed to secondary effects (459f, 915, 927a, 930, 1302, 1428, 1772).

For instance, if, in a solid solution with a luminescence yield less than 100 %, the solvent molecules surrounding the individual molecules of the luminescent compound do not have identical configurations, the excited molecules may have unequal probabilities of transferring their excitation energy to the solvent. Thus they would have slightly different mean life times and the decay curve would correspond to the superposition of numerous exponentials with slightly different exponents.

As mentioned in the foregoing section, the coefficient α in Equation (60) is a function of temperature for phosphorescence processes. In the first approximation the relation between α and the absolute temperature T is also exponential:

$$\alpha = se^{-\varepsilon/kT} \quad \text{or} \quad \log \alpha = b + c \cdot T^{-1} \quad (62)$$

where $\varepsilon = F - M$ or the heat of activation of the phosphorescence-process. s is nearly constant but varies slightly with the temperature; it determines the probability with which the process occurs when the energy ε is provided by thermal fluctuations.

The decay of a simple band whether fluorescence or phosphorescence, is always uniform for all parts of the band. This has been proved by direct observation for the slow fluorescence of uranyl salts and rare-

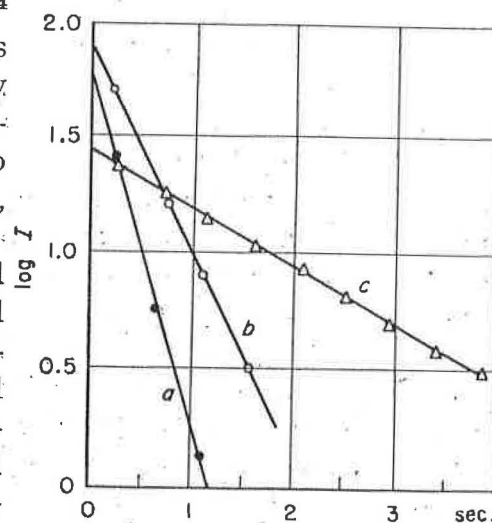


Fig. 97. Decay of the luminescence of tryptaflavine adsorbed on silica gel (Pringsheim and Vogels).

a: green phosphorescence at + 39° C. *b*: the same at - 18°.
c: orange slow fluorescence at - 180° C.

earth ions, and for the fluorescence and phosphorescence of dyes in solid solutions; it has been proved by indirect methods for the short-lived fluorescence of liquid dye solutions. In every instance where the color of the luminescence varies during the period of the afterglow, it could be shown that two emission bands of different spectral composition and with different lifetimes were superimposed. An example is the green phosphorescence band and the yellow band of slow fluorescence emitted by tryptaflavine in solid solution at -40°C (927a, 1302).

Any light emission which is excited by light absorption must have a certain period of growth or "induction" corresponding inversely to the decay period. With a long-lasting constant irradiation the luminescence reaches a limiting or equilibrium value I_0 when the number of molecules excited per second by light absorption is equal to the number deactivated by emission:

$$dn/dt = A - an_0 = 0; I_0 = an_0 = A; a = 1/\tau_0 \quad (63)$$

Absorbed energy A and emitted energy I are measured in quantum units, and no quenching processes of any kind are assumed to exist in this simple treatment.

In analogy to the mean lifetime τ_0 at the end of which the intensity has dropped from I_0 to $I = e^{-1}I_0$ after the termination of the excitation, the mean induction period ϑ can be defined as the time elapsed from the beginning of the excitation until the luminescence has attained the intensity:

$$I = (1 - 1/e)I_0 \quad (64a)$$

If the luminescence is due to the same electronic transition as the absorption and both have the same transition probability (an assumption which is valid for practically all directly excited fluorescence processes), τ_0 and ϑ are equal, irrespective of the absolute value of τ_0 . This follows from the integration of Equation (63) for $dn/dt > 0$:

$$n = n_0 (1 - e^{-t/\tau}) \text{ for } t = \tau_0 = \vartheta \quad (64b)$$

If, on the other hand, the duration of the luminescence depends partially on transition probabilities which have no influence on the absorption process, as in phosphorescence and indirectly excited slow fluorescence, the mean induction period can never be longer than the mean decay period, but it can be much shorter. Under these conditions, τ_0 and ϑ are no longer connected by a definite relation. Temperature determines the duration of phosphorescence because it determines the

transition probability from M to F , but it has no influence on the absorption process. If the intensity of the exciting irradiation is kept constant, a decrease in temperature increases the number of molecules which remain in the quasi-stable state; eventually, practically all molecules have been transferred into this state when equilibrium is reached. The phosphor is then "fully excited" or "saturated." Greater intensity of the exciting light produces saturation within a shorter time, while this leaves the decay period of the phosphorescence unaltered. Similar considerations are valid for indirectly excited slow fluorescence.

The existence of an induction period was discovered by Becquerel in luminescence processes which are now classified as slow fluorescence. The phenomenon is easily observed in the slow fluorescence of organic compounds at low temperatures (for instance, Kowalski's "progressive phosphorescence"; compare Section 136) and in the phosphorescence of many crystal phosphors (815).

100. Luminescence Intensity and "Light Sum" L . Under the conditions stated in the last section, according to which the periods of growth and decay of luminescence are equal, the relative number of excited molecules always remains small compared to the total number of unexcited molecules, even if the primary radiation has a very high intensity. Therefore, the fluorescence intensity is strictly proportional to the intensity of the exciting light over the widest obtainable range (582). This is no longer true if, in the course of a phosphorescence excitation process, a relatively great number of molecules is transferred into a quasi-stable state M . Under these conditions, the phosphorescence intensity reached at the end of the excitation process tends toward its saturation value I_m . A further increase of the primary intensity has no appreciable influence on this value. Figure 98 shows the phosphorescence intensity of fluorescein dissolved in vitrified boric acid at 18°C as a function of the strength of the primary radiation: if the intensity of the exciting light is reduced to one-half of its maximum value, the phosphorescence decreases by only about 12%. Similar curves were obtained for the slow fluorescence of the same solid solution at -185°C (930).

For any kind of fluorescence, regardless of its duration and its mode of excitation, the intensity of the secondary radiation is a direct measure of the number of excited molecules present at the moment of observation, according to Equation (63), in which constant α depends only on the nature of the luminescent molecule. On the other hand, the intensity of a phosphorescence can be very small or even zero at the

end of the excitation period in a fully excited phosphor. Hence, the number of excited molecules present at a given moment is no longer proportional to the actual intensity of luminescence but to the total

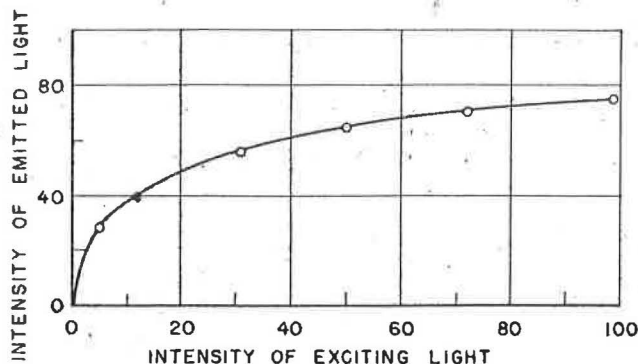


Fig. 98. Intensity of the phosphorescence of fluorescein in boric acid as a function of the exciting radiation at 18° C (Lewis, Lipkins, and Magel).

number of light quanta the substance is still able to emit without new excitation, or to the "light sum" L stored in the phosphor:

$$L_t = \int_t^{\infty} I dt \text{ or } I = -dL/dt \text{ and } L_0 = I_0 \int_0^{\infty} e^{-at} dt = I_0 \tau \quad (65)$$

If a simple exponential decay is assumed for I , L is also an exponential:

$$L = I_0 \tau e^{-at} \quad (66)$$

If τ is known, I_0 and L_0 can be derived from the measurement of I at any given moment after the end of the excitation. As long as τ is constant, I_0 and L_0 are proportional to I at any given time t , and in order to find, for instance, the relative change of I_0 or L_0 with varying intensities of the primary light it is sufficient always to measure I at the same time t after the end of excitation under the varying conditions of irradiation.

If the intensity of the primary radiation is far below the saturation value,* I_0 is equal to A [Equation (63)] as soon as the equilibrium state is reached and according to Equation (65) the light sum or the total energy stored in a phosphor at a given intensity of primary radiation increases proportionally with τ . If experimental results

* This condition is fulfilled in almost all cases of afterglow not exceeding a few seconds.

disagree with this conclusion, some kind of quenching process must compete with the luminescence emission. In the other limiting case, when saturation is reached either because the exciting radiation is extremely strong or because the lifetime τ is very long, L_0 has always the same value at the end of the excitation period, while I_0 decreases with increasing τ — for instance, when the temperature is lowered.

In a saturated phosphor, L_0 is proportional to the total yield Q even in the presence of some quenching process, while I_0 , being a function of τ , is not directly connected with Q . If, on the other hand, the phosphor is far from being saturated, I_0 is proportional to Q , regardless of the value of τ , while L_0 would increase with an increase of τ according to Equation (66). (In the case of saturation, I_0 would decrease with decreasing temperature at a constant value of Q ; far below saturation, the luminescence intensity is always $I_0 = QA$ after equilibrium is reached).

C. Emission, Absorption, and Excitation Spectra

101. Band Width, Stokes' Law, and the Franck-Condon Principle.

The energy levels of a luminescent molecule are influenced in two different ways by the continuous and fluctuating interaction with the surrounding medium. Under this influence the energy of a level is not sharply determined, but varies at every instant for differently located molecules and varies with time for every individual molecule. The broadening of the energy levels is due to the electronic rather than to the vibrational part of the total energy, since the Raman lines due to intramolecular vibrations are nearly as narrow in liquids as in vapors. Equally sharp fluorescence lines are very infrequent in condensed media; they occur exclusively in crystals at low temperatures. As a second consequence of the continuous energy exchange with the surrounding medium, no vibrational energy transferred to a molecule by the absorption process can be retained by the molecule during the period elapsing before the re-emission takes place. Therefore, the emission process always originates from one of the lowest vibrational levels of the excited molecule.

Lenard was probably the first to ascribe the great width of the bands in the emission spectra of crystal phosphors to the fluctuation of the molecular fields. The problem of the band width and of the spectral displacement of the fluorescence bands with respect to the absorption bands has been treated by Jablonski on the basis of the