PHOSPHORESCENCE AND THE RÔLE OF THE TRIPLET STATE IN THE ELECTRONIC EXCITATION OF COMPLEX MOLECULES[1]

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CONTENTS

The purpose of this paper is to present a discussion of the researches of Professor Gilbert N. Lewis and his associates which led to the identification of the phosphorescent state with the lowest triplet state of a complex molecule.[3] However, this paper does not consist of a review of all of the details of these researches. It is more in the nature of a commentary, and as such may be regarded as a supplement to the four basic papers on phosphorescence published by Lewis and his coworkers (13, 15, 16, 18). In addition to presenting highlights of previously published work, and new work reported at this Symposium, an additional section on the mechanism of excitation of the triplet state of complex molecules has been added. It may be remarked that the point of view adopted in this paper is that, since metastability of electronic levels may be due to various causes, a phosphorescent state may not be identified as a triplet state until definite physical evidence for this identification has been obtained.

I. DEFINITION OF LUMINESCENCES OF COMPLEX MOLECULES

When the total luminescence of a complex molecule, in solution in a rigid glassy medium, is excited by high-frequency ultraviolet light and recorded spectrographically, it is found that, in general, only two distinguishable luminescences are

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[3] The present discussion deals with the case of molecules having singlet ground states, which includes most of the complex molecules.

observed. The luminescence of higher frequency is readily identified, by its spectral position and (short) mean emission lifetime,[4] as the reverse of the lowest-energy normal absorption process. On the other hand, the second luminescence occurs some 2000 cm.$^{-1}$ to 20,000 cm.$^{-1}$ below the normal absorption band and has a relatively long mean lifetime. Thus, it is usually observable with a low-speed phosphoroscope (rotating alternate vane shutter). The spectroscopic (15, 16) and magnetic (13, 14) studies of the metastable excited state giving rise to this long-lived luminescence have led to the conclusion that, in many cases, this metastable state is the lowest triplet state of the molecule.

Several explanations for the long mean lifetime of phosphorescence of complex molecules (in rigid glasses) had been given previously. The apparent requirement of rigidity of the medium led to the geometrical isomer theory of phosphorescence.[5] A related idea consisted of the interpretation of the phosphorescent state as a tautomer of the normal molecule (6, 7), the return to the normal form being inhibited by the forces present in the rigid medium. However, as indicated in Section II, rigidity is not the fundamental requirement for the manifestation of phosphorescence. The requirements of the *triplet-state theory* of phosphorescence include several general points. According to this theory (15): (*a*) the long lifetime is to be ascribed chiefly to operation of the intercombination[6] selection rule, (*b*) the quasi-forbidden absorption from the ground to the phosphorescent state should be observable for cases having favorable mean phosphorescence lifetimes, and (*c*) the phosphorescent state should be paramagnetic. Each of these topics will be discussed in a later section of this paper.

Both the normal and the low-frequency luminescences are in many cases of such short duration that it is not possible to differentiate between them by the eye on the basis of mean lifetime. For this reason, and because of a belief in the generality of the triplet-state theory, it was proposed (15) that (in the field of complex molecule luminescences) the term *fluorescence* be applied to emissions involving no change in multiplicity, and the term *phosphorescence* be applied to emissions involving a transition between electronic states of dissimilar multiplicity.

In the special case of dyes, for which the normal-excited, and metastable electronic levels are separated by only 1500 to 3000 cm.$^{-1}$, thermal activation may lift molecules from the metastable to the unstable level, resulting in an emission spectrally identical with normal fluorescence, but having a relatively long mean lifetime. This emission has been named alpha-phosphorescence to distinguish it from spontaneous metastable-to-ground emission, which was named beta-phosphorescence (18). This mechanism of luminescence of dyes follows the interpretation made by Jablonski (10).

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[4] Time required for the emitted light to fall to 1/e of its intensity.

[5] This was discussed by Lewis, Lipkin, and Magel (18), together with the triplet-state theory of phosphorescence. See also Terenin (35).

[6] *Intercombination* refers to the process of combining (undergoing transition between) two electronic states of dissimilar multiplicity. *Intersystem* refers to general interrelations between states of dissimilar multiplicity.

However, metastability of an electronic level may be due to other causes than that of the simple operation of the singlet–triplet selection rule. Consequently, any absorption bands of relatively low intensity may have corresponding luminescences of relatively long mean lifetime. One example of such a low-intensity absorption is the case of the characteristic long-wave-length absorption band of carbonyl compounds. This absorption has been interpreted as corresponding to a transition in which a loosely bound electron, occupying a non-bonding orbital lying in the molecular plane and across the C—O direction, is excited to an excited molecular orbital with a node in this plane (McMurry (24)). Another example is the well-known low-intensity long-wave-length absorption band of benzene and certain substituted benzenes, for which the electronic transition is forbidden on symmetry grounds, as interpreted by Sklar, Sponer, *et al.* (8, 29, 30, 31, 33).

In some cases the long-lived luminescence may be ascribed to a triplet–singlet transition if it can be distinguished from other forbidden transitions which are possible. This may sometimes be done by its spectral position, or by a comparison of its mean lifetime with that calculated from the integrated absorption of the processes in question. In the final decision, only studies based on the paramagnetic nature of the triplet state can give an unambiguous assignment as a triplet–singlet emission. This is discussed more fully in Section X.

II. DEFINITION OF EXPERIMENTAL CONDITIONS

The literature on the luminescence of organic molecules in rigid media is sometimes complicated by failure to distinguish between emission spectra of the original molecule and species formed from it, such as various ionic forms, dimers, and higher polymers, and photochemical products produced during the illumination. Further, often no distinction is made between various physical states, such as dissolved, adsorbed, colloidal, or crystalline, in either crystalline or vitreous media. These factors often have a large influence on the optical properties of the molecule. This paper deals only with the case of dilute solution of the substance studied, in the form of homogeneous, transparent, rigid glassy media. Under such conditions it has been found that the luminescences observed are characteristic of the dissolved substance and not of the medium employed (15).

Thus, phosphorescence spectra of carbazole, in rigid glasses of dextrose (293°K.), glycerol (193°K.), and EPA (5 ether, 5 isopentane, 2 ethanol, by volume) (90°K.), were studied. These showed but relatively small differences in frequency of the highest-energy emission band and in the main vibration intervals (15). Similar experiments have been done at one temperature by Mr. R. V. Nauman of this Laboratory, in which the phosphorescence spectra were obtained for several substances in a variety of solvents, each supercooled to a rigid glassy state by means of a liquid-nitrogen bath (77°K.). The solvents used include various hydroxylic and hydrocarbon solvent mixtures, concentrated phosphoric acid, and concentrated sulfuric acid. It was found that the spectral characteristics of the phosphorescences were relatively little affected (20). A study of the vibrational structure of the phosphorescence spectra has shown that the vibrations are characteristic of the ground state of the molecule (15, 19, 25, 27).

Furthermore, it has been found that rigid media are not always essential for the observation of phosphorescence. Thus, the phosphorescence of a number of substances has been observed in glycerol solution at room temperature (2, 20). Similarly, the gas-phase luminescence of several substances was shown (16) to be *nearly identical, in spectrum and mean lifetime, with the phosphorescence* observed in rigid glasses at 77°K. Phosphorescence in fluid media is readily observed if the mean lifetime is intrinsically short, of the order of 10^{-3} sec. Substances having mean phosphorescence lifetimes of several seconds do not exhibit the phenomenon in fluid media at room temperature. From these facts it has been concluded (16) that the chief function of the rigid medium is to prevent viscosity-dependent quenching of the energy of the molecule in the metastable state. Quantitative experiments on the quantum yield of phosphorescence as a function of mean lifetime and viscosity would be very desirable.

Considering the respective rôles of the complex molecule and the rigid glassy medium in making up a complex molecule *phosphor* system, there is evidently no close analogy to the "activator" of mineral phosphor systems. The application of the term "activator" to the former system must be regarded as inaccurate and misleading.

III. PHOSPHORESCENCE OF NON-HYDROGENIC CARBON COMPOUNDS

Since it had been suggested that the phosphorescent state may correspond to a tautomer of the normal molecule (6, 7), it was of interest to investigate the phosphorescence properties of a number of molecules not containing hydrogen. The phosphorescences of a series of perchlorinated molecules were studied in rigid media (EPA, Section II) at 77°K. Data obtained for several different structural types are given in table 1. The lifetimes were estimated roughly by visual observation and are probably too long.

The data of table 1 show that even for molecules which contain no hydrogen atoms, phosphorescence of normal characteristics occurs. This of course would not be possible if normal tautomerism were operative in excitation of the phosphorescent state, in view of the absence of hydrogen in these molecules. It is possible that if very high vibrational levels were involved, resulting in a vibrationally energy-rich molecule, "tautomerism" of an abnormal nature might occur, causing a "shift" of very heavy atoms, such as would not ordinarily be expected (5). That is to say, in a highly vibrating state, a heavy atom may attain such a large displacement as to require merely a redistribution of bonds for its effectual transfer from one part of the molecule to another. However, as Professor M. Calvin has pointed out to the author, if such a "tautomerism" did occur, no mechanism would be available to explain the *spontaneous* return from the phosphorescent state to the normal state. In the emission process the molecule starts from the zero-point vibration level of the upper state, under the usual conditions of observation.

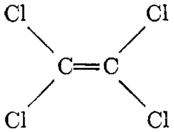
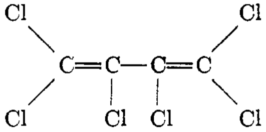
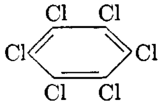
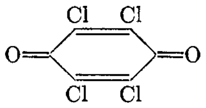
It is concluded that tautomerism does not play a fundamental rôle in phosphorescence phenomena in the case of most complex molecules.

IV. PHYSICAL CHARACTERISTICS OF (BETA) PHOSPHORESCENCE

In the case of mineral phosphor systems some evidence has been obtained for the occurrence of electron transfer during the excitation and emission processes. The independent study of electron transfer caused by illumination (by high-frequency ultraviolet light) of complex molecules in rigid glassy media (12, 17) has indicated that in the phosphorescence process in this system electron transfer is definitely not involved, as previously discussed (15).

TABLE 1

Phosphorescence characteristics of non-hydrogenic carbon compounds

COMPOUND	$\bar{\nu}_P$	APPROXIMATE MEAN LIFETIME
	cm.$^{-1}$	*sec.*
	26,000	2
	25,800	3
	24,170	0.1
	21,750	0.5

The observation of a strictly exponential decay law of phosphorescence of complex molecules, during normal time intervals (18, 22, 28, 36), is compatible with the idea of a spontaneous (unimolecular) emission. For time intervals which are long compared with the mean phosphorescence lifetime, involving a thousandfold variation in intensity of phosphorescence, it was found recently by Sveshnikov (34) that a noticeable deviation from the exponential decay law (phosphorescence of acid fluorescein dye) occurs. Also, there was found a slight dependence of the decay constant on the intensity of the exciting light.

Both these anomalies are in the direction of increased rate of decay during the existence of a higher concentration of molecules in the phosphorescent state. Professor M. Calvin has pointed out to the author that these deviations may be due to a magnetic quenching resulting from the interaction of a molecule in the triplet state with the inhomogeneous magnetic fields produced by neighboring triplet-state molecules (see Section V). As the phosphorescence decays, the influence of the fields would diminish and the quenching would decrease, as observed.[7]

Finally, three other physical characteristics of phosphorescence which have been studied deserve mention. (*a*) Beta-phosphorescence has been found to be nearly temperature-independent (18), while alpha-phosphorescence is strongly temperature-dependent, as pointed out in Section I. (*b*) Beta-phosphorescence shows very little polarization (18, 26), while alpha-phosphorescence is polarized similarly to normal fluorescence. (*c*) Wide-angle interference-pattern studies of the phosphorescence of acid fluorescein dye, by Weissman and Lipkin (38), have demonstrated that the electromagnetic radiation mechanism is *electric dipole* emission.

V. PARAMAGNETISM OF THE PHOSPHORESCENT STATE[8]

That the phosphorescent state is paramagnetic in certain cases was first demonstrated by Lewis and Calvin (13). A direct measurement of the paramagnetism of the phosphorescent state is possible in the case of complex molecules because of the phosphorescence saturation phenomenon (18) arising from the long mean lifetime (seconds), whereby a large fraction of the molecules may be held in the phosphorescent state by illumination of the phosphor with an intense light source. The experiments of Lewis and Calvin were performed on the phosphorescent state of acid fluorescein dye, using a Theorell horizontal microbalance. Later experiments (14) permitted a quantitative determination of the value for the molal paramagnetic susceptibility, the results of which are given here.

For acid fluorescein dye in the 2.5-sec. phosphorescent state in boric acid glass at room temperature, a steady-state concentration of 3.23×10^{-8} moles per centimeter length produced a boom displacement of 4.43×10^{-3} cm., corresponding to a pull of 1.17×10^{-2} dynes. These data yielded a value of 2100×10^{-6} C.G.S. units for the molal paramagnetic susceptibility of the phosphorescent-state molecules. This value is about two-thirds of the value given for the triplet state of oxygen at the same temperature. The discrepancy is attributed to the thermal depopulation of the phosphorescent state (as described in Section I) due to warming of the sample by the high-intensity exciting source. Owing to this discrepancy the experiments are being repeated at low temperatures; a full report on this research is postponed until a later date.

VI. MEAN LIFETIME OF THE PHOSPHORESCENT STATE

For the triplet-state theory of phosphorescence to be valid, it is important to establish the fact that the range of observed mean lifetimes is consistent with the transition probability expected theoretically for a triplet–singlet emission.

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[7] The effects observed by Sveshnikov could be due to warming of the sample by the high-intensity light, although it seems unlikely that the boric acid glass would cool sufficiently during the decay time to influence the decay constant.

[8] Reported at this Symposium by Professor Melvin Calvin.

Lifetimes roughly estimated by visual observation (15) indicated a range of about 10^{-4} to 50 sec., with a strong dependence on molecular structure. More recent quantitative measurements indicate that the visual estimates were somewhat long in most cases. Since the careful experimental and theoretical study of the problem of phosphorescence lifetimes of complex molecules is under way at this Laboratory (23), further discussion will not be given here. For atomic cases the quantum-mechanical treatment of intensities of singlet–triplet transitions relative to singlet–singlet transitions is well known. It is interesting that approximations for the corresponding processes in complex molecules, based on a model using atomic wave functions and assuming spin–orbit coupling, give triplet–singlet lifetimes which are of the same order of magnitude as observed phosphorescence lifetimes (1).

VII. CHANGE OF CONFIGURATION IN EXCITATION OF THE TRIPLET STATE

The excitation of a non-dissociated low-energy triplet state of a complex molecule requires the uncoupling of the spins of a pair of unsaturation electrons. The resultant triplet state may then be considered as analogous to a diradical. Thus, it is apparent that in excitation to the triplet state the configuration of the complex molecule may be affected in a direct way. It has been found interesting to attempt to construct a model for the most probable diradical configuration of the triplet state of various types of molecules in terms of classical chemical structures[9] (15).

The study of phosphorescence characteristics (15) (energy of the phosphorescent state above the ground state, as determined by highest-frequency emission band; mean lifetime of emission; vibration pattern) showed that within certain molecular types essentially similar characteristics occurred. Thus, for derivatives of an aromatic ring molecule (substituted by such saturated groups as alkyl, alkoxy, halogen), closely similar phosphorescences are obtained. For example, most benzene derivatives (20) have phosphorescent-state energies of about 80 kcal., naphthalene derivatives about 60 kcal.; and the mean emission lifetimes are in the range 5–10 sec. and 1–4 sec., respectively (23). Both benzene derivatives and naphthalene derivatives have many-banded phosphorescence spectra of sharp fine structure.

On the other hand, when a series of aromatic nitro compounds is studied, it is found that the phosphorescence characteristics are very different from those of the parent molecule, and in fact quite consistent regardless of the aromatic nucleus. Thus, most aromatic nitro compounds (e.g., nitronaphthalenes, nitrofluorenes, nitrobiphenyls) have phosphorescent-state energies of about 57 kcal., mean lifetimes of about 0.1 sec., and a characteristic spectrum consisting of an evenly spaced (in frequency) set of diffuse emission bands. Analogously, many aromatic ketones have been found to have mean phosphorescence lifetimes of about 10^{-3} sec., also with a characteristic spacing of diffuse emission bands. In

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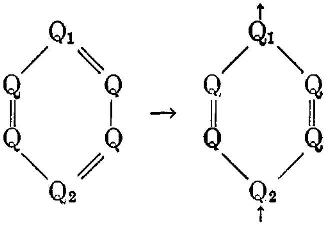
[9] The procedure of assigning energy increments for the factors contributing to the energy of the triplet state, as used in the earlier work on phosphorescence, will be omitted from the present discussions, owing to its somewhat arbitrary nature.

this case however, the energy of the phosphorescent state varies widely, depending on the ketone, presumably owing to electronic interaction of the carbonyl group with the rest of the molecule.

The consideration of such phosphorescence data led to the idea that the excitation of the triplet state involved essentially different molecular mechanisms in each structural type. Thus, in some cases the excitation could be considered as confined to a diatomic double-bonded array, involving a localized molecular orbital, pictured as follows:

$$Q_1{=}Q_2 \rightarrow \overset{\uparrow}{Q_1}{-}\overset{\uparrow}{Q_2}$$

where each Q represents an atom, one or both of which may be bonded to other atoms; the small arrows represent the parallel-spin electrons which give rise to the triplet multiplicity. There would be a characteristic change in interatomic distance expected for such an excitation. In the case of excitation of a cyclic structure, the configurational change may be pictured thus:



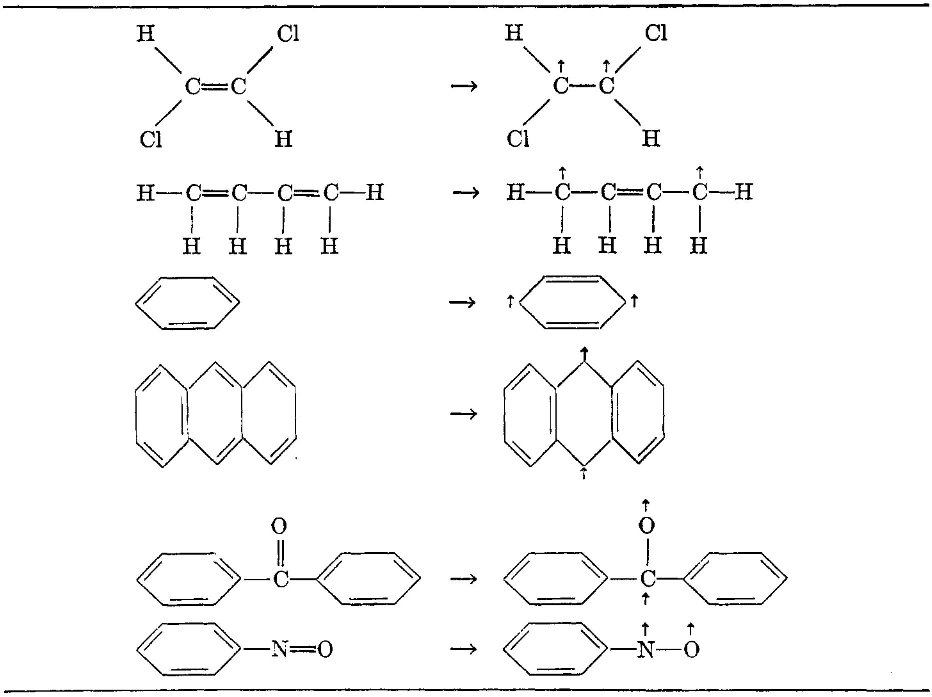
in which case the net displacement of Q_1 and Q_2 would be less than for the diatomic array (on the basis of classical structures and normal bond distances and angles). When the electrostatic repulsion of the two electrons is considered, it may be expected that (*a*) if confined to a diatomic array, the repulsion would further increase the interatomic distance for the diradical configuration, or (*b*) if the geometry of the molecule permitted, the electrons would tend to separate, e.g., favoring para positions in the above case to ortho positions.

Table 2 illustrates the postulated configurational changes for triplet-state excitation of several actual molecules. Various alternative structures would have to be considered for a more accurate picture. In such a case as benzophenone, the decision as to whether the benzene ring or the carbonyl group is the principal locus of excitation is made on the basis of phosphorescence characteristics alone. In most cases an unambiguous differentiation may be made, by comparison with the characteristics obtained for the two competing parts of the molecule when studied separately (i.e., linked to electronically inert groups). It may be pointed out that in the case of benzene the *p*-quinoid model for the triplet state is supported by the intensity relations of the phosphorescence emission spectrum (15), and by a vibrational analysis of the fine structure of the spectrum (27).

This picture of triplet-state excitation is of course very crude, but, subject to certain refinements, it does give an interpretation of the variation in phosphorescence characteristics enumerated above. Use of this model has facilitated the development of the picture of mechanism of excitation of the phosphorescent state, discussed in Section VIII of this paper. Furthermore, the model may be used to explain certain permanent changes occurring in some photochemical reactions, such as photoisomerization about a double bond. A triplet state intermediate in a number of such photochemical processes is suggested.

TABLE 2

Postulated change of molecular configuration in excitation of the triplet state



VIII. MECHANISM OF EXCITATION OF THE TRIPLET STATE

The mechanism of excitation of the phosphorescent state deserves special consideration. Let the discussion be limited at first to the cases in which the phosphorescent state is a triplet state. Excitation of this state as a result of direct transition from the ground state by light absorption may be expected to occur but rarely, i.e., with very low probability (see Section X). Thus, excitation of the triplet state must almost always involve primary absorption to one of the excited singlet states. The ratio of the mean lifetimes of normal fluorescence (${}^1\Gamma^* \rightarrow {}^1\Gamma$) (excited singlet → singlet)[10] and phosphorescence (${}^3\Gamma \rightarrow {}^1\Gamma$) (defined

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[10] *Nomenclature*: In the papers of Lewis and Kasha (15, 16) singlet states were designated by S, S', S'' and triplet states by T, T', T''. In this paper these are replaced by ${}^1\Gamma$, ${}^1\Gamma^*$, ${}^1\Gamma^{**}$ and ${}^3\Gamma$, ${}^3\Gamma^*$, ${}^3\Gamma^{**}$, in conformity with usual spectroscopic practice. Γ is an arbitrary term symbol, and the asterisks indicate simply that the states are different, but more than this is not known. $\Gamma \leftarrow \Gamma$ denotes absorption and $\Gamma \rightarrow \Gamma$ denotes emission, with the state of highest energy placed first in order.

in accordance with the limitation given above) is on the order of 10^{-8} to 1 sec., respectively. Therefore it is obvious that, assuming similar intercombination transition probabilities, the ${}^1\Gamma^* \rightarrow {}^3\Gamma$ process cannot be a radiative one (see figure 2). It was formerly postulated (6, 7, 18) that in the excitation of the phosphorescent state the molecule in the ${}^1\Gamma^*$ state is first transferred, by an internal conversion of energy, to a high vibrational level of the ${}^1\Gamma$ state. Then transfer to the phosphorescent state could occur when a favorable configuration was acquired, while *slowly (it was assumed) falling through the ${}^1\Gamma$ vibrational levels in the* neighborhood of the phosphorescent state.

An analysis of the details of the processes involved in normal absorption and emission of light indicates that the mechanism described above cannot be valid. Studies of the absorption spectra of complex molecules in rigid glasses at low temperatures indicate that the vibrational cascade to the zero-point level of the ${}^1\Gamma^*$ state, after primary absorption has occurred, is very rapid compared with the mean lifetime of the ${}^1\Gamma^*$ state. It may then be expected that vibrational cascade through the levels of the ${}^1\Gamma$ state would be just as rapid as it is in the ${}^1\Gamma^*$ state. Thus the mechanism of excitation of the phosphorescent state could not depend on a slow passage through the ${}^1\Gamma$ vibrational levels, even in a rigid medium. During the process of primary absorption the molecule remains longest at, or slightly above, the zero-point level of the ${}^1\Gamma^*$ state before normal fluorescence (${}^1\Gamma^* \rightarrow {}^1\Gamma$) occurs. Hence it is logical to assume that the radiationless internal conversion (${}^1\Gamma^* \rightarrow {}^3\Gamma$) will occur with maximum probability *at or above* the zero-point level of the ${}^1\Gamma^*$ state.

By the use of a schematic potential-curve diagram (figure 1) instead of the line energy-level diagram (figure 2), a more accurate picture of the place of interaction (on the energy diagram) may be obtained. The mechanism of excitation of the triplet state, according to this picture, involves an intersystem "crossing" of potential curves for the ${}^1\Gamma^*$ and ${}^3\Gamma$ states. The mechanism sequence may be outlined as follows: primary absorption of light (${}^1\Gamma^* \leftarrow {}^1\Gamma$), rapid vibrational cascade to the vicinity of the zero-point level of the ${}^1\Gamma^*$ state, with simultaneous intersystem crossing (${}^1\Gamma^* \rightarrow {}^3\Gamma$), followed by vibrational cascade to the zero-point level of the ${}^3\Gamma$ state. Thereafter, spontaneous phosphorescence emission (${}^3\Gamma \rightarrow {}^1\Gamma$) may occur. A detailed consideration of the factors involved leads to the conclusion that if the crossing of the potential curves occurs at the lowest point of the ${}^1\Gamma^*$ curve, the probability of internal conversion will be greater than for cases in which crossing at a higher point of the ${}^1\Gamma^*$ curve occurs.

For a complex molecule such a diagram requires a special definition of coördinates, since for such molecules a potential hypersurface would be required to show the dependence of electronic energy on the configuration for each electronic state. Here a simplification may be introduced, based on the model for triplet-state excitation presented in Section VII. A critical coördinate is first selected, corresponding to the principal axis of excitation of the triplet-state configuration. Then the schematic potential curves may be interpreted as representing time-average cross-sections of the potential-energy hypersurfaces for the electronic states along this critical coördinate. From the model it may be assumed that the $^3\Gamma$ minimum will come at larger values of interatomic distance than the minima of the $^1\Gamma^*$ and $^1\Gamma$ potential curves.

After the internal conversion to the $^3\Gamma$ state (n^{th} vibrational level) has occurred, the $^1\Gamma^* - {}^3\Gamma$ energy difference (A of table 3, Section IX) must be dissipated as vibrational energy of the $^3\Gamma$ state. This energy is often about 20–30 kcal. per mole, and although considerable, it is not of an astronomical order of magnitude compared with the 5–10 kcal. per mole which must be dissipated in the $^1\Gamma^*$ state each time that normal absorption to high vibrational quanta occurs in a complex molecule. Furthermore, in a rigid glassy medium at low temperatures, cascade by infrared radiation may become probable, as may infrared transmission by the medium, thus facilitating removal of the excess energy from the immediate neighborhood of the molecule.

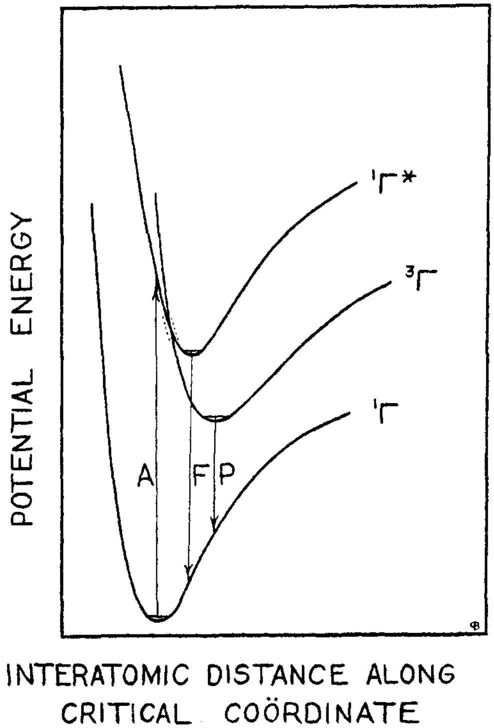

FIG. 1. Schematic potential-energy diagram of the three lowest electronic states of a complex molecule, depicting potential hypersurface cross-sections along a critical coördinate. After primary absorption, fluorescence may occur, and in addition, radiationless intersystem-crossing followed by phosphorescence.

Several interpretations of luminescence phenomena on the basis of crossing of potential curves have been made previously (3, 4, 5a, 37), but these have involved only two electronic states, or repulsive third states, and a more arbitrary definition of coördinates than is given here. From the non-destruction of the normal molecule upon repeated cycles of absorption and phosphorescence emission, it is concluded that dissociation does not occur in the excitation of the phosphorescence of complex molecules.

Throughout this section, the triplet-state theory of phosphorescence has been assumed because of the requirements imposed by the definitions of coördinates. Other metastable states may have a similar mechanism of excitation. A full discussion of this mechanism and its consequences in the optical behavior of complex molecules will be given shortly in another place by the author, together with experimental work supporting the mechanism pictured. One of the consequences of this treatment has been an interpretation of the lack of correlation (5) between the spectroscopic and thermal energy differences between the $^1\Gamma^*$ and $^3\Gamma$ states of dye molecules (11), not expected on the basis of the Jablonski mechanism of luminescence (10).

IX. THE FLUORESCENCE–PHOSPHORESCENCE FREQUENCY INTERVAL

A compilation of fluorescence–phosphorescence frequency intervals for complex molecules, giving the difference between the highest frequency bands of the two luminescences, $\bar{\nu}_F - \bar{\nu}_P$, apparently has not been made hitherto. Nevertheless, this molecular constant is of considerable aid in interpreting luminescence phenomena. Table 3 gives some examples of such data which, while not extensive, are typical for each group of molecules given.

The last column of table 3 gives A, the $^1\Gamma^* - {}^3\Gamma$ zero-point energy interval in kilocalories per mole (assuming, tentatively, a triplet metastable state), which varies widely for different structural types. Within particular groups of molecules, however, this energy interval is fairly constant. Thus, most benzene derivatives (in which the substituents are saturated groups like alkyl, alkoxy, halogen) have values of A of 23 kcal.; naphthalene derivatives about 30 kcal.; amines roughly 15 kcal. This energy interval may be considered as depending chiefly on two factors: (*a*) the configuration change involved in the excitation of the triplet state (see Section VII), and (*b*) the difference in resonance energy between the $^1\Gamma^*$ and $^3\Gamma$ states.

It will be noted that, in contrast to the moderate constancy of the interval for the cases cited above, the aromatic hydrocarbon series benzene, naphthalene, anthracene, phenanthrene, chrysene, have respective $^1\Gamma^* - {}^3\Gamma$ energy intervals of 22.1, 34.5, 28.7, 20.3, 22.4 kcal., indicating a large variation in one or both of the two critical factors. In the case of dyes, the abnormally low $^1\Gamma^* - {}^1\Gamma$ (*normal absorption band*) energy interval brings the $^1\Gamma^*$ much closer to the $^3\Gamma$ state (which latter is not correspondingly lowered by the low-energy electronic processes of dyes; *cf.* figure 2), so that the $^1\Gamma^* - {}^1\Gamma$ interval is only 5–10 kcal. As indicated in an earlier section, this small value of A leads to luminescence phenomena peculiar to dye molecules.

The strikingly large values of A occurring for most other complex molecules have been somewhat overlooked in the past, possibly owing to a disproportionate interest in the luminescence properties of dyes. A full discussion of the importance of the energy interval A in the mechanism of excitation of the phosphorescent state will be given elsewhere by the author.

X. SINGLET–TRIPLET ABSORPTION BANDS OF COMPLEX MOLECULES

Since transition probabilities for the absorption and emission of light between two electronic states are related thermodynamically, the observed mean lifetime of the phosphorescent state may be compared with the lifetime calculated from the integrated absorption of an assumed reciprocal process. This was done in a broad way by Lewis and Kasha (16), who considered also the limitations of the classical transition probability equation relating intensities when applied to spectra of complex molecules. Although the quantitative correlations of intensities which could be made were limited in number, it was definitely established that the phosphorescence emissions studied were the reverse of the quasi-forbidden absorption bands considered.

TABLE 3

Fluorescence–phosphorescence frequency relations of complex molecules

COMPOUND	$\bar{\nu}_F$	$\bar{\nu}_P$	$\bar{\nu}_F - \bar{\nu}_P$	A
	$cm.^{-1}$	$cm.^{-1}$	$cm.^{-1}$	*kcal.*
Benzene	37,037	29,325	7,712	22.1
Naphthalene	33,300	21,300	12,033	34.5
Anthracene	24,700	14,700	10,000	28.7
Phenanthrene	28,818	21,740	7,078	20.3
Chrysene	27,800	20,000	7,810	22.4
Toluene	37,037	28,800	8,237	23.6
Ethylbenzene	37,037	28,950	8,087	23.4
n-Propylbenzene	37,037	28,900	8,137	23.3
Anisole	35,461	28,200	7,261	20.8
α-Fluoronaphthalene	31,900	21,100	10,800	30.9
β-Chloronaphthalene	31,900	21,100	10,800	30.9
α-Naphthol	31,400	20,500	10,900	31.2
β-Naphthol	30,550	21,100	9,450	27.1
β-Naphthonitrile	30,000	20,600	9,400	26.9
Aniline	32,051	26,800	5,251	15.5
Diphenylamine	31,670	25,200	6,470	18.5
Carbazole	29,100	24,500	4,600	13.2
Acid fluorescein	21,000	17,700	3,300	9.5
Crystal violet	15,700	13,500	2,150	6.2
Eosin (sodium salt)	16,950	14,900	2,050	5.9
Diisopropylbromonitrosomethane	>30,000	13,600	>16,400	>47.0

It is possible to establish the reciprocal nature of two transitions for a complex molecule by other means than intensity correlation. Thus, if the absorption and emission bands each involve a single electronic transition, a correlation of the highest frequency of emission with the lowest frequency of absorption would establish the correspondence. These frequencies may be expected to be equal except for a small dissipative energy loss, the magnitude of which may be estimated from the half-width of the individual bands. A single mean lifetime for the emission spectrum establishes the singleness of an electronic transition in emission, and a "mirror-image symmetry" (21; for examples see 9, 19) of the vibration envelope of the absorption spectrum may establish the singleness for the absorption process.

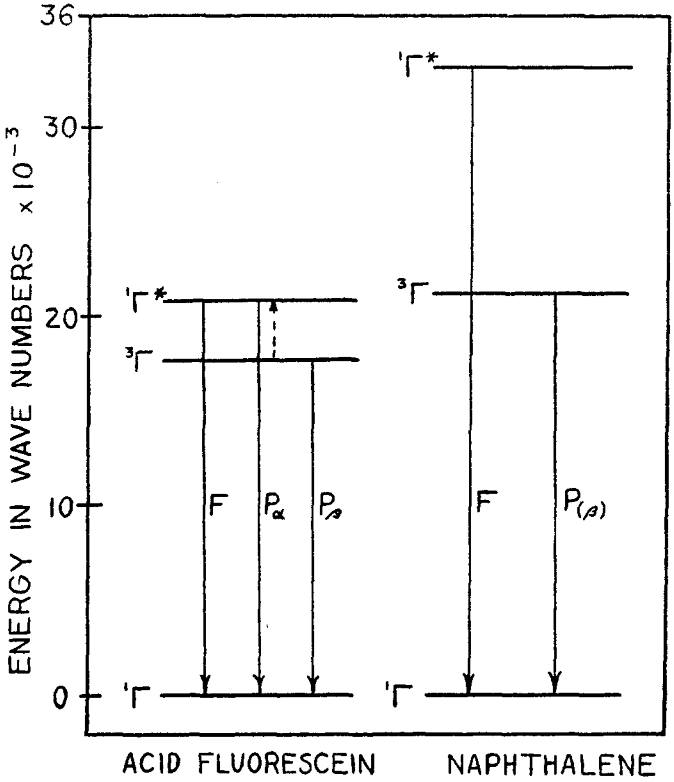

FIG. 2. Line energy-level diagrams for a typical dye and a typical complex molecule. Only the zero-point vibrational levels are shown, and the ground states are set equal arbitrarily. In the case of naphthalene the assignment of the triplet multiplicity to the lowest excited state is tentative. The $^1\Gamma^* \leftarrow {}^3\Gamma$ thermal activation is usually not observed in ordinary complex molecules at the temperatures available ($<$ 298°K.), owing to the magnitude of this energy interval relative to kT.

Although the intensity and frequency correlations may prove the correspondence between absorption and emission processes, the correlation gives no direct information as to the *nature* of the electronic transition involved. The association of forbidden electronic transitions with a triplet-singlet process may be made in three ways: (*a*) by demonstration of the paramagnetic nature of the metastable state,[3] (*b*) by comparison with assignments of triplet levels on the basis of quantum-mechanical calculations, and (*c*) by elimination, when other known interpretations of forbidden transitions can be shown not to apply.

Method (*a*) is conclusive, but has been applied only in one case, the 2.5-sec.

state of acid fluorescein dye. Unfortunately, the long mean lifetime and intense normal color make observation of the forbidden absorption process impossible. This direct paramagnetic measurement method will prove very useful in many cases, and an extensive program of investigation based on it is being planned.

Method (*b*) has been applied to the phosphorescence spectrum of benzene (15), for which the highest-frequency emission band comes at $\bar{\nu}_P = 29{,}325$ cm.$^{-1}$ (20), a value which corresponds to the weak absorption band at 29,400 cm.$^{-1}$ assigned as a $^3\Gamma \leftarrow {}^1\Gamma$ transition by Sklar (29) on the basis of quantum-mechanical calculations. The existence of this weak absorption band was corroborated by Lewis and Kasha (16), who found four maxima at 29,400, 30,300, 31,200, and 32,100 cm.$^{-1}$, with a molal absorption coefficient of $\epsilon = 0.0004$. It is interesting to note that in this case by two independent approaches—one the study of phosphorescence, and the other a quantum-mechanical treatment—the same low-intensity absorption band was tentatively assigned to a singlet–triplet transition.

Method (*c*) does not give an unambiguous identification of a forbidden transition as a singlet–triplet process, but it can give conclusive proof that a particular transition is not to be interpreted on the basis of a particular known cause of prohibition. This is well illustrated by the case of carbonyl compounds. The phosphorescence emission of many carbonyl compounds has been studied (15) and recently, accurate determination of the mean lifetimes of the phosphorescence state of these has been made (23). The emission spectra occur at frequencies a little below the characteristic long-wave-length carbonyl absorption band, for which an interpretation as a forbidden transition has been given by McMurry (24), as mentioned in Section I. However, the integrated absorption of this band predicts a mean lifetime about 100 times shorter than is observed; in other words, the carbonyl absorption is too intense by a factor of 100, for a complete identification with the long-lived (*ca.* 10^{-3} sec.) emission observed. Probably the absorption bands consist of two superposed forbidden electronic transitions. The occurrence of fine structure in the characteristic carbonyl band of some compounds suggests this to be the case, especially in the case of certain diketones (16).

Examples of known low-intensity absorption bands of complex molecules are given in table 4. It is not meant to be implied that these are all singlet–triplet bands; this table merely represents material for study as possible cases. In the case of thiobenzophenone a very good correlation between absorption and emission frequencies and mirror-image symmetry was obtained (16). The absorption coefficient as given is thought to be somewhat in error owing to an impurity of benzophenone, and the lifetime was not measured but only a lower limit established. Thus, an intensity correlation was not achieved, although it is important to do this, since McMurry (24) has suggested that his interpretation of the low-intensity carbonyl bands may apply also to thiocarbonyls. Because of its unique spectral position, it seems rather likely that the thiobenzophenone absorption band in the infrared represents a single electronic transition. A decision as to the cause of prohibition, that of intercombination or otherwise, would be of great interest. However, the suggestion made below offers some evidence for an intercombination process in this case.

In a number of instances, the low-intensity absorption bands observed for nitroso compounds have been correlated with phosphorescence emission spectra (16), though again only partly. Whether the bands are definitely singlet–triplet was not ascertained. It is of interest to point out that in many cases of thiocarbonyl and nitroso compounds the solid state is colorless, while the solutions are colored. More generally, the monomeric state is colored, while dimers and other polymers (which form readily with these compounds) are colorless. If two triplet molecules associated with intermolecular electron coupling, upon polymer formation or upon crystallization, the color would disappear if due to a singlet–triplet absorption in the monomer.

TABLE 4

Forbidden absorption bands of complex molecules

MOLECULE	COLOR	MOLAL ABSORPTION COEFFICIENT	ABSORPTION $\bar{\nu}$	EMISSION $\bar{\nu}$	$\int \epsilon \, d\bar{\nu}$	CALCULATED τ (ASSUMING $s-t$)	OBSERVED τ
			cm.$^{-1}$	*cm.*$^{-1}$		*seconds*	***seconds***
1. *Thiocarbonyl:*							
Thiobenzophenone	Blue	3	16,000	13,800	9,300	2.3×10^{-4}	$<10^{-3}$
2. *Carbonyl:*							
Biacetyl	Yellow	22	22,500	19,700	77,500	1.16×10^{-5}	1.65×10^{-3}
Glyoxal	Yellow	3.5	21,700		9,660	1.17×10^{-4}	
3. *Nitroso:*							
Nitrosodiethylaniline	Green	0.6	12,200		1,700	1.7×10^{-3}	
Diisopropylbromonitrosomethane	Blue		14,560	13,600			
4. *Azo:*							
Diazomethane	Yellow	5	25,200		27,000	3.6×10^{-5}	
Azomethane	Yellow	4.6	29,500		27,000	2.6×10^{-5}	
5. *Aromatic nuclei:*							
Benzene		0.0004	29,400	29,325	~0.5	~1	4.0*
p-Dichlorobenzene			26,400	26,000			0.01*
Phenazine		0.8	(16,000)	15,300	620	2.8×10^{-3}	$<10^{-2}$

* Reference 23, unpublished work.

The low-intensity absorption bands listed for the two simple aliphatic azo compounds are also of interest for the present discussion, but luminescence studies of these have not yet been made. For a few aromatic hydrocarbons, extremely low-intensity absorption bands have been found. Like the case of benzene, an analogous though more obscure set of bands was obtained for *p*-dichlorobenzene. The frequencies matched very well, and the intensities roughly (a large experimental error in the integration is inevitable with such low absorption).

The aspect of luminescence research considered in this section is of great importance because of the elucidation of the nature of forbidden absorption bands of complex molecules which it promises to give. Faint colors, anomalous in normal color theory, may find their explanation in intersystem[6] transitions. The lack of data in table 4 emphasizes the need for thorough quantitative work on this subject.

In the last analysis the absolute assignment of a forbidden electronic transition, as a singlet–triplet process, will probably depend on the paramagnetism of the triplet state. Other methods than the direct measurement by microbalance are available. An attempt to determine the paramagnetism of molecules in the phosphorescent state by molecular-beam techniques is being made by Harrison Shull, working with Professor G. E. Gibson at this Laboratory. Also a number of indirect methods may be found useful, e.g., the effect of applied fields in the mean phosphorescence lifetime, either external fields or fields due to molecules in the environment of the excited molecule (see also end of Section XI). The availability of such a variety of methods should make it possible to apply at least one to each case of forbidden transition in question.

XI. ABSORPTION OF LIGHT BY MOLECULES IN THE PHOSPHORESCENT STATE

The phenomenon of phosphorescence saturation, which corresponds to the building up of a high concentration of molecules in the phosphorescent state, permits the study of the properties of this state as distinguished from those of the normal molecule. The study of the magnetic properties was described in Section V; the study of optical properties of the phosphorescent state is considered in this section.

Early in the work on the optical phenomena of complex molecules in rigid glasses, it was observed that in some cases a transient colored state was produced by intense illumination, decaying upon removal of the exciting light. This transient color, it was noted, is *color by absorption* and not luminescence, although both are present simultaneously and both decay with the same mean lifetime. It was recognized that this color is due to absorption from the ground metastable level to other electronic levels of the same type ($^3\Gamma^* \leftarrow {}^3\Gamma$, $^3\Gamma^{**} \leftarrow {}^3\Gamma$) (here a metastable triplet level again is assumed). As expected, the intensity of absorption varied with the intensity of the exciting light.

The absorption spectrum of the phosphorescent state of acid fluorescein dye was determined (18), although in this instance the color of the dye due to normal absorption masks the new absorption produced. However, the absorption spectrum of diphenylamine in the phosphorescent state was also determined (17), and in this case a transient violet color is observed upon intense illumination. It was shown that the color was not due to photochemical decomposition of the molecule.

It may be expected that $^3\Gamma^* \leftarrow {}^3\Gamma$ absorption bands should be quite generally observable with complex molecules having the longer-lived phosphorescent states. Perhaps the occurrence of such an absorption could be taken as evidence for the triplet multiplicity of a metastable state,[3] since it would be difficult to account for this absorption phenomenon in the case of some of the other causes of prohibition of electronic processes.

XII. CONCLUSION

The phosphorescence spectra of several hundred complex molecules have been recorded (15, 20). In the case of acid fluorescein dye, direct measurement of paramagnetism has established the fact that the phosphorescent state is a triplet state. Indirect (but not conclusive) evidence for this identification has been obtained for benzene ($\bar{\nu}_P$ = 29,325 cm.$^{-1}$), *p*-dichlorobenzene (26,000 cm.$^{-1}$), diphenylamine (25,200 cm.$^{-1}$), thiobenzophenone (14,100 cm.$^{-1}$), and several nitroso compounds. It is believed that the phosphorescence observed at about 2000 cm.$^{-1}$ to 20,000 cm.$^{-1}$ below the normal absorption band of a complex molecule will prove to be triplet–singlet transitions in most cases.

The phenomenon of the phosphorescence of complex molecules, and the use of rigid media, must therefore be looked upon as convenient means of observing forbidden electronic transitions in emission. Whereas the absorption process becomes increasingly more difficult to observe with increasing prohibition, the emission process becomes increasingly easy to observe, since greater prohibition corresponds simply to longer mean lifetimes of the excited state.

The identification of metastable electronic states as triplet states is of more than academic interest. In addition to offering an interpretation of some low-intensity absorption bands of complex molecules, often giving rise to anomalous color, the triplet state may be expected to be of great photochemical importance. The absence of long-lived luminescence in fluid media does not mean that excitation of the metastable state does not take place, but merely that this state is deactivated, owing to viscosity-dependent quenching.

When the metastable state is a triplet state, the fact that it is long lived, has a diradical configuration, and may be excited in fluid media at ordinary temperatures, suggests an important rôle for this state in photochemical processes in ordinary chemical systems.

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